SYNTHESIS AND CHARACTERIZATION OF POLY(DIMETHYLBUTADIENE) COPOLYMERS

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Roberto Chinchilla-Pardos

Inch by inch, play by play, ‘till we’re finished.

Coach Tony D'Amato (“Any Given Sunday” 1999)

Some people don’t like change, but you need to embrace change if the alternative is disaster.

Elon Musk

Synthesis and Characterization of Poly(Dimethylbutadiene) Copolymers

Roberto Chinchilla-Pardos

ABSTRACT: 2,3-dimethyl-1,3-butadiene (DMB), typically referred to as dimethylbutadiene has been used to prepare a variety of homopolymers and copolymers by living anionic polymerization. The effect of different reaction parameters such as polarity of the solvent, temperature or initial concentration of initiator on the microstructure of poly(dimethylbutadiene) (PDMB) has been investigated.

The synthesis of a series of statistical copolymers, in benzene and *n*-heptane, of DMB with butadiene, styrene and 1,1-diphenylethylene (DPE) has been carried out with the goal of understanding the copolymerization behaviour. The reactivity ratios of each pair DMB/comonomer has been calculated.

The synthesis of randomly branched polymers of DMB via anionic chain transfer polymerization using divinylbenzene (DVB) as branching agent and potassium *tert*-butoxide as chain transfer promoter has been investigated. Different mole fractions of both DMB and DVB has been tested in order to balance the extent of crosslinking and chain-transfer with the aim of inhibiting crosslinking and producing soluble branched copolymer.

The homopolymers and copolymers has been analysed by a variety of techniques including ^{1}H-NMR spectroscopy, Differential Scanning Calorimetry (DSC) and Size Exclusion Chromatography (SEC).

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List of Abbreviations

^{1}H-NMR	Proton Nuclear Magnetic Resonance
AIBN	Azobisisobutyronitrile
ATRP	Atom Transfer Radical Polymerization
Bd	Butadiene
Đ	Dispersity
DDT	1-dodecanethiol
DEB	Diethylbenzene
DLS	Dynamic Light Scattering
DMB	2,3-dimethyl-1,3-butadiene
dn/dc	Refractive Index Increment
DPE	1,1-Diphenylethylene
DSC	Differential Scanning Calorimetry
DVB	Divinylbenzene
EGDA	Ethylene Glycol Diacetate
EGDMA	Ethylene Glycol Dimethacrylate
ε	Dielectric Constant
EVB	Ethylvinylbenzene
FT-IR	Fourier-Transform Infrared Spectroscopy
GC-MS	Gas Chomatography - Mass Spectrometry
HEX	*n*-hexane
H-H PP	Head to Head Polypropylene
IV	Intrinsic Viscosity

KOtBu	Potassium *tert*-butoxide
LDPE	Low Density Polyethylene
M_1	Monomer 1
M_2	Monomer 2
MALDI ToF	Matrix-Assisted Laser Desorption/Ionization Time-of-Flight
MMA	Methylmethacrylate
M_n	Number Average Molecular Weight
M_{target}	Target Molecular Weight
MW	Molecular Weight
M_w	Weight Average Molecular Weight
NaOtBu	Sodium *tert*-butoxide
p(DMB-*s*-Bd)	Poly(2,3-dimethyl-1,3-butadiene-*statistical*-butadiene)
p(DMB-*s*-DPE)	Poly(2,3-dimethyl-1,3-butadiene-*statistical*-1,1-Diphenylethylene)
p(DMB-*s*-Sty)	Poly(2,3-dimethyl-1,3-butadiene-*statistical*-styrene)
PDMB	Poly(2,3-dimethyl-1,3-butadiene)
PDPE	Poly(1,1-Diphenylethylene)
PE	Polyethylene
polyDMB	Poly(2,3-dimethyl-1,3-butadiene)
PP	Polypropylene
PS	Polystyrene
r_1	Reactivity Ratio of Monomer 1
r_2	Reactivity Ratio of Monomer 2
RALS	Right Angle Light Scattering

r_{Bd}	Reactivity Ratio of Butadiene
r_{DMB}	Reactivity Ratio of 2,3-dimethyl-1,3-butadiene
r_{DPE}	Reactivity Ratio of 1,1-Diphenylethylene
RDRP	Reversible Deactivation Radical Polymerization
r_{DVB}	Reactivity Ratio of Divinylbenzene
RI	Refractive Index
r_{Ip}	Reactivity Ratio of Isoprene
r_{Sty}	Reactivity Ratio of Styrene
RT	Room Temperature
SAXS	Small-Angle X-Ray Scattering
SEC	SIze-Exclusion Chromatography
Sty	Styrene
T	Temperature
t	time
T_g	Glass Transition Temperature
T_m	Melting Point
TMEDA	Tetramethylethylenediamine
TOL	Toluene
VOC	Volatile Organic Compounds
w/v	Weight/Volume
x_1	Weight Fraction Monomer 1

Statement of Copyright

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I would like to thank everyone at Synthomer who helped me feel welcome and made my time working there so enjoyable.

Thank you Pilar for being waiting on the other side of the screen. It has not been easy but now we can be together again and enjoy a life in common.

Por último no puedo acabar sin agradecer a mis padres y a mi hermana porque sin ellos jamás habría podido llegar donde estoy.

Chapter 1

Introduction

Chapter 1: Introduction

1.1. Poly(dimethylbutadiene) — The History of a Forgotten Polymer

2,3-dimethyl-1,3-butadiene (DMB), typically referred to as dimethylbutadiene or methyl isoprene is a colourless liquid monomer (boiling point 68-69 °C) whose structure is shown in *Figure 1.1*. It is a derivative of butadiene with two methyl side groups.

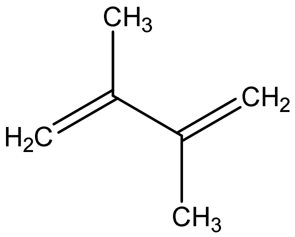
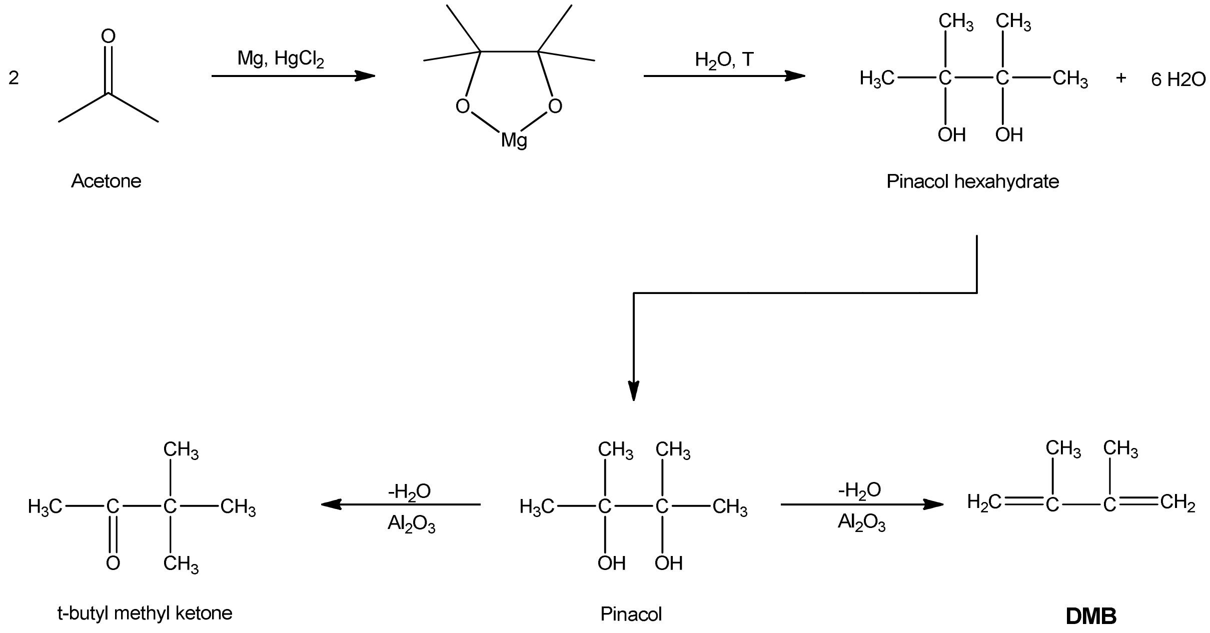


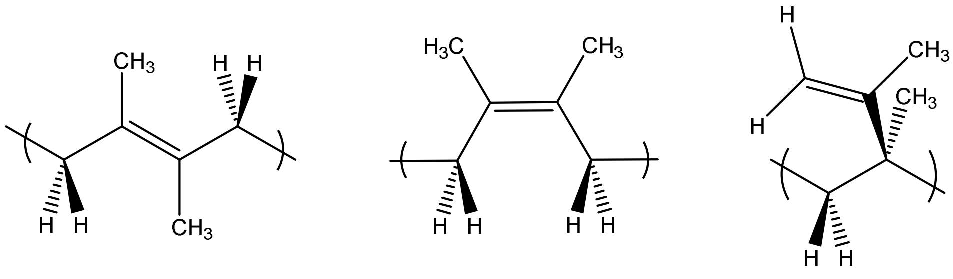
Figure 1.1: *Chemical structure of 2,3-dimethyl-1,3-butadiene (DMB).* C_6H_{10}*, molecular weight 82.14 g* mol^{-1}*.*

Currently it may be produced by four methods:[1] abstraction (by heating in the presence of an alkali) of two halogen hydride molecules from 2,3-dimethyl-2,3-dihalobutanes,[2] synthesis based on a Grignard reaction,[3] dehydration of 2,3-dimethyl-2,3-butanediol (pinacol) using a 48% HBr solution[4] and the catalytic dehydration of pinacol using Al_2O_3 catalyst. Among these methods, nowadays the catalytic dehydration of pinacol, as shown in *Scheme 1.1*, is preferred in both academia and industry. This process begins from the industrially-available acetone which is reduced to 2,3-dimethyl-2,3-butanediol hexahydrate, using magnesium amalgam, in roughly 50% yield. The latter is then converted, by azeotropic distillation with benzene, to anhydrous 2,3-dimethyl-2,3-butanediol (pinacol). Finally, pinacol is dehydrated in the presence of Al_2O_3 catalyst at temperatures between 400-500 °C, leading to DMB but also about 1-2% of *t*-butyl methyl ketone as a byproduct. Pinacol flow rate as well as the reaction temperature can affect the yield of this last step of the process which proceeds in approximately 80% yield.[1]

Poly(2,3-dimethyl-1,3-butadiene) (PDMB), also referred to as poly(methylisoprene) or more commonly methyl rubber, is considered the first commercial synthetic rubber.[5] DMB can polymerize to give polymer with three different microstructures (*Figure 1.2*) and PDMB was first synthesized by Kondakov in 1900 by heating DMB in the presence of caustic potash. It was during the First World War (1914-1918) that methyl rubber was first commercialized in Germany, playing an important role in the conflict.



Scheme 1.1: *Synthesis of DMB by catalytic dehydration of pinacol using Al_2O_3 as catalyst. This reaction leads to two possible products: DMB (right) and t-butyl methyl ketone (left).*


trans-1,4

cis-1,4

1,2

Figure 1.2: *The possible microstructures of PDMB.*

The main use of this material (produced in roughly 30 tons per month) was for the production of tyres and hard rubber pieces, with the German army being the main user during the war.[6,7] The development and commercialization of DMB was a response to the British blockade which cut off the German supplies, for both natural rubber and butadiene monomer. Hence, the prices and demand of these goods rose dramatically in a short period of time, which drove the Emperor Wilhelm II to invest in the research, development and production of alternative synthetic rubbers.

Germany focused on the development of PDMB, most likely, due to DMB monomer being more readily available than butadiene[6, 8] and during World War I, Germany produced a few thousands of tons of PDMB.[9] *Friedrich Bayer & Co.* alone produced more than 2000 tons of methyl rubber at a cost o f$ 2.80-3.21 per kilogram.[8] Nevertheless, the production and products of methyl rubber presented several drawbacks compared to natural rubber. Firstly, the production (by bulk polymerization) and processing of PDMB into the final products took a few months at room temperature.[8, 10] Another issue was that products made from crosslinked PDMB had a low level of elasticity at temperatures close to 0 °C, so tyres and other PDMB products had limited durability. These poor properties made PDMB tyres clearly inferior to tyres made of natural rubber and PDMB products failed at some applications during the conflict. For example, due to the higher glass transition temperature of PDMB (from -5 to 20 °C) compared to natural rubber, tyres made of this material were not suitable during winters as they became increasingly inelastic and brittle. However, in hindsight, it is commonly thought that this material might have been successful if it had been reinforced by carbon black, which was used very little as a filler for natural rubber prior to 1914,[6, 8, 9, 11, 12] or if DMB had been copolymerized with other monomers (e.g. other dienes).[13]

Because of the observed drawbacks of methyl rubber products and their slow production during WWI, and the lower and more stable prices for natural rubber after the hostilities ended, there was little economic interest in the development and production of PDMB synthetic rubbers after the war. However, there was a renewed interest in synthetic rubbers eight years later due to a new rise in the cost of natural rubber, but in this case, the interest in synthetic rubbers was directed towards polybutadiene as its properties were closer to natural rubber than those of PDMB.[6, 10] Unlike Kaiser Wilhelm II in WWI, Germany rejected PDMB in favour of the development of Buna S (polybutadiene) elastomers (patented by Tschunkur and Boch in 1933) leading up to the beginning of the Second World War.[7]

From an academic point of view, there is limited published data on this monomer and polymers produced from DMB. The majority of academic interest in PDMB seems to have largely died out after conclusion of WWI. This is in remarkable contrast with the other two monomers of the butadiene series (1,3-butadiene and isoprene) and their polymers which have been the subject of significant and sustained research activity from then until the present time.

That said, there have been a few notable studies on the polymerization of DMB and the key results are summarised below. In 1949 and 1952, Marvel and co-workers[14] and Orr and Williams[15] respectively, reported the emulsion free radical polymerization of PDMB and its copolymerization with 1,3-butadiene, isoprene and styrene. The authors reported reactivity ratios for the co-monomer pairs; butadiene-DMB, isoprene-DMB and DMB-styrene under such conditions (*Table 1.1*). Additionally, Gilbert *et al*. reported the influence of temperature on the reactivity ratios of the butadiene-DMB pair. As it can be seen in *Table 1.1* when the reaction temperature was raised from -18 to 5 °C the r_1 value decreased 0.41 and 0.15 in case of r_2.[16]

Table 1.1: *Reactivity ratios of butadiene-DMB, isoprene-DMB and DMB-styrene for free radical emulsion polymerization at different temperatures.*

Monomer 1	Monomer 2	T (°C)	r_1	r_2
Butadiene	DMB	5	0.85	0.63
Butadiene	DMB	-18	1.26	0.78
Isoprene	DMB	-18	1.18	0.84
DMB	Styrene	-18	0.92	0.42

In the late 1950s, T. F. Yen of *The Goodyear Tyre & Rubber Co.* research division explored the stereospecific Ziegler-Natta polymerization and properties of all *cis*-1,4[17] and all *trans*-1,4[18] PDMB using a triisobutyl aluminium-titanium tetrachloride catalyst system. Reactions were carried out at room temperature using different catalyst concentrations and varying Al to Ti mole ratios. At 60 mmol of catalyst per mol of monomer and an Al:Ti of 1.00, an all *cis*-1,4 PDMB was obtained. On the other hand, at a catalyst concentration of 3-12 mmol/mol and an Al:Ti ratio of 0.25, the 100% *trans*-1,4 polymer is produced. Yen reported that both materials were crystalline powders with melting points of 189-192 °C (all *cis*-1,4) and 260-263 °C (all *trans*-1,4). Later in 2003, Priozzi and co-workers reported the crystal structure of *cis*-1,4 PDMB.[19]

In the 1960s Szwarc carried out a series of reactions with the 1,3-butadiene monomers (butadiene, isoprene and DMB). Szwarc carried out a controlled, slow addition of each of the dienes to a sample of living polystyrene which had been synthesized by anionic polymerization.[20] The objective of this work was to explore the impact of the diene monomer structure on the rate of addition to the living polystyryl anion and revealed the significant retarding effect of the electron-donating methyl group(s). The presence of one methyl group in isoprene and two methyl groups in DMB increases the electron density in the different positions of the molecule This presence of a single methyl group in isoprene has a significant effect on the electron density on carbon 1 but much less impact on the electron density of carbon 4. However, the increase in the electron density produced by the two methyl groups in DMB is clearly more significant and has a much greater impact on the reactivity of the monomer. Thus, the increased electron density on carbons 1 and 4 of DMB, makes it less susceptible to nucleophilic attack by the polystyryl carbanion and the rate of addition of DMB to the polystyryl chain-end was reportedly 60 to 70 times slower than that of butadiene while in case of isoprene the rate of addition is just roughly half that of butadiene (*Table 1.2*).

Table 1.2: *Copolymerization of living polystyrene in THF with dienes at 25 °C.*

Co-monomer	**[diene] x 10^{-3} (m./l.)**	**[PS] x 10^{-3} (m./l.)**	**$k_{1,2}$ (l./m. sec)**
Butadiene	1.8	2.16	34.6
Isoprene	2.3	3.7	18
DMB	1.7	3.9	0.55

In the late 1960s and early 1970s Yuki and co-workers reported the anionic polymerization[21] of DMB and its copolymerization with 1,1-diphenylethylene (DPE).[22] They polymerized DMB successfully in THF, benzene and *n*-heptane at different temperatures (from -78 to 50 °C) testing different initiators (*n*-BuLi and Na and K-dispersions). The experiments were carried out on a small scale, using only about 0.50 g of monomer with target molecular weights ranging from 4 to 17 kg mol^{-1}. The polymers were prepared in THF, using *n*-BuLi as initiator, and showed a microstructure rich in 1,2 units (42-86%), also referred to as vinyl content, while the polymers prepared in non-polar solvents, also using *n*-BuLi as initiator, possessed microstructures richer in 1,4 units (vinyl content of 18% in *n*-heptane and 20-31% in benzene). It is worth noting that the vinyl content obtained in *n*-heptane (18%) contrasts with results reported later by Prud'homme *et al*. and Chiang and co-workers (3% 1,2 units in *n*-hexane).[23, 24] When THF was used as an additive (from 2 to 20 mol of THF per mol of initiator) in the polymerizations carried out in benzene, microstructures with 1,2 (vinyl) content of 45-50% resulted. Clearly, solvent polarity plays an important role in determining microstructure. Yuki also showed that the vinyl content of DMB is dependent on reaction temperature; in THF the vinyl content decreases as the reaction temperature increases whereas the opposite trend is seen in non-polar solvents. The change of initiator from *n*-BuLi to Na and K-dispersion did not seem to affect significantly the microstructure of the polymers obtained in THF but showed a notable influence on the microstructure in benzene (17% 1,2 with *n*-BuLi and 42% with K-dispersion). Yuki also explored the statistical anionic copolymerization of DMB and DPE using *n*-BuLi in both benzene and THF. DPE is a monomer that cannot homopolymerize (except using metallic sodium in bulk polymerization at 100-110 °C),[25] so its reactivity ratio is considered to be 0. As a result, alternating copolymers were obtained when DPE was fed in excess with respect DMB. Various feed ratios were tested in order to calculate the reactivity ratio of DMB in a copolymerization with DPE. Thus, the calculated average reactivity ratio for DMB in benzene was 0.23 and approximately 0 in THF. Moreover, the authors observed that the formation of 1,2 units of PDMB was less favourable when copolymerized with DPE, probably because of steric effects. Yuki reported that in the presence of DPE no 1,2 addition of DMB occurred during the copolymerization in THF, while under the same conditions the homopolymerizations of DMB in THF resulted in a polymer with 42-86% 1,2 units.[22, 26] Similar observations have been recently reported by Hutchings *et al.* for the anionic copolymerization of butadiene and DPE.[27, 28] Additionally, Yuki *et al.* reported the anionic copolymerization of *trans*-stilbene with DMB, isoprene and butadiene[29] and α-methylstyrene with DMB.[30] The copolymerization of *trans*-stilbene with DMB revealed a similar behaviour to the copolymerization of *trans*-stilbene with isoprene and a different behaviour compared to the copolymerization of *trans*-stilbene with butadiene, in terms of the resulting microstructure of the diene. Yuki suggested that in the copolymerization of *trans*-stilbene with each diene, the microstructure of the dienes in the resulting copolymers was controlled mainly by steric factors. Thus, the higher steric hindrance in DMB led to copolymers with no vinyl content and almost 0% in case of isoprene while in case of butadiene the copolymers showed 12% 1,2 content of butadiene units. Regarding the reactivity ratio for the copolymerization of stilbene with each diene monomer, Yuki reported that there is almost no difference in THF where r_1 is nearly 0 for the three dienes. However, in benzene r_1 is 8.5 for DMB while Yuki quoted that r_1 is "more than 50" for the other two dienes, assuming that r_2 is 0 (*trans*-stilbene does not homopolymerize).

Later in the 1970s, Prud'homme *et al*. reported a detailed analysis, by IR and NMR spectroscopy, of the microstructure of PDMB prepared by anionic polymerization. The chemical shifts (NMR) of the monomeric repeat units of PDMB are strongly affected by the microstructure of the adjacent repeat units. This fact was attributed to the crowded protons within the polymer chain. For example, considering a 1,2 unit in the middle of a triad, the chemical shift of the CH_3 of the vinylidene group (highlighted in *Figure 1.3*) will change depending on whether it is in between 1,2 and 1,4 units or two 1,4 units, as the environment around this group is different, as shown in *Figure 1.3*.

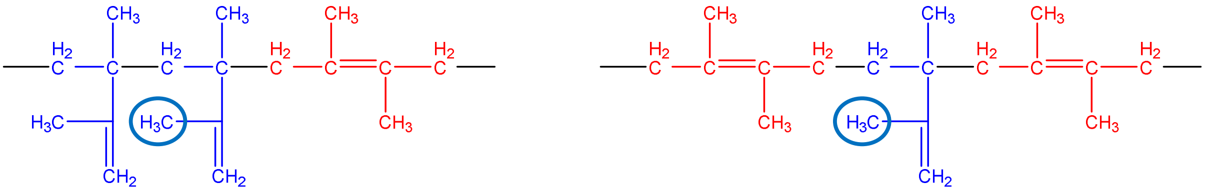
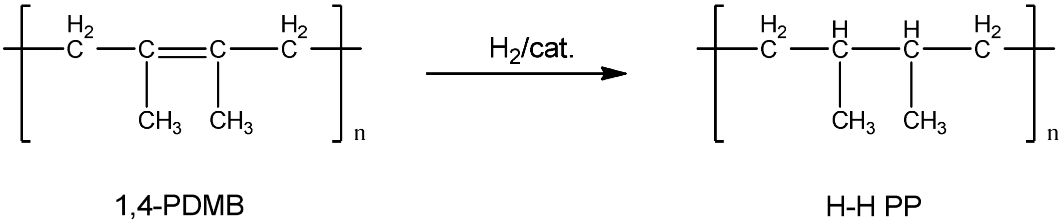


Figure 1.3: *Examples of triad in a PDMB chain: (left) 1,2—1,2—1,4 triad and (right) 1,4—1,2—1,4 triad. 1,2 units are represented in blue and 1,4 units in red.*

For this reason, the authors paid special attention to the distribution of dyads and triads of the different possible DMB units (Figure 1.2: *The possible microstructures of PDMB.Figure 1.2*).[23-31] Prud'homme reported that PDMB synthesized in cyclohexane containing 1% v/v of THF, using *n*-BuLi as initiator, at 25 °C (45% 1,2 and 55% 1,4 units) is a nearly alternating copolymer of 1,2 and 1,4 monomer units. However, a PDMB synthesized in pure THF, at -45 °C (69% 1,2 and 31% 1,4 units), has more randomly distributed sequence of 1,2 and 1,4 units. Moreover, they explored the hydrogenation of PDMB (prepared by anionic polymerization) obtaining head to head polypropylene (H-H PP), as shown in *Scheme 1.2*.[32] This synthesis and analysis of head to head polymers by hydrogenation of PDMB was further explored by Chiang and co-workers[24] and other authors.[33-39] It was reported that while PDMB rich in 1,4 units is a semi-crystalline material, the fully hydrogenated equivalent, is a totally amorphous material with a lower glass transition temperature (about -20 °C for H-H PP compared to about 5 °C for 1,4-PDMB). Chiang *et al.* also reported the influence of the vinyl content of PDMB on the thermal properties. Thus, the lower the content in 1,2 units, the lower the glass transition (ranging from -12 to 5 °C) and the higher the melting point (between 46 and 95 °C).



Scheme 1.2: *Synthesis of head to head polypropylene by catalytic hydrogenation of all cis-1,4 PDMB.*

In 1974, Yasuda *et al.* successfully synthesized PDMB by anionic polymerization using metallic K in a THF:triethylamine (2:1) mixture at 30 °C. The microstructure of the obtained polymer was 34-35% 1,2 units and 65-66% 1,4 structures.[40]

In 1976 Jenner and Khalilpour studied the impact of temperature, solvent polarity, concentration of initiator and pressure on the microstructure of DMB polymerized by anionic polymerization using *n*-BuLi as initiator.[41] The authors reported that among those parameters, the nature of the solvent influences the microstructure the most. Thus, for polymers synthesized in *n*-heptane and cyclohexane the 1,2 (vinyl) content was 14 and 12% respectively and 39-50% for the polymers prepared in ether (polar) solvents. The results of microstructure reported by Jenner and Khalilpour in alkanes (vinyl content of 12-14%) are intermediate compared to the results reported by Yuki (18% 1,2 units in *n*-heptane) and the results reported by Prud'homme and Chiang (3% 1,2 microstructures in cyclohexane). Even the presence of low concentrations (4-16 mol-% with respect the reaction solvent) of these polar solvents may increase the vinyl content up to 50%. It was also observed that increasing the temperature produces a decrease in the vinyl content in both polar and non-polar solvents which contradicts Yuki's work described above. In case of increasing pressure, it produces the opposite effect to temperature. It was reported that increasing the concentration of initiator produced a decrease in the molecular weight, and leads to polymers with lower vinyl content which is in contrast to what it is observed for butadiene.[42]

In 1980 *The Goodyear Tyre & Rubber Co.* filed a patent regarding the synthesis and analysis of rubbery tapered blocky copolymers of DMB with butadiene or isoprene with a content of DMB ranging from 20 to 80 mol-%. In this patent it is explained, in detail, the relationship between microstructure of DMB units and the final physical properties such as crystallinity, glass transition temperature or the ability of the resulting copolymer to undergo stress-induced crystallization. Henderson points out that the PDMB block is able to induce stress-crystallization in the final copolymer but both, the polybutadiene and the polyisoprene blocks, do not have this property. A microstructure of PDMB comprising of less than 20% of 1,2 units and between 60 and 65% *trans*-1,4, is required to allow stress-induced crystallisation, with the 1,2 content being the more critical parameter, since the branched 1,2 units disrupt the crystallinity. The glass transition temperature was was reported to be difficult to obtain by differential scanning calorimetry (DSC) in these copolymers, especially when the concentrations of both co-monomers were approximately equal.[43]

Although there are a number of reports discussing the polymerization and copolymerization of DMB via other mechanisms, as these are not of direct relevance to the current project, they will not be explained in detail but only mentioned. Cesca studied the synthesis of isobutylene-DMB copolymers via cationic polymerization.[44-45] In 2004, Cordoneanu and Baird published the synthesis of high molecular weight copolymers (higher than 5 x 10^5 g mol^{-1}) of isobutene and DMB, analogous to the commercial isobutene-isoprene copolymers, using a novel protic carbocationic initiator.[46] In the 1980s, Gordon 3.13 and Blumenthal published the synthesis and polymerization of a number of 2,3-disubstituted-1,3-butadienes. These monomers were synthesized using DMB as starting material and then polymerized by radical polymerization with azobisisobutyronitrile (AIBN) as initiator or by Ziegler-Natta coordination catalysts.[47] Other examples regarding copolymerization of DMB via radical polymerization are described in the literature.[48-50]

During the second half of the twentieth century and the beginning of the current one there are a few further publications regarding alternative stereospecific routes for polymerizing and copolymerizing DMB. For example radiation-induced polymerization,[51-53] photoinduced polymerization,[54] polymerization via different canal complexes and nanochannels[55-58] or via other organometallic complexes.[59-64] Also, DMB has been used in organic chemistry reactions,[65-68] especially as a reactant in Diels Alder[69, 70] and hetero Diels Alder reactions,[71, 72] and as part of organometallic complexes[73-75]

1.2. Polymers — a general introduction

Polymers have played an important role in a vast range of applications and are now ubiquitous in everyday life. As mentioned above, polymers have been around for millions of years in the form of natural biopolymers such as DNA and proteins which are essential for life. Cotton, wool and starch, also natural polymers, are examples of the first polymers used by man. Man's earliest attempts at polymer chemistry can be traced back to 1844 when Charles Goodyear patented the vulcanization of natural rubber. This process consisted of the blending of natural rubber with sulphur and white lead followed by heating. Thanks to this treatment, natural rubber chains are crosslinked to obtain a material with improved mechanical properties (e.g. tensile strength).[76]

1.3. Polymer classification

As the number of different types of polymers, structures or properties is extremely great, there are several ways of classifying polymers according to many useful criteria. The first, and most intuitive, is split them in two groups, natural and synthetic. Another example is to classify polymers according to their composition i.e. the number of monomers/co-monomers and their sequence within the polymeric chain. Alternatively, polymers can be classified according to their skeletal structure/architecture which may have an important impact in the behaviour of the material.

1.3.1. Classification according to polymer composition

A polymer can be composed of just one type of monomer, a homopolymer, or two or more monomers leading to copolymers. Due to the huge number of available monomers, copolymerizations can lead to a very wide variety of possible structures and compositions, as shown in *Figure 1.4*.

These different compositions play an important role in the final properties of the resulting material. Copolymers can be divided in two groups, statistical copolymers and block copolymers. Both groups may be further subdivided into more specific kinds of copolymers. Alternating and random copolymers belong to the group of statistical copolymers while multi-block and graft are specific types of block copolymers.

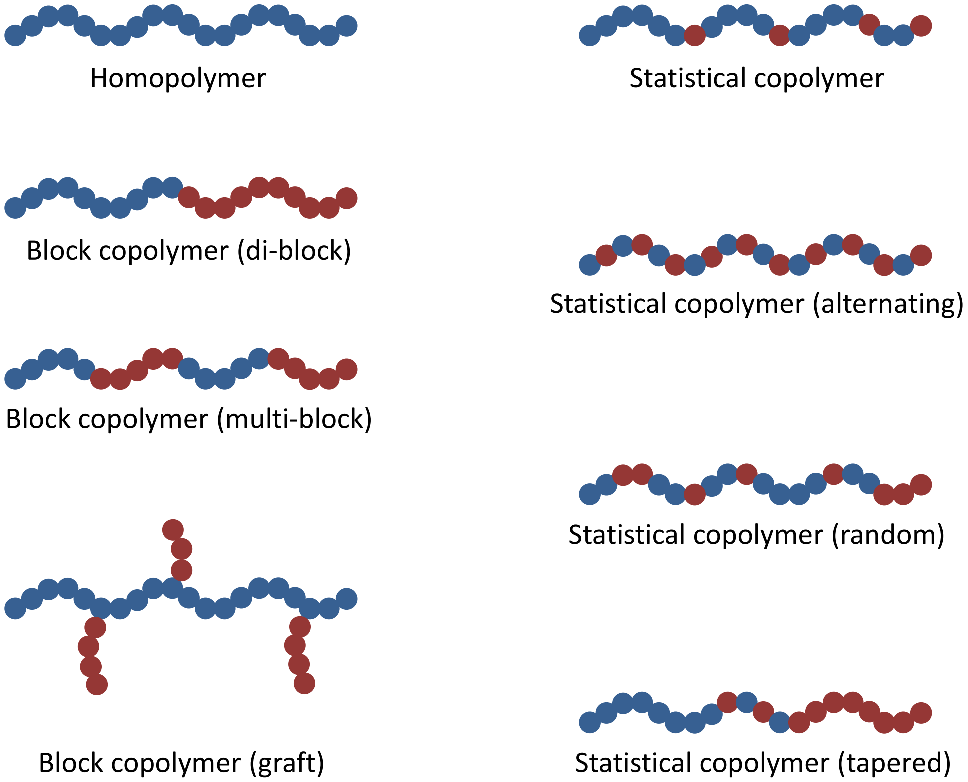


Figure 1.4: *Types of (co)polymer sequence.*

1.3.1.1. Statistical copolymers — copolymerization kinetics

Statistical copolymers are synthesized in one-pot polymerizations where all the monomers (two or more) are copolymerized simultaneously. Under such conditions, the sequence of monomers is statistically controlled according to copolymerization kinetics. As a consequence of the different reactivity of the monomers and propagating species, a compositional drift along the growing chain may result. The instantaneous copolymer composition is commonly explained using, among others, a terminal model of two monomers, monomer 1 (M_1) and monomer 2 (M_2). In this model it is assumed that the reactivity only depends on the terminal repeat unit of the growing chain and the rest of the propagating chain is neglected. In this way, for describing the addition of the two monomers into the growing chain, four possible propagation reactions are possible with rate constants k_{11}, k_{12}, k_{21} and k_{22} (*Figure 1.5*).[77, 78]

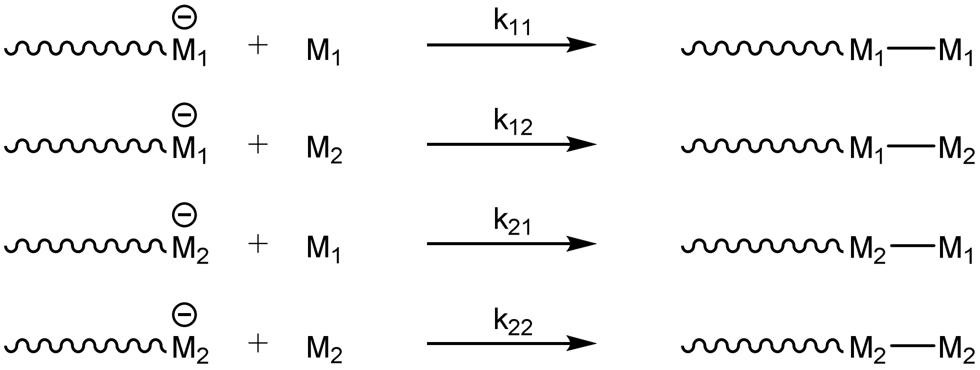


Figure 1.5: *Four propagating rate constants for the anionic copolymerization of two monomers assuming the reactivity of the chain end only depends on the terminal unit.*

Following this model, k_{11} and k_{22} represent the rate constants of self-propagation while k_{12} and k_{21} represent the rate constants for cross-propagation. From these propagation rate constants the reactivity ratios r_1 and r_2 may be calculated as follows:

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

The reactivity ratios are unique for each pair of co-monomers (and reaction conditions) and they describe the tendency of a specific pair of monomers to undergo either self-propagation or cross-propagation. Therefore, reactivity ratios give an indication of the likely structure/monomer sequence of the resulting copolymer and for many statistical copolymers (not alternating and not random) there can be significant compositional drift as a consequence of the different reactivity between the pair of monomers as the polymerization takes place. For this reason, reactivity ratios are used to elucidate the possible structures in statistical copolymerizations.

1. $r_1 = r_2 = 0$: the resulting copolymer will be an alternating chain of monomers 1 and 2.

2. $r_1 = r_2 = 1$: a truly random copolymer, where the probability of finding a given type of monomer unit at certain point in the chain is determined by the feed ratio.

3. $k_{11} > k_{12}$ then $r_1 >> 1$: M_1 will prefer to homopolymerize. Similarly, if $k_{22} > k_{21}$ then $r_2 >> 1$ and M_2 also will have tendency to homopolymerize rather than copolymerize. In this situation (r_1, $r_2 >> 1$) a "blocky" copolymer (chains with relatively long sequences of each monomer) will be obtained in the absence of termination or chain transfer.

4. $r_1 >> r_2$: a gradient (or tapered) copolymer is obtained.

5. $0 > r_1$, $r_2 > 1$: the result is a statistical copolymer.

There are an almost infinite number of outcomes for a statistical copolymerization, so the previous list has to be understood as a simplified summary of the possible cases.[77, 78] The reactivity ratios are rarely 0 or 1, and therefore alternating and random copolymers are not common.[79] The nature of the monomers involved in the polymerization is of great importance. In statistical radical copolymerization, one of the advantages is the possibility of copolymerizing monomers with very different structures. These monomers react with relatively small differences in their reactivity. In contrast, in statistical ionic copolymerization monomer reactivity is strongly dependent on the structure of the monomer. Relatively small changes in monomer structure can generate significant changes in reactivity. As a consequence ionic statistical copolymerization is only possible for limited pairs of monomers with similar structures.[80]

Statistical copolymers often have properties which are intermediate between the constituent homopolymers depending on the relative amount of the monomers that compose the final material. Statistical copolymers may show a single glass transition (T_g) if the monomers are distributed in a random manner but may show more than one T_g in the case of copolymers with blocky sequences. The precise value of T_g in a random/statistical copolymer can be predicted, taking into account the mole fraction of each component within the final copolymer and in such cases T_g approximates to a linear function of composition.[81] As many properties of the final polymer are closely related to the monomer sequence along the chains, understanding the statistics in the addition of each monomer to the growing chains has acquired great importance.[77] An investigation into reactivity ratios and the impact on thermal properties is a further aim of this project.

1.3.2. Classification according to polymer architecture

Polymer can have different skeletal structures or architectures which have a significant impact on their properties. From the point of view of the polymer architecture, the possibilities are endless but broadly speaking, polymers can be classified into three main categories: linear, branched and crosslinked, as shown in *Figure 1.6*.

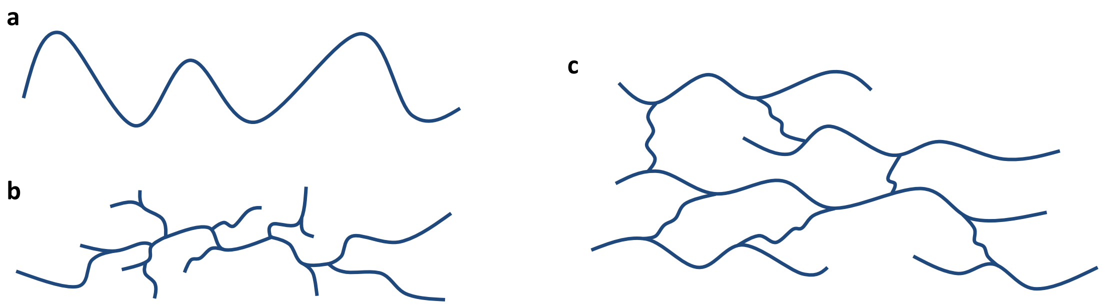


Figure 1.6: *Examples of polymer architectures: a) linear, b) branched (randomly branched) and c) crosslinked (network).*

Linear polymers are the simplest type of architecture and consist of macromolecular chains without any branching. The introduction of branching points in the polymeric structure opens the door to a wide range of possible architectures (i.e. stars, comb or H-shaped). This branching can be random, leading to irregular branched polymers, or controlled, leading to perfectly regular branched architectures. When the degree of branching is high the polymers are termed hyperbranched. If an elevated degree of branching is combined with perfectly regular structures, the obtained polymers are referred to as dendrimers. Crosslinked polymers are composed of chains interconnected by several branching points creating a network-like macromolecule. These networks can have a higher or lower degree of crosslinking which affects greatly the properties.[82]

1.4. General strategies for polymer synthesis

Polymers can be synthesised via many different polymerization reactions. Historically, these reactions have been divided into two general groups, taking into account their mechanisms: step-growth polymerization and chain-growth polymerization.

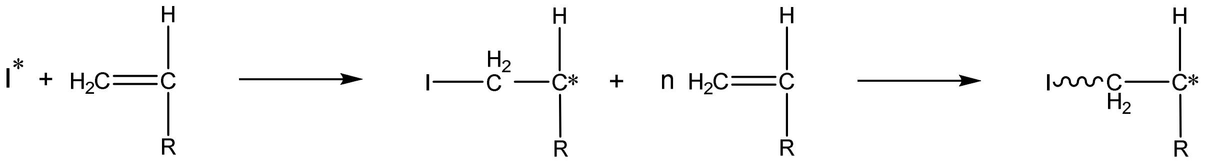
This scheme has also been used for distinguishing between polymers according to their synthetic mechanism. The evolution of these polymerization processes over the years has opened new possibilities of tailored materials with promising applications in a wide range of fields.

1.4.1. Step growth polymerization

Step growth polymerization consists of many independent steps where monomers are linked together by common organic reactions. The process carries on as a sequence of these accidental and independent reaction events until final chains are formed. In this kind of polymerizations monomer is consumed in the early stages of the process and initiator is not needed. These reactions can be further subdivided into two groups taking into account whether by-products are eliminated during the process (polycondensation) or not (polyaddition).[83]

1.4.2. Chain growth polymerization

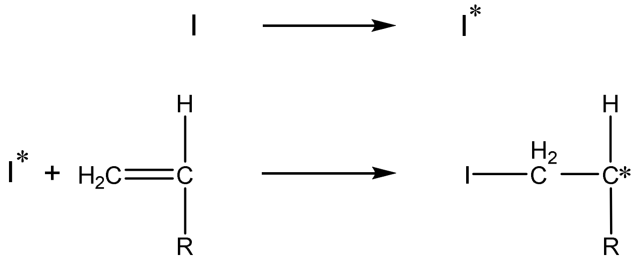
Chain growth polymerization, also referred to as addition polymerization, involves the synthesis of polymeric chains by the addition of the activated monomeric units, one by one, to the growing chain. Chain growth reactions are usually carried out by opening of the double bond of alkene monomers with an initiator (e.g. free radical or ionic). In this case no by-products are produced. A general mechanism of chain growth polymerization can be described as follows:



Scheme 1.3: *Chain growth polymerization.*

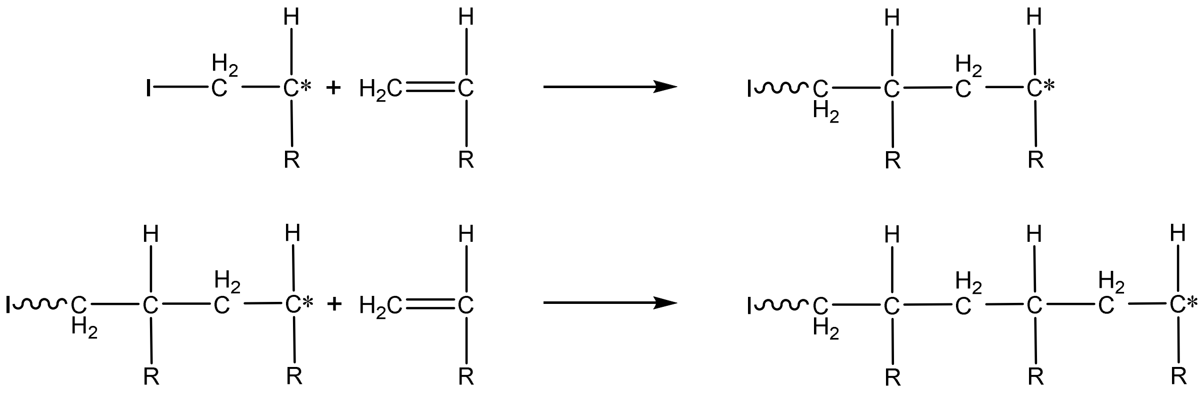
Chain growth polymerization is considered a three steps process:

Initiation is the process where the active species (initiator) reacts with the first monomer molecule giving a reactive unimer.



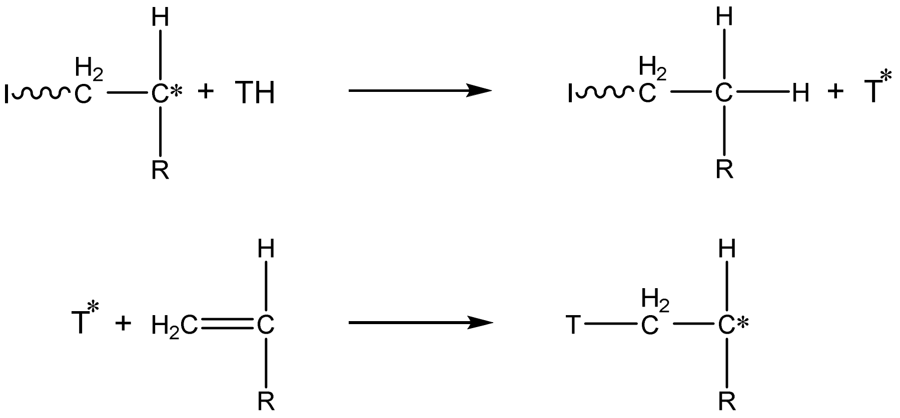
Scheme 1.4: *Initiation in chain growth polymerization.*

During propagation, many identical chain-growth reactions occur, stimulated by the products obtained from the initiation step. The active species (radical, ion etc) are always carried at the end of the chain so the reactions are always carried out at that location.



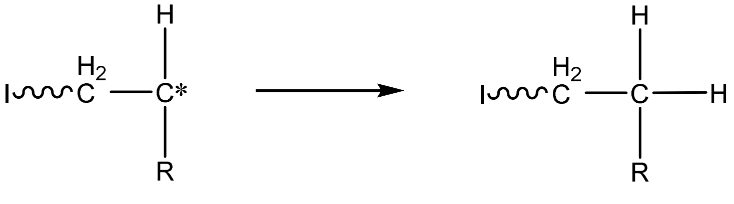
Scheme 1.5: *Propagation in chain growth polymerization.*

An additional process that might take place during propagation under certain conditions is chain transfer. This process consists of the transfer of the active propagating species to a molecule of solvent (chain transfer to solvent) or monomer (chain transfer to monomer) followed by the re-initiation of chain growth. As this re-initiation does not have to occur only in chain ends but can occur on the polymer backbone (chain transfer to polymer), chain transfer processes can lead to branched macromolecules.



Scheme 1.6: *Chain transfer process. TH may be a molecule of solvent or monomer.*

Propagation occurs until either the monomers are completely consumed or the active centres are deactivated, also called termination step (*Scheme 1.7*).



Scheme 1.7: *Termination in chain growth polymerization.*

1.5. Controlled polymerization methods — Ionic polymerizations

In the distant past, control over molecular weight, molecular weight distribution and polymer architecture was considered impossible or very limited. However, in many cases, for many applications, the control over these parameters is of significant importance. This control is nowadays achieved thanks to polymerization techniques developed in the second half of the twentieth century. These mechanisms are the family of the controlled radical polymerizations and ionic polymerizations, with anionic polymerization being the gold standard.

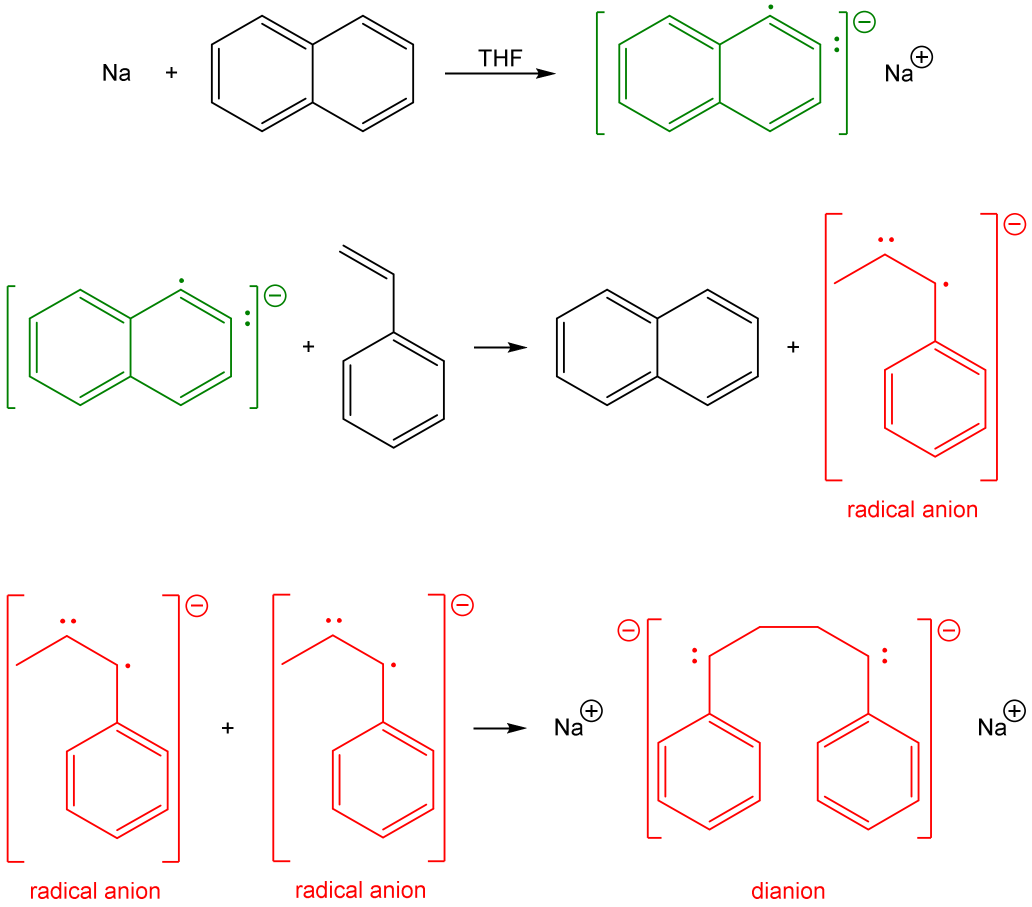
As mentioned above ionic polymerization is a kind of chain growth process in which the reaction begins when a monomer reacts with an initiator to create an ionic active species. Propagation follows the same process already described for chain-growth polymerizations. In contrast with radical polymerization, ionic polymerization is in many cases greatly affected by the nature of initiator or solvent. In radical polymerization, collision of two active species normally leads to the termination by recombination or disproportionation. In the case of ionic polymerization recombination is not possible and hence, the life and concentration of the active molecules is constant. In many cases, ionic polymerization may proceed in the complete absence of chain transfer and termination reactions. Under such conditions the obtained macromolecules are called living polymers.

Ionic polymerization is considered cationic when the active terminal group is positively charged. On the other hand, if the active terminal group carries a negative charge the ionic polymerization is referred to as anionic polymerization.[84] As all the polymers in this research project were synthesized by anionic polymerization, this technique will be described in detail in the next section.

1.6. Living anionic polymerization

Anionic polymerization involves the synthesis of polymers via negatively charged active species. This technique was initially exploited more than 100 years ago by the rubber producing industry with reports in the first decade of the 20th century of the generation of viscous materials obtained from the anionic polymerization of dienes with alkali metals.[85] Even though there are many early publications about anionic polymerization, the living nature of this procedure was first described by Szwarc and co-workers in 1956, who synthesized polystyrene in THF with sodium naphthalide as the initiator, as shown in *Scheme 1.8*.[86] After the reaction of naphthalide with sodium, a green coloured species was obtained which immediately reacted with styrene obtaining a radical anion with a characteristic dark red colour. The use of the term *living* originally described a mechanism where the polymer chain could only propagate and not suffer chain transfer or irreversible termination.[87]

Szwarc's discovery is considered an important milestone in polymer science and led other researchers in both industry and academia to apply this concept of livingness to other monomers. Also, other living polymerization techniques were developed after Szwarc's breakthrough. Anionic polymerization is a technique that requires strict reaction conditions as it is a very sensitive to impurities and therefore the number of monomers suitable for polymerization by this technique is limited. Currently, anionic polymerization is the most common technique used in the tyre and rubber industries.[88-91]



Scheme 1.8: *Swarc's mechanism for the polymerization of styrene with sodium naphthalide.*

1.6.1. Criteria for living polymerization

For any polymerization mechanism to be considered a truly living process, a list of criteria must be fulfilled — these criteria are described in detail by Hsieh and Quirk.[42]

Criterion 1: *Polymerization proceeds until all of the monomer is consumed. Further addition of monomer results in further polymerization.*

This first criterion appears in the original report about the livingness of anionic polymerization by Szwarc and co-workers in 1956.[86] It is probably the most relevant criterion when regarding whether a polymerization is living and suggests that all the growing chains in the system must keep their active centres while the experiment is being carried out. In order to verify this criterion, size exclusion chromatography (SEC) can be used before and after the addition of fresh monomer. If the system is living the molecular weight of the polymer after the addition of new monomer has to be higher (elution times lower) than before the addition. In case of chain termination or chain transfer reactions occurring during the process, the dead macromolecules will not increase the molecular weight when more monomer is added.

Criterion 2: *The number average molecular weight, M_n, is a linear function of conversion.*

This criterion is based on the fact that the degree of polymerization is related to the degree of monomer conversion and the stoichiometry of the reactants. The number average molecular weight is related to the mass (in grams) of the monomer by *Equation 1.1*:

$$\boldsymbol{M_n = \frac{g_{monomer}}{mole_{initiator}}} \qquad \textbf{Equation 1.1}$$

Hence, at an intermediate degree of conversion *Equation 1.1* becomes:

$$\boldsymbol{M_n = \frac{g_{monomer\ consumed}}{mole_{initiator}}} \qquad \textbf{Equation 1.2}$$

This linear relationship is not valid if chain transfer reactions occur as the number of chains increases. However, if termination reactions occur (in the absence of chain transfer), the total number of chains remains unaltered and the M_n will still be a linear function of conversion. Thus, this criterion will detect chain transfer reactions but it is not sensitive to partial termination. Alone, this criterion is not robust enough to elucidate if a system is truly living or not, since a linear plot will be obtained even if termination processes take place, if there is not chain transfer reactions.

Criterion 3: *The number of polymer molecules (and active propagating sites) is constant, which is sensibly independent of conversion.*

This criterion is subject to the limitations explained in *Criterion 2*. This criterion is not met if there are chain transfer reactions, since they will increase the number of polymer molecules. However, this criterion is not a good diagnostic test for termination reactions as the presence of termination will not change the total number of polymer molecules. Therefore, *Criterion 2* and *Criterion 3* should be used only in conjunction with other criteria.

Criterion 4: *The molecular weight can be controlled by the stoichiometry of the reaction.*

Again this criterion cannot be used alone for determining if a system is living. This criterion depends on the quantitative utilization of the initiator before the monomer is completely consumed. As shown in *Equation 1.1*, for a living polymerization, the target molecular weight can be calculated as the ratio between mass of monomer and the moles of initiator. Therefore, this criterion is sensitive to impurities, since the presence of impurities can reduce the number of active molecules of initiator and result in an increase in the molecular weight. Chain transfer reactions can also reduce molecular weight by prematurely terminating chains and initiating new ones, thus chain transfer reactions add active chains into the system leading to a reduction of the molecular weight.

Criterion 5: *Polymers with a narrow molecular weight distribution are produced.*

Generally, a molecular weight distribution is considered as narrow when Đ is equal or lower than 1.10. Low dispersity values are a consequence of: a) all active centres being introduced at the outset of the polymerization, resulting in nearly simultaneous initiation of all chains, b) the absence of termination or chain transfer, c) irreversible propagation, d) all active species having equal reactivity towards the monomer and e) the growth of each macromolecule arising by the consecutive addition of monomers to an active terminal group.

However, a living polymerization can result in a broad molecular weight distribution in certain cases. Additionally, relatively narrow molecular weight distributions can be also obtained by other non-living systems such as the already mentioned RDRP techniques (Đ values of 1.10-1.50). For this reason this criterion cannot be used alone.

Criterion 6: *Sequential monomer addition leads to the synthesis of block copolymers*

This criterion is one of the key tests of whether a polymerization is living. As in case of *Criterion 1* it states that upon addition of further monomer, the polymerization continues. This characteristic allows for the production of block copolymers, if a different monomer is added to the system. This criterion is extremely sensitive to termination and chain transfer reactions, which lead to heterogeneities which can be detected by SEC.

Criterion 7: *Chain-end functionalized macromolecules can be produced in quantitative yield.*

In principle, if a functionalized terminating agent is used it can quantitatively react with the active chains in a controlled termination. However, most functionalization reactions do not proceed quantitatively. Therefore, this is not an ideal method for testing whether a polymerization is actually living.

Criterion 8: *The kinetic plot of rate of propagation versus time is linear as represented in Equation 1.3.*

$$\ln\frac{[M]_0}{[M]} = k_{obs}t \qquad \textbf{Equation 1.3}$$

$[M]_0$ ≡ initial monomer concentration

$[M]$ ≡ monomer concentration during polymerization

k_{obs} ≡ rate constant of propagation

t ≡ time of polymerization

Criterion 9: *Determination of linearity of a kinetic plot of the left side of Equation 1.4 versus time, t.*

$$\ln\left(1-\frac{[I]_0}{[M]_0}\overline{DP_n}\right) = -k_p[I]_0t \qquad \textbf{Equation 1.4}$$

$[I]_0$ ≡ initial initiator concentration

k_p ≡ rate constant of polymerization

DP_n ≡ number average degree of polymerization

A plot of the left side of *Equation 1.4* vs time is a simple way of determining whether or not chain transfer or termination is present in the system. In the absence of both, a linear plot is obtained.

It can be concluded that no single criterion can be used for determining if a system is living, as each criterion is sensitive to different parameters. Only by utilising all of the criteria together, it is possible to define a system as truly living. Anionic polymerization is a process that can fulfil, in most cases, every criterion listed above and so it can be considered as a truly living system. However, in some cases special measures need to be taken e.g. anionic polymerization of MMA at room temperature is not a living process and therefore must be carried out at low temperatures. The possibility of obtaining well-defined polymers with a wide range of molecular architectures is also a characteristic of anionic polymerization that few other techniques can match.

Living anionic polymerization is a versatile tool for the production of consistent and well-defined polymers. It provides excellent control over a number of structural and compositional parameters such as molecular weight and molecular weight distribution, branching, composition (in the case of synthesis of copolymers) and microstructure (when dienes are polymerized). Moreover, it offers the possibility of introducing chain-end functionality. As a living polymerization, the absence of termination or chain-transfer reactions, allows the propagating species to remain active even after all the monomer has been completely consumed.

Living anionic polymerization can be carried out with a variety of monomers (though limited), solvents, initiators and end-capping agents. The choice of monomer, solvent or initiator may have an effect on different parameters of the final material. For example, the choice of solvent can have an impact on microstructure (in the case of dienes), rate of polymerization and copolymerization kinetics.

1.6.2. Monomers

Carbanions are strongly basic nucleophiles, which limits the range of monomers which may be used in anionic polymerization. Thus, electrophilic groups or proton-donating groups such as amino, hydroxyl or carboxyl cannot be present in the monomer or, if present, they have to be protected by conversion to a suitable derivative as these groups may terminate the polymerization. Moreover, any monomer successfully used in anionic polymerization must be able to form stable carbanions under polymerization conditions. Monomers that are susceptible to anionic polymerization are generally classified into two main groups: i) vinyl, diene and carbonyl-types and ii) cyclic. In the first group, bifunctionality is provided by one or more double bonds, while in the second group it is provided by a ring opening reaction triggered by a nucleophilic attack. A list of typical monomers susceptible to anionic polymerization is shown in *Table 1.3*.[42, 92]

Table 1.3: *List of suitable monomers for anionic polymerization.*

Vinyl monomers	Dienes	Styrenes	Methacrylates
	Vinyl pyridines	Alkyl acrylates	Nitroethylenes
Cyclic monomers	Lactones/lactides	Lactams	Carbonates
	Cycloethers	Siloxanes	Sulphides

For vinyl monomers, the double bond must have substituents such as aromatic rings, double bonds, ester, cyano, carbonyl or sulfonic groups which stabilize the negative charge, promoting the nucleophilic attack from other species. That is also the case for 2,3-dimethylbutadiene (DMB) which is able to stabilize the negative charge due to the presence of two conjugated double bonds, as shown in *Figure 1.7*.[92]

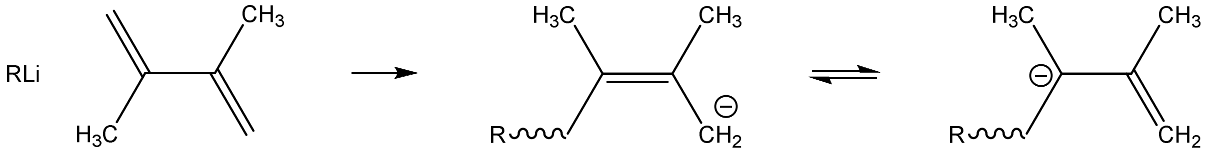


Figure 1.7: *Stability of the DMB molecule carbanion.*

The polymers and copolymers synthesised in this project will be prepared using monomers from the vinyl group, and specifically dienes (butadiene and DMB) and styrene (and some derivatives).

1.6.3. Initiators

A variety of initiators have been successfully used for anionic polymerization over the years. These initiators include alkali metals, radical anions, alkyl-lithium compounds, diphenylmethane based carbanions or ester enolate initiators.

Among them, the alkyl-lithium compounds (*Figure 1.8*) are the most widely used because of their high efficiency as anionic initiators. Moreover, these compounds are readily available commercially in a reasonable selection of common hydrocarbon solvents such as hexane and cyclohexane. Alternatively they can be easily synthesized by the reaction of lithium metal with the corresponding alkyl chloride.

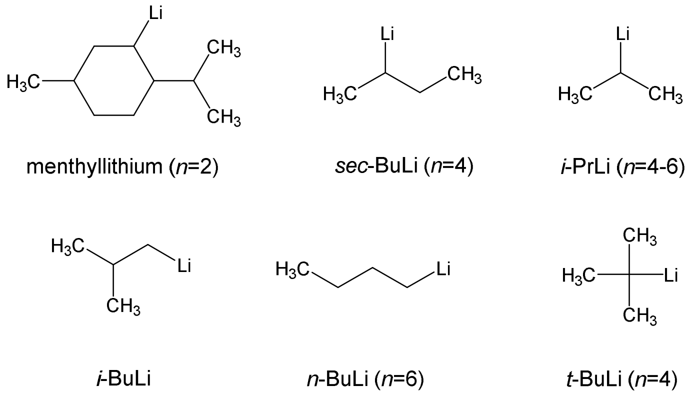

menthyllithium (*n*=2)
sec-BuLi (*n*=4)
i-PrLi (*n*=4-6)
i-BuLi
n-BuLi (*n*=6)
t-BuLi (*n*=4)

Figure 1.8: *Chemical structure of alkyl-lithium initiators used in anionic polymerization of styrene and dienes. n value in brackets represents the degree of association of the different alkyl-lithiums being n=2 (dimer), n=4 (tetramer) and n=6 (hexamer).*

The reactivity of these organometallic compounds as initiators (in non-polar solvents) depends strongly on the degree of association, *n*, in solution. *n*-BuLi and *i*-PrLi in non-polar hydrocarbon solution are aggregated as hexamers ($n = 6$). The degree of aggregation is a function of the steric bulk of the alkyl fragment. If there is chain branching in α- or β- position, *n* drops to 4 and the compound aggregates in the form of tetramers. Only when the alkyl group is very bulky it does the compound aggregate as a dimer ($n = 2$). The less aggregated (or the lower the degree of association) the more reactive they are.[93] However, from a practical point of view, commercial *t*-BuLi is reported to be very unreactive for styrene polymerization even having a bulky alkyl group. It was reported that this fact is due to a 4-5% content of impurities present in the commercial *t*-BuLi. Parameters that affect the degree of association and hence, the reactivity, are the kind of monomer to be polymerized, solvent, temperature or concentration.[92] Aromatic solvents tend to decrease the degree of association to a certain extent. However, a polar solvent (e.g. THF) or the addition of a Lewis base is needed to promote complete dissociation. As a consequence, reaction rates in polar solvents are much higher than in aromatic solvents and these in turn are higher than in aliphatic solvents. In general, reaction rates for the initiation (R_i), *Equation 1.5*, of styrene and dienes (monomers used in this project) can be summarized as follows:

Styrene polymerization: menthyllithium > *sec*-BuLi > *i*-PrLi > *i*-BuLi > *n*-BuLi > *t*-BuLi

Diene polymerization: menthyllithium > *sec*-BuLi > *i*-PrLi > *t*-BuLi > *i*-BuLi > *n*-BuLi

$$\boldsymbol{R_i = k_i K_d [BuLi]^{1/n} [M]}$$ **Equation 1.5**

k_i ≡ rate constant of initiation

K_d ≡ dissociation constant

For example, it is observed in *Equation 1.5* that the kinetics of initiation exhibit a one sixth order dependence on initiator concentration for *n*-BuLi (n = 6) while for *sec*-BuLi (n = 4) it is a one fourth order dependence. The most commonly used alkyl-lithiums are *sec*-butyl lithium (*sec*-BuLi) and *n*-butyl lithium (*n*-BuLi). They are employed commercially in the syntheses of polystyrene and polydienes. In the case of polydiene syntheses, the use of these initiators leads to microstructures with a high 1,4-content (> 90%) in non-polar solvents. *n*-BuLi shows a high degree of aggregation (usually hexameric) and higher reaction temperatures are required. *sec*-BuLi is considered a good initiator for the polymerization of styrene, because the rate of propagation is lower than the rate of initiation. Generally a rapid initiation is preferable. For that reason *sec*-BuLi is preferred over *n*-BuLi for the synthesis of both polystyrene and polydienes. Solubility of *sec*-BuLi in polar solvents such as

THF is also a good characteristic which is favourable for its use. However, in industry *n*-BuLi is preferred over *sec*-BuLi because of its lower price.

These initiators are also used for the synthesis of statistical/random copolymers of styrene and dienes. However, large differences between styrene and diene reactivity makes it necessary in some cases, to add a small amount of an alkali metal alkoxide or Lewis base additive, which act as randomizers if random sequences are desired.[42]

1.6.4. Solvents

The range of suitable solvents for anionic polymerization is limited as a consequence of the high reactivity of the initiators and propagating species present in the system. The choice of solvent for the anionic polymerization of styrene and dienes is restricted to ether solvents (in case of dienes) aromatic hydrocarbons, alkanes (not in case of styrene) and cycloalkanes. Protic and halogenated solvents cannot be used in anionic polymerization.

In case of using alkanes and toluene as the solvent, chain transfer reactions can occur in the presence of Lewis bases at relatively high temperatures. Benzene and toluene result in greater initiation and propagation rates than alkanes. Though, under certain experimental conditions both solvents can undergo chain transfer and metalation reactions. The contribution of these chain transfer reactions increases as the temperature increases and also in the presence of polar additives such as ethers, metal alkoxides or amines.[42]

1.6.5. Impurities

Living anionic polymerization as a technique is very sensitive to impurities. As explained previously, initiators and propagating carbanionic species are highly reactive and they are highly susceptible to reactions with environmental impurities such as water, carbon dioxide and oxygen or other protic impurities. These impurities react with the active centres leading to undesired premature terminations and in some cases to chain coupling. For this reason a very important feature of any living anionic polymerization is the strict elimination of all potential impurities.[42] At a laboratory scale, this is accomplished by; a) the thorough purification and degassing of all monomers, reagents and solvents used in the polymerization and b) using high vacuum techniques[92, 94] with specialized glass reaction apparatus (thoroughly cleaned) which is described in more detail in the Experimental section.

If necessary this kind of polymerization can also be carried out under an inert gaseous atmosphere such as nitrogen or argon.

1.7. Mechanical properties of polymers

The mechanical properties of a material are physical properties that a material shows when it is submitted to different forces. As has been already mentioned, polymeric materials are widely used for various applications due to their exceptional and versatile mechanical properties, at a low cost. The mechanical properties of a macromolecular material are therefore of great importance however, these properties are highly dependent on many different parameters, which makes very difficult to classify these polymers according to their mechanical properties. These parameters are not only structural and compositional but also include external variables such as temperature. With regard to the structural parameters, mechanical properties are affected for example by molecular weight, crosslinking, polymer architecture, co-monomers, presence of plasticizers or fillers, blending or crystallinity. Examples of external variables include temperature and thermal history, pressure, stress/strain amplitude, type of deformation or presence of moisture around the polymer.

Currently, many different mechanical tests are available including creep tests, stress-relaxation tests, dynamic mechanical tests and stress-strain tests. Among them, stress-strain (tensile) tests are one of the most used. *Figure 1.9* shows an example of typical stress-strain curves for different behaviours of polymers.

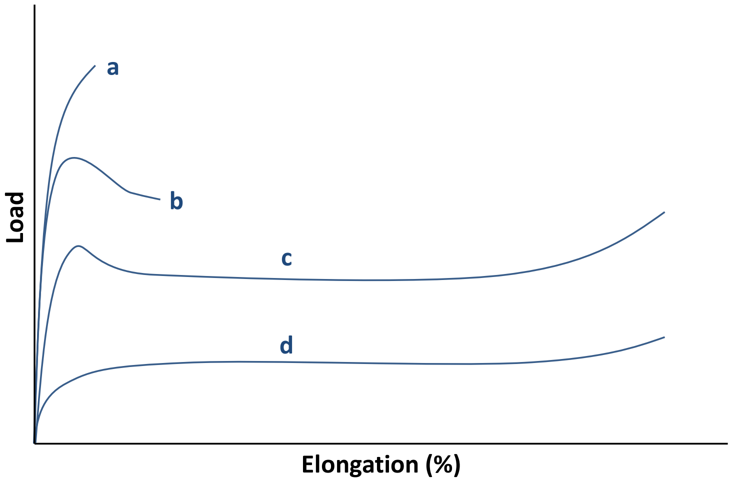


Figure 1.9: *Examples of Load vs Elongation curves for different types of polymer behaviour: a) brittle, b) ductile, c) cold drawing and d) rubber-like behaviour.*

Curve (a) shows the brittle behaviour of a solid polymer, way below its T_g. Stress increases until the breaking point at very low deformations. When the sample temperature gets closer to but still below the T_g, the polymer behaves similarly to a ductile metal (*Figure 1.9b*). The stress reaches a maximum before the yield point. Curve (c) shows a phenomenon called necking or cold drawing. After stress maximum, deformation occurs easily at lower constant stress up to 1000% elongation when the fracture point is reached. This behaviour is observed when the solid polymer is very close but still below to its T_g. Curve (d) shows an elastic rubber-like behaviour.[95, 96]

1.7.1. Stress-induced crystallization

Certain elastomers show a property referred as to strain-induced crystallisation or stress-induced crystallisation. This phenomenon consists of an ordering of the polymer chains when a sufficient stress is applied. As a result of this alignment, the degree of order increases and the polymer is able to crystallise. Once the stress is released the crystallised elastomer returns to the rubbery state.[97] This property was recognized in natural rubber (a polymer of isoprene with minor organic impurities and water) around two hundred years ago and has been exploited ever since. However, this phenomenon was formerly discovered by Katz in 1925 and has been extensively studied both from a theoretical and experimental perspective. Natural rubber has always been considered a material with excellent mechanical properties. These features are usually attributed to its ability to stress-crystallise.[98-100]

In the case of natural rubber, the crystallinity attained upon elongation is ruled by the microstructure (100 % content in *cis*-1,4 structures) of the polymer backbone and a content of roughly 6% of natural non-rubber components (proteins, phospholipids, carbohydrates and metal ions). High levels of stress-crystallizability are possible due to the high stereoregularity of the polymer backbone. This high regularity is observed in natural rubber which makes its performance superior in comparison to synthetic rubbers. It has been observed that stress-crystallisation improves the resistance to crack growth of the materials. Materials that show this characteristic have better fatigue properties than the materials that do not have it.[97, 99]

The strain/stress induced crystallisation has been analysed by a number of techniques including X-ray diffraction, infrared absorption, NMR, birefringence or electron microscopy.[99, 101, 102]

1.8. Aims and objectives

The present research was in part motivated by academic curiosity but also in part by potential industrial application. *Synthomer Ltd.*, the main sponsor of the project, manufacture a range of products from natural and synthetic rubber so this work is of direct interest to them. Natural rubber is a material with good properties (e.g. stress-crystallization) that has been exploited extensively over the years. However, the supply of natural rubber is not enough to meet demand. Additionally, a small proportion of the population are allergic to natural rubber[103] and the use of natural rubber latex in gloves for medical applications becomes a risk. Although the synthetic rubbers represent an alternative, most of them, especially those produced by anionic polymerization, do not show stress-induced crystallization, which is a highly desirable property as described in the previous section. Given that PDMB has been shown to display this feature,[43] it makes DMB an interesting monomer to explore. The overarching aim of this project is to explore the properties and characteristics of polymers and copolymers of DMB produced by living anionic polymerization. Syntheses will be carried out in one-pot reactions. Special emphasis will be put on the impact of various reaction conditions (e.g. solvent polarity) on the microstructure of DMB polymers. One goal is to obtain PDMB with a microstructure that allows the polymers to be stress-crystallizable. According to Henderson[43] the range of microstructures for obtaining stress-crystallization in PDMB is < 20% of 1,2 units and 60-65% of *trans*-1,4 structures.

First, the synthesis of lower (10 kg mol^{-1}) and higher (> 50 kg mol^{-1}) molecular weight homopolymers will be described. Although the synthesis of DMB homopolymers was already described in the litrature, there are discrepancies between different authors about the effect of reaction conditions on the microstructure of PDMB. For example, Yukie *et al.* reported a vinyl (1,2) content of 18% when PDMB was synthesized by anionic polymerization in *n*-heptane while Prud'homme *et al*. and Chiang and co-workers reported a vinyl content of 3% in *n*-heptane under similar conditions. Additionally, the synthesis of DMB homopolymers was used for learning the techniques used throughout the present work in a simple homopolymer system. Therefore, the first objective is to test/understand the impact of different experimental parameters such as temperature and solvent polarity on the microstructure of the resulting DMB homopolymers and to compare the obtained results with the reported previously in the literature. The resulting homopolymers will be analysed by ^{1}H-NMR (microstructure), SEC (molecular weight and dispersity) and DSC (thermal properties). Special emphasis will be put in testing if the obtained homopolymers show any inherent crystallization, which is a property that polybutadiene and polyisoprene synthesized by anionic polymerization are not capable of. Additionally, solubility experiments will be carried out in order to obtain qualitative information about, for example, processability and crystallinity of the obtained polymers.

Anionic polymerization is widely used in industry to produce statistical copolymers with a wide variety of properties for many different applications. The most relevant example is the butadiene/styrene pair copolymerized in solution by anionic polymerization, first marketed as *Solprene 1205* by *Phillips* in 1962. Zelinski at and co-workers discovered that the statistical copolymerization of this pair gave as a result a tapered block copolymer. The addition of small amounts of ether or tertiary amine was necessary for avoiding the block formation. However, this addition of polar compounds incresases the vinyl addition of the diene which have an impact in certain properties (for example an increase of glass transition temperature).[42] The synthesis of a series of statistical copolymers, in different polarity solvents, of DMB with butadiene, styrene and 1,1-diphenylethylene (DPE) is proposed. The goal is to understand the copolymerization kinetics of DMB with those comonomers. The influence of those comonomers on the physical properties (solubility, T_g, etc.), as well as on the microstructure of DMB will be studied. As a key purpose, the reactivity ratios of each pair DMB/comonomer will be calculated as, to the best of our knowledege, no previous reported reactivity ratios were found for the proposed pairs of comonomers in the literature, which may add a new valuable information from both academic and industrial perspective. Then, the impact of the resulting co-monomer sequence on the resulting physical properties will be explored. In case PDMB can crystallise, it will be studied if the copolymers retain or not that inherent crystallinity.

It is also proposed to investigate the synthesis of randomly branched polymers of DMB via anionic chain transfer polymerization. The synthesis will be adapted from the so called Strathclyde route originally developed for radical polymerization. Divinylbenzene (DVB) will be used as branching agent and toluene acts as both solvent and chain transfer agent, with sodium and potassium *tert*-butoxide used to promote chain transfer. Different concentrations of both DMB and DVB will be tested in order to balance the extent of crosslinking and chain-transfer with the aim of inhibiting crosslinking and producing soluble branched copolymer. Additionally, the influence on the microstructure of the obtained polymers of the two butoxides will be tested and compared.

Finally, the possibility of scaling up the synthesis of PDMB homopolymers and copolymers will be studied. This work will be carried out within the research labs at *Synthomer Ltd.* The one-pot anionic polymerizations carried out in a laboratory scale will be scaled-up by one order of magnitude. Other parameters such as reaction temperatures and times, solvents and initiators will be modified as far as possible, in order to adapt the process to the industrial way as much as possible.

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Chapter 2

Synthesis and characterisation of poly(2,3-dimethyl-1,3-butadiene)

Chapter 2: Synthesis and characterization of poly(2,3-dimethyl-1,3 butadiene)

As mentioned in *Chapter 1*, the synthesis of polybutadiene and polyisoprene by anionic polymerization have been very widely studied over the past century, but the polymerization of DMB much less so. One of the key aims of this project is to study the impact of various experimental parameters, such as solvent polarity, temperature and initial concentration of initiator, on the microstructure of polyDMB and, in particular, how the impact of such parameters on the polymerization of DMB compares to the impact of the same parameters on the polymerization of butadiene and isoprene.

This is of particular interest, from both an academic and commercial perspective, given the reported potential for polyDMB, with a high 1,4-microstructure, to undergo stress-induced crystallisation, something that neither polybutadiene or polyisoprene (prepared by anionic polymerization) are capable of.

In order to analyse the impact of solvent polarity on the microstructure of polyDMB, and as a starting point of the project, a series of DMB homopolymers have been synthesized via anionic polymerization in four different low polarity aromatic and aliphatic solvents: benzene, toluene, *n*-hexane and cyclohexane. Initially low molecular weight homopolymer of DMB were prepared with the additional aim of learning the challenging synthetic techniques required for living anionic polymerization that would be used throughout the project. Moreover, although the homopolymerization of DMB by anionic polymerization has been previously reported in the literature, significant discrepancies exist between such reports from different authors regarding the impact of solvent polarity on the microstructure of PDMB. Therefore, the results obtained from these initial studies are of interes and will be compared with the data previously reported in the literature. A series of higher molecular weight polymers (≥ 50 kg mol^{-1}) have also been synthesized in order to study the impact of the initial concentration of initiator upon polymer microstructure which in all cases has been analysed by ^{1}H-NMR. Molecular weights and molecular weight distributions have been obtained by triple detection Size Exclusion Chromatography (SEC) and thermal properties (glass transition temperature and crystallinity) have been characterized by Differential Scanning Calorimetry (DSC).

2.1. Synthesis of low molecular weight polyDMB

The initial step of the project involved the synthesis of a series of low molecular weight (*ca.* 10,000 g mol^{-1}) homopolymers of DMB. The aim of these experiments was to understand the basic features of the anionic polymerization of DMB and to establish/optimize reaction conditions such as time of reaction, temperature, etc., that will be followed (with modifications where appropriate) for the rest of project. Benzene was selected for the first experiments due to its favourable characteristics as a solvent in anionic polymerization as explained in *Chapter 1*. *Sec*-BuLi was chosen as an initiator due to its well-understood performance with respect to other initiators (higher initiation rate than propagation rate). In order to anticipate viscosity or solubility issues during the polymerization, it was decided to establish a concentration of DMB of 10% w/v (10 g of monomer in 100 mL of solvent).

Regarding reaction time and temperature, it was expected that DMB would polymerize more slowly than butadiene due to the two extra methyl groups in carbon 2 and 3 of the monomer. As mentioned in *Chapter 1*, these methyl groups are expected to result in a significant increase in the electron density of the terminal carbons of DMB with respect to butadiene, slowing the rate of polymerization of DMB in comparison to butadiene.[1] An initial experiment with a target molecular weight (M_{target}) of 10 kg mol^{-1} in benzene was carried out at room temperature (RT). After 48 h of reaction a polymer with a lower molecular weight than the target (M_n = 7 kg mol^{-1}) was obtained in a yield of just 28%. These results suggest that the polymerization of DMB proceeds much more slowly than butadiene. Experience would suggest that an analogous polymerization with butadiene at room temperature would be complete in less than 48 h. In order to speed up the reactions it was decided to carry out subsequent experiments at a temperature of 40 °C. Moreover, the low yield and the obtained M_n suggest the presence of some impurities. Even considering that a certain amount of polymer may be lost during the precipitation and recovery, if 7000 g mol^{-1} corresponds to a yield of 28% then 100% monomer conversion would result in a polymer with a molar mass of more than 20000 g mol^{-1} — significantly higher than intended.

2.1.1. Analysis of DMB monomer

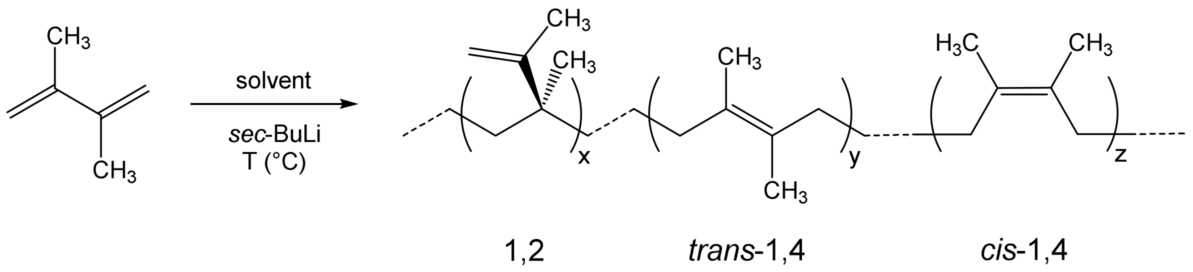
Before proceeding with the subsequent polymerizations, a sample of DMB monomer was analysed in order to identify possible impurities that might have resulted in the deactivation of initiator. The sample was analysed by headspace GC-MS and FT-IR.

Headspace GC-MS was used for identifying the volatile organic compounds (VOC) present in the DMB monomer. This analysis revealed that apart from DMB, the sample contained 1,2-dimethyl cyclopropane, 2-pentane, and 2,4-hexadiene, which are not expected to cause termination, and *t*-butyl methyl ketone which might be responsible for the premature termination of the polymerization — carbanions may react readily with carbonyl compounds. The presence of *t*-butyl methyl ketone was also observed by FT-IR analysis where the ketone carbonyl (C=O) stretch was observed at approximately 1750 cm^{-1}.

As mentioned in *Chapter 1*, the catalytic dehydration of pinacol using Al_2O_3 catalyst leads to the production of both DMB and *t*-butyl methyl ketone. This explains the presence of *t*-butyl methyl ketone in the purchased batch of DMB. As mentioned, this ketone might kill a small amount of the initiator injected, affecting the M_n of the resulting polymers ($M_n > M_{target}$). In order to overcome the presence of this impurity, the monomer was subjected to a sacrificial pre-polymerization step using *n*-BuLi. Thus, DMB was distilled under high vacuum into a Young's ampoule and initiated/purified with 1 mL of *n*-BuLi added via a rubber septum. The foundation of this sacrificial pre-polymerization step is that *n*-BuLi will react with traces of any residual impurities, but may also initiate propagation. Although *n*-BuLi has a relative slow rate of initiation and DMB propagates slowly, it is anticipated that a small proportion of the monomer will be "sacrificed" in order to ensure that the remaining monomer is completely pure. The process was allowed to proceed for 5 minutes at room temperature, in order to ensure the complete reaction with impurities before the residual unreacted and purified DMB was distilled under high vacuum into the reaction apparatus.

2.1.2. The impact of solvent polarity on microstructure of polyDMB

Having dealt with the issue of monomer impurities, a series of experiments was carried out under the established conditions (10% solution concentration of monomer, *sec*-BuLi as initiator and 40 °C), as shown in *Scheme 2.1*. Reactions were performed using four different solvents (*n*-hexane, cyclohexane, benzene and toluene) of low but varying polarity (dielectric constant, ε, from 1.89 to 2.38). At intermediate reaction times (after 24 to 72 h), samples were collected, terminated and analysed in order to follow the progress of the reaction.



Scheme 2.1: *Anionic polymerization reaction for the synthesis of PDMB. DMB can polymerize to give three different microstructures: 1,2, trans-1,4 and cis-1,4. Solvents: toluene, benzene, cyclohexane or n-hexane. T: RT or 40 °C.*

Both, intermediate samples and the final polymers were analysed by SEC, see *Table 2.1*. The molar mass data was obtained using a triple detection calibration (with light scattering) using the *dn/dc* value of polyisoprene (0.130 mL/g) since no previously reported value of *dn/dc* for PDMB was found. By using the *dn/dc* value for the (structurally similar) polyisoprene it is accepted that the obtained values of M_n (and hence, the conversion) will not be absolutely accurate. However, in the context of this research a perfectly accurate value of the molar mass is perhaps less important than the impact of solvent polarity on the microstructure of PDMB. Nevertheless, as all the homopolymers will be affected by the same (small) error, valuable qualitative and comparative observations about molar mass can be made. Dispersity values will not be impacted by a small error in the *dn/dc* (*Table 2.1*).

Reported yields are for the final polymer and do not include losses due to sampling. In all cases high yields (> 80%) were obtained which suggests that all the reactions went to (more or less) full conversion. If one assumes that the final polymer did indeed represent 100% conversion, the conversion at intermediate reaction times was calculated as follows:

$$\%\ \boldsymbol{conversion} = \frac{\boldsymbol{M_{n,sample}}}{\boldsymbol{M_{n,final\ polymer}}} \qquad \textbf{Equation 2.1}$$

When considering the conversion of the polymer at various times, it is clear that the reaction rate increases when the polarity of the solvent is increased. Experiments carried out in aromatic solvents (toluene and benzene) showed higher conversions (< 85%) after 24 h and full conversion after 48 h. On the other hand, polymerizations using alkanes as solvent only reached conversions of around 45% within the first 24 h and approximately 80% conversion after 48 h. This observation agrees with the expectations as higher polarity solvents (benzene and toluene) tend to dissociate the propagating species more than the lower polarity solvents (*n*-hexane and cyclohexane).[2] The molecular weights obteined by SEC (reported in *Table 2.1*) of the final polymers are in close agreement with the M_{target} (10 kg mol^{-1}) for all the experiments. The dispersity (Đ) values are also within the expected range for anionic polymerization (Đ < 1.10)[2] with the exception of experiment 2.4 which has a dispersity value of 1.32, which is considered high for anionic polymerization.

Table 2.1: *Molecular weight data obtained by SEC of the resulting polymers synthesized by anionic polymerization of DMB. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, T = 40 °C.*

Experiment	Solvent (ε)	t (h)	M_n (g mol^{-1})	Đ	% conversion[a]	% yield
2.1	Toluene (2.38)	24	11400	1.08	86	92
		48	13300	1.05	100	
2.2	Benzene (2.27)	24	10800	1.07	88	98
		48	12600	1.13	100	
		120	12200	1.09	100	
2.3	Cyclohexane (2.02)	24	5800	1.04	49	86
		48	9400	1.04	80	
		96	11700	1.04	100	
2.4	*n*-hexane (1.89)	24	4000	1.04	44	86
		72	9900	1.09	100	
		120	9200	1.32	100	
2.5[b]	*n*-hexane (1.89)	24	7900	1.06	31	81
		48	19100	1.06	74	
		92	25700	1.08	100	

a) Calculated as M_n (sample)/M_n (final polymer) x 100; b) T = 50 °C and M_{target} = 20 kg mol^{-1}.

Analysing the SEC chromatograms (*Figure 2.1*) a pronounced low MW tail is observed for the polymer obtained in *n*-hexane (experiment 2.4 — *Figure 2.1c*). This tailing was also observed in the intermediate samples. This is probably a consequence of a slow leak in the reactor. The impurities that are introduced in the reactor terminate slowly a small proportion of the propagating chains as the polymerization proceeds. The leak is likely a consequence of a poor seal caused by imperfect rubber septum. In the case of PDMB synthesized in benzene (*Figure 2.1a*), a second, small peak can be observed to lower retention volumes (higher molecular weight). The M_n of that undesired peak is approximately double that of the main peak and is a consequence of chain coupling reactions occurring during the termination process. These chain coupling reactions arise due to the presence of environmental impurities (O_2/CO_2) in the methanol that is used for termination. Commonly, the methanol used for termination is sparged with nitrogen gas for several minutes in an attempt to remove dissolved O_2 and CO_2 however, this process is not always 100% successful. Attempts to further limit the presence of O_2 in the methanol for termination involved degassing the methanol using freeze/pump/thaw cycles and storing it under high vacuum. However, the nitrogen used for creating a positive pressure (needed for extraction of methanol by injection) may also contain a low level of O_2 which will produce chain coupling to a greater or lesser extent depending on the content of O_2. Although the effects of impurities on either molar mass and/or dispersity are undesirable such impurities will have no impact on the microstructure, the key parameter under investigation.

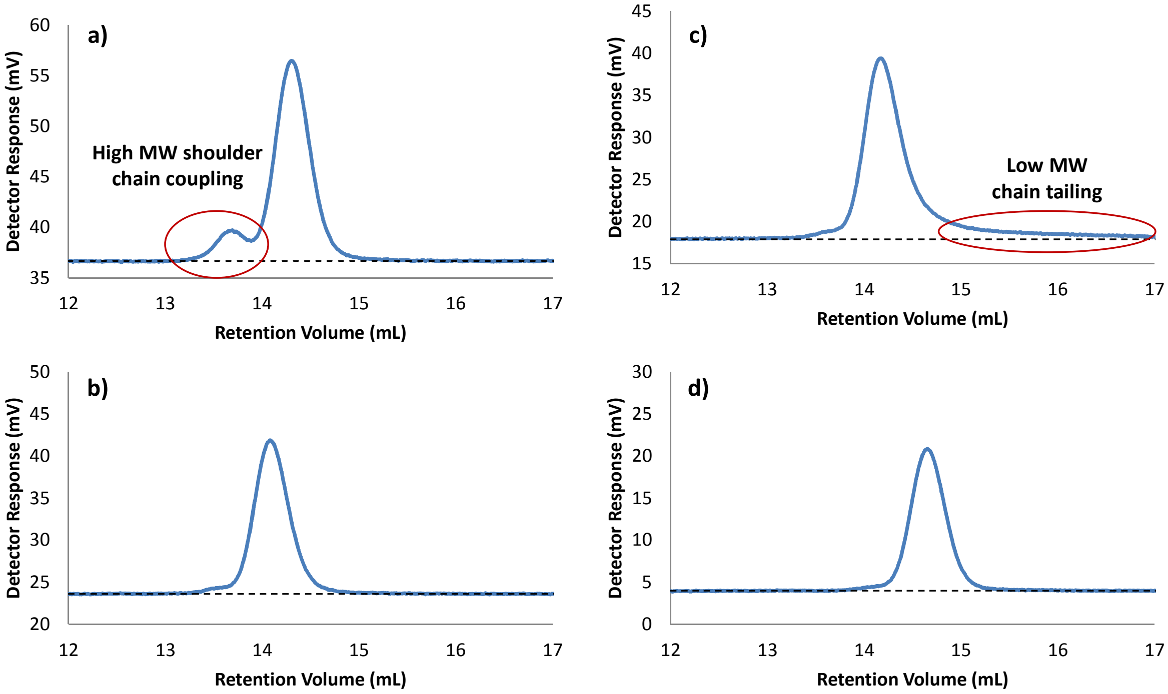


Figure 2.1: *SEC chromatogram of PDMB obtained in: a) benzene, b) toluene, c) n-hexane and d) cyclohexane.*

The resulting polymers were also analysed by ^{1}H-NMR in order to determine the impact of solvent polarity on the microstructure. The microstructure plays an important role in the final properties of the material. Of particular interest, and as mentioned in *Chapter 1*, PDMB is able to undergo stress-induced crystallization but this phenomena is very much microstructure dependent. It has been reported that a microstructure consisting of less than 20% of 1,2 units, between 60 and 65% of *trans*-1,4 units and the rest of *cis*-1,4 units, is required to enable stress-induced crystallization to occur.[3] Examples of the ^{1}H-NMR spectra for PDMB synthesised in benzene and *n*-hexane, to illustrate the key signals used to calculate the microstructure are shown in *Figure 2.2* and *Figure 2.3*.

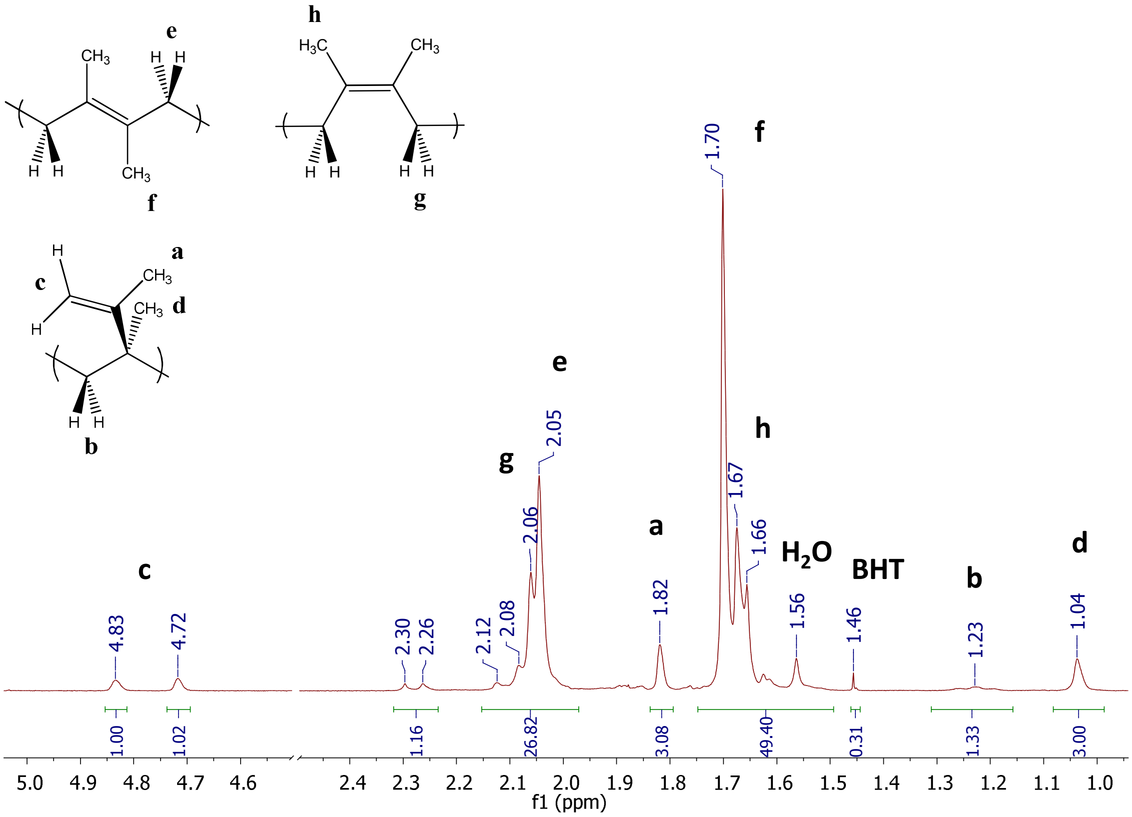


Figure 2.2: ^{1}*H-NMR spectrum of PDMB synthesized in benzene (CDCl$_3$, 400 MHz) δ (ppm).*

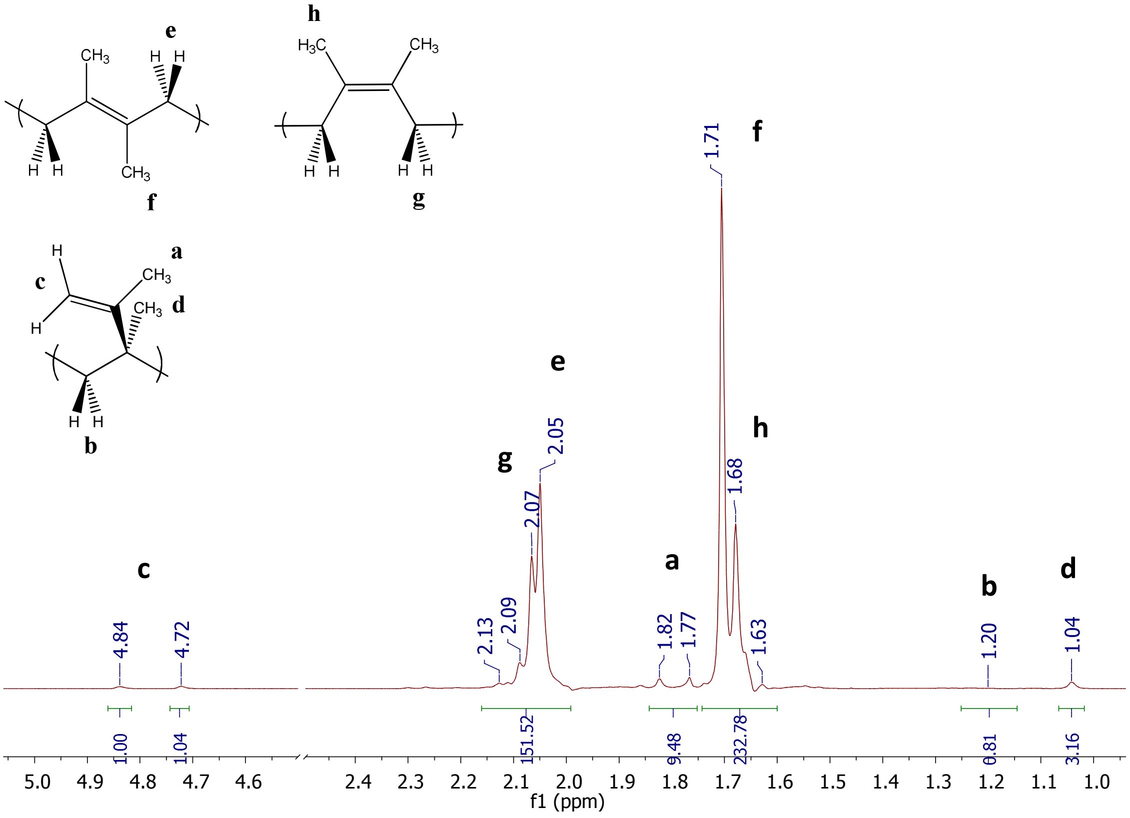


Figure 2.3: ^{1}*H-NMR spectrum of PDMB synthesized in n-hexane (CDCl$_3$, 400 MHz) δ (ppm).*

Peaks were assigned taking into account previously published data.[4-8] As can be seen in the spectra above, there is a degree of overlapping of signals ***e*** (2.05 ppm) and ***g*** (2.06-2.07 ppm) and signals ***f*** (1.70-1.71 ppm) and ***h*** (1.67-1.68 ppm) corresponding to *cis*- and *trans*-1,4 microstructures. In contrast with polyisoprene, the methyl groups of the *cis*-1,4 units of polyDMB are more shielded than the *trans*-1,4 units.[4] These *cis*- and *trans*-1,4 signals of polyDMB appear at 1.65-1.66 and 1.68 ppm respectively. However, the situation is the opposite for the methylene groups of *cis*- and *trans*-1,4 of polyDMB whose resonances are observed at 2.04 and 2.02-2.03 ppm respectively. Unassigned weaker peaks (signals at 2.30-2.26, 2.13-2.08, 1.77 and 1.66-1.46 ppm) correspond to different arrangements of 1,2 and 1,4 units (dyads and triads) within the polymer structure which, according to Blodin, change the chemical shift of the peaks.[4, 8] These unassigned peaks appear around the signals corresponding to the methyl and methylene groups of *cis*- and *trans*-1,4 units. When *Figure 2.2* (16% 1,2 units PDMB) and *Figure 2.3* (3% 1,2 units PDMB) are compared it is clear that these unassigned signals are weaker in the latter, where the vinyl content is low. This might suggest that these unassigned signals correspond to 1,4 units adjacent to one or two 1,2 units. The amount of each microstructure was calculated following a method reported by Chiang and co-workers, by using the areas under the peaks ***c*** (4.84-4.72 ppm), ***f*** (1.70-1.71 ppm) and ***h*** (1.67-1.68 ppm). In this case the calculation was carried out in duplicate, using the normalized areas under the peaks ***c***, ***e*** and ***g*** and peaks ***c***, ***f*** and ***h*** given by the analysis software, as the resolution of the spectra is higher. Using both results, an average microstructure composition was calculated. The equations used for calculating microstructure composition using signals ***c***, ***f*** and ***h*** is shown below (with *n* being the number of protons corresponding to each signal):

$$\%\,\mathbf{1,2} = \frac{area_c/n_c}{\left(\frac{area_c}{n_c}+\frac{area_f}{n_f}+\frac{area_h}{n_h}\right)} \qquad \textbf{Equation 2.2}$$

$$\%\,\boldsymbol{cis-1,4} = \frac{area_h/n_h}{\left(\frac{area_c}{n_c}+\frac{area_f}{n_f}+\frac{area_h}{n_h}\right)} \qquad \textbf{Equation 2.3}$$

$$\%\,\boldsymbol{trans-1,4} = \frac{area_f/n_f}{\left(\frac{area_c}{n_c}+\frac{area_f}{n_f}+\frac{area_h}{n_h}\right)} \qquad \textbf{Equation 2.4}$$

In case of the method reported by Chiang *et al.*, *Equation 2.4* included a correction term to overcome the overlapping of signals ***a*** (1.82 ppm) and ***f*** (1.70-1.71 ppm). In the current study this correction term was not necessary as no overlapping between those signals was observed, which makes this calculation more accurate. However, because of the considerable degree of overlapping between signals ***e*** (2.05 ppm) and ***g*** (2.06-2.07 ppm) and signals ***f*** (1.70-1.71 ppm) and ***h*** (1.67-1.68 ppm) and taking into account that the calculation method is based on software estimation, a certain amount of error has to be assumed anyway. The results of microstructure composition calculations of the final polymers are reported in *Table 2.2*.

Table 2.2: *Molecular characteristics of DMB homopolymers synthesized in different polarity solvents. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, T = 40 °C.*

Experiment	Solvent (ε)	% 1,2	% *cis*-1,4	% *trans*-1,4
2.1	Toluene (2.38)	21	24	55
2.2	Benzene (2.27)	16	23	61
2.3	Cyclohexane (2.02)	4	30	66
2.4	*n*-hexane (1.89)	3	32	65
2.5[a]	*n*-hexane (1.89)	3	32	65
polybutadiene[9, 10]	Toluene (2.38)	10	90	
	Benzene (2.27)	9	91	
	Cyclohexane (2.02)	8	92	
	n-hexane (1.89)	8	92	
polyisoprene[11]	Benzene (2.27)	7[b]	66	27
	Cyclohexane (2.02)	5[b]	80	15

a) T = 50 °C and M_{target} = 20 kg mol^{-1}; b) For polyisoprene: % 3,4 units.

Previously published data, for polybutadiene and polyisoprene, on the impact of solvent polarity on microstructure has shown that the vinyl (1,2) content increases with increasing solvent polarity. By way of an example it has been reported that the 1,2 content of polybutadiene synthesized in *n*-hexane is 8% (see *Table 2.2*) and 67% when synthesized in THF.[2] The PDMB obtained in the current set of experiments follow this expected trend (see *Table 2.2*). PDMB obtained in aromatic solvents (toluene and benzene) showed a significantly higher content in 1,2 units than the same polymers synthesized in the extremely non-polar alkanes (*n*-hexane and cyclohexane). Moreover, although the general trend for PDMB is consistent with previously reported trends for polybutadiene and polyisoprene, when the obtained results for polyDMB are compared to data previously reported for polybutadiene and polyisoprene, significant differences are observed. Hadjichristidis *et al*. reported that the vinyl (1,2) content of polybutadiene obtained by anionic polymerization in benzene and other non-polar solvents is 10% and 8% respectively (see *Table 2.2*).[9, 10] In the case of polyisoprene obtained by anionic polymerization, the addition of 3,4 units is more favoured than the addition of 1,2 units, due to the electron density of carbon 4 being lower than in carbon 1.[1] For this reason, the anionic polymerization of isoprene results in negligible amounts of 1,2 units. Morton and co-workers reported the anionic polymerization of isoprene in benzene and cyclohexane. The obtained polymers showed microstructures of 0% 1,2-, 7% 3,4-, 66% *cis*-1,4 and 27% *trans*-1,4 for the polymers obtained in benzene and 0% 1,2-, 5% 3,4-, 80% *cis*-1,4 and 15% *trans*-1,4 units in cyclohexane (see *Table 2.2*).[11] In both cases, polybutadiene and polyisoprene, the difference in the vinyl content of the polymers synthesized in aromatic solvents and alkanes is not great (1-2%). Taking into account the signal to noise ratio of the ^{1}H-NMR spectra this 1-2% difference in the vinyl content may not be considered significant, which was not surprising considering that the difference in the polarity is not great ($1.89 < \varepsilon < 2.38$). However, it seems that the microstructure of polyDMB is much more sensitive to the polarity of the polymerization solvent than polybutadiene and isoprene. When the impact of solvent polarity on microstructure for polybutadiene, polyisoprene and polyDMB is compared (*Figure 2.4*) it is observed that within the same range of polarity (ε from 1.89 to 2.38) the vinyl content of polyDMB changes from 3 to 21% while the content of 1,2 units hardly varies for polybutadiene, remaining between 8 and 10% and, in case of polyisoprene, the variation of the vinyl content, which is the % 3,4 units, is also very small (5% in cyclohexane and 7% in benzene).

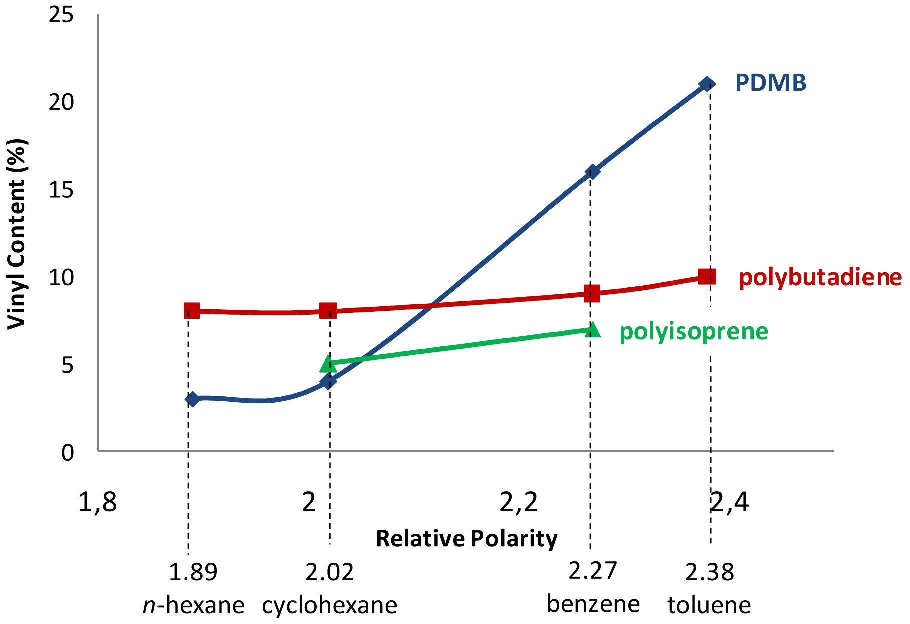


Figure 2.4: *Evolution of vinyl content with the solvent dielectric constant (1.89 to 2.38) in PDMB (3 to 21%) and polybutadiene (8 to 10%) and polyisoprene (5 to 7%).*[9-11]

The difference in the microstructure of polyDMB obtained in the different solvents can be easily seen by comparing the ^{1}H-NMR spectra of the different polymers, as shown in *Figure 2.5*. As expected, polymerizations carried out in solvents with similar polarities gave polymers with similar ^{1}H-NMR spectra and hence, similar microstructures. It is observed in *Figure 2.5* that as the vinyl content of the resulting polyDMB gets lower, the signals corresponding to the 1,2 units (***a***, ***b***, ***c*** and ***d***) become weaker. On the other hand, the signals corresponding to *cis*- (***g*** and ***h***) and *trans*-1,4 (***e*** and ***f***) appear clearer with less overlap (peaks corresponding to different 1,2-1,4 units sequences as mentioned above) when the content of 1,2 is lower. For the experiments carried out in aromatic solvents (2.1 and 2.2) it can be seen that the vinyl content rises significantly from 16% in benzene to 21% in toluene, when the dielectric constant of the solvent rises by only 0.11. However, in case of the polymerization reactions carried out in alkanes (experiments 2.3 to 2.5) the variation in the vinyl content is just from 3% to 4% when the difference in the dielectric constant is similar (0.12).

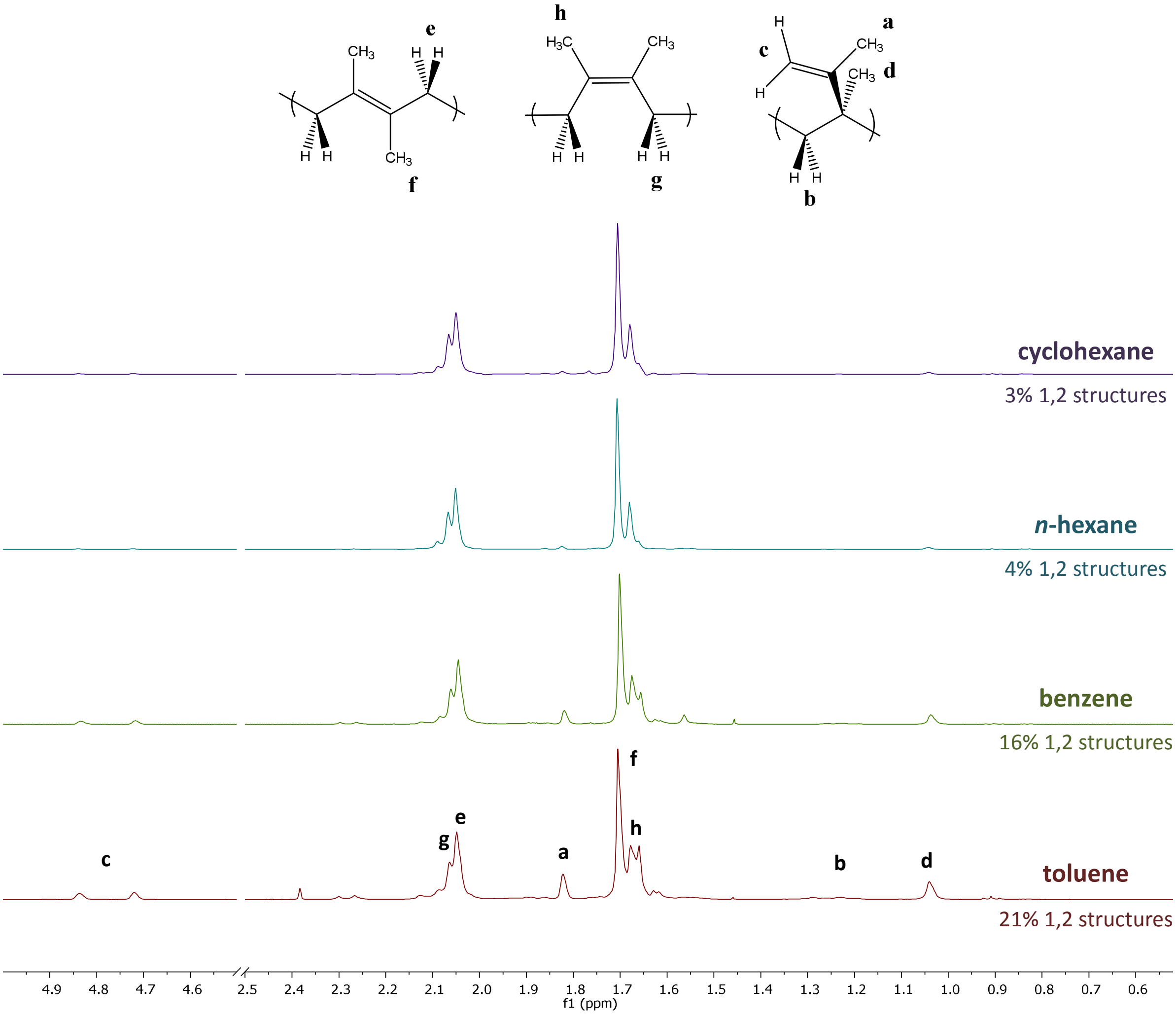


Figure 2.5: *Comparison between ^{1}H-NMR spectra of polymers synthesized in toluene, benzene, cyclohexane and n-hexane ($CDCl_3$, 400 MHz) δ (ppm).*

It is noteworthy to mention that the difference between 3% and 4% of 1,2 microstructures cannot be considered significant. Given the ^{1}H-NMR signals corresponding to the 1,2 microstructures (***c*** in *Figure 2.3*) are very small, the errors occurring when the microstructure is calculated from ^{1}H-NMR spectra will make the %1,2 microstructures of both experiments 2.3 and 2.4 the same within error.

This might suggest that the evolution of the vinyl content of polyDMB reaches a lower limit at low polarities and a further reduction in the content of 1,2 units is not possible even using solvent with lower polarities (e.g. pentane, ε = 1.84).

In the polymerizations of DMB in aromatic solvents (experiments 2.1 and 2.2) it was observed that the colour of the reaction turned to yellow after initiation (*Figure 2.6 left*), similar to the anionic polymerization of butadiene.

Figure 2.6: *Anionic polymerization of DMB approximately 24 h after initiation using sec-BuLi (left) in benzene and (right) in n-hexane.*

The microstructures obtained in experiments 2.1 and 2.2 were compared with values previously reported by H. Yuki *et al.*[7] (*Table 2.3*). The data suggests that the 1,2 content of polymers prepared in this study, is similar to the data extracted from the literature. The small differences can be explained by variations in the experimental parameters (e.g. reaction temperature, initiator concentration or chemical structure of initiator) which also exert an impact on the microstructure and are not identical to those used in the current study. According to Yuki, an increase in the temperature leads to a decrease in the content of 1,4 units (from 80% at 30 °C to 69% at 50 °C). This trend is consistent with reported data for the anionic polymerization of butadiene in hydrocarbon solvents. However, within the same range of temperature the content of 1,4 units of polybutadiene decreases only from approximately 92% to 90%.[2] This further example demonstrating that, the microstructure of polyDMB seems to be much more sensitive to the experimental conditions than polybutadiene. In all the experiments reported in the literature, the concentration of DMB monomer was roughly half the concentration used in experiments 2.1 and 2.2. However, this parameter does not affect the microstructure significantly. Experiments carried out by Yuki also differ in the molecular weight of the resulting polymers and hence, in the concentration of initiator. According to Quirk, in the case of butadiene, a higher concentration of initiator (lower molecular weight) leads to polymers with a lower 1,4 content. This trend seems to be the same in the case of polyDMB. According to Yuki (*Table 2.3*), the lower molecular weight polymers (Yuki 2 and Yuki 3) have a content in 1,4 units of 80-82% and the higher molecular weight polyDMB (Yuki 4) has a 1,4 content of 87%.

Table 2.3: *Comparison between the results for experiments in aromatic solvents (experiments 2.1 and 2.2) with data previously reported.*[7]

Experiment	Solvent	T (°C)	[BuLi] (mM)	[DMB] (g/mL)	% 1,2	% *cis*-1,4	% *trans*-1,4
2.1	Toluene	40	9.52	0.10	21	24	55
2.2	Benzene	40	12.18	0.12	16	23	61
Yuki 1	Benzene	50	6.40	0.05	31	69	
Yuki 2	Benzene	30	6.40	0.05	20	80	
Yuki 3	Benzene	30	12.80	0.05	18	82	
Yuki 4	Benzene	30	3.21	0.05	13	87	

In the anionic polymerization of DMB in alkanes (experiments 2.3 and 2.4), it was observed that after approximately 24 h, the reaction turned from completely transparent to an opaque milky appearance, as shown in *Figure 2.6 (right)*. This was unexpected but is probably due to a low solubility of the resulting polyDMB in both *n*-hexane and cyclohexane. This behaviour prompted an investigation into the solubility of the resulting PDMB in various solvents,to be discussed later in *section 2.1.4*. The results obtained in experiments 2.3 to 2.5 were compared with the data previously reported by Blodin,[4] Chiang,[5] Jenner[6] and Yuki[7] in *Table 2.4*.

The four authors each reported the synthesis of PDMB by anionic polymerization under various conditions. In case of the experiments carried out by Blodin and Chiang, the authors did not report the initial concentration of BuLi, and although the results reported from Blodin are consistent with the results described here, it is difficult to account for the significant variations in microstructure reported by Chiang. For that reason, comparisons with these experiments need to be considered carefully. The very low content of 1,2 units (3-4%) obtained in experiments 2.3 and 2.4 agreed with the experiments carried out by Blodin and Chiang but differed from the experiments carried out by Jenner and Yuki. In order to check the reproducibility of the results obtained in experiments 2.3 and 2.4, the polymerization in *n*-hexane was repeated but with an increased M_{target} of 20 kg mol^{-1}. Moreover, the reaction temperature was increased to 50 °C as soon as the reaction mixture started to lose its transparency and become milky, to test whether the solubility of the polymer in *n*-hexane would improve at a higher temperature. The solubility did not appear to improve at the higher temperature and the reaction mixture remained milky. Moreover, it can be seen from the results reported in *Table 2.2*, that the polymer prepared in the second experiment in *n*-hexane (experiment 2.5) showed exactly the same microstructure as experiment 2.4 (3% 1,2, 30% *cis*-1,4 and 65% *trans*-1,4). Therefore, the results of experiments 2.3-2.5 can be considered consistent and consistent with Blodin and Chiang (with the exception of experiments Chiang 1 and Chiang 2, as shown in *Table 2.4*, with no apparent explanation).

Table 2.4: *Comparison between the results for experiments in alkanes (experiments 2.3, 2.4 and 2.5) with data previously reported.*[4-7]

Experiment	Solvent	T (°C)	[BuLi] (mM)	[DMB] (g/mL)	% 1,2	% *cis*-1,4	% *trans*-1,4
2.3	Cyclohexane	40	10.36	0.10	4	30	66
2.4	*n*-hexane	40	11.20	0.11	3	32	65
2.5	*n*-hexane	50	5.18	0.10	3	32	65
Blodin 1	Cyclohexane	60	—	—	3	23	74
Chiang 1	Cyclohexane	40	—	—	27	22	51
Chiang 2	Cyclohexane	40	—	—	29	19	52
Chiang 3	Cyclohexane	40	—	—	3	14	83
Chiang 4	Cyclohexane	40	—	—	4	21	75
Chiang 5	Cyclohexane	40	—	—	3	22	75
Chiang 6	Cyclohexane	40	—	—	3	29	78
Jenner 1	Cyclohexane	30	120.00	0.33	12	88	
Jenner 2	*n*-heptane[a]	30	120.00	0.31	14	86	
Yuki 1	*n*-heptane[a]	40	6.40	0.05	18	82	

a) ε = 1.92.

2.1.3. The impact of microstructure on the physical appearance of polyDMB

This microstructure of the resulting polymers also has a noticeable impact upon their physical appearance, as shown in *Figure 2.7*. The samples with a higher 1,2 content (synthesized in aromatic solvents) are white solids that showed a slight rubber-like texture. On the other hand, the samples with a very low 1,2 content (synthesised in *n*-hexane and cyclohexane) are white compact waxy solids, which are easily crumbled. However, the resulting powdery polymers are not free flowing powders like, for example, polystyrene. This observation might be the consequence of a degree of crystallinity in the polymers with a high 1,4 content.

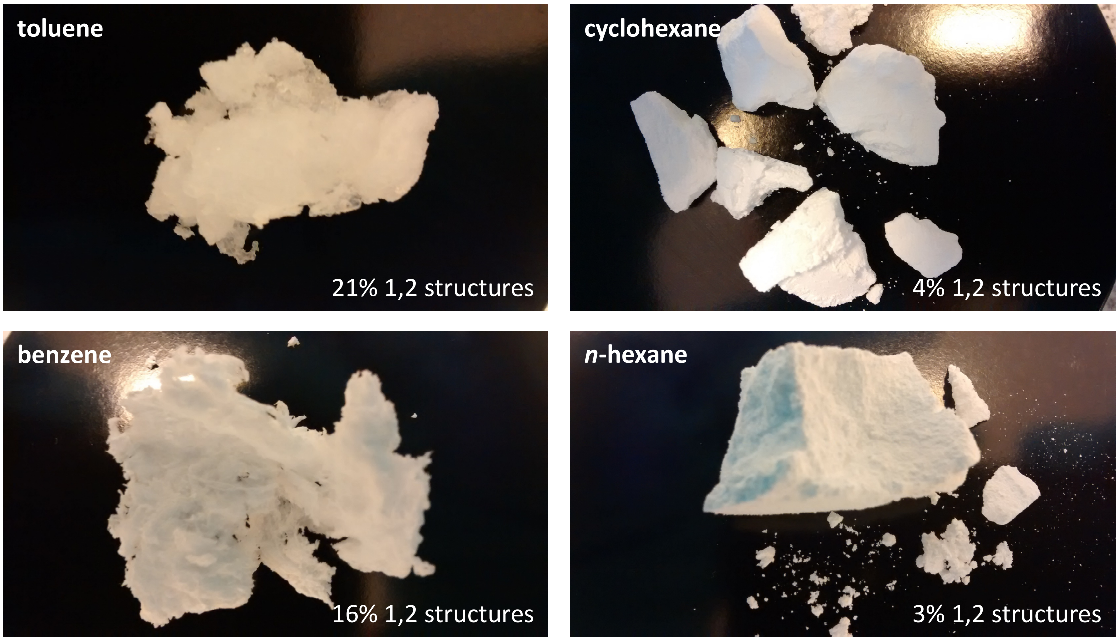


Figure 2.7: *Images of the resulting PDMB homopolymers synthesized in different polarity solvents: toluene (experiment 2.1), benzene (experiment 2.2), cyclohexane (experiment 2.3) and n-hexane (experiment 2.4) after precipitation and being dried in vacuum oven overnight.*

2.1.4. The impact of microstructure on solubility of polyDMB

The solubility of PDMB with different microstructures was evaluated in three different solvents, selected according to their polarity index, with a view to investigate the impact of microstructure on solubility. THF (high dielectric constant, 7.58), toluene (intermediate dielectric constant, 2.38) and *n*-hexane (low dielectric constant, 1.89) were the solvents used in this investigation. 10% (w/v) solutions of the polymers in each solvent (500 mg of polymer in 5 mL of solvent) were prepared in sealed vials and put on a roller-mixer for 24 h. The results of this qualitative solubility test are shown in *Figure 2.8*. This test was motivated in part because of the industrial relevance of, for example, processability of the resulting polymers and in part by the milky solution observed in the polymerizations in alkanes (experiments 2.3, 2.4 and 2.5). Moreover, solubility may give some indirect evidence of crystallinity, which often serves to reduce the solubility of polymers.

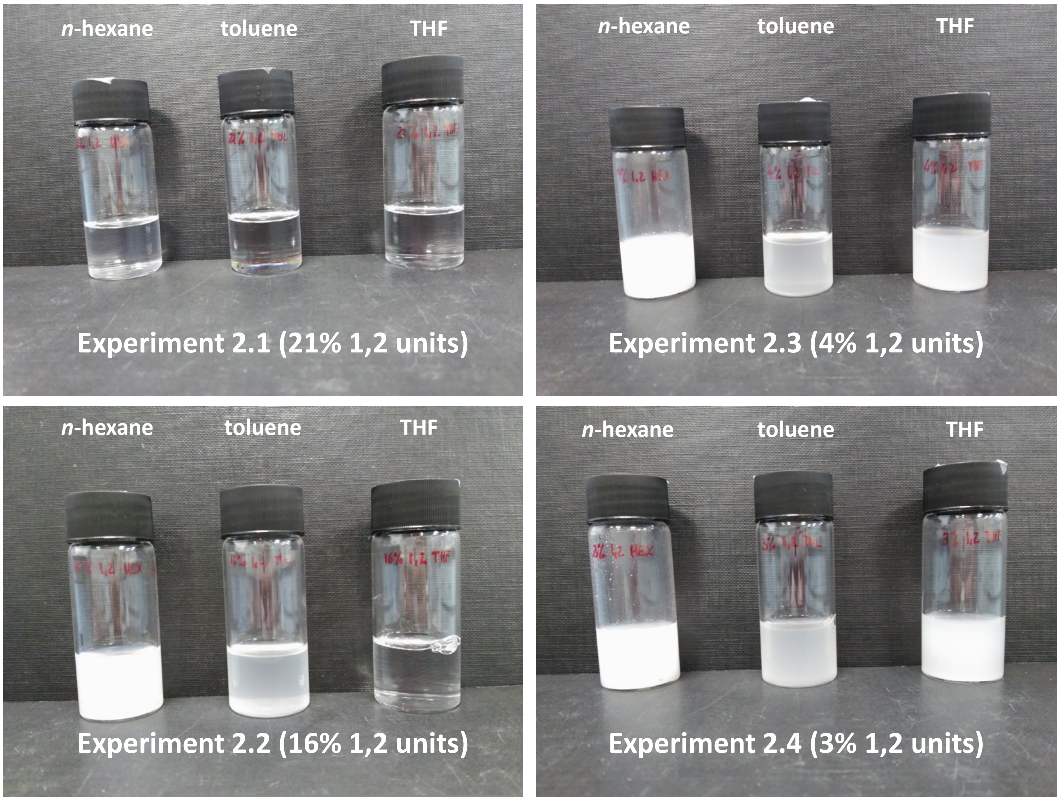


Figure 2.8: *Impact of PDMB microstructure on solubility in various solvents. Samples of 500 mg of polymer were dissolved in 5 mL of different polarity solvents: THF (ε = 7.58), toluene (ε = 2.38) and n-hexane (ε = 1.89).*

As can be observed, the lowest polarity solvent, *n*-hexane, is not a good solvent for any of the polymer samples. It can be seen that the solubility of the PDMB samples in non-polar solvents (toluene and *n*-hexane) decreases with the decreasing content of 1,2 microstructures. It is surprising the difference in the solubility in toluene of experiments 2.1 (21% 1,2 microsturctues) and 2.2 (16% 1,2 microstructures) considering the small difference in the microstructure, which suggests an important influence of the %1,2 on the solubility. THF seems to be a good solvent only for the samples with higher %1,2 (2.1 and 2.2) but samples with lower %1,2 (2.3 and 2.4) remained unsoluble. This result suggests a very strong dependence of solubility on microstructure (specially the content of 1,2 microstructures), which is not observed for polybutadiene and polyisoprene. According to Van Krevelen,[12] highly crystalline polymers such as polyethylene are not soluble in any solvent at room temperature as a direct result of the crystallinity. Yen reported that both, 100% *cis*- and 100% *trans*-1,4 PDMB (produced by stereospecific Ziegler-Natta polymerization) are crystalline powders, as the structure of both, *cis*- and *trans*-1,4 units is regular enough to allow efficient chain-packing.[13, 14] However, according to Henderson, the presence of 1,2 units significantly disrupts the crystallinity of PDMB. Therefore, the resulting PDMB of experiments 2.3 and 2.4 (96-97% 1,4 units) might be expected to have a certain degree of crystallinity, and probably a lower solubility. The low solubility of PDMB samples 2.3 and 2.4 would also explain the milky solution formed during these polymerization reactions. It is also worth noting that this is another example of where PDMB differs from polybutadiene and polyisoprene which are both completely soluble in hexanes at room temperature.

Van Krevelen also reported that highly crystalline polymers may be dissolved in certain solvents at high temperatures (e.g. polyethylene is soluble in xylene above 80 °C) as the additional energy helps to overcome the intermolecular forces binding the crystalline domains. Therefore, a qualitative test of the solubility as a function of temperature was carried out with PDMB samples 2.2, 2.3 and 2.4. The same 10% (w/v) samples used in the previous test were kept in a water bath at 40 °C for 1 h. After checking the solubility at 40 °C, the temperature of the water bath was raised to 60 °C for 1 h and solubility was checked accordingly. Further increases in temperature were not considered as the boiling point of *n*-hexane (68 °C) and THF (66 °C) made it unsafe. Finally, the samples were stored outside the water bath and allowed to cool down to room temperature in order to check if they became insoluble again on cooling. The results of these qualitative tests are shown in *Figure 2.9*.

It is observed that the solubility of PDMB from experiment 2.2 (16% 1,2 units) is clearly improved by increasing the temperature in the three solvents tested. In the case of samples 2.3 and 2.4, the solubility is improved in toluene and THF with the increasing temperature. However, the solubility of samples 2.3 and 2.4 in *n*-hexane shows no apparent improvement, even at 60 °C. In all the experiments, the solubility of the PDMB after cooling back to room temperature appeared to be the same as in the initial state. The obtained solubility results provide valuable information for potential handling in industry as they establish a temperature at which the resulting polymers can be dissolved in toluene (a general use solvent at *Synthomer Ltd.*). This in turn is relevant in terms of polymer processability and the post-reaction work-up (e.g. reactor cleaning or pipe blocking).

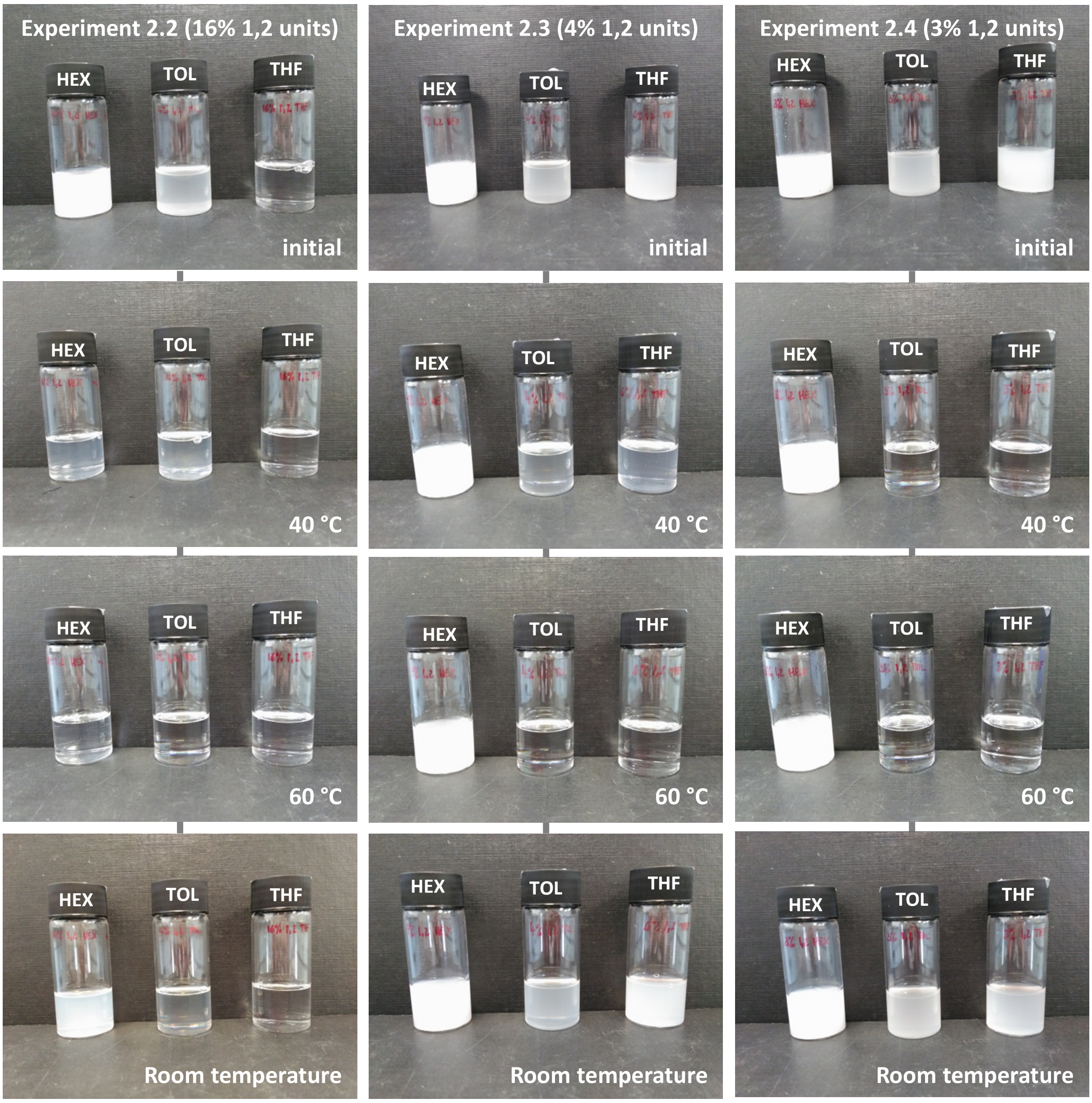


Figure 2.9: *Solubility of resulting polymers from experiments 2.2 (left), 2.3 (middle) and 2.4 (right) as a function of temperature. Initial situation: room temperature. Samples of 500 mg of polymer were dissolved in 5 mL of different polarity solvents: THF (ε = 7.58), toluene (ε = 2.38) and n-hexane (ε = 1.89).*

2.2. Synthesis of high molecular weight polyDMB

High molecular weight polymers are often of more interest from a commercial perspective. Given the relatively long reaction times required for the synthesis of 10 kg mol^{-1} polyDMB, suitable reaction conditions for higher molecular weight DMB homopolymers needed to be explored. From a commercial point of view, it was expected that an increase in the MW of PDMB would improve, to some extent, the mechanical properties of the final material. Moreover, as mentioned previously, a lower concentration of initiator (leading to higher molecular weight polymers) results in PDMB with a lower vinyl content. Taking into account this effect (a lower vinyl content), the resulting higher molecular weight PDMB was expected to show higher degree of crystallinity. Additionally, the degree of crystallinity in higher molecular weight polymers could be higher due to intramolecular crystallinity.

In order to obtain high molecular weight polyDMB in a reasonable reaction time, some changes in the experimental conditions were introduced. Firstly, the reaction temperature was raised from 40 °C to 60 °C with the aim of increasing the reaction rate and hence, reducing the reaction time. As a consequence of using a higher reaction temperature, *n*-hexane (boiling point = 69 °C) was replaced by *n*-heptane (boiling point = 98 °C).

The synthesis of high molecular weight PDMB was carried out according to the experimental conditions described in the previous section (for low molecular weight PDMB) but at the higher temperature as indicated above. Only benzene and *n*-heptane were used as solvents since *n*-hexane/cyclohexane yield almost identical results in terms of microstructure and in the case of aromatic solvents, toluene previously gave a microstructure which was slightly outside the range reported to produce stress-crystallisable PDMB. The synthesis of 100 kg mol^{-1} (in benzene and *n*-heptane) and 200 kg mol^{-1} (in benzene) linear PDMB was attempted. In the case of 200 kg mol^{-1} PDMB, the process was scaled up to 20 g of monomer in 200 ml of benzene, as the amount of initiator is very low (< 50 µL). This change was introduced with the goal of reducing the chances of failed polymerizations.

The four polymerizations were left for (conservatively) long reaction times (5-6 days) due to the increase in the M_{target}, and to ensure full conversion of the monomer. In experiments 2.6, 2.7 and 2.8, samples at 24 and 48 h were collected and both samples and final polymers were analysed by SEC in order to study the progress of the polymerization over time. In experiment 2.9, no samples were collected due to concerns that the sampling process itself might introduce impurities into the reaction vessel resulting in partial termination as the concentration of active species was very low, 0.56 mM. SEC results are summarized in *Table 2.5*. The SEC data was obtained as indicated in the previous section for low molecular weight PDMB. Therefore, the same small errors associated with the use of the *dn/dc* value of polyisoprene (0.130 mL/g) will exist. For each experiment a gradual increase in the viscosity was observed which after approximately 24 h prevented the magnetic follower from stirring the reaction.

Table 2.5: *Molecular weight data obtained by SEC of the resulting higher MW polymers synthesized by anionic polymerization of DMB. Initiator: sec-BuLi, T = 60 °C.*

Experiment	**Solvent**	**M_{target} (g mol^{-1})**	**t (h)**	**M_n (g mol^{-1})**	**Đ**	**% conversion**	**% yield**
2.6	Benzene	100K	24	108800	1.06	80	96
			48	122500	1.14	90	
			168	135900	1.17	100	
2.7	*n*-heptane	100K	24	117700	1.85	—	40[a]
			48	159000	1.45	—	
			144	114800	1.90	—[a]	
2.8	*n*-heptane	100K	24	176500	1.28	100	91
			48	182700	1.26	100	
			144	169700	1.28	100	
2.9	Benzene	200K	144	216700	1.32	—[a]	54[a]

a) Conversion cannot be considered 100% as the yield is too low.

Another consequence of the high viscosity is the increased likelihood of additional chain-coupling reactions during termination step. When the terminating agent, methanol, is injected into the reaction mixture, it diffuses very slowly through the highly viscous solution and therefore termination is not instantaneous. Any traces of environmental CO_2/O_2 introduced with the methanol may diffuse faster than the methanol and chain-coupling reactions can compete with termination via protonation. Due to this, a shoulder (double the M_n) to lower retention volume (higher MW) is observed in the SEC chromatograms (see *Figure 2.10* and *Figure 2.111*).

The 135.9 kg mol^{-1} homopolymer, prepared in benzene (experiment 2.6) was obtained in 96% yield after 168 h and the M_n is in reasonable agreement with the M_{target}, which suggests that the reaction was 100% complete. Intermediate samples collected after 24 h and 48 h had molar masses which correspond to conversions of approximately 80 and 90% respectively. This suggests that the synthesis of approximately 100 kg mol^{-1} PDMB can be achieved in 3-4 days at 60 °C in benzene. In the case of the 216.7 kg mol^{-1} PDMB (experiment 2.9) the lower yield (54%) suggests that the reaction was not complete by the time the terminating agent was injected. However, although the experimental M_n is close to the M_{target}, the low yield would suggest that some of the initiator died as a consequence of impurities. As mentioned above, the amount of initiator used is very low and as a consequence, the presence of even very small quantities of impurities can lead to a significant reduction in the concentration of active chains, which will result in major changes in the final M_n (higher than the expected M_{target}). The obtained results suggest that it is possible to reach a MW of approximately 200 kg mol^{-1} in around 6 days of reaction. In both experiment 2.6 and 2.9, the Đ values are high for anionic polymerization (Đ > 1.10), especially in experiment 2.9 where Đ is equal to 1.32. These higher than expected Đ values arise for two reasons (see *Figure 2.10*). First, a second higher MW peak, at lower retention volume can be observed and analysis indicates that this second peak has a molar mass which is approximately double that of the main peak. As mentioned above, this second peak arises as a consequence of chain-coupling reactions during termination. Secondly, in the case of experiment 2.9, the chromatogram shows a notable tailing to the low molecular weight side of the main peak. This is due to slow premature termination of active chains during the anionic polymerization, arising from the presence of impurities, due to a possible leak into the reaction vessel.

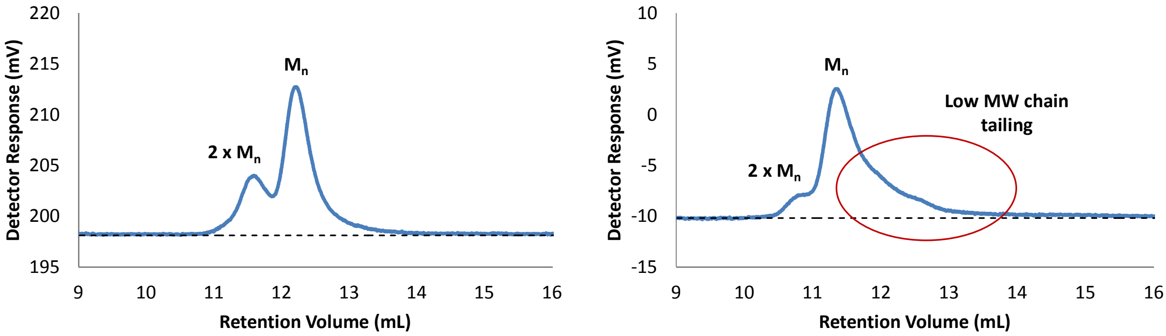


Figure 2.10: *SEC chromatogram of PDMB synthesized in benzene. (left) experiment 2.6 (135.9 kg mol*$^{-1}$*) and (right) experiment 2.9 (216.7 kg mol*$^{-1}$*).*

Although the presence of traces of impurities does have a significant impact on the molar mass and Đ, it is not expected that the vanishingly low level of impurities will have any impact at all on the resulting microstructures. It is absolutely certain that in case of the impurities introduced during the termination step can have no impact on the microstructure since the polymerization is complete.

In case of the experiments carried out in *n*-heptane solution, the reaction mixture once again became milky after few hours. Experiment 2.7 was repeated as a consequence of its low yield (40%) and its very high Đ value (1.90). The SEC chromatogram of experiment 2.7 (*Figure 2.11*) reveals that there is a very long tail in the lower MW region, due to premature termination of active chain produce by impurities, probably as a consequence of a leak in the reaction vessel. Due to the low yield (40%) the reaction cannot be considered to have gone to 100% completion. However, the resulting M_n is close to M_{target}. This might be a consequence of *sec*-BuLi killed by impurities present in the reaction vessel prior the initiation. As mentioned, this lower concentration of initiator leads to an increase in theM_{target}. The repeat experiment (2.8) gave a satisfactory high yield (91%) which suggests that the polymerization went on to completion. However, the obtained M_n (approximately 170 kg mol^{-1}) is significantly higher than the M_{target} (100 kg mol^{-1}) which suggests that approximately 40% of the initiator was killed before initiation, probably as a consequence of traces of impurities present in the reaction vessel as explained in previous experiments. In experiment 2.8 the polymerization appeared to have reached 100% conversion after 24 h of reaction — at least there was no apparent increase in the molar mass of the three (apparently) identical samples from experiment 2.8, which have an average M_n of 176300 g mol^{-1} and a variation of approximately ± 4%. This level of error is not unusual for SEC analysis and may in this case have arisen from "human error" in setting the baseline and integration limits, which can be a challenging when dealing with peak tailing. The fact that the reaction in *n*-heptane was apparently comple after 24 h is somewhat surprising as higher reaction rates were expected for experiments in aromatic solvents than in alkanes.

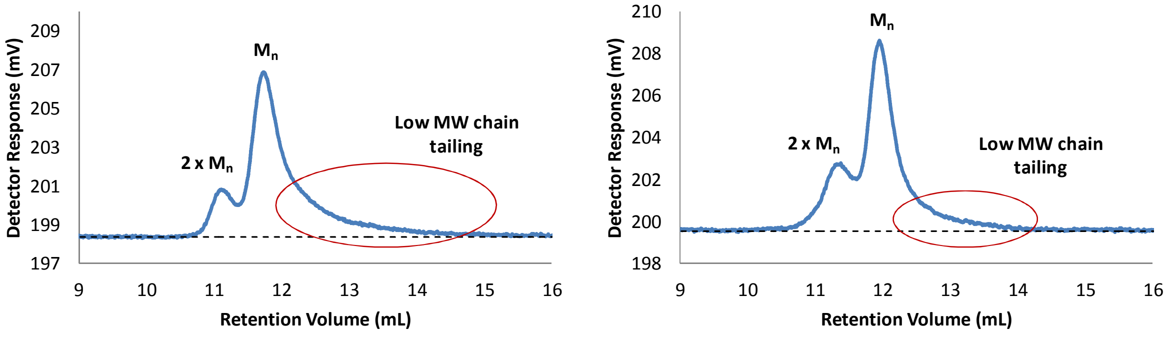


Figure 2.11: *SEC chromatogram of PDMB synthesized in n-heptane. (left) experiment 2.7 and (right) experiment 2.8.*

Intermediate samples and the final polymers were also analysed by ^{1}H-NMR in order to obtain their microstructure. The microstructures (*Table 2.6*) were calculated form ^{1}H-NMR spectra as explained previously for the lower molar mass linear PDMB (M_{target} of 10 kg mol^{-1}). It is perhaps also worth pointing out that although the presence of impurities has had an impact upon both the molar mass and dispersity of some of the samples, we do not believe that the presence of traces of impurity will have had any impact at all on the microstructure of the resulting polymers. Although the less than perfect control of molar mass and dispersity is not ideal, understanding the impact of experimental conditions, and in particular solvent polarity on microstructure is the primary aim of these experiments. The microstructure data in *Table 2.6*, which will be discussed in more detail below, supports this conclusion in so much that the two experiments in *n*-heptane had very different degrees of success in terms of control of molar mass, dispersity and conversion and yet have almost identical microstructures.

Table 2.6: *Molecular characteristics of high MW DMB homopolymers synthesized in different polarity solvents. Initiator: sec-BuLi, T = 60 °C.*

Experiment	Solvent	t (h)	% conversion	% 1,2	% *cis*-1,4	% *trans*-1,4
2.6	Benzene	24	80	12	34	54
		48	90	14	25	61
		168	100	12	33	55
2.7	*n*-heptane	24	100	2	38	60
		48	100	2	38	60
		144	100	3	38	59
2.8	*n*-heptane	24	100	3	34	63
		48	100	3	34	63
		144	100	3	35	62
2.9	Benzene	144	100	11	43	46

The microstructures of each high molecular weight polymer are consistent with those reported above for the low molecular weight samples of PDMB. However, it is noteworthy that the 1,2 content of the high molecular weight PDMB produced in benzene (2.6 and 2.9) is lower in both cases (12% and 11% respectively) than the 1,2 content of the low molecular weight PDMB (16% of 1,2 microstructure for 12.2 kg mol^{-1}). These results agree with expectations as, according to Quirk and Yuki, the higher the molecular weight of the polydiene (lower the concentration of initiator) the lower the content in 1,2 structures.[2, 7] In the case of high molecular weight PDMB prepared in *n*-heptane (2.7 and 2.8) the 1,2 content was almost identical (2-3%) to that observed for the analogous low molecular weight samples prepared in *n*-hexane (3%). It should be pointed out that the dielectric constant of *n*-hexane (1.89) and *n*-heptane (1.92) are almost identical. The 1,2/1,4 microstructures ratio appeared to be constant between intermediate samples and final polymer from the same experiment (very small variations were observed in experiment 2.6). This is probably due to the possibility of obtaining accurate integrals of the 1,2 signals (***c***) in the ^{1}H-NMR spectra given that the 1,2 signals are quite distinct from the 1,4 signals(***e***, ***f***, ***g*** and ***h***), see *Figure 2.5*. However, the analysis/calculation of the *cis*/*trans*-1,4 ratio reveals some variation between identical samples — e.g. the intermediate and final samples from the same experiment. This variation is probably due to the difficulty of assigning accurate integrations to overlapping peaks as the signals that allow the calculation of the *cis*/*trans*-1,4 ratio are not resolved (protons ***e*** and ***g*** and ***f*** and ***h***), see *Figure 2.5*.

Therefore, it could be claimed with confidence that the changes in the %1,2 microstructures as function of solvent polarity are real and significant. Nevertheless, that is not the case of the *cis*/*trans*-1,4 ratio data due to the errors explained above.

2.2.1. The impact of molar mass on microstructure

As mentioned previously, the concentration of initiator exerts an effect on the microstructure of polydienes (polybutadiene, polyisoprene and PDMB). According to Quirk and Yuki, for the three polydienes, an increase in the concentration of initiator leads to lower molecular weight polymers with higher vinyl content.[2, 7] In this section the microstructure of the resulting linear PDMB (in both, benzene and alkanes) with different MW's was compared.

The microstructure of the polymers from experiments 2.2, 2.6 and 2.9, all carried out in benzene, with M_n of 12.2, 135.9 and 216.7 kg mol^{-1} were compared. As can be seen in *Table 2.6*, there is a trend of decreasing vinyl content with the increasing M_{target} and hence, with the decreasing concentration of initiator (16% at [BuLi] = 10.16 mM, 12% at [BuLi] = 0.89 mM and 11% at [BuLi] ≈ 0.51 mM) — in line with expectation. Given the fact that the 1,2 signals are quite distinct, it is possible to calculate the %1,2 with a considerable degree of accuracy, see *Figure 2.12*. There will of course be some potential error due to signal to noise ratio but the difference between 16% (sample 2.2) and 12% 1,2 microstructures (sample 2.6) is high enough to be considered real and significant. However, the difference between 12% (sample 2.6) and 11% (sample 2.9) is very low so the vinyl content of samples 2.6 and 2.9 may well be the same within error. On the other hand, because the signals used to calculate the *cis*/*trans*-1,4 ratio are not fully resolved (signals ***e*** and ***g***), as shown in *Figure 2.12*, the potential for error is higher. The content of *cis*-1,4 increases (23 to 33 to 43%) and the content of *trans*-1,4 decreases (61 to 55 to 46%) with the decreasing concentration of initiator until they are close to equal in the 216 kg mol^{-1} polymer (43% *cis*-1,4 and 46% *trans*-1,4). The differences in *cis*/*trans*- content between each sample seem to be high enough to be considered significant. However, due to the potential error in the calculation of the *cis*/*trans*-1,4 ratio mentioned previously, these differences should be considered carefully.

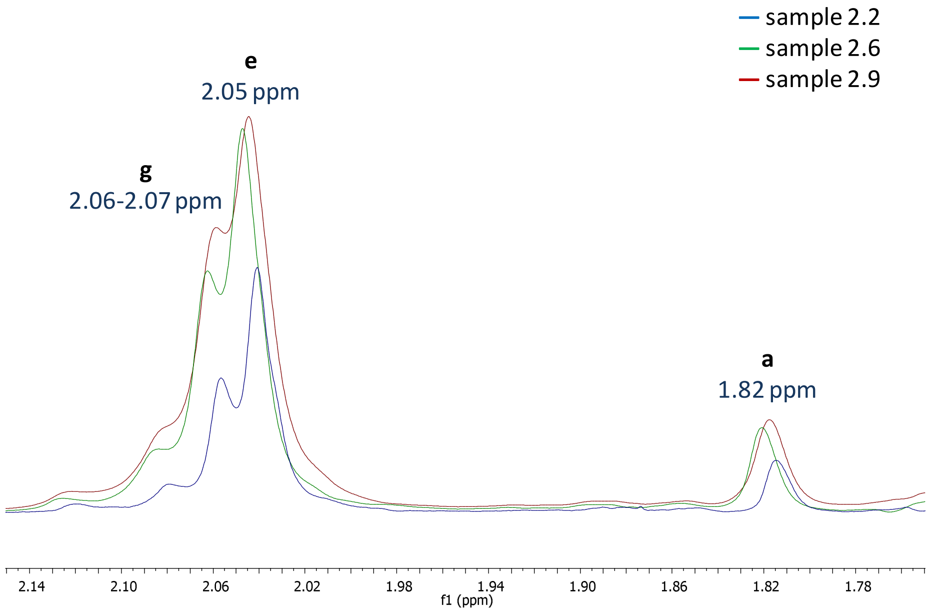


Figure 2.12: *Superimposed spectra of samples 2.2 (12.2 kg mol^{-1}), 2.6 (135.9 kg mol^{-1}) and (216.7 kg mol^{-1}).*

In case of the experiments 2.4 (M_{target} = 10 kg mol^{-1} in *n*-hexane) and 2.8 (M_{target} = 100 kg mol^{-1} in *n*-heptane), it is observed that, in contrast with the experiments in benzene, the vinyl content does not vary with the concentration of initiator (3% 1,2 units in both experiments), as shown in *Table 2.6*. This might suggest that the vinyl content of PDMB synthesized by anionic polymerization with *sec*-BuLi cannot be further reduced unless very low concentrations of initiator are used ([BuLi] >> 1.26mM). The *cis/trans* ratio in 1,4 microstructure for PDMB prepared in alkanes shows a similar trend to that for PDMB made in benzene. It is observed that the content of *cis*-1,4 increases slightly (32 to 35%) and the content of *trans*-1,4 (65 to 62%) decreases with the decreasing concentration of initiator. However, it is observed that this variation in the *cis/trans* ratio is much less pronounced for PDMB prepared in alkanes and due to the overlapping of signals ***e*** and ***g*** (corresponding to *cis*- and *trans*-1,4 microstructures), it is not possible to claim that the differences are real and significant. Therefore, it can be concluded that the microstructures of PDMB synthesized in alkanes do not vary significantly with the concentration of initiator in the range of 12.12 mM < [BuLi] < 0.72 mM.

2.3. Scale-up of synthesis of polyDMB

Polybutadiene and polyisoprene have been widely produced by anionic polymerization in industry since the beginning of the twentieth century. However, the industrial production of polyDMB was stopped after the conclusion of WWI, since the production of the other polydienes was preferred.

In order to explore the transition from laboratory to the potential industrial production of polyDMB by anionic polymerization, a series of scaled-up experiments were carried out in both, laboratory and industrial reactors. The scaled-up synthesis of polyDMB was attempted in three solvents; toluene, *n*-hexane and *n*-heptane. These solvents were chosen to produce polymers with different microstructures and for being more practical from an industrial point of view than benzene (carcinogen) or cyclohexane (more expensive than *n*-hexane). The transition from academic laboratory to industry also saw *sec*-BuLi replaced with *n*-BuLi, since the latter is more commonly used in industry due to its lower price.

Thus, two sets of experiments were carried out. The first set was carried out using the same design of reactor as described above, but on a scale 5 times greater (50 g of monomer in 500 mL of solvent) than the previous experiments (10 g of monomer in 100 mL of solvent), using *n*-BuLi as initiator. The second set was carried out on a larger scale again (100 g of monomer in 1 L of solvent) in an industrial reactor provided by *Synthomer Ltd*. Due to the confidentiality agreement signed with *Synthomer Ltd* some information regarding the reactor (e.g. size, set-up, stirring blades shape) will not be reported in the present document.

2.3.1. Laboratory scaled-up synthesis of polyDMB

40-50 g of monomer and 400-500 mL of solvent (10% solution) were distilled into the reactor prior to initiation using *n*-BuLi. The M_{target} was 10 kg mol^{-1} and, in order to speed up the reaction, the reaction temperature was set at 60 °C. As in previous experiments, conservatively long reaction times were used, in order to ensure the full consumption of the monomer. In these experiments, samples at intermediate reaction times were not collected.

The resulting polymers were analysed by SEC using a triple detection calibration (with light scattering) using the *dn/dc* value of polyisoprene (0.130 mL/g). The results are reported in *Table 2.7*.

Table 2.7: *Molecular weight data obtained by SEC of the resulting polymers synthesized by anionic polymerization of DMB. Initiator: n-BuLi,* M_{target} *= 10 kg mol*$^{-1}$*, T = 60 °C.*

Experiment	**Solvent (ε)**	**t (h)**	**M_n (g mol^{-1})**	**Đ**	**% yield**
2.10	Toluene (2.38)	96	14500	1.11	100
2.11	*n*-heptane (1.92)	96	18800	1.14	100

In both, experiments 2.10 and 2.11, the resulting polymers were obtained in quantitative yield (100%). The obtained M_n is somewhat higher than M_{target} in experiment 2.10 and in the case of experiment 2.11, the experimental M_n is significantly higher (88%) than $M_{targtet}$. This is almost certainly due to the presence of traces of impurities in the reactor before initiation. Additionally, the SEC chromatogram of experiment 2.11 (*Figure 2.13*) shows a low MW tail which is probably produced by impurities leaked into the reactor during polymerization. In both experiments, the obtained Đ values are reasonable for an anionic polymerization although in experiment 2.10, there is evidence of chain coupling during termination (*Figure 2.13*), as discussed previously in *section 2.1.2*.

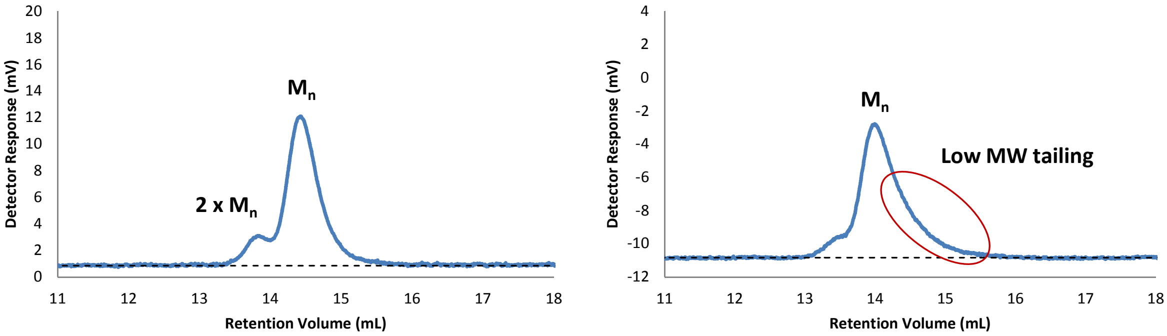


Figure 2.13: *SEC chromatogram of experiment 2.10 (left) and 2.11 (right).*

The resulting polymers were also analysed by ^{1}H-NMR in order to obtain the microstructures. The content of the three different microstructures was calculated from the ^{1}H-NMR spectra in the same way explained above for the previous polymerizations of DMB. Results are reported in *Table 2.8*.

Table 2.8: *Molecular characteristics of DMB homopolymers synthesized in different polarity solvents. Initiator: n-BuLi, M_{target} = 10 kg mol^{-1}, T = 60 °C.*

Experiment	Solvent (ε)	% 1,2	% *cis*-1,4	% *trans*-1,4
2.10	Toluene (2.38)	15	25	60
2.11	*n*-heptane (1.92)	3	33	64

The results reported in *Table 2.8* are entirely consistent with previous observations. It was not expected that scaling up the process would have an impact on the microstructure and changing the initiator from *sec*- to *n*-BuLi was not expected to make any difference.[2, 5, 6]

2.3.2. Industrial scaled-up synthesis of polyDMB

Next, the synthesis of linear polyDMB on a larger scale was attempted using industrial stainless steel reactors. The scale of the reactions was 100 g of monomer in 1 L of solvent (10% w/v solutions). Toluene and *n*-hexane were used as solvents as they are preferred in industry over benzene (carcinogen) and cyclohexane (more expensive). The polymerizations were carried out under a nitrogen atmosphere instead of high vacuum. As a consequence of the lack of high vacuum equipment, the solvents and the monomer were not purified under high vacuum conditions as in the lab scale experiments. Instead, both, monomer and solvents were (only) dried and stored over molecular sieves until they were charged into the reactor. In case of DMB, the bottles were also purged with a nitrogen stream and stored in a fridge at 4 °C prior to use. The polymerizations were initiated by *n*-BuLi and a target molecular weight of 10 kg mol^{-1} was chosen for three reasons:

1. The synthesis of high molecular weight PDMB involves a significant increase in the viscosity of the reaction mixture and this was considered unsuitable for the "industrial" reactor as the viscous solution could block the stirrer and the reactor outlet.

2. Due to local safety regulations, the reactions had to be completed in less than 8 h.

3. As a consequence of the limited purification of the monomer, success in the synthesis of higher MW PDMB was considered unlikely due to the potential for significant levels of impurities in the monomer that might kill the initiator due to the lower concentration of initiator at high M_{target}.

Following initiation the polymerization reactions were stirred under a nitrogen atmosphere, for 5 h and then terminated and isolated by precipitation. The resulting polymers were analysed by SEC using a triple detection calibration (with light scattering) and *dn/dc* value of polyisoprene (0.130 mL/g) and the results are reported in *Table 2.9*.

In experiment 2.12, carried out in toluene, the experimental M_n (4200 g mol^{-1}) is lower than the M_{target}, the polymer was obtained in a very low yield (< 20%) and the Đ value (2.30) is very high for an anionic polymerization. The SEC chromatogram (*Figure 2.14*) shows a very long tail in the low MW region, which is probably due to premature termination by impurities leaking into the reactor. Furthermore, the tailing might also be due to slow reacting impurities e.g. *t*-butyl methyl ketone, (see *Section 2.1.1.*) present in the monomer which was not extensively purified prior to use in this case. Experiment 2.12 was repeated, experiment 2.13, obtaining a polymer in 62% yield with a M_n closer to the M_{target} (8800 g mol^{-1}) and a Đ of 1.55. This clearly represents an improvement on the previous experiment but is still some way from optimised. Experiment 2.14, carried out in *n*-hexane, gave a polymer in a 36% yield, with an M_n of 7200 g mol^{-1} and a Đ of 1.33. This might suggest that the protic terminating agent was added before all the monomer was consumed and the reaction was not well controlled. As in the case of experiment 2.12 and 2.13, the SEC chromatogram of 2.14 (*Figure 2.14*) shows tailing in the low MW region (premature termination). Additionally, it can be seen a second peak (2 x M_n) in the high MW region (chain coupling).

Table 2.9: *Molecular weight data obtained by SEC of the resulting polymers synthesized by anionic polymerization of DMB. Initiator: n-BuLi, M_{target} = 10 kg mol^{-1}, T = 60 °C.*

Experiment	Solvent (ε)	t (h)	M_n (g mol^{-1})	Đ	% yield
2.12	Toluene (2.38)	5	4200	2.30	< 20
2.13	Toluene (2.38)	5	8800	1.55	62
2.14	*n*-heptane (1.92)	5	7200	1.33	36

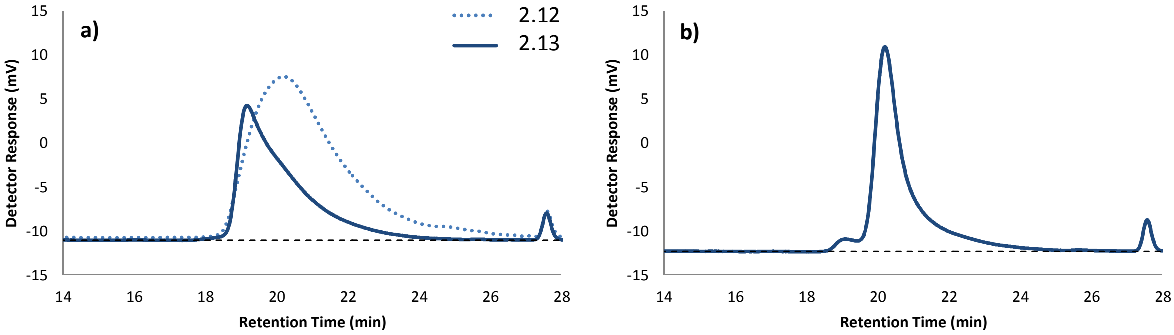


Figure 2.14: *SEC chromatogram of PDMB synthesized by anionic polymerization in an industrial reactor: a) experiments 2.12 and 2.13 (toluene) and b) experiment 2.14 (n-heptane).*

The polymers were also analysed by ^{1}H-NMR. The microstructures were calculated from the NMR spectra using the method explained previously and are summarized in *Table 2.10*. The polymer obtained in experiment 2.12 was not analysed due to the low yield and M_n and the very high Đ value.

Table 2.10: *Molecular characteristics of DMB homopolymers synthesized in different polarity solvents. Initiator: n-BuLi, M_{target} = 10 kg mol^{-1}, T = 60 °C.*

Experiment	Solvent (ε)	% 1,2	% *cis*-1,4	% *trans*-1,4
2.12	Toluene (2.38)	-	-	-
2.13	Toluene (2.38)	15	26	59
2.14	*n*-heptane (1.92)	3	34	63

In *Table 2.10* it is observed that the microstructures of experiments 2.13 and 2.14 are almost identical to experiments 2.10 and 2.11 respectively (see *Table 2.8*). Therefore, it can be concluded that scaling up the process had little or no impact on the resulting microstructure.

The results obtained clearly evidence that the scaled-up process still needs some work and especially a more extensive purification process. For example, degassing and storing the monomer under reduced pressure and its addition by injection would remove significantly the amount of impurities and therefore the results obtained.

2.4. Thermal analysis of polyDMB

The thermal properties e.g. glass transition temperature (T_g) and melting temperature (T_m) also represent a key element in the characterisation of polymers, as they correlate mechanical properties to temperature. Thus, the thermal properties define the temperature range within which the polymer has the desired properties or above which, the polymer can be processed. The thermal properties may be analysed by different techniques, with Differential Scanning Calorimetry (DSC) a popular choice. DSC measures the difference in the heat flow between the sample to be analysed and a reference, as a function of temperature (which is controlled by a defined temperature program). DSC has many applications but is most commonly used in the field of polymer science for the determination of various phase transition temperatures including the T_g and T_m. T_g is a characteristic of amorphous polymers where the chains are randomly orientated. The irregularity of the polymer chains does not allow effective packing. Below T_g the polymer is a brittle, rigid material and above T_g the polymer softens and behaves as a viscous liquid. When the chains are regular enough to allowing packing into highly ordered structures, the polymer is able to crystallise and semi-crystalline polymers result. In this case the polymer will possess both, a T_g and T_m. In a DSC thermogram the T_g is observed as a step in the baseline while the T_m is detected as a peak. 100% crystalline polymers do not exist as it is not possible to have all the chains within the polymer completely ordered.

The thermal properties of PDMB (and other diene polymers) are strongly related to the polymer microstructure.[15] Thus it has been reported that PDMB with a high *cis*-1,4 or *trans*-1,4 microstructure (especially *trans*-1,4) is able to crystallise. As mentioned previously in *section 1.1*, 100% *cis*-1,4 and 100% *trans*-1,4 PDMB are (semi-)crystalline powders with melting points ranging from 189 to 192 °C[13] and 260 to 263 °C[14] respectively. Both polymers crystallise under quiescent condition. The difference in the melting point in these two cases is due to the structure of the *trans*-1,4 unit allowing the chains to more easily pack than the *cis*-1,4 and thus, *trans*-1,4 PDMB is more crystalline. In a patent published by *The Goodyear Tyre & Rubber Co.* in 1980 it was reported that 1,2 units disrupt crystallinity much more than *cis*-1,4, so, if it is desirable to have a certain amount of crystallinity in PDMB, the 1,2 content in the final polymer should not exceed 20%.

2.4.1. The impact of heating rate on the glass transition of polyDMB

As is known from data previously published, the T_g obtained by DSC shows a dependence on the heating and cooling rate. At lower heating rates more accurate T_g are obtained as any thermal lag is minimized. However, in some cases, at low heating rates, the T_g may be too small to be detected. At higher heating rates a larger amount of heating power is required when passing through the T_g faster. Therefore, a greater change in the heat flow is observed for the T_g at higher heating rates. However, due to the thermal lag produced by the faster heating rates, the T_g values are usually shifted to higher temperatures[16, 17] and the extent to which the T_g is shifted will increase with heating rate. It is also well-known that the glass transition is sometimes difficult to detect by DSC but the apparent size of the transition can be "magnified" by increasing the heating rate. With this in mind, a study of how much the T_g varies with increasing the heating rate (from 10 to 100 °C/min) in the DSC analysis was carried out for the lower molar mass linear PDMB homopolymers (with a M_{target} of 10K g mol^{-1}) obtained in benzene (experiment 2.2) and *n*-hexane (experiment 2.4). This study was carried out in order to inform the thermal analysis of the materials described in the current and subsequent chapters. The results for this study are shown in *Table 2.11*.

The results are in line with expectations. The data for sample 2.2 in *Table 2.11* and in *Figure 2.15* and *Figure 2.16*, confirm that a higher heating rate results in an increase in T_g, from 3.5 °C at 20 °C/min to 16.4 °C at 300 °C/min. Additionally, as explained above, the transitions at higher heating rates (50-300 °C/min) appear enhanced in magnitude and therefore clearer than the transitions at lower heating rates (10-30 °C/min). The data presented in *Figure 2.15* and *Figure 2.16* for sample 2.2 is typical and the DSC thermograms for sample 2.4, not reported here, illustrated the same behaviour. In case of the analyses at 10 °C/min in both cases the glass transition was not detected and the calculation of T_g was not possible.

Table 2.11: *DSC analysis of the evolution of T_g of 10 kg mol^{-1} PDMB synthesized in benzene (sample 2.2) and n-hexane (sample 2.4) at different heat rates.*

SAMPLE 2.2 (benzene; %1,2 = 16%)		**SAMPLE 2.4 (*n*-hexane; %1,2 = 3%)**	
Heating rate (°C/min)	**T_g (°C)**	**Heating rate (°C/min)**	**T_g (°C)**
10	—[a]	10	—[a]
20	3.5	20	-1.6
30	4.0	30	0.9
50	6.1	50	4.0
100	8.6	100	6.6
200	10.6	200	8.3
300	16.4	300	13.9

a) Transitions not clear enough for an accurate calculation of T_g.

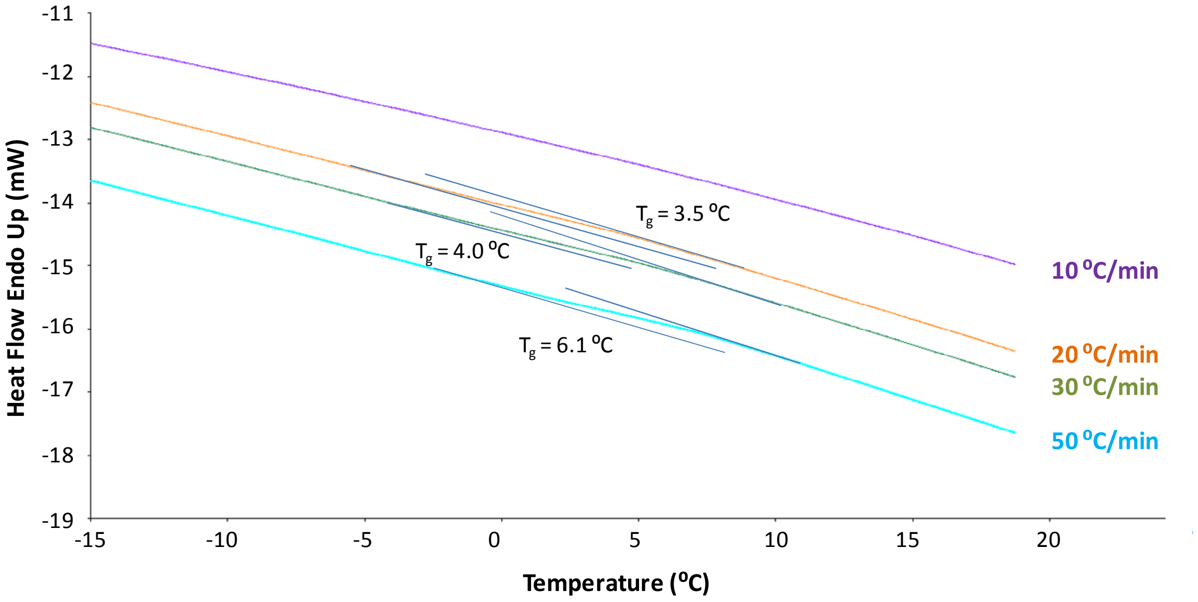


Figure 2.15: *DSC thermograms for sample 2.2 (PDMB synthesized in benzene), showing the T_g observed upon heating at 10 (purple line), 20 (orange blue line), 30 (green line) and 50 (light blue line).*

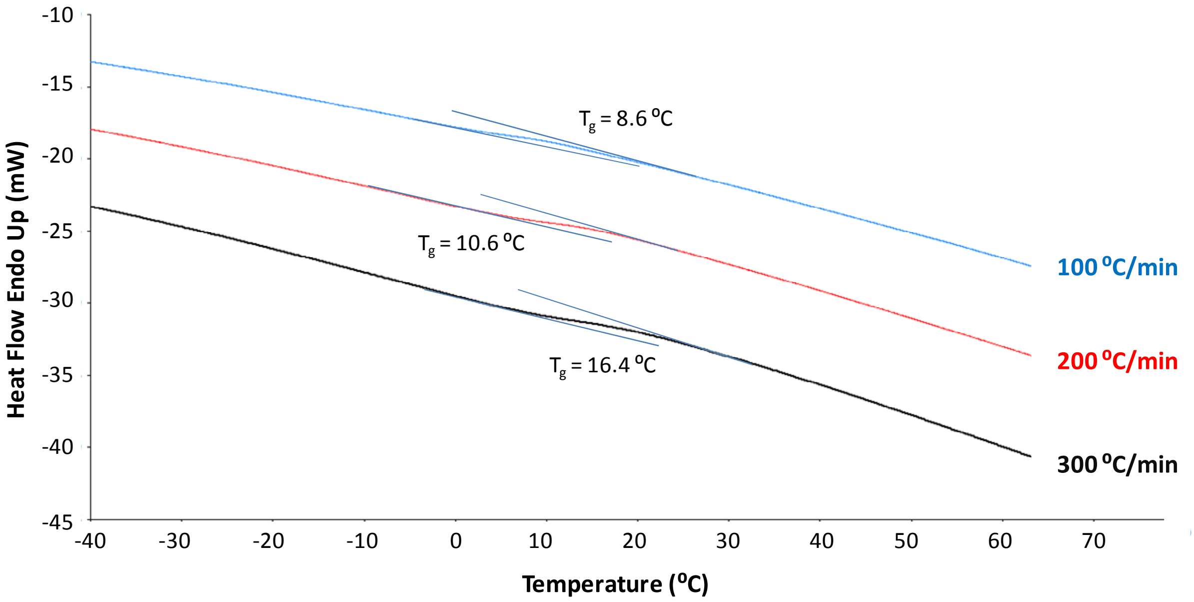


Figure 2.16: *DSC thermograms for sample 2.2 (PDMB synthesized in benzene), showing the T_g observed upon heating at 100 (blue line), 200 (red line) and 300 (black line).*

Chiang and co-workers previously reported the thermal analysis of polyDMB with a vinyl content ranging from 3 to 29% with an associated T_g in the range -4.6 °C to 5.2 °C.[5] The data reported in *Table 2.11* is broadly in line with expectation and the relationship between T_g and microstructure consistent with Chiang in that sample 2.2 with 16% 1,2 units has a consistently higher T_g than sample 2.4 with 3% 1,2 units.

2.4.2. The impact of microstructure on thermal properties of polyDMB

To understand the relationship between microstructure and the thermal properties of polyDMB, the four lower molar mass polymers from experiments 2.1, 2.2, 2.3 and 2.4 (M_{target} = 10 kg mol^{-1}) were analysed by DSC. The analysis was carried out in a temperature range from -100 to 100 °C at two different heat rates (200 and 300 °C/min) in order to ensure clearer transitions (*Figure 2.18*) as previous DSC analysis at lower heating rates on the same samples gave weak and poorly defined transitions. Three heating/cooling cycles were carried out at each heating rate and an average T_g was calculated from the three observed glass transitions. DSC results are shown in *Figure 2.17*. *Figure 2.18* shows an example of the DSC thermograms obtained for sample 2.1 at 200 and 300 °C/min. The rest of the samples gave very similar thermograms and so the thermograms are not reported.

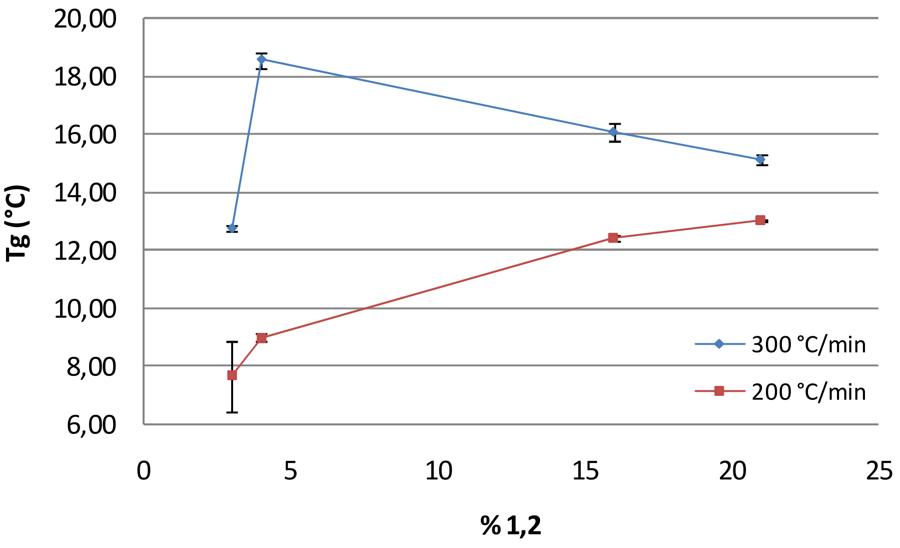


Figure 2.17: *T_g of low molar mass DMB homopolymers (M_{target} = 10 kg mol^{-1}) with different microstructures synthesized in aromatic solvents and alkanes: sample 2.1, toluene, 21% 1,2, sample 2.2, benzene, 16% 1,2, sample 2.3, cyclohexane, 4% 1,2 and sample 2.4, n-hexane, 3% 1,2.*

The T_g's obtained for the polymers produced in this study are out of the range described previously by Chiang who reported a T_g of between -4.6 °C at 3% 1,2 units to 5.2 °C at 29%.[5] However, the difference might be a consequence of different experimental conditions as Chiang does not report experimental details and in particular does not specify the heating rate — the heating rates used in the current study are very high. As mentioned before, higher heating rates shift the T_g to higher values due to the thermal lag and, as shown in *section 2.4.1.*, differences of more than 10 degrees in T_g can arise when using much higher heating rates. Therefore, any comparison to other data has to be considered carefully. It is clear that there is a general trend to a lower glass transition temperature for PDMB with a lower 1,2 microstructure. The T_g for sample 2.1 (with 21% 1,2 units) is 13.0 °C at 200 °C/min while the T_g for the other samples is 12.4 °C (sample 2.2, 16% 1,2), 9.0 °C (sample 2.3, 4% 1,2) and 7.7 °C (sample 2.4, 3% 1,2) at 200 °C/min. However, the result for sample 2.3 at 300 °C/min (18.6 °C) is somewhat higher than the trend of other results would imply, with no obvious explanation. However, leaving that result aside, the T_g of the various samples range from 7.7 to 13.0 °C at 200 ^{o}C/min and from 12.8 to 16.0 °C at 300 °C/min. The data shows evidence of good reproducibility of the T_g measurements at 200 and 300 °C/min. Thus in all cases a single sample was run three times with T_g falling within about 1 °C variation. The only exception being sample 2.4 at 200 °C/min, which showed greater variation. The data in *Figure 2.17* shows that samples with similar vinyl content showed very similar T_g. The difference between the T_g of 2.1 and 2.2 is less than 1 °C (variation between runs) so it might be argued that the difference between the two samples is not significant. On the other hand, the difference between 2.1-2.2 (with a 1,2 content of 16 and 21%

respectively) and 2.3-2.4 (4 and 3% 1,2 respectively) is about 3 to 4 °C (which is higher than the variation between runs), and therefore, the impact of microstructureon T_g is statistically significant and confirms that the difference in microstructure really does impact the T_g. Additionally, the trends in the data are consistent with Chiang's observation that T_g generally increases with increasing 1,2 (vinyl) content albeit with some minor variation (less than 1 °C) from the expected trend for the data obtained at 300 °C/min.[5] This might be explained as a consequence of the extremely high heating rate producing inaccuracies due to thermal lag or by some small element of human error in analysing the data.

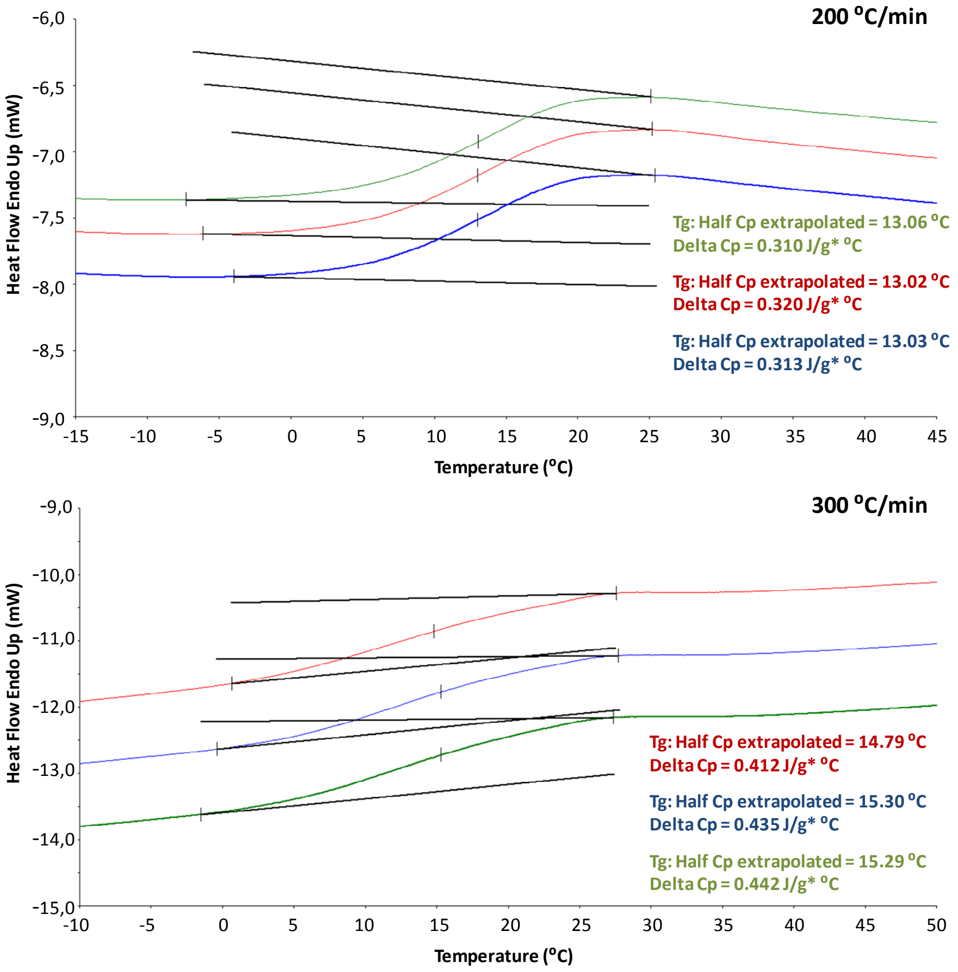


Figure 2.18: *DSC thermogram for sample 2.1 (PDMB synthesized in toluene), showing the T_g observed upon heating at 200 °C/min and 300 °C/min.*

Comparing the DSC results for the various samples of polyDMB, with the T_g previously reported for polyisoprene (-68 °C)[18] and polybutadiene (-90 °C),[2] it is clear that the T_g of polyDMB is dramatically higher than the other polydienes. As it can be seen, the difference between the T_g of polybutadiene and polyisoprene (ΔT_g = 22 °C) is much less than the difference between polyisoprene and polyDMB (ΔT_g = 70 °C). This comparison suggests that the presence of the two methyl groups on carbons 2 and

3 of DMB seem to exert a surprisingly more significant impact on the thermal properties of PDMB than the single methyl group on carbon 2 of isoprene. This impact on T_g is almost certainly the consequence of the bond dipole caused by the two electron releasing $-CH_3$ groups, that in turn will increase intermolecular forces of attraction. However, the magnitude of the effect caused by the second $-CH_3$ group on the thermal properties was unexpected and is considered surprising.

The relatively high T_g of the resulting polyDMB (close to room temperature) goes a long way towards explaining the limitations of the tyres manufactured in Germany during WWI (see *Chapter 1*). These polymers will be below T_g at northern winter temperatures, making them unsuitable for being used in tyre production.

2.4.3. Thermal analysis of high molecular weight polyDMB

The higher molar mass linear PDMB homopolymers with a M_{target} of 100K g mol^{-1} (samples 2.6 and 2.8) were also analysed by DSC, in order to check the impact of the molecular weight on the thermal properties of polyDMB. An empirical equation that relates the M_n to the T_g is the Flory-Fox equation, *Equation 2.5*,[19, 20] where $T_{g,\infty}$ is the value of the glass transition temperature at infinite molecular weight and *K* is a constant for a given polymer that is related to the free volume of the polymer.

$$\boldsymbol{T_g(M_n) \approx T_{g,\infty} - {}^{K}\!/_{M_n}} \qquad \textbf{Equation 2.5}$$

According to *Equation 2.5*, an increase in the M_n would increase the T_g. On the other hand, as mentioned in *section 2.2.1.*, a higher molar mass (lower concentration of propagating chain ends) results in a lower vinyl content of PDMB, and that in turn will push the T_g down (as shown in *section 2.4.2.*). The vinyl content of the resulting PDMB as well as the Đ are also expected to have an impact on the thermal properties. According to Henderson,[3] the 1,2 units of PDMB disrupt crystallinity more than *cis*-1,4. Therefore, samples with higher %1,2 are expected to be less crystalline. Additionally, in samples with high Đ (especially those with low MW tailing) there is a possibility that the low molar mass chains act as plasticizers pushing down the T_g and disrupting crystallinity.

Three heating/cooling cycles were carried out (from -50 to 250 °C) at three different heat rates (20, 100 and 200 °C/min) for each polymer. The cycle at 20 °C/min was carried out in order to eliminate any thermal history but the transitions were not expected to be clear enough for accurate calculations of T_g and T_m, considering previous results, see s*ection 2.4.1*. The heating/cooling cycles at 100 and 200 °C/min were carried out in order to obtain clear transitions. The DSC thermograms for samples 2.6 and 2.8 are shown in *Figure 2.19* and *Figure 2.20* respectively. The T_g and T_m are reported in *Table 2.12*.

Table 2.12: *DSC analysis of the higher molar mass linear PDMB homopolymers (with a M_{target} of 100K g mol^{-1}) at two different heat rates.*

Sample	Solvent	% 1,2	Heat rate (°C/min)	T_g (°C)	T_m (°C)
2.6	Benzene	12	100	12.4	90.6
			200	21.2	106.4
2.8	*n*-heptane	3	100	10.2	115.0
			200	15.0	114.4

In line with expectations and the data presented earlier T_g increases with the increasing 1,2 microstructures and thus, the polyDMB prepared in benzene with 12% 1,2 units has a T_g of 12.4-21.2 °C (depending on heating rate) while the polymer obtained in *n*-heptane with a lower vinyl content (3%) shows a lower T_g of 10.2-15.0 °C. However, when samples 2.2 (12.2 kg mol^{-1}) and 2.6 (136.0 kg mol^{-1}) are compared, an increase in the glass transition temperature from 12.4 to 21.2 °C at 200 °C/min is observed. Two contrasting effects are expected here. On the one hand, one would expected to see a decrease in the T_g of sample 2.6 (12% 1,2 units) compared to the T_g of sample 2.2 (16% 1,2 units) as a consequence of the lower vinyl content of sample 2.6. On the other hand, one would also expect to see an increase in T_g as a consequence of the significantly higher molar mass of sample 2.6 (M_n = 136000 g mol^{-1}) versus sample 2.2 (M_n = 12200 g mol^{-1}). Considering the results for samples 2.2 and 2.6, it seems that the effect of the molecular weight on the T_g of the resulting PDMB is more significant than the effect of the relatively small change in microstructure. In case of samples 2.4 and 2.8, both with a vinyl content of 3%, the same impact of molar mass on T_g is observed. Thus, sample 2.4 (9.2 kg mol^{-1}) has a T_g of 7.7 °C at 200 °C/min while sample 2.8 (169.7 kg mol^{-1}) showed a higher T_g of 15.0 °C at 200 °C/min.

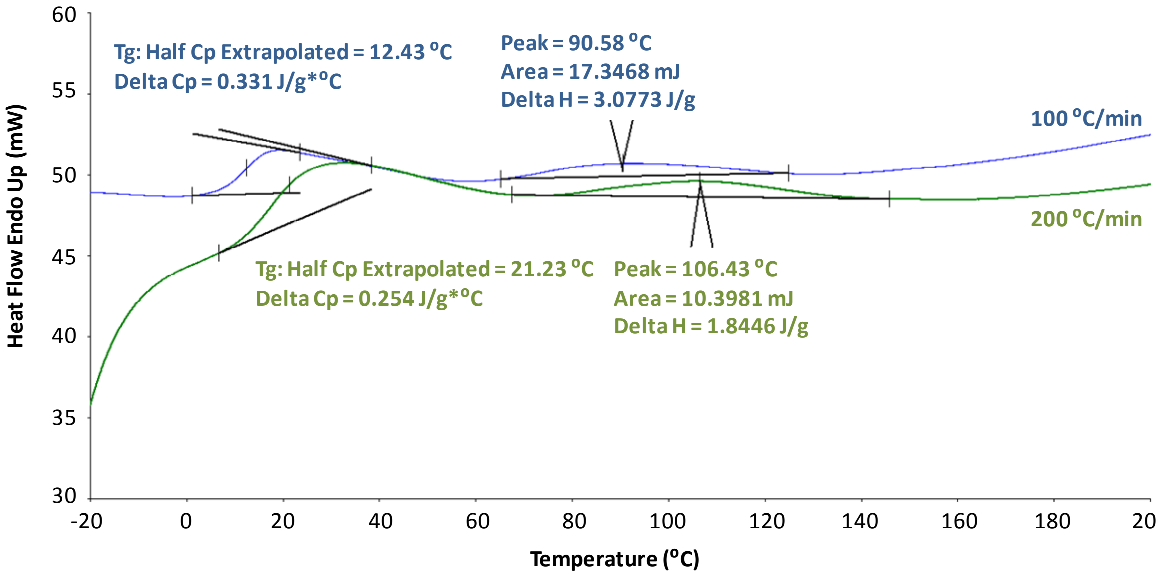


Figure 2.19: *DSC thermogram obtained for sample 2.6 (136.0 kg mol^{-1} PDMB synthesized in benzene), showing the T_g and T_m observed upon heating at 100 °C/min (blue line) and 200 °C/min (green line).*

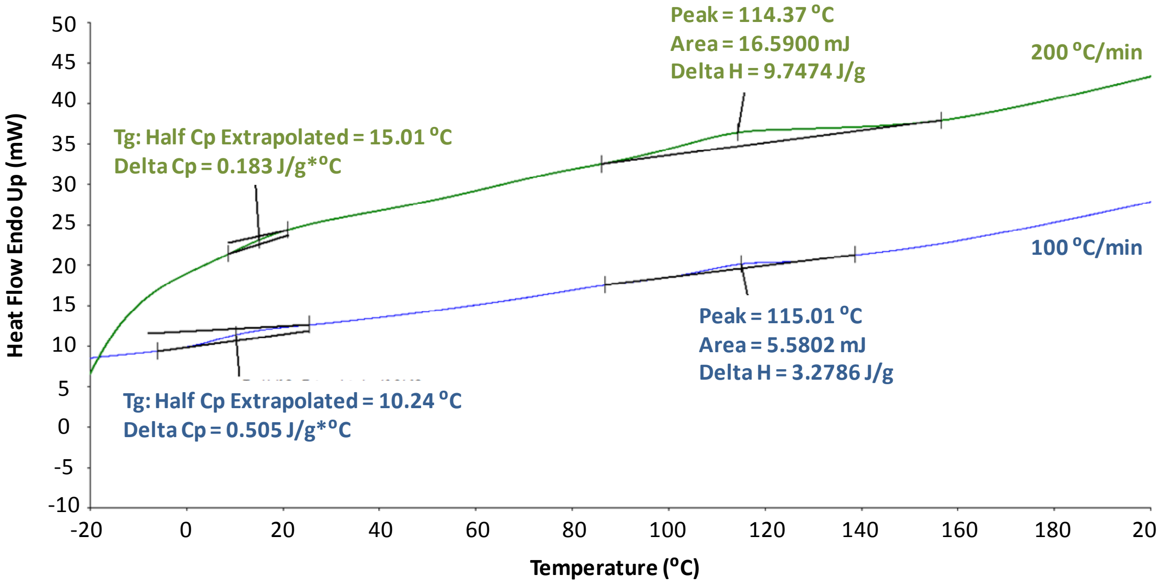


Figure 2.20: *DSC thermogram obtained for sample 2.8 (169.7 kg mol^{-1} PDMB synthesized in n-heptane), showing the T_g and T_m observed upon heating at 100 C/min (blue line) and 200 °C/min (green line).*

Regarding the crystallinity of the resulting polymers, it was expected that the samples of PDMB with a higher 1,4 content would show a higher degree of crystallinity and possibly a higher T_m due to easier chain packing. According to Yen,[13, 14] a 100% *trans*-1,4-polyDMB shows a T_m at 260 °C while a 100% *cis*-1,4 polyDMB shows a T_m at 189 °C. Considering that the polymers produced in the current project do not have a 100% 1,4 microstructure, it was expected that T_m would be below 189 °C. DSC analysis revealed that sample 2.6 (M_n = 136000 g mol^{-1}, 12% 1,2 content) has a T_m at 90.6 and 106.4

°C at heating rates of 100 and 200 °C/min respectively (*Figure 2.19*). On the other hand, sample 2.8 (M_n = 170000 g mol^{-1}, 3% 1,2 content) showed a T_m peak at a temperature around 115 °C at both, 100 and 200 °C/min (*Figure 2.20*). Regarding the enthalpy of melting (Delta H in *Figure 2.19* and *Figure 2.20*), experiment 2.6 (vinyl content of 12%) shows an enthalpy of 3.08 and 1.84 J/g at 100 and 200 °C/min respectively. On the other hand, experiment 2.8 (vinyl content of 3%) shows a higher enthalpy of melting of 3.30 and 9.75 J/g at 100 and 200 °C/min respectively. As the enthalpy of melting is proportional to the degree of crystallization, this experimental observation might suggest that the crystallinity of sample 2.8 is higher than sample 2.6 under the conditions of the experiment. This would be in agreement with the expectations as the 1,2 units disrupt the crystallization of PDMB.[3] However, it is noteworthy that T_m transitions are broad and very weak. Typical DSC thermograms of well-known commercial semicrystalline polymers (e.g. PE, PP, PET) show very intense T_m transitions compared to the T_g, which is not the case for samples 2.6 and 2.8. Therefore, even though DSC evidence support that samples 2.6 and 2.8 are showing some crystallisation, the degree of crystallization is very low. Additionally, samples 2.6 and 2.8 showed Đ of 1.17 and 1.29 respectively which are expected to disrupt crystallinity in some extent due to the presence of low M_n chains acting as plasticisers (especially in case of sample 2.8 where a significant low MW tailing was observed, see *section 2.2*). As a consequence the differences in Delta H for both samples might not be significant and it cannot be claimed with confidence that the degree of crystallinity varies with the vinyl content in the studied range of microstructures (3-12% 1,2). Therefore, it can be concluded that the resulting higher M_n linear PDMB homopolymers (with a M_{target} of 100K g mol^{-1}) undergo crystallisation in the absence of stretching but the degree of crystallinity is very low for both samples.

Crystallinity in the quiescent state has also been observed in the both polybutadiene and polyisoprene. It is reported that both show a certain degree of crystallinity when their microstructure is nearly 100% *trans*-1,4.[21, 22] However, the range of microstructures available in polybutadiene and polyisoprene synthesised by anionic polymerization do not allow any crystallisation in quiescent samples.

2.5. Summary

Linear DMB homopolymers with M_n of approximately 10 kg mol^{-1} have been successfully synthesized in four different polarity solvents (toluene, benzene, cyclohexane and *n*-hexane). The polymerization of DMB showed a lower rate than butadiene and isoprene due to the higher electron density on carbons 1 and 4, induced by the two methyl groups on carbons 2 and 3. The microstructure of polyDMB varied significantly as a function of solvent polarity, from 21% 1,2 units in toluene (ε = 2.38) to 3% 1,2 units in *n*-hexane (ε = 1.89). The microstructure of polyDMB has proved to be more sensitive to the polarity of the reaction solvent than polybutadiene where the vinyl content is relatively unchanged (8-10% 1,2 microstructure) within the same polarity range. Moreover, it has been shown here that the microstructure of the resulting polyDMB plays an important role on the polymer's physical appearance and properties. The polyDMB samples with a higher 1,2 content (16-21% 1,2 units) have a white solid appearance with a slight elasticity. On the other hand, the polyDMB with lower 1,2 content (3-4% 1,2 units) were white compact waxy solids. The difference in the physical appearance is possibly a consequence of a higher degree of crystallinity in the polyDMB obtained in alkanes due to the higher 1,4 content (96-97%) than the polyDMB obtained in aromatics (79-84% 1,4 units). Moreover the higher T_g (12.4-16.0 °C) of the polymers synthesized in aromatic solvent (a consequence of the 16-21% 1,2 units) compared to the analogous samples synthesized in alkanes (7.7-12.8 °C) will be a contributing factor. The solubility tests revealed that polyDMB shows decreasing solubility (in THF, toluene and *n*-hexane) with increasing content in 1,4 units and hence, with increasing crystallinity. An increase in temperature (up to 60 °C) improved the solubility of the resulting polyDMB obtained in benzene, cyclohexane and *n*-hexane. It is also worth noting that the solubility of PDMB is notably different to that of polybutadiene, which is fully soluble in the three solvents tested (THF, toluene and *n*-hexane).

Linear polyDMB of approximately 100 kg mol^{-1} has been successfully synthesized in benzene and *n*-heptane in approximately 48-72 h at 60 °C. The initial concentration of initiator and hence, the molecular weight of the polymer, exerted a significant effect on the microstructure of the resulting polyDMB obtained in benzene. Thus, the lower molar mass linear PDMB homopolymers (with a target MW of 10K g mol^{-1}) obtained in benzene showed a vinyl content of 16% while the higher M_n equivalent (M_{target} = 100 kg mol^{-1}) showed a lower vinyl content of 12%. The effect of the initial concentration of initiator on the microstructure of polyDMB (lower vinyl content at lower concentrations of BuLi) was similar to the effect on the microstructure of both polybutadiene and polyisoprene. In case of the polymers synthesized in *n*-alkanes, no change in the microstructure was observed at lower concentrations of initiator which might suggest that the vinyl content of polyDMB reaches a minimum at 3% and further reduction is not easy to achieve.

A series of scaled-up experiments were carried out in order to explore the transition from academic to the industrial synthesis of polyDMB. Two experiments at a scale of 50 g of monomer in 500 mL of solvent (toluene and *n*-heptane) have been carried out using *n*-BuLi as initiator (preferred in industry) in a glass reactor under vacuum. The increase of temperature from 40 to 60 °C seemed to play a significant role in the microstructure of PDMB synthesized in toluene. At 40 °C, a vinyl content of 21% was observed while at 60 °C the resulting PDMB showed a lower content in 1,2 units of 15%. On the other hand, the resulting PDMB synthesized in *n*-alkanes proved to be insensitive to the increase of temperature (3% at both 40 and 60 °C). Next, a series of polymerizations at a scale of 100 g of monomer in 1000 mL of solvent (toluene and *n*-hexane) was carried out using *n*-BuLi as initiator in an industrial stainless steel reactor. The resulting polymers showed a SEC chromatogram with broad dispersity due to a long low molecular weight tail as a consequence of premature termination of active chains throughout the polymerization. This is probably a consequence of impurities present in the monomer and solvents.Full purification was not possible prior to initiation as the process was not carried out under high vacuum but under N_2 atmosphere. These observations suggest that the industrial synthesis of PDMB under the selected conditions has still to be optimized.

Finally, the lower (M_{target} of 10 kg mol^{-1}) and the higher molar mass (M_{target} of 100 kg mol^{-1}) PDMB were analysed by DSC in order to explore the thermal properties, and specifically the T_g and the T_m. First, a study of the variation of T_g of the lower molar mass linear PDMB homopolymers (with a target MW of 10 kg mol^{-1}) samples synthesized in benzene and *n*-hexane with the DSC heating rate was carried out. The glass transitions at lower heating rates (10, 20, 30 and 50 °C/min) were not always clear enough for accurate analysis. However, as expected, the T_g shifted to higher values with the increasing heating rate (0.04 and 0.05 °C per 1 °C/min for benzene and *n*-hexane respectively) and the transition became easier to detect. Then, the low M_n PDMB samples synthesized in toluene, benzene, cyclohexane and *n*-hexane (M_{target} = 10 kg mol^{-1})were re-analysed by DSC at 200 and 300 °C/min in order to ensure clear transitions. The T_g of PDMB synthesized in aromatic solvents (with a 1,2 content of 16-21%) ranged from approximately 12 to 16 °C. On the other hand, the PDMB synthesized in alkanes (3-4% 1,2 content) showed a T_g ranging from 8 to 13 °C. In all cases the T_g of PDMB was shown to be much higher than polybutadiene (-90 °C) and polyisoprene (-68 °C), suggesting that the second methyl group in carbon 3 of DMB plays a fundamental and significant role in the physical properties of PDMB. The analysis of the higher M_n linear PDMB homopolymers (with a target M_n of 100K g mol^{-1}) samples revealed that the T_g of higher MW PDMB is higher (12-21 in benzene and 10-15 °C in *n*-heptane) than the lower MW samples — as expected. Additionally, a weak crystalline melting peak was observed in both the high molar mass samples of PDMB synthesized in benzene (T_m 91-106 °C) and in *n*-heptane (T_m 114-115 °C). The enthalpy of melting suggests that even though there is evidence that there is a certain crystallinity in quiescent conditions for both samples, the degree of crystallisation is low. This inherent crystallinity of PDMB synthesised in this study via anionic polymerization is a property that both polybutadiene and polyisoprene are only capable of when their microstructures are nearly 100% 1,4 units.

Nevertheless, the range of microstructures for polybutadiene and polyisoprene synthesised by anionic polymerization do not allow the inherent crystallisation in the absence of stretching that was observed in PDMB.

The results obtained in this chapter have revealed the strikingly different behaviour of polyDMB compared to polybutadiene and polyisoprene. The microstructure of PDMB has proved to be more sensitive to the change of polarity of the reaction solvent. Moreover, 97% 1,4-PDMB can be synthesized just by switching to a non-polar solvent such as *n*-hexane or *n*-heptane which is not possible in the case of polybutadiene (92% 1,4 microstructure in *n*-hexane). The PDMB samples synthesized herein showed a certain degree of inherent crystallinity, which is a property that polybutadiene and polyisoprene synthesized by anionic polymerization do not have. Probably as a consequence of this inherent crystallinity, PDMB showed a very low solubility in *n*-hexane and a poor solubilities in toluene and THF, which contrast with the high solubility of polybutadiene in the three solvents tested.

2.6. References

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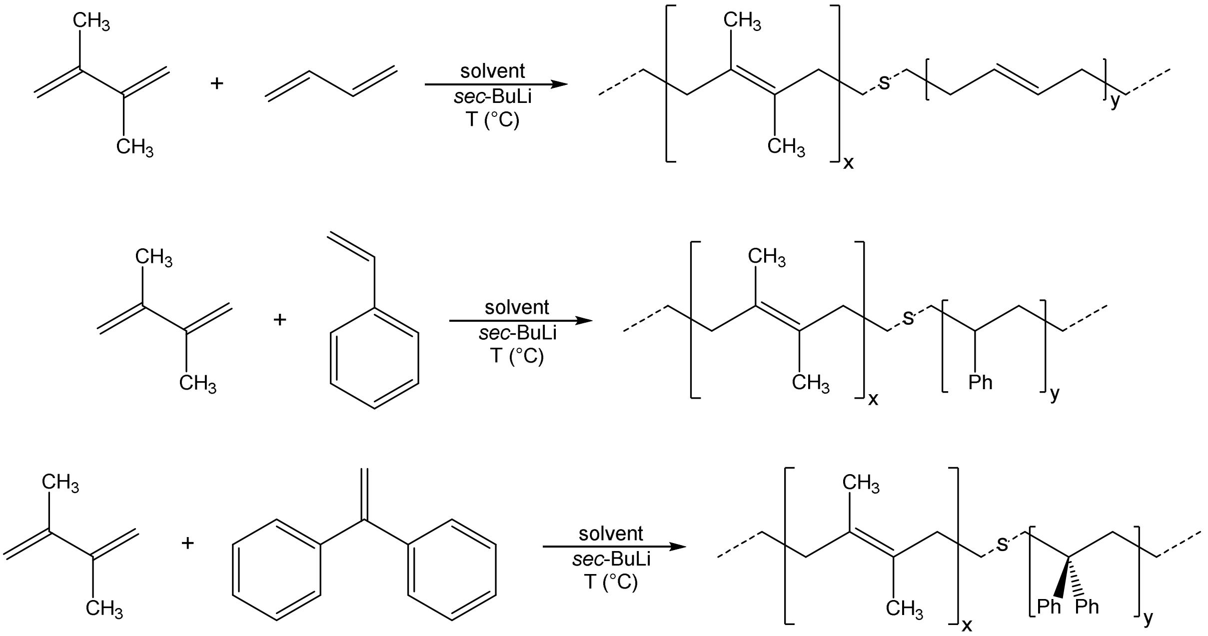
Chapter 3

Synthesis of 2,3-dimethyl-1,3-butadiene copolymers and characterisation of co-monomer sequence distributions

Chapter 3: Synthesis of 2,3-dimethyl-1,3-butadiene copolymers and characterisation of co-monomer sequence distributions

This chapter will focus on the anionic copolymerization of DMB with three different co-monomers: butadiene, styrene and 1,1-diphenylethylene, as shown in *Scheme 3.1*. As mentioned in *Chapter 1*, the syntheses will be carried out in a one-pot process. Thus, the two monomers will be mixed together before initiation takes place. In other words, all the experiments described in this chapter will be statistical copolymerizations.



Scheme 3.1: *Statistical anionic copolymerization of DMB with butadiene, styrene and 1,1-diphenylethylene (DPE). Solvents: benzene, n-hexane or n-heptane. T: 40 or 60 °C.*

The purpose of these experiments is understand the copolymerization behaviour of each pair of monomers and to obtain the reactivity ratios. As described in *Chapter 1*, in statistical copolymerizations the different co-monomers have different reactivities as a consequence of their specific chemical structure. This relative reactivity is responsible for the monomer sequence of the resulting copolymers (random, blocky, etc.) which in turn will strongly influence the final properties and hence, which applications the copolymers are suitable for. For example, a random copolymer of DMB will show a single T_g and the inherent crystallinity shown by PDMB, see *Chapter 2*, would likely be inhibited. On the other hand, if the copolymerization of DMB and the co-monomer leads to a blocky copolymer, two T_g values will be observed, and the DMB block might retain its crystallinity. For that reason, understanding how these pairs of monomers react together is of great importance and the calculation of reactivity ratios will be a key issue within this chapter. To the best of our knowledge, reactivity ratios for the anionic copolymerization of DMB-Bd and DMB-Sty have not been reported previously. Also, the influence of the (non-DMB) co-monomer on the microstructure of DMB units, as well as how the co-monomer affects different parameters such as reaction rate or polymer solubility will be reported. As mentioned in *Chapter 1*, the copolymerization behaviour of butadiene and isoprene in anionic polymerization has been well-known for many decades and comparisons will be made between the behaviour of DMB and the more commonly used dienes.

For calculating the reactivity ratios, the Fineman-Ross linearization method was used. This linear equation was published by Fineman and Ross in 1950.[1] It is based on the linearization of the Lewis-Mayo equation:

$$\frac{m_1}{m_2} = \frac{r_1[M_1]^2+[M_1][M_2]}{r_2[M_2]^2+[M_1][M_2]} \qquad \textbf{Equation 3.1}$$

Where r_1 and r_2 are the reactivity ratios of monomer 1 and monomer 2 respectively, m_1 and m_2 correspond to the copolymer composition and $[M_1]$ and $[M_2]$ represent the monomer feed ratio. In using the above equation for estimating the reactivity ratios it is assumed that the instantaneous feed ratio ($[M_1]/[M_2]$) is the same than the initial feed ratio. However, due to the different reactivity of the co-monomers, the instantaneous feed ratio changes constantly throughout the copolymerization. Therefore, using *Equation 3.1* requires the collection and analysis of copolymerization samples at very low monomer conversions (< 5-10%) when the instantaneous feed ratio is still approximately equal to the initial feed ratio. As the Fineman-Ross linearization is based on *Equation 3.1*, the collection of samples at low conversion will be critical for calculating reactivity ratios. The rearrangement of *Equation 3.1* gives:

$$G = r_1 H - r_2 \qquad \textbf{Equation 3.2}$$

Where:

$G = X(Y-1)/Y$

$H = X^2/Y$

$X = m_1/m_2$

$Y = [M_1]/[M_2]$

A plot of *Equation 3.2*, *G* vs *H*, should give a straight line whose slope is r_1 and whose intercept is minus r_2. Alternatively, *Equation 3.1* can be rearranged in a different way:

$$\frac{G}{H} = -r_2 \frac{1}{H} + r_1 \qquad \textbf{Equation 3.3}$$

In this case, a plot of *Equation 3.3*, *G*/*H* vs 1/*H*, gives a straight line whose slope is minus r_2 and the intercept r_1. This alternative method is known as Inverted Fineman-Ross linearization.

In the case of both the Fineman-Ross and inverted Fineman-Ross linearizations, the confidence intervals were calculated using the least squares fitting method, *Equation 3.4* and *Equation 3.5*, where *n* is the number of samples (*n* = 5).

$$error_{slope} = \pm \sqrt{\frac{\sum_i^n (G_i - slope \times H_i - intercept)^2}{(n-2) \times \sum_i^n \left(\frac{H_i - \sum_i^n H_i}{n}\right)^2}} \qquad \textbf{Equation 3.4}$$

$$error_{intercept} = \pm \sqrt{\left(\frac{1}{n} + \frac{\left(\frac{\sum_i^n H_i}{n}\right)^2}{\sum_i^n \left(\frac{H_i - \sum_i^n H_i}{n}\right)^2}\right) \times \left(\frac{\sum_i^n (G_i - slope \times H_i - intercept)^2}{n-2}\right)} \qquad \textbf{Equation 3.5}$$

In addition, reactivity ratios were also calculated by the Kelen-Tudos method. The Kelen-Tudos method is also based on the Mayo-Lewis equation so, as is the for the Fineman-Ross linearization method, the samples collected have to be at low monomer conversion. According to Kelen and Tudos the method provides some advantages over Fineman-Ross, such as reduced potential error in the slope of the line arising from small variations in the polymer composition or invariant reactivity ratios, by re-indexing of the monomers, and thus Kelen-Tudos represents a more robust method. The Kelen-Tudos method uses the following equation:[2]

$$\eta = \left(r_1 + \frac{r_2}{a}\right) \xi - \frac{r_2}{a} \qquad \textbf{Equation 3.6}$$

Where:

$\eta = G / (a + H)$

$\xi = H / (a + H)$

The arbitrary constant *a* (*a* > 0) is used for an optimum distribution of the data. The calculation of the most feasible value of *a* is carried out by using *Equation 3.7* where H_m and H_M represent the lowest and the highest values of *H* respectively, from the series of measurements:

$$a = \sqrt{H_m H_M} \qquad \textbf{Equation 3.7}$$

By plotting the η against ξ, which can only take values in the range $0 < \xi < 1$, a straight line is obtained. Extrapolation to $\xi = 0$ and $\xi = 1$, gives $-r_2/a$ and r_1 respectively (both as intercepts). The confidence intervals were obtained as shown in *Equation 3.8* and *Equation 3.9*, using a t_β *(n-2)* (tabulated value of the Student distribution) of 3.18 (95% confidence) where *n* equals 5 samples.[2-4]

$$\Delta r_1 = \pm t_\beta(n-2)\sqrt{\frac{S_{min}^2}{n-2} \times \frac{\sum_i^n(1-\xi_i)^2}{D}} \qquad \textbf{Equation 3.8}$$

$$\Delta r_2 = \pm \propto t_\beta(n-2)\sqrt{\frac{S_{min}^2}{n-2} \times \frac{\sum_i^n \xi_i^{\,2}}{D}} \qquad \textbf{Equation 3.9}$$

Where S_{min}^2 is the minimum value calculated by *Equation 3.11* and *D* represents:

$$D = \sum_i^n \xi_i^2 \times \sum_i^n (1-\xi_i)^2 - \left[\sum_i^n \xi_i(1-\xi_i)\right]^2 \qquad \textbf{Equation 3.10}$$

$$S^2 = \sum_i^n \left[n_i - r_1\xi_i + \frac{r_2}{\alpha}(1-\xi_i)\right]^2 \qquad \textbf{Equation 3.11}$$

For all the copolymerization experiments discussed herein, DMB will be designated as monomer 1 (M_1) and the co-monomer (butadiene, styrene or DPE) as monomer 2 (M_2). Reactions with different feed ratios ($[M_1]/[M_2]$) were studied in order to calculate reactivity ratios. All the copolymerization reactions were carried out using the experimental conditions established in *Chapter 2* i.e. *sec*-BuLi as initiator and temperatures of 40 or 60 °C. As in the previous chapter, solvents with different polarities were tested — namely benzene and *n*-alkanes (*n*-hexane and *n*-heptane). Benzene was selected because of its good characteristics for anionic polymerization and *n*-alkanes because of the extraordinary low vinyl content of PDMB achieved. The reactivity ratios in anionic copolymerizations have been shown to be very sensitive to solvent polarity. For example, for the butadiene-styrene copolymerization, r_{Bd} and r_{Sty} are 10.4 and 0.04 respectively in benzene ($\varepsilon = 2.27$) at 30 °C and 7.0 and 0.1 in *n*-heptane ($\varepsilon = 1.92$) at the same temperature.

3.1. Synthesis of DMB-Bd statistical copolymers

3.1.1. Synthesis of low molecular weight DMB-Bd statistical copolymers

Firstly a set of DMB-Bd copolymerizations with an M_{target} of 10 kg mol^{-1} was attempted with the goal of checking the relative (qualitative) reactivity of each co-monomer pair by collecting and analysing samples at intermediate reaction times. This study is composed of three copolymerizations, each with a different feed ratio ($[M_1]/[M_2]$) and each carried out using two solvents of different polarity (benzene and *n*-hexane). As previously mentioned, the experimental conditions were those established in *Chapter 1*. Two samples from each polymerization were collected and terminated at different intermediate reaction times.

3.1.1.1. SEC analysis of low molecular weight DMB-Bd statistical copolymers

Both, intermediate samples and final copolymers were analysed by SEC and ^{1}H-NMR. SEC results were obtained using triple detection analysis. As in *Chapter 2* (DMB homopolymers), a nominal value of 0.130 mL/g was used as the *dn/dc* for the SEC analysis of the copolymers described in this chapter. This is the *dn/dc* of polyisoprene, which once again will introduce an error into the calculation of M_n, and the impact of this error must be considered in the context of the DMB-Bd copolymers. The chemical structures of DMB and butadiene are very similar to isoprene which suggests that the use of the *dn/dc* of polyisoprene in a statistical copolymer of DMB and butadiene will not introduce a large error. Moreover, the precise magnitude of the error will vary with copolymer composition and will be a function of the mole fraction of monomers. However, as mentioned in *Chapter 2*, this small error in molar mass will have no impact on the analysis of the copolymer composition/microstructure via ^{1}H-NMR and hence, will not contribute to any error in the reactivity ratios that will be reported later in the this chapter. The SEC data for reactions carried out in both benzene and *n*-hexane are reported in *Table 3.1* and *Table 3.2*respectively.

Table 3.1: *SEC results of resulting DMB-Bd copolymers and their intermediate samples. Initiator: sec-BuLi,* M_{target} *= 10 kg mol*$^{-1}$*, solvent: benzene and T = 40 °C.* M_1*: DMB and* M_2*: butadiene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.1	71/29	4	3300	1.06	20	85
		8	3800	1.07	23	
		144	16300	1.07	100	
3.2	52/48	24	8000	1.07	54	86
		48	9800	1.08	67	
		144	14700	1.06	100	
3.3	25/75	24	8500	1.07	73	83
		48	10200	1.12	88	
		144	11600	1.12	100	

As can be seen above, polymers were recovered in relatively high yields (> 80%), especially when considering that two intermediate samples were collected during each reaction. When samples at low conversions are collected, these samples contain polymer, solvent and a significant amount of unreacted monomer that will not be part of the final copolymer. Therefore, this “lost” monomer will inevitably reduce the final yield. Experimental M_n values are somewhat higher than the M_{target} especially in the case of experiment 3.1. One obvious source of inaccuracy will be that the *dn*/*dc* value of polyisoprene was used in the SEC analysis as explained above, although we do not believe that the small error arising from this can account for the discrepancy between target and experimental molar masses in *Table 3.1*. A more likely explanation is the introduction of traces of environmental impurities, which will deactivate a portion if the initiator, leading to increases in M_n with respect to M_{target}. The reasonably high yields suggest that each reaction reached full (100%) conversion. Assuming full conversion, the conversion of intermediate samples was calculated as described previously in *Equation 2.1*. The Đ values obtained for the copolymers produced in experiments 3.1 and 3.2 agree with the expectations of anionic polymerization (Đ < 1.10)[5] although the Đ value for experiment 3.3 might be considered slightly high (1.12). Comparing experiments 3.2 and 3.3 (qualitatively) with the synthesis of DMB homopolymer in benzene (experiment 2.2), it was observed that in the presence of butadiene, the overall reaction rate is lower. Thus, in experiment 2.2, conversions of roughly 90% were achieved after 24 h, in experiments 3.2 and 3.3 conversions of only 54% and 73% respectively were reached in the same reaction time. This decrease in reaction rate seems to be slightly less pronounced when the fraction of butadiene in the feed increases (54% conversion in 52/48 copolymer versus 73% in 25/75 copolymer after 24 h). It is also clear that the intermediate samples collected in experiments 3.2 and 3.3 showed too high a conversion (>> 10%) to be used for the calculation of reactivity ratios. For that reason, samples in experiment 3.1 were collected and terminated at earlier reaction times (4 and 8 h). However, these samples also showed conversions which were too high (≥ 20%) to be used in the calculation of reactivity ratios.

Table 3.2: *SEC results of resulting DMB-Bd copolymers and their intermediate samples. Initiator: sec-BuLi,* M_{target} *= 10 kg* mol^{-1}*, solvent: n-hexane and T = 40 °C.* M_1*: DMB and* M_2*: butadiene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.4	74/26	24	Insufficient sample		—	74
		48	4500	1.07	48	
		144	9600	1.24	100	
3.5	51/49	24	4300	1.04	34	82
		48	Insufficient sample		—	
		164	12500	1.07	100	
3.6	43/57	2	2400	1.01	29	67
		4	3300	1.02	40	
		120	8300	1.10	100	
3.7	24/76	4	4900	1.03	49	82
		8	6400	1.04	63	
		167	10000	1.10	100	

A subsequent set of experiments were carried out in *n*-hexane (*Table 3.2*). The resulting copolymers were obtained at lower yields (67-82%) than the equivalents synthesized in benzene (83-86%). This observation can in part be explained by difficulties in isolating the polymers; the resulting DMB-Bd copolymers were soft sticky solids. However, of more significance is the collection of samples at early reaction times. The polymerization reaction apparatus did not easily allow the collection of accurate volumes in the side-arms for sampling, thus the experiments with lower yields might be a consequence of higher volumes collected of the intermediate samples. Considering the impact of these issues on the yields, taking into account that the experimental M_n values are in close agreement to M_{target}, and the conservatively long reaction times, we feel justified in assuming that reactions went to completion. A comparison of experiments 3.4 and 3.5 (in *n*-hexane, *Table 3.2*) with experiments 3.2 and 3.3 (in benzene, *Table 3.1*) reveals that lower conversions are achieved in *n*-hexane than in benzene after 24 and 48 h. This suggests that the copolymerization reaction rate is higher in benzene than in *n*-hexane. This agrees with expectations, as it is well known that reaction rates in anionic polymerization increase when the polarity of the solvent increases.[5] Again it is observed that the presence of butadiene as a co-monomer seems to decrease the overall reaction rate of the copolymerization (roughly 90% conversion in the homopolymerization of DMB versus less than 50% conversion in the copolymerizations, after 24 h in *n*-hexane). It should also be noted that the amount of copolymer (low molecular weight liquid material) in the samples collected after 24 h in experiment 3.4 and after 48 h in experiment 3.5 were of insufficient quantity to allow SEC analysis. It can be seen in *Table 3.2*, that once again, the conversion of the intermediate samples is too high to allow them to be used for the calculation of reactivity ratios. In experiments 3.6 and 3.7 intermediate samples were collected at earlier stages of the reaction (2 to 8 h) with the goal of obtaining samples at lower conversions. Nevertheless, the conversion of these samples was too high, making the data unsuitable for the Fineman-Ross linearization method. It is clear that collecting samples at low conversion, and low molecular weight is particularly challenging and for this reason a series of much higher molecular weight copolymers was prepared, see *Section 3.1.2*. However, the samples described in this section were still analysed by ^{1}H-NMR to give useful qualitative information about the relative rate of consumption of the two monomers.

3.1.1.2. Composition and microstructure of low molecular weight DMB-Bd statistical copolymers

The composition of both the intermediate samples and final copolymers, were calculated by ^{1}H-NMR. By way of an example, the ^{1}H-NMR spectrum of a 50/50 DMB-Bd copolymer prepared in *n*-hexane can be seen in *Figure 3.1*. Peaks were assigned for the different microstructures as shown in the figure (inset). The areas under the peaks were used to calculate the relative amount of each microstructure. In this case, the areas of peaks ***1***, ***6*** and ***8*** were used for butadiene and peaks ***c***, ***f*** and ***h*** for DMB.

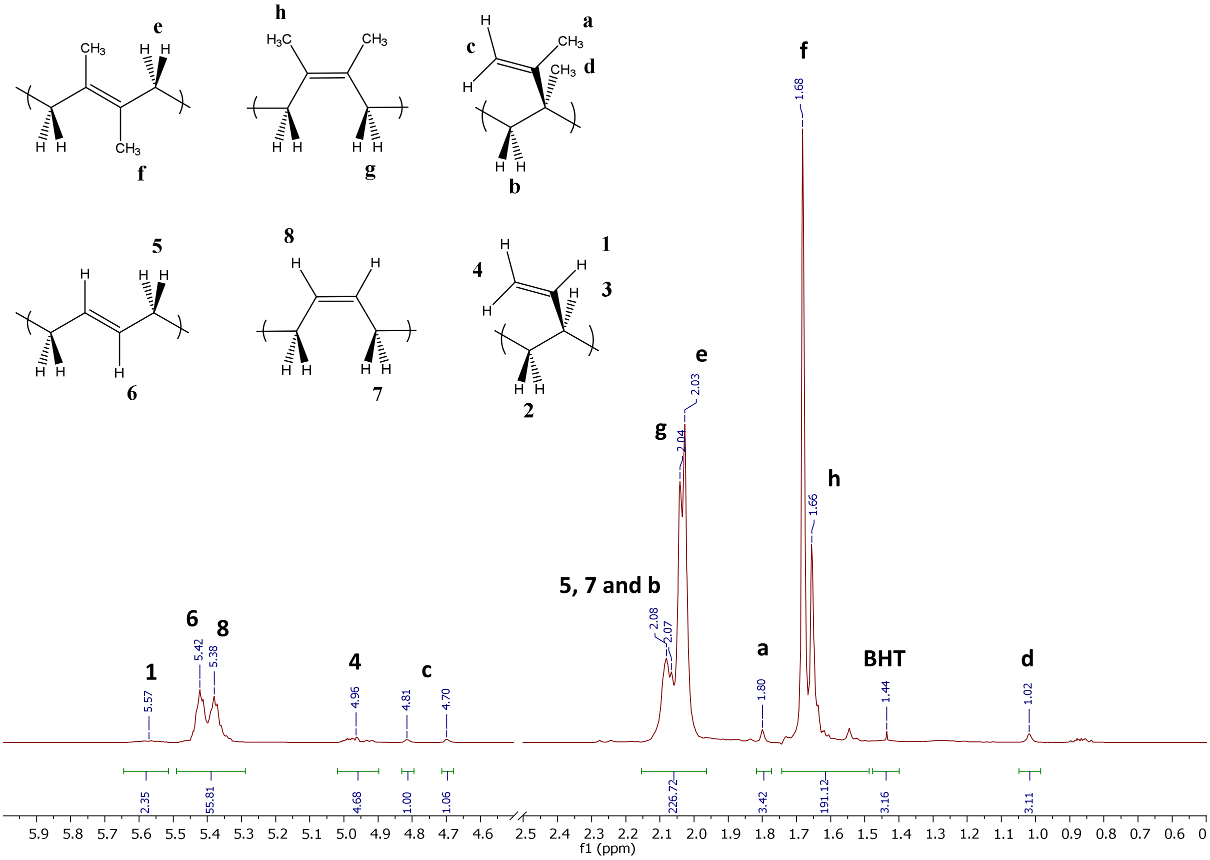


Figure 3.1: *^{1}H-NMR spectrum of p(DMB-s-Bd)-50/50 in n-hexane (CDCl$_3$, 400 MHz) δ (ppm).*

In order to calculate the composition of the resulting copolymer i.e. mole ratio of DMB:Bd, it is first necessary to calculate the relative amount of each microstructure. The relative number of moles of DMB (m_{DMB}) was calculated as the sum of the normalized areas (area divided by number of protons corresponding to that peak) of the peaks corresponding to the three different possible microstructures (1,2, *cis*-1,4 and *trans*-1,4) as follows:

$$\boldsymbol{Area\ c\ (2H): normalized\ c = \frac{Area_c}{2}}$$ **Equation 3.12**

$$\boldsymbol{Area\ h\ (6H): normalized\ h = \frac{Area_h}{6}}$$ **Equation 3.13**

$$\boldsymbol{Area\ f\ (6H): normalized\ f = \frac{Area_f}{6}}$$ **Equation 3.14**

$$\boldsymbol{m_{DMB} = normalized\ c + normalized\ h + normalized\ f}$$ **Equation 3.15**

In the same way, the mole of butadiene (m_{Bd}) was calculated as follows:

$$\boldsymbol{Area\ 1\ (1H): normalized\ 1 = \frac{Area_1}{1}}$$ **Equation 3.16**

$$\boldsymbol{Area\ 6\ (2H): normalized\ 6 = \frac{Area_6}{2}}$$ **Equation 3.17**

$$\boldsymbol{Area\ 8\ (2H): normalized\ 8 = \frac{Area_8}{2}}$$ **Equation 3.18**

$$\boldsymbol{m_{Bd} = normalized\ 1 + normalized\ 6 + normalized\ 8}$$ **Equation 3.19**

Once the combined mole fractions of the different microstructures of DMB and butadiene are calculated, it is possible to calculate the composition of the copolymer and the vinyl content and the contents of *cis*-1,4 and *trans*-1,4 structures of the different co-monomers:

$$\boldsymbol{{m_1}/{m_2} = \frac{m_{DMB}}{m_{Bd}}}$$ **Equation 3.20**

$$\boldsymbol{\%microstructure_{DMB} = \left(\frac{normalized_{c,h\ or\ f}}{m_{DMB}}\right)}$$ **Equation 3.21**

$$\boldsymbol{\%microstructure_{Butadiene} = \left(\frac{normalized_{1,6\ or\ 8}}{m_{Butadiene}}\right)}$$ **Equation 3.22**

The copolymer composition and contribution of each microstructure, calculated as described above, are summarized in *Table 3.3* (benzene as solvent) and *Table 3.4* (*n*-hexane as solvent). In calculating these values a certain amount of error is to be expected. The microstructures of DMB for the samples with very low DMB mole fractions (< 10% DMB) were not calculated as the corresponding ^{1}H-NMR signals are very small. The poor signal to noise ratio and the high degree of overlap between signals corresponding to 1,4-DMB microstructures (***e*** with ***g*** and ***f*** with ***h*** in *Figure 3.1*) dramatically increases the potential errors, meaning that any data is unacceptable in terms of confidence. Moreover, although microstructure data for both DMB and Bd has been quoted in most cases, given the overlap between signals, and differences in the *cis*/*trans* ratios for different samples may not be significant.

Table 3.3: *Composition of resulting DMB-Bd copolymers and their intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, solvent: benzene and T = 40 °C. M_1: DMB and M_2: butadiene.*

Exp.	**$[M_1]/[M_2]$**	**% conversion**	**m_1/m_2**	**% DMB**			**% Bd**		
				1,2	***cis*-1,4**	***trans*-1,4**	**1,2**	***cis*-1,4**	***trans*-1,4**
3.1	71/29	20	2/98	Very low DMB mole fraction			18	39	43
		23	17/83	15	45	40	18	40	42
		100	75/25	17	21	62	6	55	40
3.2	52/48	54	44/56	12	37	51	18	44	38
		67	43/57	17	22	61	7	52	41
		100	47/53	17	22	61	7	42	51
3.3	25/75	73	17/83	15	36	49	15	39	46
		88	30/70	17	24	59	15	38	47
		100	28/72	17	24	59	12	29	59

As expected for a living polymerization, the final copolymers (100% conversion) showed a composition (m_1/m_2) that is close to the feed ratio. The slight discrepancies might be a consequence of small errors associated with the calculation from the ^{1}H-NMR spectra or the collection of intermediate samples.

As mentioned above, the intermediate samples of these experiments cannot be used for the calculation of the reactivity ratios because of their relatively high conversions. However, a qualitative trend can be observed when the data is analysed. The ratio of monomers within the polymeric chain (m_1/m_2) of the intermediate samples is lower than the feed ratio ($[M_1]/[M_2]$). This suggests that the mole fraction of butadiene (M_2) in the growing chain is higher than the initial mole fraction of butadiene. This is especially evident in the case of the low conversion samples of experiment 3.1 where butadiene is present in the feed at only 29 mol-%. In this experiment the samples collected at 20% and 23% conversion contain extremely low levels of DMB in the growing chain (m_1/m_2 = 2/98) and (m_1/m_2 = 17/83) respectively. In the other two experiments, where butadiene is present in the feed at the same or higher mole fraction than DMB (experiments 3.2 and 3.3) a difference between copolymer composition and feed ratio is also observed but it is less remarkable. This qualitative observation suggests that in benzene, butadiene reacts in preference over DMB, which is in agreement with previously published qualitative observations of analogous copolymerizations[6, 7] whereby Henderson reported that the anionic statistical copolymerization of

DMB and butadiene gives rise to a tapered blocky copolymer. However, Henderson did not report reactivity ratios for the DMB-Bd pair.

In the next set of copolymerizations, carried out in *n*-hexane, there was insufficient quantity of the first sample of experiment 3.4 to obtain clear signals in the ^{1}H-NMR spectrum. For that reason the calculation of composition and microstructures was not possible. In experiment 3.5, ^{1}H-NMR analysis of the sample collected at 34% conversion, revealed no signals at all corresponding to DMB (*Figure 3.2*). This lack of visible signals does not mean necessarily that DMB is not present at all in the growing chain but does suggest that if present, the fraction of DMB is too low to be seen.

Table 3.4: *Composition of resulting DMB-Bd copolymers and their intermediate samples calculated from* ^{1}*H-NMR. Initiator: sec-BuLi,* M_{target} *= 10 kg mol*$^{-1}$*, solvent: n-hexane and T = 40 °C.* M_1*: DMB and* M_2*: butadiene.*

Exp.	**$[M_1]/[M_2]$**	**% conversion**	**m_1/m_2**	**% DMB**			**% Bd**		
				1,2	***cis*-1,4**	***trans*-1,4**	**1,2**	***cis*-1,4**	***trans*-1,4**
3.4	74/26	—	Insufficient sample						
		48	36/64	4	32	64	7	48	45
		100	69/31	4	28	68	5	50	45
3.5	51/49	34	0/100	No DMB signals observed			6	48	46
		—	15/85	2	52	46	6	52	42
		100	53/47	3	36	61	6	62	32
3.6	43/57	29	2/98	Very low DMB mole fraction			11	34	65
		40	2/98	Very low DMB mole fraction			12	33	55
		100	47/53	5	28	67	11	39	50
3.7	24/76	49	3/97	Very low DMB mole fraction			10	35	55
		63	2/98	Very low DMB mole fraction			10	36	54
		100	32/68	5	28	67	10	35	55

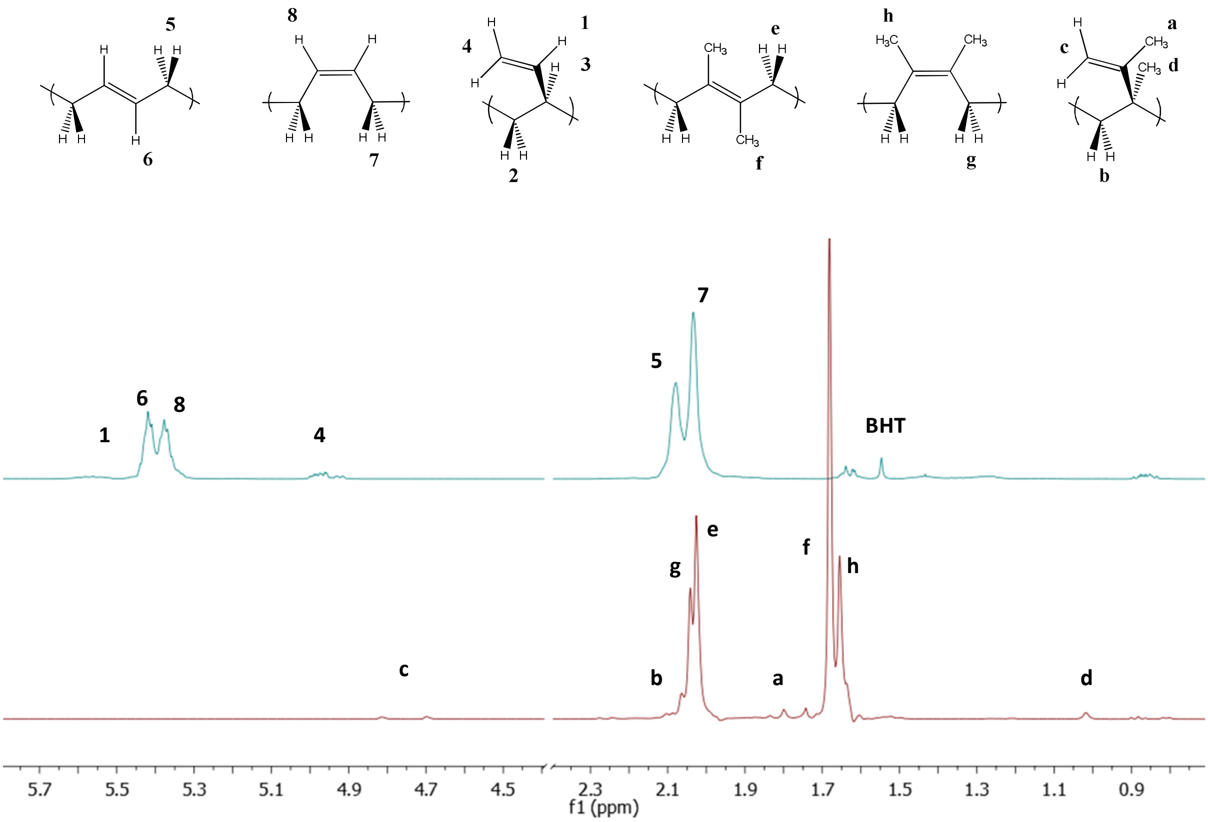


Figure 3.2: *Offset spectra of 34% conversion sample of experiment 3.5 (blue line) and PDMB synthesized in n-hexane (experiment 2.4, red line).*

Again, it is observed that the ratio of monomers within the final copolymers (at 100% conversion) is close to the feed ratio. As previously observed for DMB homopolymers, the use of *n*-hexane as the copolymerization solvent results in a dramatic reduction in the vinyl content of DMB from 17% in benzene to 3-5% in *n*-hexane. It might be argued that the switch from benzene to *n*-hexane also had an impact on the vinyl (1,2) content of butadiene but the differences are perhaps less significant.

When considering evolution in the composition of the copolymers, it is again observed that in the intermediate samples m_1/m_2 is lower than $[M_1]/[M_2]$. However, in *n*-hexane this trend is sharper. This trend is especially obvious in the samples collected at low conversion in experiments 3.5, 3.6 and 3.7 where butadiene is present at the start of the reaction at similar or higher concentrations than DMB. In these samples, the presence of DMB within the polymeric chain was very low or even undetectable: m_1/m_2 = 0/100 in experiment 3.5, 2/98 in experiment 3.6 and 3/97 in experiment 3.7. This reinforces the observation reported above, that butadiene reacts in strong preference over DMB with a pronounced tendency for butadiene to undergo homopolymerization in both alkane and aromatic solvents. In this way, it is expected that the resulting DMB-Bd copolymers will be tapered/blocky copolymer with a first "block" that is rich in butadiene, a middle segment with a gradient sequence and a second "block" rich in DMB, as illustrated in *Figure 3.3*. However, as already mentioned, these samples cannot be used for calculating reactivity ratios so a more accurate conclusion cannot be stated at this point.

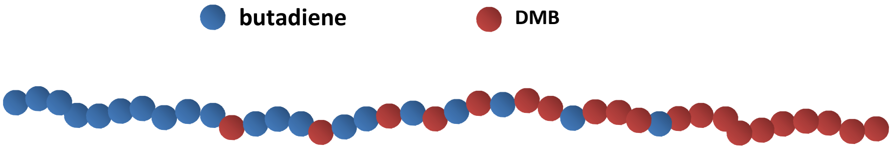


Figure 3.3: *Proposed cartoon model for the sequence distribution of resulting DMB-s-Bd copolymers.*

3.1.1.3. The solubility of low molecular weight DMB-Bd statistical copolymers

Next, solubility experiments were carried out, on the copolymers described above, in the same way as described in *Chapter 2* for the PDMB homopolymers. These studies were carried out in order to investigate the influence of the addition of butadiene on the solubility of PDMB copolymers. The solvents selected were of varying polarity; THF (intermediate dielectric constant, 7.58), toluene (low dielectric constant, 2.38) and *n*-hexane (very low dielectric constant, 1.89). 10 wt-% solutions of the copolymers in each solvent were prepared and put on a roller-mixer for 24 h. The results can be seen in *Figure 3.4*. Compared to the DMB homopolymers (*Figure 2.8*) the solubility seems to be generally improved by the presence of butadiene. This effect is particularly visible in the case of the copolymers prepared in *n*-hexane, which show much improved solubility compared to PDMB prepared in *n*-hexane, which has a very high 1,4 microstructure (96-97%) and, as a result of the resulting crystallinity, generally showed poor solubility in the three selected solvents. The general improvement in solubility is unsurprising given the known high solubility of polybutadiene in all three solvents, as shown in *Figure 3.5*. The copolymers synthesized in *n*-hexane (experiments 3.4, 3.5 and 3.7) are clearly soluble in THF and toluene at room temperature, although sample 3.4, (31 mol-% butadiene) is a little milky. However, these copolymers are not very solublein *n*-hexane, even for a sample with a mole fraction of 47% butadiene (experiment 3.5). Based on the qualitative information about comonomer consumption above and these observations, we might assume that the resulting copolymers have a blocky sequence, (*Figure 3.3*), in which the butadiene-rich block is soluble in *n*-hexane and the semi-crystalline DMB-rich block remains insoluble. In case of experiment 3.7 (m_1/m_2 = 32/68) the turbid solution/dispersion in *n*-hexane could be the consequence of the formation of micelles, where the short PDMB block would remain in the core and the long polybutadiene block would form the corona. Additionally, during experiment 3.7 (68 mol-% butadiene) the reaction solution became slightly turbid, possibly indicating the onset of polymerization induced self-assembly arising from the delayed consumption of DMB and the formation of a blocky sequence with the less soluble DMB-rich block formed after the preferential consumption of butadiene. This might be the first example of polymerization induced self assembly in an anionic polymerization. However, since it is only based on experimental observation and not hard evidence, further work would be required to prove it beyond any doubt and it will be proposed as future work later in *Chapter 6*. The preference for the consumption of butadiene is less pronounced when the copolymerization was carried out in benzene, resulting in a more tapered sequence and this, coupled with a higher 1,2 content in the DMB (which inhibits crystallinity) could account for the enhanced solubility of the copolymers prepared in benzene (*Figure 3.4*).

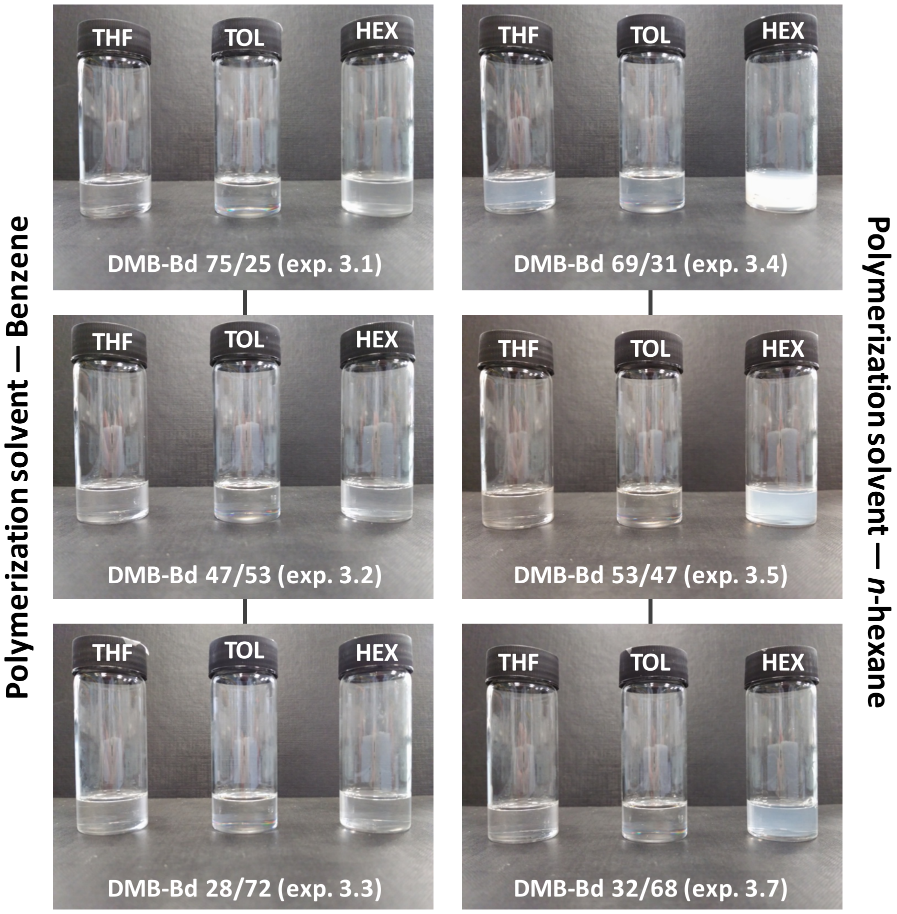


Figure 3.4: *Solubility tests of the DMB-s-Bd copolymers. Samples of 500 mg of polymer were dissolved in 5 mL of different polarity solvents: THF (ε = 7.58), toluene (ε = 2.38) and n-hexane (ε = 1.89).*

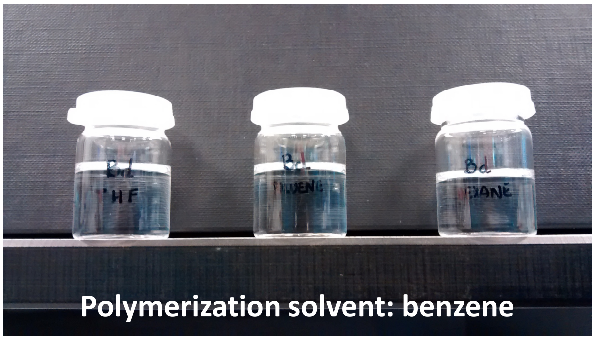


Figure 3.5: *Solubility of polybutadiene synthesized in benzene (M_n approximately 10 kg mol^{-1}). Samples of 500 mg of polymer were dissolved in 5 mL of different polarity solvents: THF (ε = 7.58), toluene (ε = 2.38) and n-hexane (ε = 1.89).*

3.1.2. Synthesis of high molecular weight DMB-Bd statistical copolymers

As reactivity ratios could not be obtained via the synthesis of lower molar mass DMB-Bd copolymers (M_{target} of 10 kg mol^{-1}), due to the high conversion of the collected samples and the difficulty in recovering samples of low molecular weight polymer at intermediate conversion, a second set of copolymerizations were carried out with M_{target} of 100 kg mol^{-1}. For these reactions the temperature was raised to 60 °C to increase the reaction rate and reduce reaction times. For safety reasons, *n*-hexane was switched for *n*-heptane in order to avoid using a solvent whose boiling point (68 °C) is too close to the reaction temperature. Moreover, the intermediate samples were collected and terminated at shorter reaction times (in the order of tens of minutes at the latest) in order to obtain samples at monomer conversions lower than 10%. All other experimental conditions were the same as used for the lower M_n copolymers (with M_{target} of 10 kg mol^{-1}): namely, *sec*-BuLi as initiator, benzene as aromatic solvent and same monomer feed ratios (approximately 75/25, 50/50 and 25/75). However, in this set of experiments two additional feed ratios (roughly 60/40 and 40/60) were used, to yield a wider data set, in order to calculate reactivity ratios more accurately. To ensure complete consumption of the monomers, reactions were allowed to proceed for between 3 and 5 days.

3.1.2.1. SEC analysis of high molecular weight DMB-Bd statistical copolymers

Both intermediate samples and final copolymers were analysed by triple detection SEC. In the cases where the MW was too low for an adequate light scattering signal, a conventional PS calibration was used. Triple detection SEC analysis was carried out in the same way as described earlier for the lower molar mass DMB-Bd copolymers (M_{target} = 10 kg mol^{-1}) and hence, the same (small) errors associated with the use of the *dn/dc* of polyisoprene are applicable throughout this section. However, because this work will primarily use ^{1}H-NMR data to obtain copolymer compositions to enable reactivity ratio calculations, these errors in SEC analysis are not expected to impact on reactivity ratios. Intermediate samples were collected at very short reaction times in order to ensure conversions under 10% and were analysed by conventional PS calibration when necessary (M_n < 5000 g mol^{-1}). In such very low molar mass samples the inaccuracy in the M_n associated with the use of *dn/dc* of polyisoprene is not relevant. However, the use of a conventional calibration, with polystyrene standards, will also result in inaccuracies in obtained molar masses. The SEC data for copolymerizations carried out in both benzene and *n*-heptane are reported in *Table 3.5* and *Table 3.6*.

Table 3.5: *SEC results of resulting DMB-Bd copolymers and their intermediate samples. Initiator: sec-BuLi,* M_{target} *= 100 kg mol*$^{-1}$*, solvent: benzene and T = 60 °C.* M_1*: DMB and* M_2*: butadiene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.8	63/37	0.05	Insufficient sample		—	69
		0.10	2900^a	1.07	1	
		96	202200	1.39	100	
3.9	57/43	0.05	1200^a	1.16	1	68
		0.12	5900	1.12	4	
		96	148100	1.23	100	
3.10	49/51	0.03	700^a	1.20	1	55
		0.08	2200^a	1.08	2	
		72	115900	1.21	100	
3.11	38/62	0.10	3300^a	1.48	3	84
		0.15	13300	1.03	11	
		72	122000	1.17	100	
3.12	25/75	0.05	3400^a	1.09	2	69
		0.10	16100	1.05	8	
		120	207100	1.28	100	

a) Obtained using a conventional SEC calibration using PS standards.

Recovered yields were significantly lower than the previous low molar mass copolymers (M_{target} = 10 kg mol^{-1}) and in one case as low as 55%. This could be due to two experimental issues. The first one is related to the physical appearance of the resulting copolymers. As a consequence of the presence of butadiene, these copolymers have a glass transition temperature which is below room temperature (see later) and the polymers are sticky and difficult to handle, particularly when the mole fraction of butadiene is high. Hence, part of the copolymer is lost during the reaction work-ups. However, a second more significant issue, is related to the collection of samples at intermediate times. The intermediate samples (approximately 20 mL of reaction solution for each sample) were collected at very short reaction times, to ensure low conversion, and as such the sampled reaction mixture contains only a small amount of polymer and a large amount of unreacted monomer. Therefore, a significant portion of the monomer is taken out of the system each time a sample is collected, which will affect the final mass of the copolymer and hence, the yield. By way of an example, if a 20 mL sample is collected at 1% conversion, the sample will contain approximately: 0.02 g of copolymer and 1.98 g of unreacted monomers. Another consequence of this sampling is that the first samples of some experiments did not contain sufficient mass of polymer for its analysis by SEC. Taking this into account, considering that the M_n of the polymers is similar to or higher than M_{target}, and the prolonged reaction times, it can reasonably be assumed that the reactions reached full conversion.

The resulting copolymers at (assumed) full conversion had M_n values which are higher than M_{target} in most experiments and significantly higher in experiments 3.8 and 3.12. This is almost certainly the consequence of some impurities in the reaction vessel killing part of the initiator before initiation takes place. As the M_{target} is high, very small changes in the amount of initiator can lead to significant changes in the final M_n. The Đ values are somewhat higher than expected for anionic polymerization (Đ > 1.10). The higher dispersities can be ascribed to i) impurities introduced during the sampling process, resulting in premature termination of some growing chains and ii) chain coupling reactions occurring during the slow termination of the high viscosity of the reaction mixture. The former can be seen in the SEC chromatograms as tailing or bumps in the lower MW (higher retention volume) region and the latter as a shoulder in the high MW (low retention volume) region. Both effects can be seen to some extent in all the experiments (see *Figure 3.6*) however, it should be noted that the issues leading to higher dispersity will not have an impact on the reactivity ratios; the primary objective of this series of experiments. Regarding the reaction rates, it can be seen that where samples have been collected from reactions where DMB is the major component in the feed (i.e. experiment 3.8), the conversions are lower than for analogous reactions where the feed ratio of butadiene is higher. This agrees with expectations as the propagation rate of DMB is slower due to higher electron density in carbons 1 and 4 compared to butadiene.

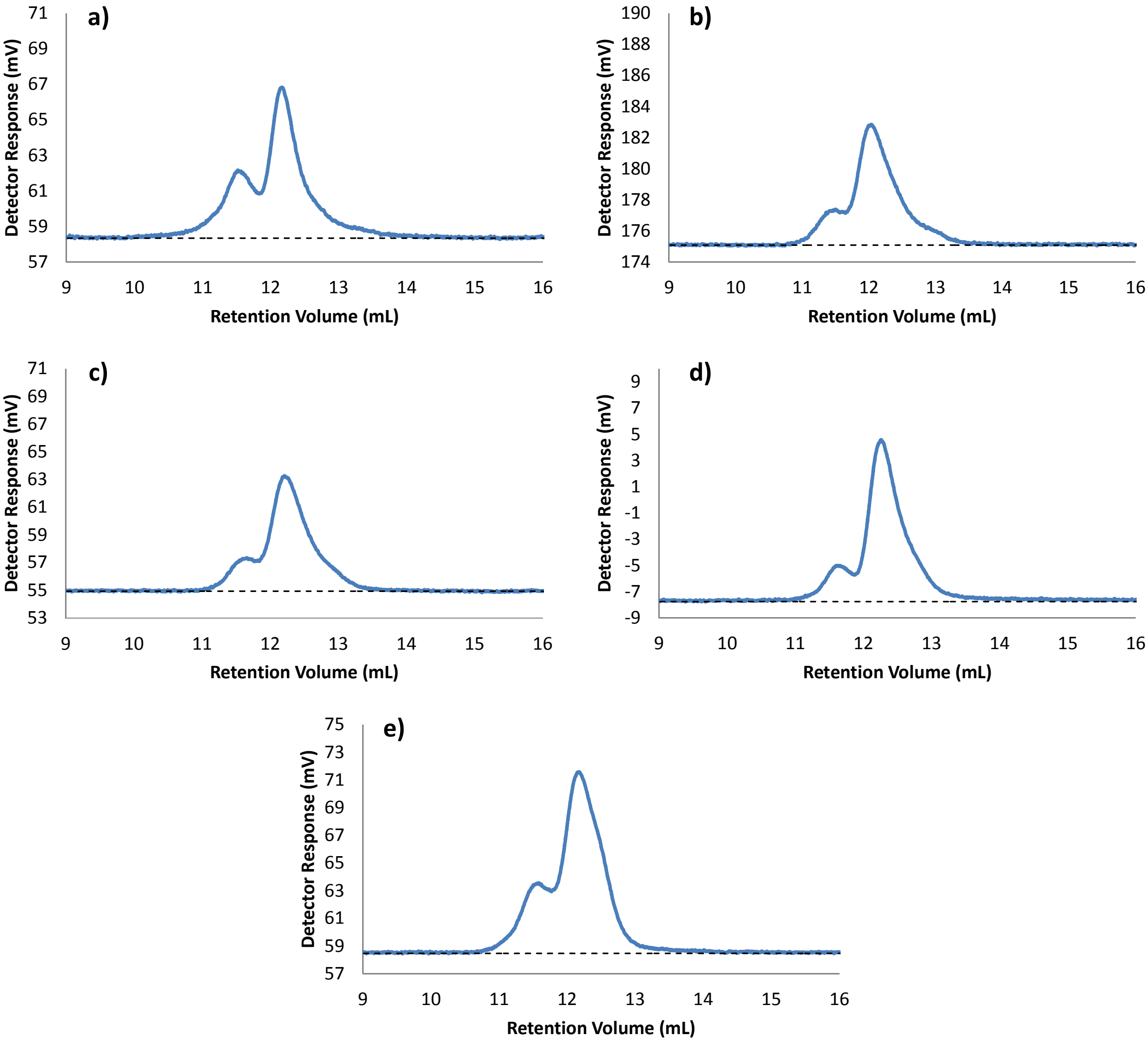


Figure 3.6: *SEC chromatograms of resulting DMB-Bd copolymers synthesized in benzene: a) experiment 3.8, b) experiment 3.9, c) experiment 3.10, d) experiment 3.11 and e) experiment 3.12.*

Table 3.6: *SEC results of resulting DMB-Bd copolymers and their intermediate samples. Initiator: sec-BuLi,* $M_{target} = 100$ *kg mol*$^{-1}$*, solvent: n-heptane and T = 60 °C.* M_1*: DMB and* M_2*: butadiene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.13	73/27	0.07	Insufficient sample		—	77
		0.13	1400[a]	1.13	1	
		72	152200	1.32	100	
3.14	58/42	0.08	Insufficient sample		—	75
		0.15	2100[a]	1.06	2	
		96	109100	1.33	100	
3.15	50/50	0.07	Insufficient sample		—	59
		0.13	2400[a]	1.09	2	
		96	125200	1.26	100	
3.16	37/63	0.10	Insufficient sample		—	65
		0.15	3800[a]	1.02	3	
		72	119200	1.17	100	
3.17	23/77	0.07	Insufficient sample		—	75
		0.17	5500	1.03	5	
		72	106000	1.18	100	

a) Obtained using a conventional SEC calibration using PS standards.

For the copolymerization reactions carried out in *n*-heptane (see *Table 3.6*) the resulting polymers presented M_n values which were in reasonable agreement with M_{target} with the exception of experiment 3.13 where the molar mass was 50% above target. Again, Đ values are somewhat higher than expected for anionic polymerization (Đ > 1.10). The SEC chromatograms (*Figure 3.7*) indicate that these high values are probably due to the two effects mentioned above for the copolymerizations in benzene; namely the impact of sampling and inefficient termination. It should be noted that the shape of the chromatogram of experiment 3.16 is very unusual and much different from the expected Gaussian peak for anionic polymerization (*Figure 3.7d*) — we have no obvious explanation for this discrepancy.

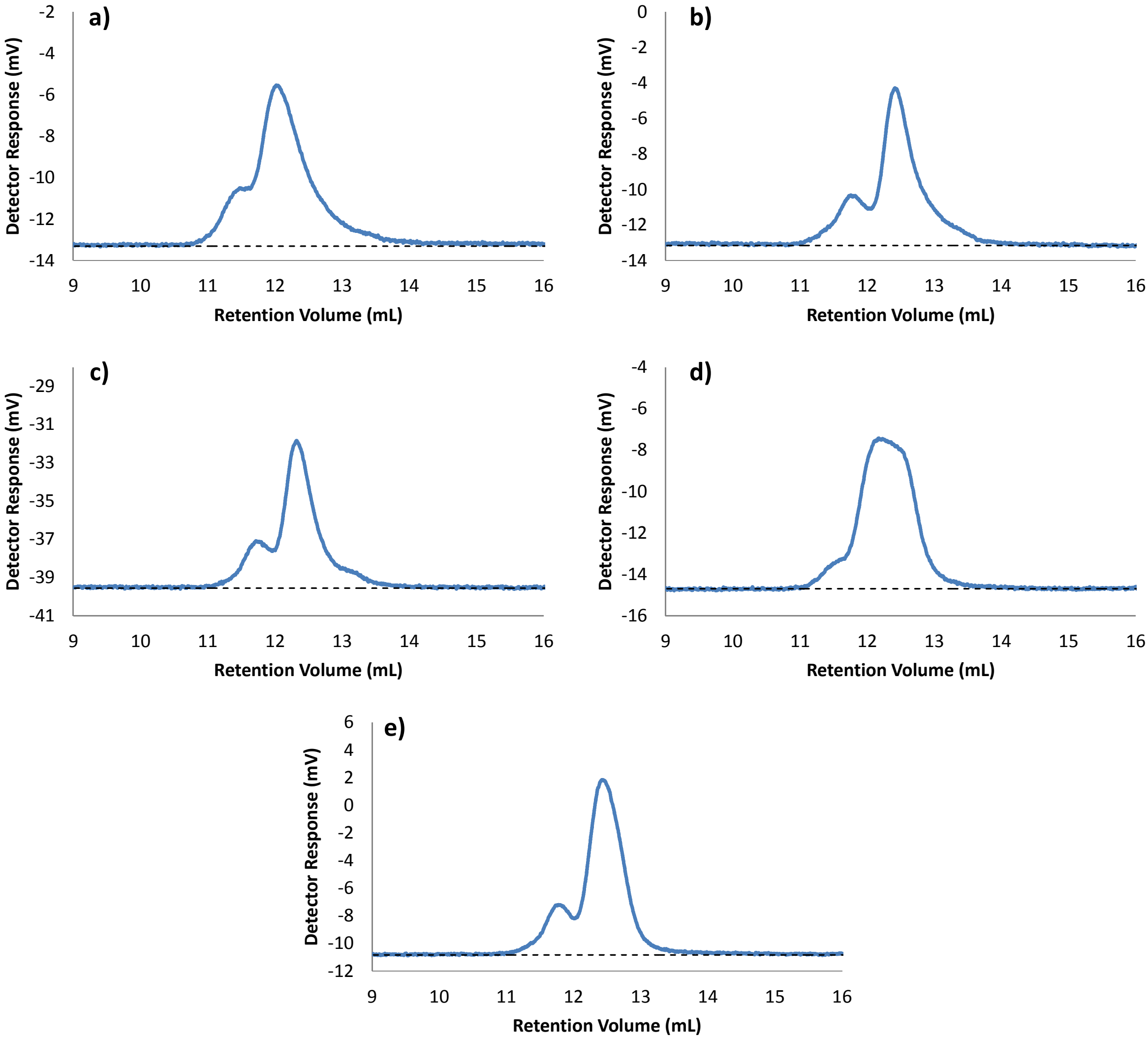


Figure 3.7: *SEC chromatograms of resulting DMB-Bd copolymers synthesized in n-heptane: a) experiment 3.13, b) experiment 3.14, c) experiment 3.15, d) experiment 3.16 and e) experiment 3.17.*

3.1.2.2. Composition and microstructure of high molecular weight DMB-Bd statistical copolymers in benzene — calculation of reactivity ratios

The composition and microstructure of the resulting copolymers were calculated from ^{1}H-NMR data using the method described previously, for the analogous lower molar mass copolymers (M_{target} = 10 kg mol^{-1}) and the results reported in *Table 3.7*. As mentioned in Section 3.1.1.2, the microstructure of DMB repeat units for samples with a composition containing less than 10 mol-% DMB were not calculated because the associated ^{1}H-NMR signals are very weak, leading to potential high errors.

Table 3.7: *Composition of resulting DMB-Bd copolymers and their intermediate samples calculated from* ^{1}*H-NMR. Initiator: sec-BuLi,* M_{target} *= 100 kg mol*$^{-1}$*, solvent: benzene and T = 60 °C.* M_1*: DMB and* M_2*: butadiene.*

Exp.	$[M_1]/[M_2]$	% conversion	m_1/m_2	% DMB			% Bd		
				1,2	*cis*-1,4	*trans*-1,4	1,2	*cis*-1,4	*trans*-1,4
3.8	63/37	—	5/95	—			17	44	39
		1	2/98	—			16	41	43
		100	62/38	13	29	58	11	45	44
3.9	57/43	1	6/94	—			13	58	29
		4	1/99	—			8	53	39
		100	56/44	11	32	57	10	50	39
3.10	49/51	1	4/96	—			15	45	40
		2	1/99	—			8	53	39
		100	50/50	10	36	54	9	55	36
3.11	38/62	3	1/99	—			8	53	39
		11	1/99	—			9	51	40
		100	33/67	14	27	59	9	52	39
3.12	25/75	2	1/99	—			16	41	43
		8	1/99	—			16	46	38
		100	19/81	14	26	59	10	51	39

As can be seen in *Table 3.7*, the comonomer composition of the final copolymers is close to the feed ratio in all cases, as expected. However, when the composition of the intermediate samples is considered, the same compositional drift that was described above for the lower molar mass (M_{target} of 10 kg mol^{-1}) copolymers ($m_1/m_2 << [M_1]/[M_2]$) is also observed. At low conversions the incorporation of DMB into the growing chains is extremely low, even where DMB is the major component of the feed. This effect is particularly evident in experiments 3.11 and 3.12, where the feed ratio gets lower (high fraction of butadiene).

As the intermediate samples had conversions of less than 10%, the first sample from each of the five experiments was used to generate data for Fineman-Ross and inverted Fineman-Ross linearization and Kelen-Tudos models, for the calculation of reactivity ratios as described at the beginning of this section. The calculated reactivity ratios are reported in *Table 3.8* and it is clear that the reactivity ratios calculated by each methods are similar and confirm the qualitative trend observed previously.

Table 3.8: *Reactivity ratios calculated for the anionic copolymerization of DMB and butadiene in benzene.*

Method	r_{DMB}	r_{Bd}
Fineman-Ross	-0.24±0.54	25.78±18.47
Inverted Fineman-Ross	-0.07±0.50	29.98±10.00
Kelen-Tudos	-0.22±0.30	26.11±8.11

As can be seen in Table 3.8 r_{Bd} is significantly higher than r_{DMB} and of equal importance is that r_{Bd} is significantly greater than 1.0 and r_{DMB} is significantly less than 1.0. These values confirm that k_{12} >> k_{11} and that k_{22} >> k_{21} and the consumption of butadiene is favoured strongly. As a result, for the copolymerization of DMB and Bd in benzene, the blocky comonomer sequence proposed in *Figure 3.3* would seem reasonable. It should also be noted that although negative values of r_{DMB} were obtained by all three methods, a negative value is not possible and makes no sense. However, the values are very close to 0 and within error could be positive yet still very close to 0. The reactivity ratios are derived from the ^{1}H-NMR spectra and it is clear that the samples collected at extremely low conversions, contain almost no DMB (see *Figure 3.8*). The error on the integral of the DMB signals is likely to be high, which will propagate through to errors in the reactivity ratio calculations. However, the relative magnitudes of the calculated reactivity ratios are entirely consistent with the ^{1}H-NMR data, and the (potentially) high errors in the ^{1}H-NMR data and reactivity ratio calculations are almost inevitable for a copolymerization in which one monomer is almost totally excluded from the reaction in the early stages.

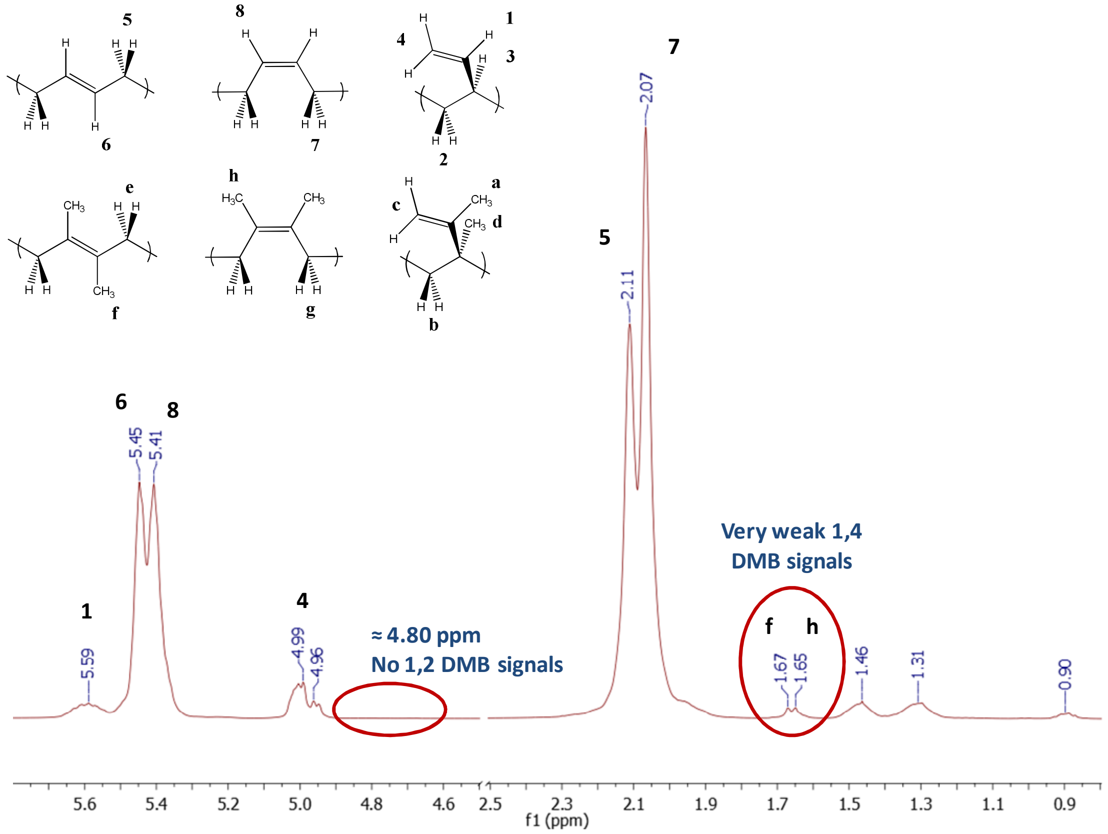


Figure 3.8: *^{1}H-NMR spectrum of first sample (1% conversion; m_1/m_2 = 4/96) of experiment 3.10 ($CDCl_3$, 400 MHz) δ (ppm).*

As a point of interest, it is worth comparing the results discussed above for the copolymerization of DMB and butadiene, with data for the copolymerization of butadiene and isoprene in hydrocarbon solvents. Reactivity ratios for the copolymerization of butadiene and isoprene have been reported and the resulting copolymers have a blocky/gradient comonomer sequence with a preference for the addition of butadiene as $r_{Bd} > r_{Ip}$. However, the difference between the reactivity ratios for a butadiene-isoprene copolymerization is far less dramatic than in case of the DMB-butadiene copolymerization. In benzene at 40 °C r_{Bd} is 3.70 (higher than 1 so a preference for homopolymerization) and r_{Ip} 0.50 (lower than 1 so tendency to cross-propagate).[5]

3.1.2.3. Composition and microstructure of high molecular weight DMB-Bd statistical copolymers in *n*-heptane — calculation of reactivity ratios

The composition and microstructure of the analogous high molar mass (with M_{target} of 100 kg mol^{-1}) copolymers prepared in *n*-heptane were also calculated from the ^{1}H-NMR spectra, using the calculation method described above for the lower molar mass (with M_{target} of 10 kg mol^{-1}) copolymers. The results are reported in *Table 3.9*. For reasons previously discussed, the microstructure of DMB repeat units for samples containing less than 10 mol-% DMB were not calculated.

Table 3.9: *Composition of resulting DMB-Bd copolymers and their intermediate samples calculated from* ^{1}*H-NMR. Initiator: sec-BuLi,* M_{target} *= 100 kg mol*$^{-1}$*, solvent: n-heptane and T = 40 °C.* M_1*: DMB and* M_2*: butadiene.*

Exp.	[M$_1$]/[M$_2$]	% conversion	m$_1$/m$_2$	% DMB			% Bd		
				1,2	*cis*-1,4	*trans*-1,4	1,2	*cis*-1,4	*trans*-1,4
3.13	73/27	—	8/92	—			13	44	43
		1	2/98	—			8	62	29
		100	68/32	4	36	59	7	48	44
3.14	58/42	—	5/95	—			13	44	43
		2	1/99	—			7	50	43
		100	61/39	5	37	58	7	49	44
3.15	50/50	—	6/94	—			13	44	43
		2	1/99	—			8	63	29
		100	53/47	3	40	57	8	50	43
3.16	37/63	—	2/98	—			12	47	41
		3	1/99	—			7	50	43
		100	23/77	4	31	65	7	49	44
3.17	23/77	—	1/99	—			8	63	29
		5	1/99	—			7	49	44
		100	20/80	3	30	67	8	49	43

The change of the copolymerization solvent to *n*-heptane does not seem to alter significantly the qualitative trends observed for the copolymerizations in benzene. Again there is a strong preference for the addition of butadiene units over DMB, as seen for the analogous experiments in benzene.

In the same way as described previously in *Section 3.1.2.3.*, the first sample from each of the five experiments was used to generate data for Fineman-Ross and inverted Fineman-Ross linearization and Kelen-Tudos models, for the calculation of reactivity ratios. The reactivity ratios calculated by the three methods are reported in *Table 3.10* and it is clear that for the anionic copolymerization of DMB and butadiene in *n*-heptane, the reactivity ratios are extremely different with r_{Bd} being approximately 25 and r_{DMB} is close to zero. This would again lead to a very strong preference for the initial consumption of butadiene and a block-like monomer sequence. It should also be noted that high errors are observed (again) for the reactivity ratios, although perhaps smaller than for the data associated with the copolymerizations in benzene (*Table 3.8*). When comparing the copolymerization behaviour of DMB in *n*-heptane, with the more common diene monomers, we once again see stark differences. The statistical copolymerization of butadiene and isoprene in *n*-hexane at 40 °C, has reactivity ratios which are: r_{Bd} = 2.18 (tendency to homopolymerize) and r_{Ip} = 0.35 (preference for cross-propagation)[5] which would suggest that the anionic copolymerization of butadiene and isoprene would lead to tapered/gradient copolymers rather than the very block-like sequence for butadiene and DMB.

Table 3.10: *Reactivity ratios calculated for the anionic copolymerization of DMB and butadiene in n-heptane.*

Method	r_{DMB}	r_{Bd}
Fineman-Ross	-0.05±0.11	23.38±4.66
Inverted Fineman-Ross	0.18±0.38	28.53±5.87
Kelen-Tudos	0.00±0.00[a]	24.83±0.11

a) r_{DMB} = 0.002±0.004.

A comparison of the data in *Table 3.8* and *Table 3.10* shows that the reactivity ratios obtained in both benzene and *n*-heptane are very similar. This might suggest that the relatively small differences in the polarity of the solvent does not play a significant role in the copolymerization of DMB and butadiene within the studied range of dielectric constant (1.92-2.27). The reactivity ratios confirm that in both solvents a block-like copolymer with a tapered region appearing close to the point when butadiene is almost all consumed (*Figure 3.3*) will result.

The apparent insensitivity to solvent polarity of the reactivity ratios for the copolymerization of DMB and Bd is in contrast to the anionic copolymerization of butadiene and isoprene, where the difference between the reactivity ratios in benzene and *n*-heptane is more significant. The r_{Bd} varies from 3.70 to 2.18 and r_{Ip} from 0.50 to 0.35 when the solvent is changed from benzene to *n*-heptane.[5] In case of the DMB-butadiene reactivity ratios, DMB seems to be less sensitive to the polarity of the solvent than the other two dienes, which was unexpected considering previous results where DMB proved to be more sensitive to slight changes in the polarity (e.g. in the microstructure of the resulting homopolymers, see *Chapter 2*) than butadiene and isoprene.

3.2. Synthesis of DMB-Sty statistical copolymers

3.2.1. Synthesis of low molecular weight DMB-Sty statistical copolymers

Following the strategy described in the previous section, a series of low molecular weight DMB-Sty copolymers with M_{target} of 10 kg mol^{-1} was prepared with the goal of obtaining an initial qualitative understanding of the copolymerization kinetics for this system. For this, two samples at intermediate reaction times were collected, terminated and analysed. Three different feed ratios ($[M_1]/[M_2]$) were evaluated using two solvents of slightly different polarity (benzene and *n*-hexane). The experimental conditions used were those established previously and described in *Chapter 1*.

3.2.1.1. SEC analysis of low molecular weight DMB-Sty statistical copolymers

All polymer samples were analysed by triple detection SEC using 0.130 mL/g as *dn/dc* (polyisoprene). In this case the error associated to the use of *dn/dc* of polyisoprene will be greater than in the case of the DMB-Bd copolymers described previously, as the co-monomer here is not a diene. As a consequence, the assumed error will increase as the content of styrene increases in the copolymer. Nevertheless, as discussed previously, the inaccuracy in the calculation of M_n will have no impact on calculation of reactivity ratios, which is the main goal of this section. SEC data for samples prepared in both benzene and *n*-hexane are reported in *Table 3.11* and *Table 3.12* respectively.

In the experiments carried out in benzene (3.18, 3.19 and 3.20), the copolymers were recovered in high yields (≥ 94%) and in each case the M_n was close to the M_{target}. Considering the high yields and the experimental M_n, it can reasonably be assumed that the reactions reached 100% monomer conversion. It was observed that immediately after initiation, the reaction mixture turned dark orange, and the colour grew more intense and darker as the mole fraction of styrene in the feed increased, as illustrated in *Figure 3.9*. This is clearly an indication that the styrene was being consumed from the outset, as polystyryl lithium shows a characteristic dark orange colour. In all cases the Đ values are in line with expectations. It was also observed that the rate of polymerization for this pair of monomers seemed to be significantly faster than for DMB and Bd and rate appeared to increase as the amount of styrene rises. Thus, in experiment 3.18 where $[M_1]/[M_2] = 72/28$ (with DMB being M_1 in all cases), a conversion of 73% was reached in 4 h whereas in experiment 3.20 where the amount of styrene in the feed is approximately three times that of DMB ($[M_1]/[M_2] = 24/76$), full conversion was achieved in just 2 h. This might be ascribed to the fast rate of polymerization of styrene in benzene — the anionic polymerization of styrene in benzene with an M_{target} of 10 kg mol^{-1} is known to reach full conversion in 1-2 h at room temperature. Since the conversion of the intermediate samples is much higher than 10% they were not used for calculating reactivity ratios.

Table 3.11: *SEC results of resulting DMB-Sty copolymers and their intermediate samples. Initiator: sec-BuLi,* M_{target} *= 10 kg mol*$^{-1}$*, solvent: benzene and T = 40 °C.* M_1*: DMB and* M_2*: styrene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.18	72/28	4	8800	1.06	73	94
		8	9000	1.06	74	
		144	12100	1.09	100	
3.19	43/57	24	15100	1.09	92	98
		40	15500	1.06	95	
		142	16400	1.10	100	
3.20	24/76	2	12800	1.05	100	95
		4	13000	1.05	100	
		72	12800	1.09	100	

Figure 3.9: *Picture of the polymerization of p(DMB-s-Sty)-24/76 in benzene (experiment 3.20) immediately after initiation.*

In the DMB-Sty copolymerization reactions carried out in *n*-hexane (experiments 3.21, 3.22, 3.23 and 3.24) the reaction mixture also took on an orange colour right after initiation, which again implies that styrene is consumed from the outset. However, the reaction proceeded without any further notable change in colour or shade, which suggests that the concentration of polystyryl lithium chain ends remains close to constant throughout the reaction, implying a random copolymerization. Moreover, it also was observed that after few hours, an (orange) insoluble portion appeared in the reaction mixture. Experiment 3.21 ($[M_1]/[M_2]$ = 72/28) appeared to be a cloudy orange solution after approximately 24 h, whereas in experiments 3.22, 3.23 and 3.24 an orange solid was seen to be floating around the reaction solvent after 4-5 h, as shown in *Figure 3.10*. The orange colour suggests that the reaction is still living after the formation of the solid and that a portion of the chain ends are polystyryl lithium. It would therefore appear that the solubility of the DMB-Sty copolymers is significantly lower than the linear PDMB or the DMB-Bd copolymers in *n*-hexane, which is not unexpected as PDMB (96-97% 1,4 microstructure) and PS are both insoluble in *n*-hexane. Despite the poor solubility of the copolymers, each was obtained in high yield (> 90%) and with the M_n close M_{target}, as such it can be assumed that monomers were completely consumed. In this system, it would appear that slight changes in solvent polarity does not seem to significantly impact on the reaction rate, as a similar (apparent) rate of conversion was observed in both solvents. Moreover, the anionic copolymerization of DMB and styrene in *n*-hexane appears to proceed well despite the fact the growing polymer chains become insoluble. Again, the samples obtained in *n*-hexane cannot be used for the calculation of reactivity ratios as the conversions are too high (% conversion >> 10%).

Table 3.12: *SEC results of resulting DMB-Sty copolymers and their intermediate samples. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, solvent: n-hexane and T = 40 °C. M_1: DMB and M_2: styrene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.21	70/30	25	10300	1.05	79	91
		48	11100	1.06	85	
		120	13000	1.06	100	
3.22	49/51	24	14100	1.06	91	96
		48	15600	1.10	100	
		143	15500	1.08	100	
3.23	49/51	2	9500	1.09	83	95
		4	11800	1.11	100	
		72	11400	1.06	100	
3.24	24/76	24	Insufficient sample			100
		48	16700	1.05	100	

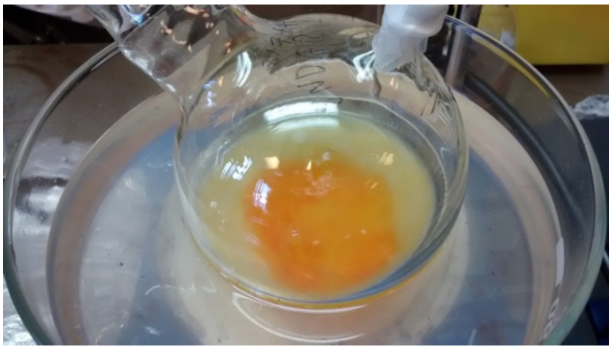


Figure 3.10: *Picture of the polymerization of p(DMB-s-Sty)-24/76 in n-hexane (experiment 3.24) immediately before termination.*

3.2.1.2. Composition and microstructure of low molecular weight DMB-Sty statistical copolymers

All intermediate samples and final copolymers were analysed by ^{1}H-NMR in order to calculate copolymer composition and microstructures. Peaks were assigned taking into account previous spectra from PDMB and PS as shown in *Figure 3.11*. In this case a high degree of overlap between the aliphatic protons of PS and the aliphatic protons of PDMB was observed and the presence of solvent peaks, even after long periods inside an oven under reduced pressure. As a consequence it was not possible to distinguish between *cis*-1,4 and *trans*-1,4 PDMB as the signals corresponding to such microstructures cannot be seen in the spectrum. Therefore, the fraction of 1,4 units was calculated as a combination of both *cis*- and *trans*-1,4. For the calculation of compositions and microstructures of the DMB-Sty copolymers, the values of integrals (i_1, i_2 and i_3) had to be used as follows (*PS* being the relative number of moles of polystyrene and DMB_i the moles of the different microstructures of DMB):

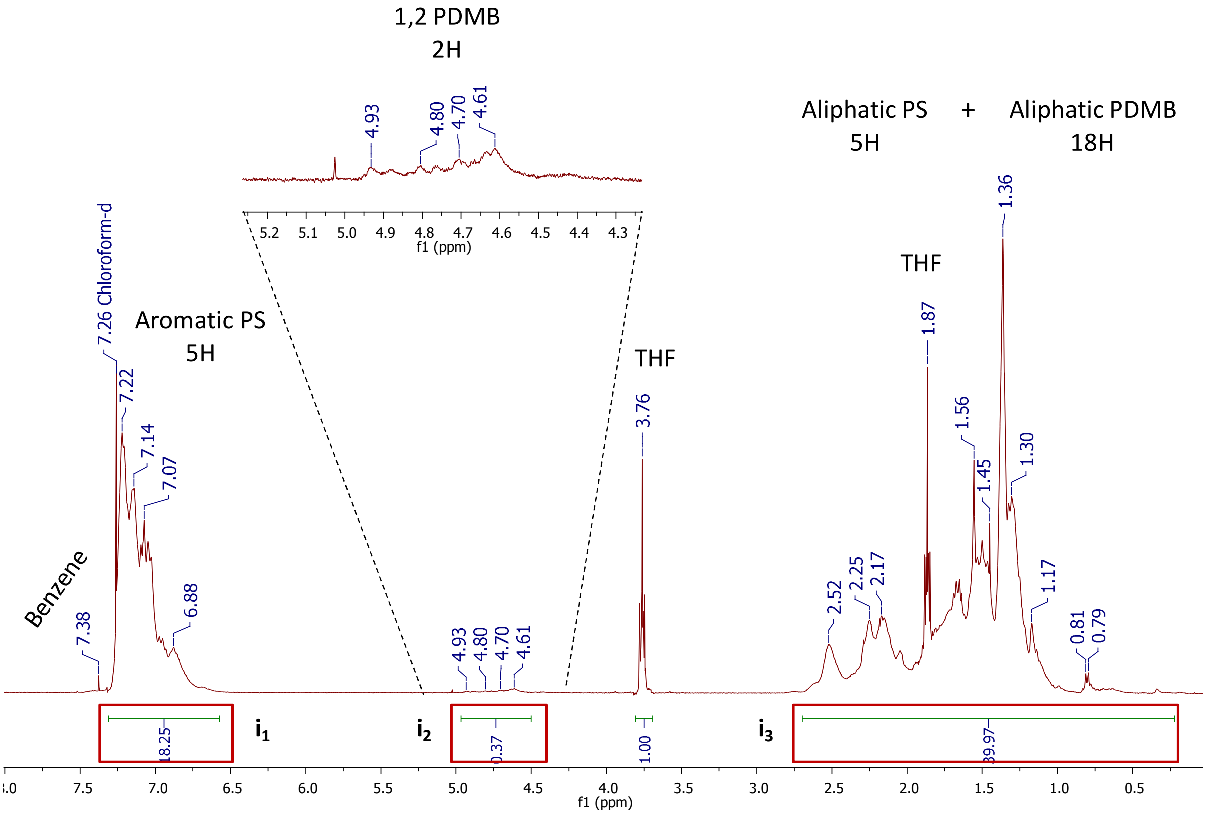


Figure 3.11: *^{1}H-NMR spectrum of p(DMB-s-Sty)-50/50 in benzene (CDCl$_3$, 400 MHz) δ (ppm).*

$$PS = \frac{i_1}{5}$$ **Equation 3.23**

$$DMB_{1,2} = \frac{i_2}{2}$$ **Equation 3.24**

$$i_3 - 3 \times PS - i_{THF} = 10 \times DMB_{1,4} + 8 \times DMB_{1,2}$$ **Equation 3.25**

Equation 3.25 is rearranged to give the relative number of moles of the 1,4 structures of DMB:

$$DMB_{1,4} = \frac{i_3 - 3 \times PS - i_{THF} - 8 \times DMB_{1,2}}{10}$$ **Equation 3.26**

$$DMB = DMB_{1,2} + DMB_{1,4}$$ **Equation 3.27**

$$^{m_1}/_{m_2} = \frac{DMB}{PS}$$ **Equation 3.28**

The copolymer composition and microstructure, calculated in the way described above, are reported in *Table 3.13* and *Table 3.14*Table 3.14. As expected the composition of the final copolymers is close to the feed ratio, as polymerizations proceeded to full conversion. As mentioned above, it was not possible to calculate reactivity ratios from these experiments, however qualitative conclusions can be drawn from these data. For example, all the copolymerizations of DMB with styrene turned to dark orange immediately after the addition of *sec*-BuLi, which suggests that living polystyryl species are formed after initiation.

In polymerizations carried out in benzene (*Table 3.13*), where the mole fraction of styrene is equal to or higher than that of DMB (experiments 3.19 and 3.20), it was not possible to observe compositional drift because the copolymerization was virtually complete (92% conversion) before the first intermediate sample was collected. However, when the mole fraction of DMB is higher than the mole fraction of styrene (experiment 3.18), the overall rate of copolymerization is slower and the intermediate samples collected at 73-74% conversion show a copolymer with a composition which is richer in styrene units than the feed ratio ($m_1/m_2 < [M_1]/[M_2]$) at 73-74% conversion. This might suggest that the consumption of styrene units is somewhat preferred to the incorporation of DMB, which is consistent with the appearance of a dark orange colour immediately after initiation. Moreover, in the case of the DMB-Sty copolymerization in benzene, the presence of styrene as a comonomer seems to have an impact on the microstructure of the DMB repeat units. While the vinyl (1,2) content in DMB homopolymers synthesized in benzene is 16%, this drops to 8-10% in the DMB-Sty copolymers. We believe this is a genuine/significant observation and can be explained in terms of the steric bulk of the phenyl side-group of styrene, which partially inhibits the incorporation of 1,2 DMB units, which contain a bulky vinylidene side-group, see *Figure 3.12*.

Table 3.13: *Composition of resulting DMB-Sty copolymers and their intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, solvent: benzene and T = 40 °C. M_1: DMB and M_2: styrene.*

Experiment	$[M_1]/[M_2]$	% conversion	m_1/m_2	% DMB	
				1,2	*cis*-1,4 + *trans*-1,4
3.18	72/28	73	60/40	8	92
		74	63/37	9	91
		100	73/27	10	90
3.19	43/57	92	45/55	8	92
		95	45/55	8	92
		100	45/55	8	92
3.20	24/76	100	27/73	7	93
		100	26/74	8	92
		100	29/71	8	92

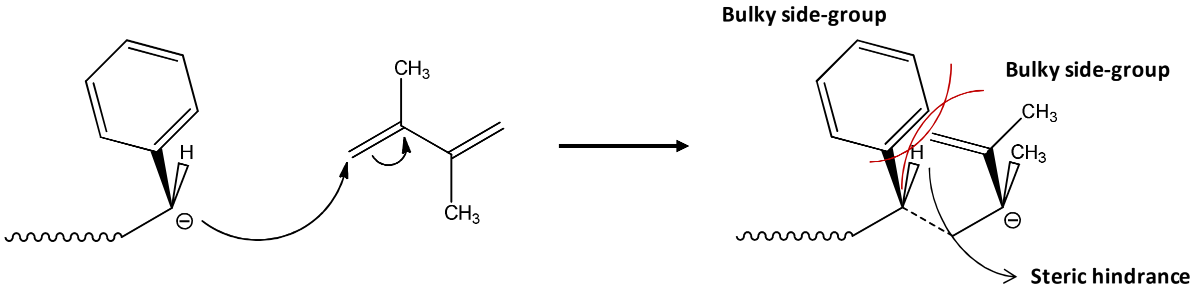


Figure 3.12: *Schematic diagram showing the addition of a $DMB_{1,2}$ unit to a DMB-s-Sty growing chain containing a styrene unit at the chain end.*

A slight compositional drift from styrene to DMB was also observed in experiments 3.21, 3.22, 3.23 and 3.24, carried out in *n*-hexane (*Table 3.14*).

Table 3.14: *Composition of resulting DMB-Sty copolymers and their intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, solvent: n-hexane and T = 40 °C. M_1: DMB and M_2: styrene.*

Experiment	**$[M_1]/[M_2]$**	**% conversion**	**m_1/m_2**	**% DMB**	
				1,2	***cis*-1,4 + *trans*-1,4**
3.21	70/30	79	63/37	6	94
		85	66/34	4	96
		100	72/28	4	96
3.22	49/51	91	48/52	5	95
		100	49/51	5	95
		100	51/49	5	95
3.23	49/51	83	49/51	2	98
		100	47/53	2	98
		100	49/51	4	96
3.24	24/76	≤ 100	Insufficient sample		
		100	27/73	2	98

Thus, in experiments 3.22, 3.23 and 3.24, where the mole fraction of styrene is equal or higher than that of DMB, no drift was observed as the samples were already at high conversion (≥ 83%) and as a consequence the m_1/m_2 is very close to the feed ratio. However, when the DMB mole fraction was higher than styrene (experiment 3.21), and conversions were lower for the intermediate samples, the samples with 79 and 85% conversion showed a m_1/m_2 which was slightly lower than the feed ratio (m_1/m_2 of 63/37 and 66/34 respectively). This might suggest that, as in the copolymerizations in benzene, the styrene units are to some extent preferentially consumed over the DMB, although to be certain, samples would need to be collected at much lower conversions. To this end a series of high molecular weight DMB-Sty copolymers were prepared and these will be discussed later.

Whilst the presence of styrene did appear to impact on the DMB microstructure when benzene was the solvent, the same observation was not made for the copolymers made in *n*-hexane. However, it should be noted that the microstructure of PDMB synthesized in alkanes (*n*-hexane and cyclohexane) shows an extraordinary low content of 1,2 microstructures (3-4%) and a further reduction might not be expected, see *Chapter 2*.

3.2.1.3. The solubility of low molecular weight DMB-Sty statistical copolymers

Solubility tests were carried out using THF (intermediate polarity, $\varepsilon = 7.58$), toluene (low polarity, $\varepsilon = 2.38$) and *n*-hexane (very low polarity solvent, $\varepsilon = 1.89$). 10% solutions were prepared of the copolymers in each solvent (500 mg of polymer in 5 mL of solvents) and the vials put on roller-mixer for 24 h. The results can be seen in *Figure 3.13* and were compared with the solubility of polyDMB homopolymer (*Figure 2.8*). The solubility of the DMB-Sty copolymers in THF and toluene seems to be generally improved by the presence of styrene. This effect is particularly evident for copolymers which were polymerized in *n*-hexane — polyDMB prepared in *n*-hexane has a very high 1,4 content, is partially crystalline and has limited solubility in THF/toluene. However, the solubility of the copolymers in *n*-hexane is clearly worse due to the presence of styrene, which is unsurprising, given that whilst polystyrene is very soluble in THF and toluene, it is insoluble in *n*-hexane, see *Figure 3.14*. Additionally, the presence of styrene statistically distributed with the DMB units throughout the copolymer is likely to inhibit the inherent crystallization of the low vinyl content PDMB (synthesized in alkanes) which also would improve the solubility of the resulting copolymers.

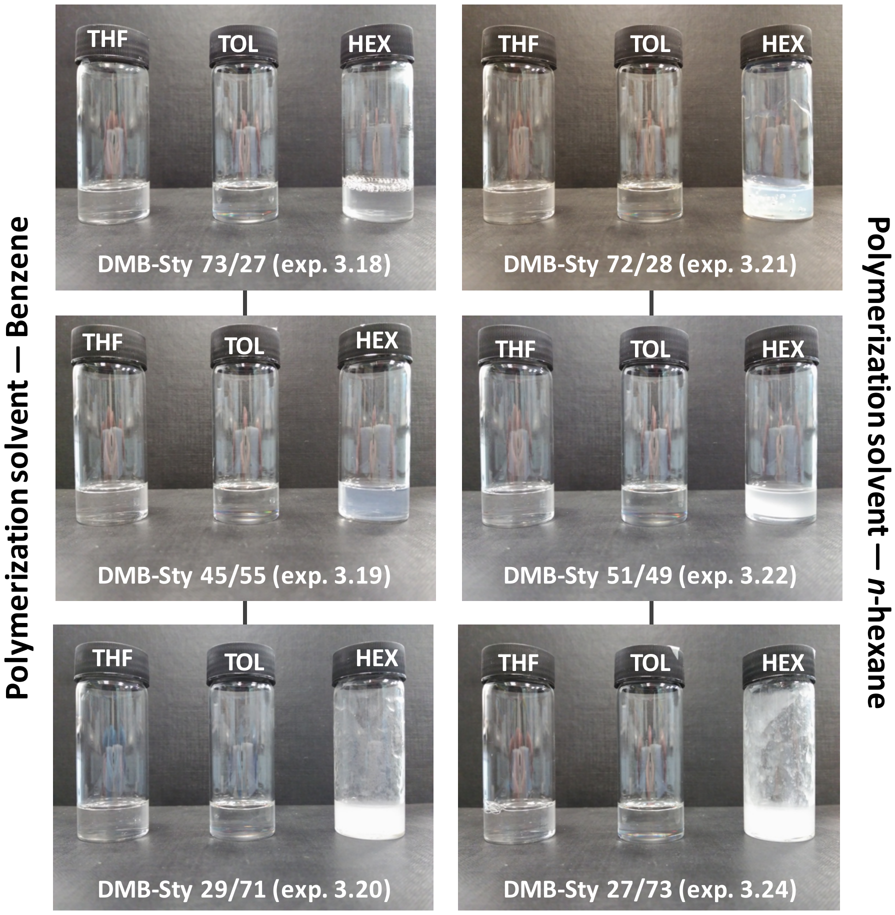


Figure 3.13: *Solubility of the resulting DMB-s-Sty copolymers. Samples of 500 mg of polymer were dissolved in 5 mL of different polarity solvents: THF (ε = 7.58), toluene (ε = 2.38) and n-hexane (ε = 1.89).*

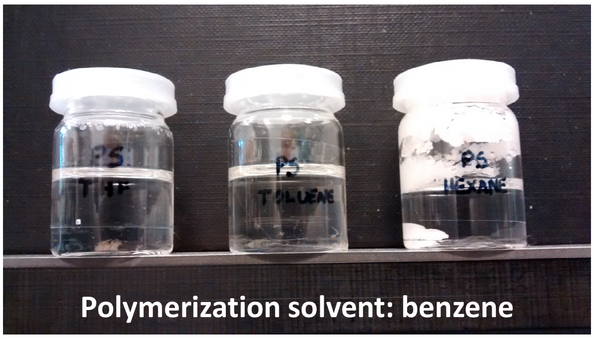


Figure 3.14: *Solubility of polystyrene synthesized in benzene (M_n approximately 10 kg mol^{-1}). Samples of 500 mg of polymer were dissolved in 5 mL of different polarity solvents: from left to right, THF (ε = 7.58), toluene (ε = 2.38) and n-hexane (ε = 1.89).*

3.2.2. Synthesis of high molecular weight DMB-Sty statistical copolymers

In order to calculate reactivity ratios, two new sets of DMB-Sty copolymerizations were carried out with an M_{target} of 100 kg mol^{-1} and using reaction conditions established in previous sections (*sec-*

BuLi, 60 °C in benzene or *n*-heptane). Samples were collected and terminated after short reaction times, in order to obtain samples with low conversions (< 10%). The feed ratios investigated were consistent with the analogous DMB-Bd copolymers i.e. 75/25, 60/40, 50/50, 40/60 and 25/75. In order to ensure full consumption of monomers, reactions were allowed to proceed for up to 5 days.

3.2.2.1. SEC analysis of high molecular weight DMB-Sty statistical copolymers

Molar masses for intermediate samples and final copolymers were calculated by SEC with the results reported in *Table 3.15* and *Table 3.16*. The results will be subject to the same inaccuracies as discussed in detail previously.

The copolymers synthesized in benzene (*Table 3.15*) were obtained in high yields (≥ 74%) although the M_n of some of these copolymers, especially experiments 3.25, 3.28 and 3.29 is significantly higher than M_{target}. As is usually the case with anionic polymerization, when the experimental molar mass is higher than M_{target} the cause is impurities. Considering that the collection of samples at low conversions removes significant quantities of unreacted monomer, it can be assumed the reported yields are representative of reactions that went to completion. The intermediate samples collected in these experiments all had conversions of less than 10% and were therefore suitable for the calculation of reactivity ratios. Most of the copolymers had dispersity values that were only slightly outside the expected range for anionic polymerization; the exception being the polymer produced in experiment 3.25 which had a dispersity of 1.50. This high value can be explained by a combination of chain coupling reactions (second peak 2 x M_n) during the termination process and impurities introduced during the sampling, leading to a significant low molecular weight tail (*Figure 3.15*).

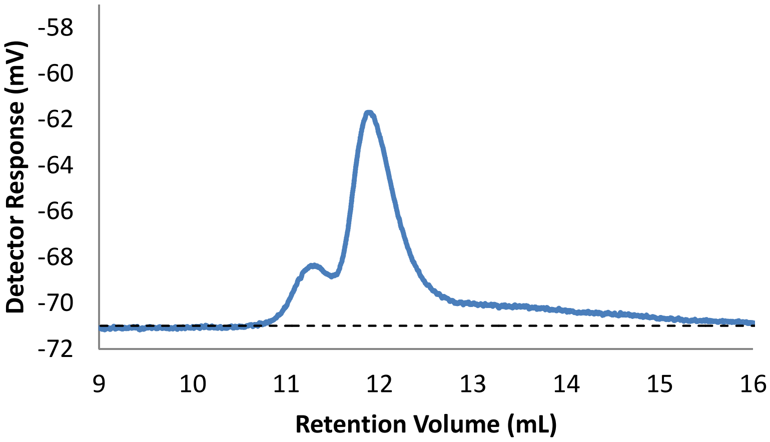


Figure 3.15: *SEC chromatograms of experiment 3.25.*

Table 3.15: *SEC results of resulting DMB-Sty copolymers and their intermediate samples. Initiator: sec-BuLi, M_{target} = 100 kg mol^{-1}, solvent: benzene and T = 60 °C. M_1: DMB and M_2: styrene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.25	70/30	0.07	3800	1.10	2	82
		0.12	10100	1.13	5	
		72	196100	1.50	100	
3.26	62/38	0.05	5000	1.12	4	74
		0.12	13700	1.05	10	
		48	143900	1.13	100	
3.27	49/51	0.08	15500	1.08	9	97
		0.17	33000	1.05	20	
		48	163900	1.14	100	
3.28	48/52	0.05	2800	1.19	1	82
		0.10	8500	1.16	3	
		120	283900	1.15	100	
3.29	25/75	0.05	10200	1.08	5	97
		0.10	35300	1.05	16	
		96	219600	1.18	100	

Yields for the copolymers prepared in *n*-heptane (3.30, 3.31, 3.32, 3.33 and 3.34 — *Table 3.16*) were generally lower (67-80%) than the analogous reactions in benzene. This might be explained by the fact that that in many cases the intermediate samples collected were at lower conversions than the samples collected in the experiments in benzene, meaning that the samples collected in *n*-heptane contain a larger amount of unreacted monomer that will not form part of the final copolymer. The lower conversions mentioned above are probably a consequence of a lower rate of reaction in (the less polar) *n*-heptane. In experiments 3.30, 3.31 and 3.34 the experimental molar mass is significantly higher than intended, probably the consequence of a significant amount (especially in case of experiment 3.30) of impurities present in the reaction vessel before initiation. The high values of Đ (> 1.10) can be explained, as in case of the copolymers in benzene, as a consequence of chain coupling competing with termination and the introduction of impurities during sampling.

Table 3.16: *SEC results of resulting DMB-Sty copolymers and their intermediate samples. Initiator: sec-BuLi, M_{target} = 100 kg mol^{-1}, solvent: n-heptane and T = 60 °C. M_1: DMB and M_2: styrene.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.30	72/28	0.05	Insufficient sample		—	79
		0.12	4100	1.09	2	
		72	267300	1.28	100	
3.31	57/43	0.05	7400	1.09	4	67
		0.10	14700	1.07	8	
		72	180700	1.17	100	
3.32	50/50	0.08	12800	1.07	9	74
		0.17	32000	1.05	21	
		72	149300	1.03	100	
3.33	40/60	0.05	2200	1.17	2	80
		0.10	6700	1.10	5	
		48	147100	1.14	100	
3.34	26/74	0.05	Insufficient sample		—	78
		0.10	4200	1.08	2	
		48	171900	1.30	100	

3.2.2.2. Composition and microstructure of high molecular weight DMB-Sty statistical copolymers in benzene — calculation of reactivity ratios

The copolymer composition and DMB microstructure for the intermediate samples and final polymers were obtained via ^{1}H-NMR analysis using the same calculation methods described earlier. The resulting data for copolymers prepared in benzene are reported in *Table 3.17* and in each case compositional drift was observed. However, surprisingly it seems that the extent of compositional drift and preference of monomer consumption is dependent on the feed ratio. Thus, when DMB is the major component in the feed and in excess over styrene, the mole fraction of DMB in the intermediate samples is lower than the mole fraction of DMB in the feed ratio (e.g. experiment 3.25: $[M_1]/[M_2]$ = 70/30 and m_1/m_2 = 61/39 at 2% conversion). This suggests that when a high mole fraction of DMB is present, the addition of styrene is slightly favoured over the addition of DMB. The opposite effect is observed when styrene is the major component in the feed and the addition of

DMB seems to be somewhat preferred over the addition of styrene. At feed ratios close to unity, i.e. almost equal mole fractions of each monomer, the composition of the early samples collected at low conversion are very close to the feed ratio suggesting that when both co-monomers are in similar amounts, the copolymerization behaves in a close to random manner. These results are unusual, unexpected and difficult to explain.

Table 3.17: *Composition of resulting DMB-Sty copolymers and their intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 100 kg mol^{-1}, solvent: benzene and T = 60 °C. M_1: DMB and M_2: styrene.*

Experiment	$[M_1]/[M_2]$	% conversion	m_1/m_2	% DMB	
				1,2	*cis*-1,4 + *trans*-1,4
3.25	70/30	2	61/39	5	95
		5	57/43	5	95
		100	66/34	8	92
3.26	62/38	4	50/50	7	93
		10	50/50	5	95
		100	61/39	10	90
3.27	49/51	9	45/55	6	94
		20	46/54	5	95
		100	48/52	6	94
3.28	48/52	1	48/52	5	95
		3	46/54	7	93
		100	51/49	5	95
3.29	25/75	5	39/61	4	96
		16	34/66	4	96
		100	26/74	5	95

The presence of styrene appears to effect the microstructure of DMB, as observed previously for the analogous low M_n copolymers (with a M_{target} of 10 kg mol^{-1}) prepared in benzene. Thus styrene as a comonomer seems to lead to a significantly lower vinyl (1,2) content in DMB compared to that observed for a homopolymer of DMB, where vinyl content has been shown to be 16%, see *Chapter 2*. Moreover, this effect is more evident when the mole fraction of styrene increases, resulting in 8% vinyl DMB at 70/30 feed ratio and 5% at 25/75 feed ratios. As proposed previously (*Section 3.1.2.1.*), we believe that this effect is a consequence of the steric hindrance between the phenyl group of styrene with the vinyl group of the 1,2 structures of DMB, as shown in *Figure 3.12*.

As the samples collected had conversions of less than 10% and the first samples were used as data points in the Fineman-Ross/inverted Fineman-Ross linearizations and Kelen-Tudos method, for the calculation of reactivity ratios. The calculated reactivity ratios, reported in *Table 3.18*, confirm that both monomers show tendency for cross-propagation as r_{DMB} and r_{Sty} are significantly lower than 1. This would suggest that the copolymerization of DMB and styrene in benzene behaves in a statistical (almost alternating) manner with a slight preference for the addition of styrene ($r_{DMB} < r_{Sty}$). However, the differences between the reactivity ratios are small and the errors relatively high, and so r_{DMB} and r_{Sty} may be almost identical within error in the case of Fineman-Ross and inverted Fineman-Ross linearizations. The reactivity ratios calculated via the Kelen-Tudos method show much smaller errors and as such suggest the slight preference for the consumption of styrene is significant. This is consistent with the observations made above in relation to compositional drift. In order to confirm the unexpected trend in reactivity ratios (as a function of feed ratio) it would be advisable to repeat the experiments and it will be proposed as Future Work (see *Section 6.2.*).

Table 3.18: *Reactivity ratios calculated for the anionic copolymerization of DMB and styrene in benzene.*

Method	r_{DMB}	r_{Sty}
Fineman-Ross	0.27±0.10	0.38±0.21
Inverted Fineman-Ross	0.14±0.07	0.21±0.03
Kelen-Tudos	0.18±0.01	0.25±0.01

3.2.2.3. Composition and microstructure of high molecular weight DMB-Sty statistical copolymers in *n*-heptane — calculation of reactivity ratios

The composition and microstructure of samples and final polymers prepared in *n*-heptane (*Table 3.19*) were also calculated using ^{1}H-NMR data according the method described above.

These copolymers showed a similar trend in terms of compositional drift as the analogous copolymers prepared in benzene, in so much that compositional drift appeared to be dependent on the feed ratio. When DMB is the major component in the feed, i.e. in excess over styrene, the mole fraction of DMB in the initial sample is lower than the mole fraction of DMB in the feed. However, when styrene is in excess over DMB, the mole fraction of DMB is higher than the mole fraction of DMB in the feed. It can also be seen that the vinyl content of the DMB units ranges from 2 to 5%, which is entirely consistent with the data in *Table 3.14* and suggests that there is no evidence to suggest that styrene has a significant impact on the vinyl content of DMB.

Table 3.19: *Composition of resulting DMB-Sty copolymers and their intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 100 kg mol^{-1}, solvent: n-heptane and T = 60 °C. M_1: DMB and M_2: styrene.*

Experiment	$[M_1]/[M_2]$	% conversion	m_1/m_2	% DMB	
				1,2	*cis*-1,4 + *trans*-1,4
3.30	72/28	—	61/39	4	96
		2	59/41	3	97
		100	70/30	2	98
3.31	57/43	4	49/51	8	92
		8	48/52	7	93
		100	56/44	3	97
3.32	50/50	9	45/55	8	92
		21	45/55	3	97
		100	51/49	5	95
3.33	40/60	2	45/55	3	97
		5	42/58	2	98
		100	40/60	2	98
3.34	26/74	—	55/45	4	96
		2	40/60	3	97
		100	28/72	3	97

The initial samples with low conversions (< 10%) were used as data points in the Fineman-Ross and inverted Fineman-Ross linearizations and Kelen-Tudos method for the calculation of reactivity ratios. The reactivity ratios, reported in *Table 3.20*, suggest that the copolymerization of DMB and styrene in *n*-heptane leads to statistical/close to alternating copolymers as, considering the confidence limits, r_{DMB} and r_{Sty} are almost the same, within error. When comparing the results for the polymerizations carried out in benzene and *n*-heptane, it can be seen that the reactivity ratios are, in general, lower for the copolymers synthesized in *n*-heptane. Data obtained using the Fineman-Ross method resulted in almost no difference between r_{DMB} and r_{Sty} in benzene and *n*-heptane. However, in the case of inverted Fineman-Ross and Kelen-Tudos methods (which are more accurate than the

Fineman-Ross linearization), r_{DMB} in benzene is 0.14-0.18 and r_{Sty} 0.21-0.25, while in *n*-heptane the reactivity ratios are 0.02-0.03 and 0.02-0.09 for DMB and styrene respectively. Both, r_{DMB} and r_{Sty}, decrease significantly, even when considering the errors, which suggest that the polarity of the solvent does play a role in the copolymerization kinetics of DMB and styrene, resulting in a copolymerization in which both monomers show a very strong preference for cross-propagation ($r_{DMB} \approx r_{Sty} \approx 0$). Such behaviour will lead to a nearly-alternating monomer sequence.

Table 3.20: *Reactivity ratios calculated for the anionic copolymerization of DMB and styrene in n-heptane.*

Method	r_{DMB}	r_{Sty}
Fineman-Ross	0.27±0.07	0.34±0.15
Inverted Fineman-Ross	0.02±0.10	0.09±0.03
Kelen-Tudos	0.03±0.06	0.02±0.04

3.2.2.4. Comparison between the copolymerization of DMB and other dienes with styrene

The reactivity ratio values reported above were compared with values previously reported in the literature for the anionic copolymerization of butadiene-styrene and isoprene-styrene, initiated by alkyllithium initiators in both, aromatic and aliphatic solvents (*Table 3.21*).

Table 3.21: *Reactivity ratios of diene-styrene anionic copolymerizations initiated by alkyllithium initiators.*

M_1	M_2	Solvent	T (°C)	r_1	r_2
Butadiene	Styrene	Benzene	30	10.00	0.04
		n-heptane	30	7.00	0.10
Isoprene	Styrene	Benzene	30	7.70	0.13
		Cyclohexane	40	16.60	0.05
DMB[a]	Styrene[a]	Benzene	60	0.18	0.25
		n-heptane	60	0.03	0.02

a) Reactivity ratios calculated by Kelen-Tudos method.

It is clear from the data in *Table 3.21* that the copolymerization kinetics for DMB differs dramatically from the other dienes when copolymerized with styrene. In each case styrene shows strong preference for cross-propagation as r_{Sty} (r_2) << 1 in all the reported examples. Statistical copolymers of both butadiene and isoprene with styrene will have a blocky sequence.[5] In both cases, the diene shows a very strong tendency to homopolymerize (r >> 1) and styrene shows a strong tendency to copolymerize. However, in the DMB-styrene copolymerization, the reactivity ratios show a more statistical/random behaviour ($r_{DMB} \approx r_{Sty} << 1$). In clear contrast with butadiene and isoprene, DMB shows a pronounced tendency to cross-propagate.

3.3. Synthesis of DMB-DPE statistical copolymers

1,1-Diphenylethylene (DPE) is a high boiling liquid monomer (270 °C) whose chemical structure is shown in *Figure 3.16*. DPE has attracted attention as co-monomer in anionic polymerization because of its inability to homopolymerize ($r_{DPE} = 0$) due to the steric bulk of the propagating centre. The synthesis of dimers of DPE has been reported when DPE is initiated by *n*-BuLi and when DPE is in large excess with respect to the concentration of initiator,[8] but it is widely accepted that in most cases the homopolymerization of DPE does not occur. However, DPE is able to copolymerize with other monomers, and with certain co-monomers, DPE can be used for the synthesis of alternating copolymers. Moreover, the use of derivatives of DPE can lead to the synthesis of a variety of functionalized copolymers.[9, 10]

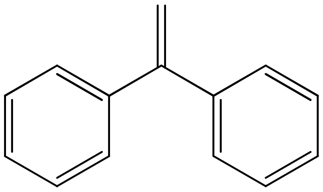


Figure 3.16: *Chemical structure of 1,1-diphenylethylene (DPE). $C_{14}H_{12}$, molecular weight 180.25 g mol^{-1}.*

Nature has perfected the control over the monomer sequence in natural copolymers, however, the possibility of obtaining that degree of control in synthetic copolymers might be considered one of the great challenges in polymer chemistry.[11, 12] As mentioned in *Chapter 1,* alternating copolymers, where r_1 and r_2 are equal to 0, are not common. Yuki *et al.* reported in 1969 the anionic copolymerization of DMB with DPE in benzene. The syntheses reported in that paper were small scale copolymerizations (*ca.* 1 g of monomers in 15 ml) using *n*-BuLi as initiator with target molecular weights around 10 kg mol^{-1}. The copolymerizations were carried out at various feed ratios where DPE was in equal or higher fraction than DMB (*ca.* from 50/50 to 40/60). The average calculated r_{DMB} for the DMB-DPE pair was 0.23,[13] which implies that DMB shows tendency to cross-propagate and the resulting sequence is close to alternating. This behaviour was consider surprising given what we know about the copolymerization of butadiene with DPE and prompted a brief investigation.

3.3.1. Synthesis of low molecular weight DMB-DPE statistical copolymer

In non-polar solvents (for example benzene) the statistical anionic copolymerization of DPE and butadiene results in a homopolymer of polybutadiene as a consequence of the very high value of r_{Bd} (r_{Bd} = 54 and r_{DPE} = 0 in benzene).[5] With a view to investigate the copolymerization kinetics of DMB-DPE copolymerization, a low molar mass sample, with an M_{target} of 10 kg mol^{-1} was initially prepared in benzene at 40 °C. Also, the influence of DPE on the reaction rate and microstructure of DMB was studied. When the initiator was injected, an immediate colour change to dark red/orange was observed, which indicates the presence of polydiphenylethyl lithium chain ends and suggesting that DPE was consumed from the outset. The reaction was allowed to proceed for 72 h, with samples collected after 24 and 48 h. The reaction did not undergo further changes in colour/shade until it was terminated. This suggests a nearly constant concentration of polydiphenylethyl lithium chain ends. The absence of any change in the reaction colour, even up to point of termination, might also suggest that all of the DMB monomer was consumed before all of the DPE and at the end of the reaction all chain ends were carried terminal DPE units. The presence of unreacted DMB following the complete consumption of DPE, would have led to the end capping of a portion of the chains with DMB, which would have resulted in a change of colour since the dimethylbutadienyl lithium chain ends are virtually colourless.

3.3.1.1. SEC analysis of low molecular weight DMB-DPE statistical copolymer

The intermediate samples and final copolymer were analysed by triple detection SEC (see *Table 3.22*) as described in previous sections. According to Hutchings and co-workers, the *dn*/*dc* value of a nearly perfect alternating copolymer of butadiene and DPE is 0.189 mL/g, with 0.124 being the *dn*/*dc* value of polybutadiene.[10] Therefore, the expected *dn*/*dc* value for an equivalent DMB-DPE copolymer would be higher than 0.189 mL/g. As a consequence, the value used in the SEC analysis (0.130 mL/g) is significantly lower than the true value and the resulting M_n will be underestimated. However, as it will be explained later in *Section 3.3.1.2.*, for the calculation of reactivity ratios in this system it was not necessary to collect samples with < 10% conversion, so errors affecting M_n and hence, conversion are not critical in this case.

Table 3.22: *SEC results of resulting DMB-DPE copolymer and its intermediate samples. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, solvent: benzene and T = 40 °C. M_1: DMB and M_2: DPE.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.35	50/50	24	11800	1.11	81	76
		48	13100	1.13	90	
		72	14600	1.10	100	

The DMB-DPE copolymer was obtained in high yield (76%), but with a M_n which is significantly higher than the M_{target}, especially when considering that the value of M_n obtained by SEC significantly underestimates the true value. This suggests that impurities present in the reactor killed a portion of the BuLi before initiation. The Đ values are slightly higher than expected in anionic polymerization (Đ ≥ 1.10) which might be also ascribed to the introduction of impurities during sampling.

3.3.1.2. Composition and microstructure of low molecular weight DMB-DPE statistical copolymer — calculation of reactivity ratios

Intermediate samples and the final copolymer were also analysed by ^{1}H-NMR — the ^{1}H-NMR spectrum for DMB-DPE copolymer is shown in *Figure 3.17*. Peaks were assigned as indicated by the inset structures. The presence of peaks (at 5.5 ppm) corresponding to the unreacted vinyl group of DPE monomer was observed in the final copolymer (*Figure 3.17*) and intermediate samples. As DPE cannot homopolymerize (r_{DPE} = 0), the presence of DPE in the final copolymer suggests that all the DMB was consumed but some DPE remained unreacted at the end of the polymerization. The high boiling point of DPE made the removal of all traces of DPE very difficult — it was observed that traces of DPE remained in the copolymer even after precipitating three times in methanol. This is particularly difficult in the case of the intermediate samples as the polymers were isolated by evaporation (the mass of sample was too low for precipitation) of solvent and unreacted monomers.

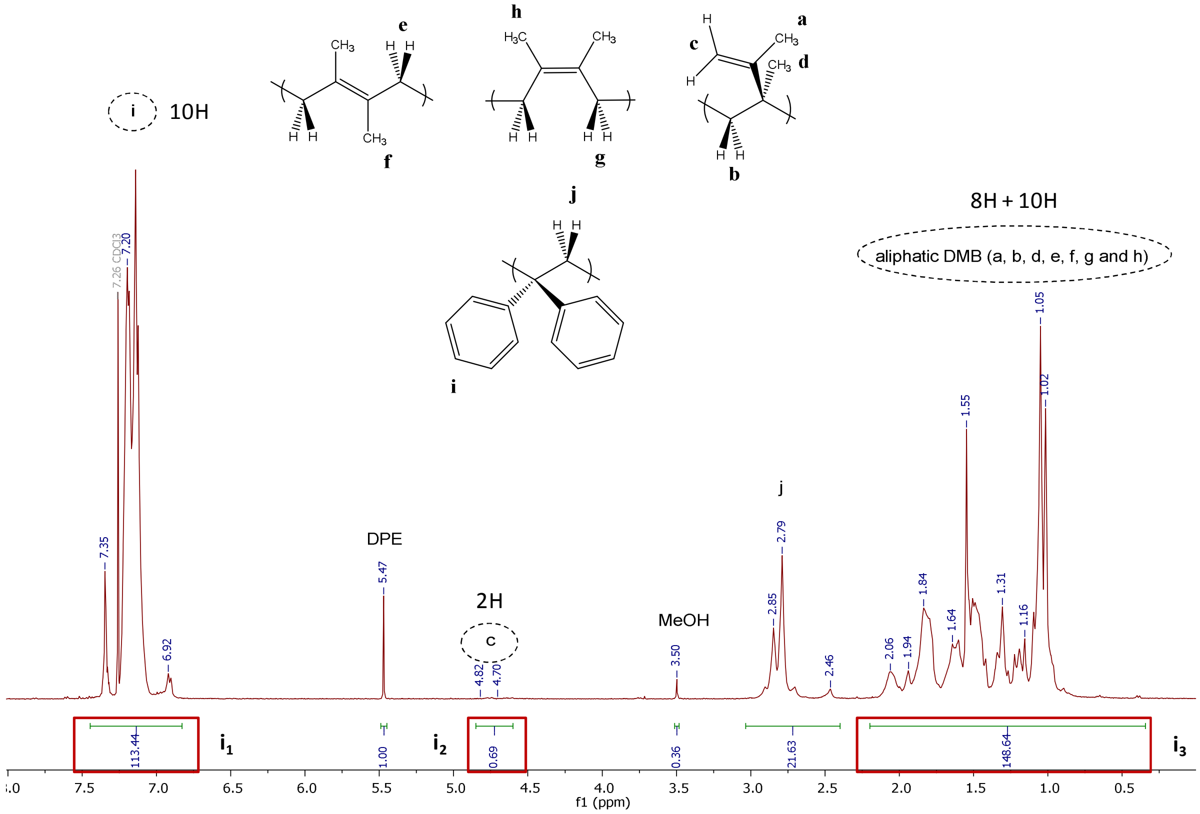


Figure 3.17: *^{1}H-NMR spectrum of p(DMB-s-DPE)-50/50 in benzene, experiment 3.35 (final copolymer) ($CDCl_3$, 400 MHz) δ (ppm).*

The copolymer composition and DMB microstructure were calculated in a similar way to the analogous DMB-Sty copolymers. Again, due to the high degree of peak overlap, the integrals of an entire region, e.g. the aliphatic region (from 2.2 – 0.5 ppm), were used instead of the integrals for the individual peaks. Therefore, it was not possible to distinguish between *cis*- and *trans*-1,4 structures of DMB and it was only possible to calculate the combined 1,4 units. *DPE* (*Equation 3.29*) is the relative number of moles of DPE, which takes account of any unreacted DPE monomer, and DMB_i the number of moles of the combined microstructures of DMB.

$$\boldsymbol{DPE = \frac{i_1 - 10 \times {}^{i_{DPE}}/_{2}}{10}}$$

Equation 3.29

$$\boldsymbol{DMB_{1,2} = \frac{i_2}{2}}$$

Equation 3.30

$$\boldsymbol{i_3 = 10 \times DMB_{1,4} + 8 \times DMB_{1,2}}$$

Equation 3.31

Equation 3.31 is rearranged to give the relative number of moles of the 1,4 units of DMB:

$$\boldsymbol{DMB_{1,4} = \frac{i_3 - 8 \times DMB_{1,2}}{10}}$$

Equation 3.32

$$\boldsymbol{DMB = DMB_{1,2} + DMB_{1,4}}$$ **Equation 3.33**

Once the moles of both DMB and DPE are known, the composition of the copolymers was calculated as follows:

$$\boldsymbol{{}^{m_1}/_{m_2} = \frac{DMB}{DPE}}$$ **Equation 3.34**

The resulting compositions and microstructures for the DMB-DPE copolymers calculated in the way described above are reported in *Table 3.23*.

Table 3.23: *Composition of resulting DMB-DPE copolymer and its intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, solvent: benzene and T = 40 °C. M_1: DMB and M_2: DPE.*

Experiment	**$[M_1]/[M_2]$**	**% conversion**	**m_1/m_2**	**% DMB**	
				1,2	***cis*-1,4 + *trans*-1,4**
3.35	50/50	81	58/42	3	97
		90	57/43	3	97
		100	57/43	3	97

It is noteworthy to mention immediately that a significant degree of DPE consumption is observed when DMB is copolymerized with DPE, which is in stark contrast to the copolymerization of butadiene and DPE where, as mentioned previously, a homopolymer of butadiene is obtained.[5] Then data in *Table 3.23* indicates that the composition of the intermediate samples is very close to the composition of the final polymer and that the each sample is slightly richer in DMB than the feed ratio. Therefore, the resulting polymer cannot have a perfectly alternating sequence. Another interesting point is that the vinyl content of the DMB units is significantly lower (3%) than for a DMB homopolymer (16%) produced in the same solvent, benzene. This is probably due to the high steric hindrance produced by the two bulky phenyl groups of DPE making the addition of DMB in the form of 1,2 units very unfavourable. The propagating DMB chain end will experience considerably less steric hindrance by reacting via the 4-carbon. Hutchings *et al.* reported a similar observation in that an alternating copolymer of butadiene-DPE prepared by anionic polymerization in THF contains polybutadiene units with a microstructure comprising only 36% 1,2-PBd, whereas the homopolymerization of butadiene in THF leads to polybutadiene with approximately 90% 1,2 microstructure. Hutchings ascribed this reduction in the content of 1,2 microstructures of polybutadiene to the steric crowding caused by the two phenyl groups on DPE.[10]

The reactivity ratios for DMB (r_{DMB}) were calculated by an iterative method using the following equation derived from the Mayo-Lewis equation by Yuki *et al.*:[14]

$$\ln\frac{[M_2]}{[M_2]_0}+\frac{1}{r_1-1}\ln\left[\frac{[M_1]_0}{[M_2]_0}(r_1-1)+1\right]=0$$ **Equation 3.35**

$[M_2]$ ≡ final concentration of DPE

$[M_1]_0$ ≡ initial concentration of DMB monomer

$[M_2]_0$ ≡ initial concentration of DPE monomer

r_1 ≡ reactivity ratio of DMB

A number of conditions need to be met for this method to be valid; i) r_1 cannot be equal to 1.0, which would make the term $1/(r_1\text{-}1)$ meaningless (1/0), ii) the reaction must proceed to completion and iii) the mole fraction of DPE monomer ($[M_2]$) at completion has to be greater than 0 — since ln 0 (*Equation 3.35*) is meaningless. In the current study, the final copolymer sample (including unreacted DPE) was recovered by evaporation of solvent. It is assumed that with a boiling point of 270 °C, any unreacted DPE will not evaporate. For the calculationof the reactivity ratio, the instantaneous monomer feed ratios are required. As mentioned at the beginning of this chapter, the monomer feed ratio varies during the polymerization and hence, reactivity ratios are typically calculated at low monomer conversion when the monomer feed ratio is nearly equal to the initial monomer feed ratio. However, when DPE is used as a co-monomer, the calculation of reactivity ratios at 100% DMB conversion is possible provided the conditions mentioned above are met — crucially there must be unreacted DPE monomer present at the end of the reaction. Upon complete consumption of M_1 (the non-DPE comonomer), DMB in the present work, the polymerization will end as DPE cannot homopolymerize (r_{DPE} = 0). At this point it is possible to calculate the final mole fraction of DPE monomer, determine the final monomer feed ratio and hence, calculate the reactivity ratios. However, if the DPE monomer (M_2) is not in excess in the feed, then M_2 could be all consumed (depending on r_1) at which point M_1 will continue to homopolymerize to complete consumption, and the final copolymer composition will inevitably be equal to the monomer feed ratio. For this reason the reactivity ratios have only been calculated when the molar feed fraction of DPE was equal to or in excess of the DMB monomer. Furthermore, if the reaction had not reached completion, then it is also not possible to calculate the reactivity ratio as the concentration of the non-DPE co-monomer (M_1) will not be equal to 0 and the instantaneous molar feed ratios cannot be determined.

The reactivity ratio for DMB was calculated as described above for experiment 3.35 and a value of r_{DMB} = 0.54 was obtained. Therefore, in experiment 3.35 both co-monomers have preference for cross-propagation as $r_{DMB} < 1$ and r_{DPE} is assumed to be 0. Thus, under the established copolymerization conditions the resulting copolymer will have a close-to-alternating sequence with a clear preference for the addition of DMB over the addition of DPE ($r_{DMB} > r_{DPE}$). As the calculated value for r_{DMB} differs from the value previously obtained by Yuki and co-workers ($r_{DMB} = 0.23$)[13] the synthesis of higher molar mass DMB-DPE copolymers was attempted.

3.3.2. Synthesis of high molecular weight DMB-DPE statistical copolymers

Following Yuki's work,[13] a series of high molecular weight DMB-DPE copolymers were synthesized, in benzene, with a target molar mass of approximately 100 kg mol^{-1}. The feed ratios tested in this case cover the situations where DMB is in molar excess in the feed in some cases and DPE is in excess in other cases (from 75/25 to 25/75). Each feed ratio was polymerized in duplicate and samples collected at very short reaction times (around 5-10 min after initiation) in the first set of experiments and at longer reaction times (15 min to 1 h) in the second. Although not strictly needed, samples were collected with the goal of obtaining information regarding the composition of the copolymers at early stages of the copolymerization. This work also includes the calculation of reactivity ratios for the DMB-DPE pair.

3.3.2.1. SEC analysis of high molecular weight DMB-DPE statistical copolymers

Molecular weight data was obtained by SEC (see *Table 3.24*) using triple detection (as in the case of the lower molar mass, with a M_{target} of 10 kg mol^{-1}, copolymer) or using a conventional PS calibration when the molar mass was too low to give a reasonable light scattering response. This was usually the case for samples collected at very low conversions (≤ 1%) with molecular weights < 1000 g mol^{-1}.

In terms of reaction rate, as expected, the steric hindrance of the two bulky phenyl groups of DPE slows down the reaction. The data in *Table 3.24* shows that the conversions of the samples are very low (lower than 1% in some cases). This was especially the case for experiments with an excess of DPE, where conversions of less than 10% were obtained 1 h after initiation, which clearly suggests that the reactions with DPE as co-monomer proceed at a slower rate than copolymers of DMB with either butadiene or styrene. The final copolymers were obtained in moderate yields (≤ 60%), probably as a consequence of sampling at very low conversions and the inability of DPE to homopolymerize — thus once all the DMB is consumed the reaction will stop and any unreacted DPE will reduce the yield of copolymer. In experiments 3.37 and 3.39 the polymers were obtained in very low yields (17% and 28% respectively). The low yields can be explained by the two factors alluded to above; namely, the collection of samples at very low conversions, which removes a significant portion of unreacted monomers and the presence of unreacted DPE at the end of the reaction. Thus, experiments with a molar excess of DMB and a molar feed ratio of 75/25 (DMB/DPE — experiments 3.36 and 3.37) would be expected to result in a higher potential yield because of the likely full conversion of DPE. On the other hand, reactions with a molar excess of DPE i.e. experiments 3.40 and 3.41 with a 25/75 (DMB/DPE) feed ratio might be expected to result in a lower yield due to the inability of the excess DPE to be consumed. However, in the case of experiment 3.37, which does not follow the relationship between feed ratio and potential yield explained above, the low molar mass and unacceptably high dispersity (1.44) of the final copolymer would suggest that the polymerization was prematurely terminated, probably by impurities introduced during the collection of the second sample — the Đ values of the earlier samples are much lower.

Table 3.24: *SEC results of resulting DMB-DPE copolymers and their intermediate samples. Initiator: sec-BuLi,* M_{target} *= 100 kg mol*$^{-1}$*, solvent: benzene and T = 60 °C.* M_1*: DMB and* M_2*: DPE.*

Experiment	$[M_1]/[M_2]$	t (h)	M_n (g mol^{-1})	Đ	% conversion	% yield
3.36	75/25	0.03	500	1.11	< 1	60
		0.08	600	1.21	1	
		96	123200	1.25	100	
3.37	75/25	0.50	4900	1.15	10	17
		1	9700	1.07	20	
		144	49800	1.44	100	
3.38	50/50	0.05	Insufficient sample		—	58
		0.10	500	1.15	< 1	
		96	147800	1.15	100	
3.39	50/50	0.25	1100	1.23	1	28
		0.50	2400	1.24	2	
		96	114900	1.30	100	
3.40	25/75	0.05	500	1.23	< 1	33
		0.10	600	1.43	< 1	
		96	92100	1.13	100	
3.41	25/75	0.50	4700	1.23	4	27
		1	10000	1.15	9	
		96	111200	1.28	100	

3.3.2.2. Composition and microstructure of high molecular weight DMB-DPE statistical copolymers — calculation of reactivity ratios

The analysis of the ^{1}H-NMR spectra and calculation of copolymer composition and DMB microstructure of the intermediate samples and final copolymers was carried out according to the method described previously. Results are reported in *Table 3.25* and they clearly show that, once again, the steric bulk of DPE has a significant impact on the vinyl (1,2) content of the DMB.

Table 3.25: *Composition of resulting DMB-DPE copolymers and their intermediate samples calculated from ^{1}H-NMR. Initiator: sec-BuLi, M_{target} = 100 kg mol^{-1}, solvent: benzene and T = 60 °C. M_1: DMB and M_2: DPE.*

Experiment	**$[M_1]/[M_2]$**	**% conversion**	**m_1/m_2**	**% DMB**	
				1,2	***cis*-1,4 + *trans*-1,4**
3.36	75/25	< 1	75/25	6	94
		1	74/26	5	95
		100	76/24	7	93
3.37	75/25	10	69/31	5	95
		20	70/30	5	95
		100	70/30	6	94
3.38	50/50	—	76/24	15	85
		< 1	75/25	20	80
		100	59/41	2	98
3.39	50/50	1	61/39	3	97
		2	59/41	3	97
		100	58/42	2	98
3.40	25/75	< 1	46/54	45	55
		< 1	42/58	51	49
		100	49/51	2	98
3.41	25/75	4	54/46	2	98
		9	53/47	2	98
		100	51/49	2	98

Moreover, there appears to be a correlation between the amount of DPE in the feed and the DMB vinyl content. Thus, when DPE is present in the feed at low mole fractions (experiments 3.36 and 3.37), a vinyl content of 6-7% was obtained. However, when the mole fraction of DPE was raised, in experiments 3.40 and 3.41, the content of 1,2 units dropped dramatically to 2%. As mentioned previously, this is due to the high steric hindrance between the bulky side-groups of DPE and the bulky vinylidene group of the 1,2 units of DMB, as shown in *Figure 3.18*. The microstructure of the low conversion samples is in general very similar (or identical in case of experiment 3.41) than the microstructure of the final copolymers, which is in line with what was observed in the DMB-Sty copolymerizations (see *Table 3.17* and *Table 3.19*). However, the samples of experiments 3.38 and 3.40 are out of this trend, which can be ascribed to potential errors in the calclation from ^{1}H-NMR spectra (e.g. poor signal to noise ratios and high degree of overlapping). Therefore, the microstructure of these samples should be disregarded.

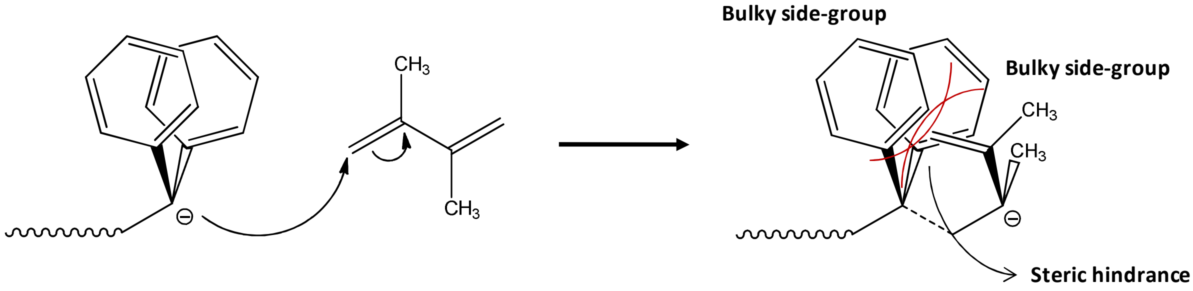


Figure 3.18: *Schematic diagram showing the addition of a DMB$_{1,2}$ unit to a DMB-s-DPE growing chain containing a DPE unit at the chain end.*

The copolymer composition of the intermediate samples and final copolymers are highly dependent upon the feed ratio. At a 75/25 (DMB/DPE) molar feed ratio (experiments 3.36 and 3.37), m_1/m_2 (the copolymer composition) is almost identical to the feed ratio ($[M_1]/[M_2]$) and does not vary significantly with conversion — which suggests an almost uniform distribution of monomers throughout the copolymer chains. When the molar feed ratio is 50/50 (experiments 3.38 and 3.39), once again there is virtually no evidence of compositional drift. We should probably discount the data from the first two samples in experiment 3.38 because with a molar mass of just a few hundred, implying a degree of polymerization of only 4 or 5, the degree of polymerization is too low to be of statistical value. Instead, we should consider the data from experiment 3.39, where the first sample has a molar mass in excess of 1000 g mol^{-1} and degree of polymerization of 8 or 9. In experiment 3.39 we see that m_1/m_2 is almost constant (with respect to conversion) at *ca.* 60/40, but higher than $[M_1]/[M_2]$ at 50/50. It is worth noting that the composition of the final copolymer of experiment 3.38 is 59/41. These data suggest that DMB is consumed in preference over DPE, which is perhaps not surprising since $k_{11} \neq 0$ and $k_{22} = 0$. The final composition does not match the feed ratio because upon complete consumption of DMB, the reaction ends and unreacted DPE remains as monomer. When DPE is in molar excess in the feed (25/75), as in experiments 3.40 and 3.41, the composition of the resulting copolymers is almost 50/50. It should be noted that the composition of the intermediate samples in experiment 3.40 show a mole fraction of DPE which is > 0.5. In theory this is not possible since DPE cannot homopolymerize, however, these samples are very low molecular weight, with a very low degree of polymerization and the apparently anomalous result is probably a consequence of the presence of short oligomers,where DPE is both the first and the last unit, e.g. a DPE-DMB-DPE trimer sequence has a molar mass of approximately 450 g mol^{-1} and would have a molar ratio (m_1/m_2) of 33/67. The final sample of experiment 3.40 has a composition of 49/51 (DMB/DPE) but the apparent molar excess of DPE is not likely to arise from the chains having DPE at both chain-ends. Instead this might be the consequence of errors associated with the ^{1}H-NMR analysis. *Figure 3.19*, shows the ^{1}H-NMR spectrum the final copolymer of experiment 3.40 and the sample contains traces presence of both benzene (7.38 ppm) and chloroform (7.26 ppm) which overlap the region where the aromatic protons of DPE appear.

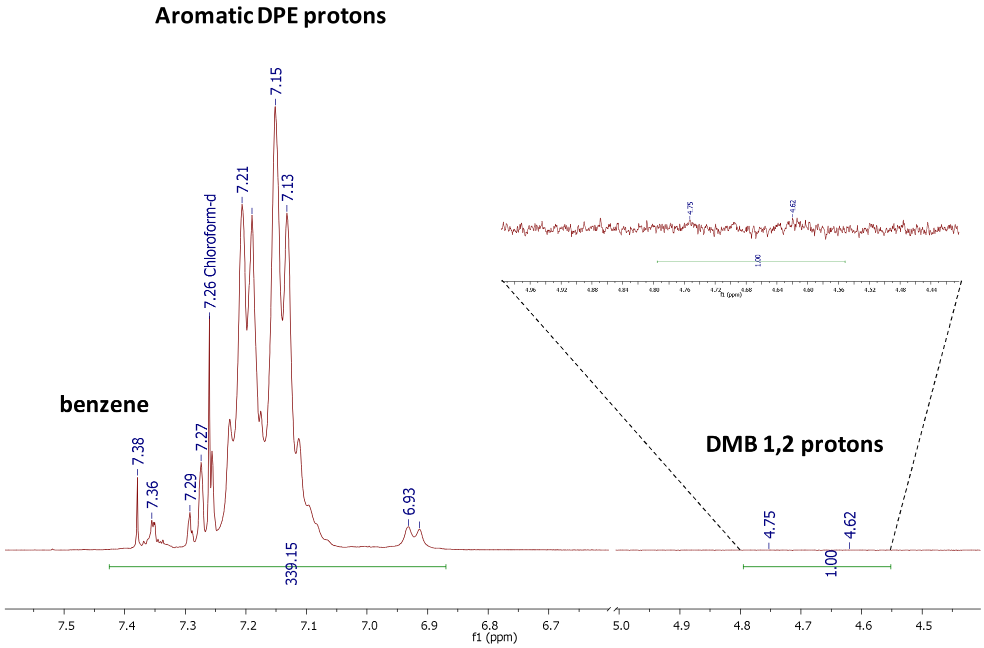


Figure 3.19: *^{1}H-NMR spectrum of experiment 3.40 showing the 7.6-6.6 ppm and 5.0-4.5 ppm regions ($CDCl_3$, 400 MHz) δ (ppm).*

Although these solvent peaks are not very large, they will result in a slight overestimation, maybe by 1 or 2%, of the mole fraction of DPE with respect to DMB. Additionally, as shown in *Figure 3.19*, the signal to noise ratio of protons corresponding to 1,2-PDMB (4.75 and 4.62 ppm) is very low, which will introduce a small error into the calculation of the mole fraction of DMB using *Equation 3.30*, *Equation 3.32* and *Equation 3.33* (see *Section 3.3.1.2*). However, even assuming an error of ±100% in the integral corresponding to the vinyl protons of DMB (4.75 and 4.62 ppm) the calculation of m_1/m_2 gave as a result 49/51 — the same reported in *Table 3.25*. It is therefore reasonable to suggest that the final composition m_1/m_2 of 49/51 might be considered to be 50/50 within error and therefore not anomalous. We will revisit this discussion in *Section 3.4.3* in the context of the thermal analysis of the reported copolymers. Experiment 3.41 showed remarkably little compositional drift (within error) and a copolymer composition comprising of a little more than 50 mol-% DMB. This would suggest that with DPE as the major component in the feed, a nearly alternating copolymer results, but implies that DMB is incorporated preferentially.

Figure 3.20 shows a schematic with illustrative monomer sequences, deduced from the results of *Table 3.25*, of the resulting copolymers of DMB and DPE synthesized at different feed ratios. The potential sequence varies significantly with the initial feed ratio, obtaining alternating or very close to alternating DMB-DPE copolymers ($m_1/m_2 \approx 50/50$) at feed ratios of 25/75. However, in order to confirm the alternating sequence of the copolymers, MALDI ToF mass spectrometry analysis would be necessary.

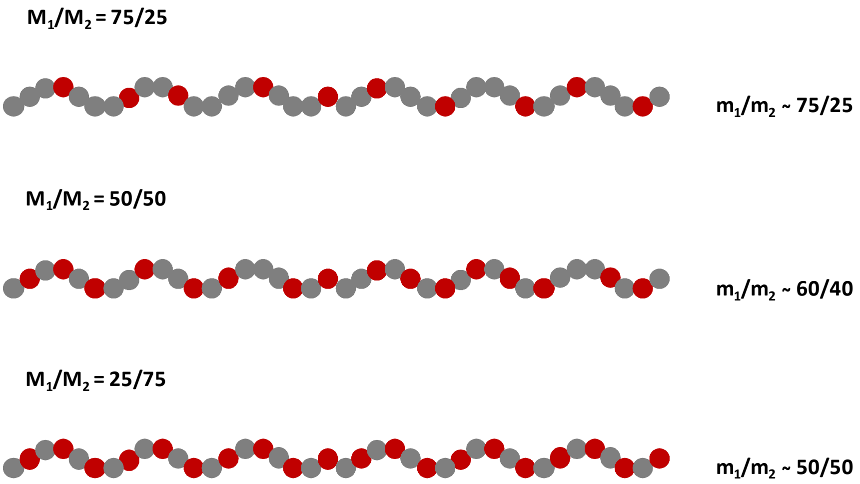


Figure 3.20: *Schematic diagram to show the potential sequence of poly(DMB-s-DPE) deduced from the reported results of composition at different feed ratios. The M_1 is represented by grey balls (DMB) and M_2 by red balls (DPE).*

The reactivity ratios were calculated using the same iterative method described for the low molecular weight DMB-DPE copolymer with an apparent M_n of 14.6 kg mol^{-1}. As mentioned above, the calculation is carried out using data from the final copolymer, and was possible only in the cases where DPE was fed in equal or higher mole fraction than DMB (experiments 3.38 to 3.41) — the results are reported in *Table 3.26*. The calculation of reactivity ratios for experiment 3.40 was not possible as the composition of the final copolymer is richer in DPE than in DMB — which of course is not possible given the inability of DPE to homopolymerize. The data reported in *Table 3.26* shows that there is some inconsistency in the reactivity ratios. Reactivity ratios for experiments 3.38 and 3.39 ($[M_1]/[M_2]$ = 50/50, r_{DMB} = 0.59-0.64) are higher than the value obtained for experiment 3.41 (r_{DMB} = 0.33). As the reactivity ratios are an inherent value for any pair of monomers, the difference in obtained reactivity ratios for the three experiments may be the consequence of different possible sources of error. It is worth noting that in the iterative method based on Mayo-Lewis equation (*Equation 3.35*) described in *Section 3.3.1.2* the mole fraction of unreacted DPE ($[M_2]$) is a key parameter in the calculation of reactivity ratios. This $[M_2]$ value was calculated as the difference between the initial and the final mole fractions of DPE given by the feed ratio and m_1/m_2. However, the unreacted DPE taken in the sampling was not/could not be taken into account. Whilst this will undoubtedly introduce an error and may account for the inconsistencies in reactivity ratio, it should be noted that the error is likely to be highest where the feed ratio of DPE is highest — experiment 3.40 and 3.41. We would therefore argue that the reactivity ratios obtained in experiments 3.38, 3.39 and 3.35 (the low molar mass analogue), r_{DMB} = 0.64, 0.59 and 0.54 respectively, are more accurate, even though a value of 0.33 is in better agreement with Yuki, who reported r_{DMB} = 0.23.[13]

Table 3.26: *Reactivity ratios of DMB-DPE anionic copolymerizations initiated by sec-BuLi in benzene at 60 °C. It is assumed that $r_2 = 0$.*

Experiment	$[M_1]/[M_2]$	m_1/m_2	r_{DMB}
3.38	50/50	59/41	0.64
3.39	50/50	58/42	0.59
3.40	25/75	49/51	—
3.41	25/75	51/49	0.33

It has also been observed that DPE clearly exerts a significant impact upon the physical appearance of the resulting copolymers, as shown in *Figure 3.21*. As the resulting copolymers have a nearly alternating sequence, their physical properties, e.g. T_g, are expected to be intermediate[15] between PDMB and the theoretical DPE homopolymer, see *section 3.4.3*. Experiment 3.36 (m_1/m_2 = 76/24) comprises of a majority of DMB units and has a similar appearance to the product of experiment 2.6 (PDMB synthesized in benzene) but harder and more brittle. The copolymers obtained in experiment 3.38 (m_1/m_2 = 59/41) and 3.40 (m_1/m_2 = 48/52) appeared as white powdery solids, similar in appearance to polystyrene, and with no elastic behaviour whatsoever.

Figure 3.21: *Pictures of resulting DMB-DPE copolymers: a) experiment 3.36 (m_1/m_2 = 76/24), b) experiment 3.38 (m_1/m_2 = 59/41) and c) experiment 3.40 (m_1/m_2 = 48/52).*

3.4. Thermal analysis of polyDMB copolymers

As mentioned in previous chapters, the thermal properties of a polymer are of great technological importance as they determine appropriate processing conditions and they influence the mechanical properties and hence, the possible applications. For example, PDMB is not suitable for the production of tyres due to its relatively high T_g (7.7-16.0 °C), as the tyres would become inelastic and brittle during autumn/winter (T < 7.7 °C).

It is known that a way of modulating the T_g of a polymer to fit it to a specific purpose is copolymerization. Depending on the type of copolymer, different effects on the T_g are exerted. If the resulting copolymer has a random/statistical sequence of comonomers, a single T_g is obtained with a value intermediate between the T_g of homopolymers of the constituent co-monomers; the T_g of the copolymer will be approximately a linear function of composition.[15] On the other hand, if the result of the copolymerization is a blocky copolymer, multiple T_g's may result — one for each block. In this study, the high molecular weight copolymers of DMB with butadiene, styrene and DPE as co-monomers, were analysed by DSC in order to obtain their T_g and T_m (if present) and to check the impact of composition on thermal properties.

3.4.1. Thermal analysis of high molecular weight DMB-Bd statistical copolymers

According to the calculated reactivity ratios, see *Section 3.1.2.2.* and *Section 3.1.2.3.*, the expected sequence of the DMB-Bd copolymers produced in this study is a blocky arrangement (r_{Bd} two orders of magnitude higher than r_{DMB} in benzene and *n*-heptane— see *Table 3.8* and *Table 3.10*). Hence, two T_g corresponding to the two “blocks” of PDMB and polybutadiene were expected. According to previous experiments, see *Chapter 2*, the T_g of the PDMB “block” is expected to be around 10-12 °C depending on the microstructure. On the other hand, the polybutadiene “block”, having a high 1,4 content was expected to show a T_g around -90 °C.[16] Moreover, if the resulting copolymers have a block-like sequence, it was expected that the PDMB "block" may retain its inherent crystallinity, see *Chapter 2*. Therefore, the presence of a T_m at approximately 90-115 °C was anticipated.

The DSC analysis was carried out at three heating/cooling rates of 100, 200 and 300 °C/min, high enough to ensure clear transitions and over a temperature range of between -150 and 250 °C. Two typical examples of the obtained thermograms for DMB-butadiene copolymers are shown in *Figure 3.22* and *Figure 3.23* respectively. In each thermogram two glass (step) transitions can be seen, one at approximately -80 °C (polybutadiene "block") and a second at between 0 and 25 °C (PDMB "block"). Additionally, in the same DSC thermograms weak peaks, which may correspond to a melting transition T_m, are observed at approximately 100-106 °C (for copolymers synthesized in benzene) and 115-122 °C (for copolymers synthesized in *n*-heptane). As the T_m values are consistent with the values observed for the higher molar mass linear PDMB (with M_{target} of 100 kg mol^{-1}) i.e. 90-106 °C in benzene and 114-115 °C in *n*-heptane, see *Chapter 2*, this would seem to suggest that the PDMB "block" does indeed retains its inherent crystallinity. However, it is noteworthy to mention that the melting peak of the copolymers synthesized in benzene is rather weak (*Figure 3.22*) so whilst there may be some residual crystallinity, the degree of crystallinity is probably not high. Thus, the previous data (see the reported r_{DMB} and r_{Bd} in *Table 3.8* and *Table 3.10*) suggesting a blocky arrangement of monomers within the polymeric chain is reinforced.

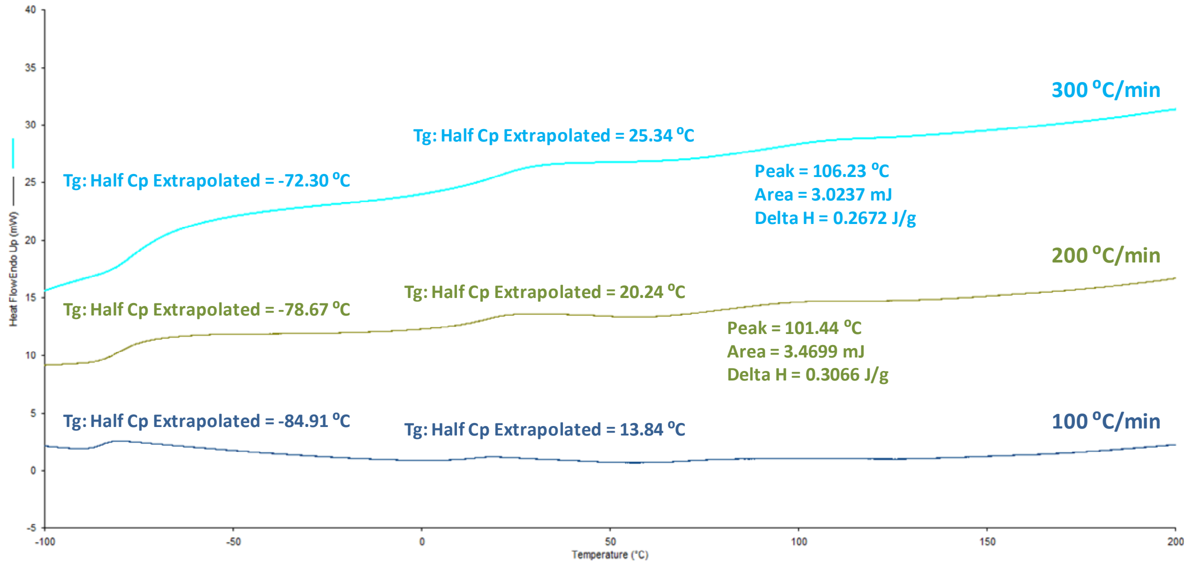


Figure 3.22: *DSC thermogram obtained for experiment 3.10 (poly(DMB-s-Bd)-50/50 synthesized in benzene), showing the T_g and T_m observed upon heating at 100 (dark blue line), 200 (green line) and 300 °C/min (light blue line).*

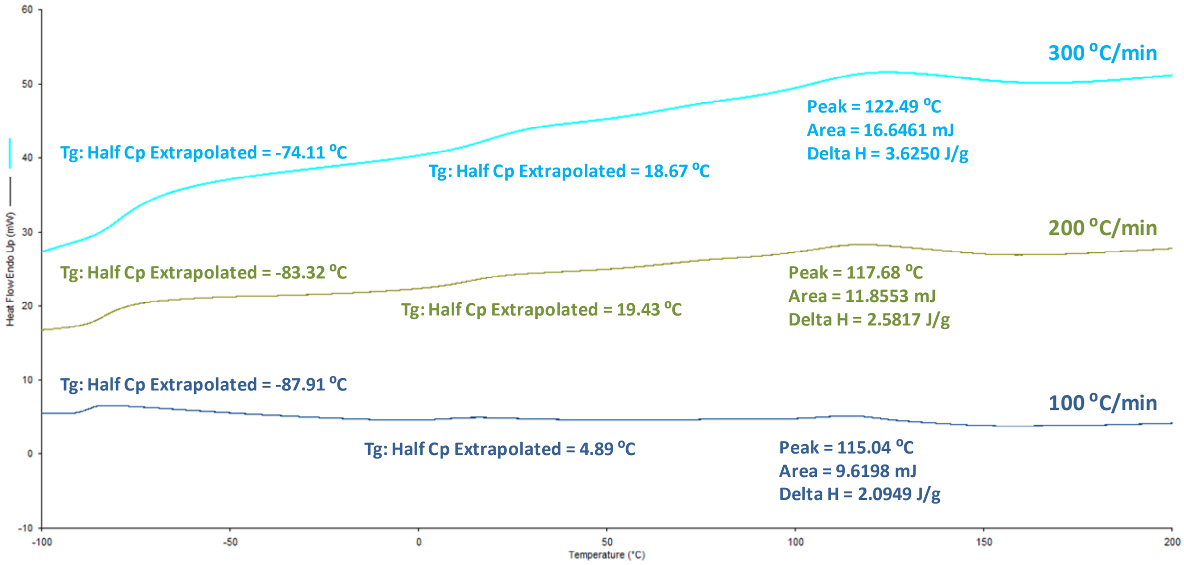


Figure 3.23: *DSC thermogram obtained for experiment 3.15 (poly(DMB-s-Bd)-53/47 synthesized in n-heptane), showing the T_g and T_m observed upon heating at 100 (dark blue line), 200 (green line) and 300 °C/min (light blue line).*

The results for all five DMB-Bd copolymers synthesized in benzene are reported in *Table 3.27* and for those synthesized in *n*-heptane, *Table 3.28*. The values for T_g and T_m obtained at a heating rate of 300 °C/min were reported as the high heating rate ensured clearer transitions.

Table 3.27: *DSC analysis of the resulting high molar mass (M_{target} = 100 kg mol^{-1}) DMB-Bd statistical copolymers synthesized in benzene at 300 °C/min.*

Experiment	m_1/m_2	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH (J/g)
3.8	62/38	-72.3	22.4	105.5	0.50
3.9	56/44	-74.7	21.8	107.1	0.21
3.10	50/50	-72.3	25.3	106.2	0.27
3.11	33/67	-75.4	18.6	108.5	0.02
3.12	19/81	-73.5	18.8	106.1	0.15

As can be seen in *Table 3.27*, for all compositions the resulting copolymers showed two glass transitions: $T_{g,\ Bd}$ between -72.3 and -75.4 °C and $T_{g,\ DMB}$ ranging from 18.6 to 25.3 °C. As explained in *Chapter 2*, at higher heating rates the T_g shifts to higher values due to thermal lag, which explains the deviation of $T_{g,\ Bd}$ of the polybutadiene “block” from the reported value (-90 °C).[5] In case of PDMB “block”, the T_g agrees with the values previously reported for PDMB synthesized in benzene (12.4-21.2 °C), see *Chapter 2*. When the copolymers with different compositions are compared, the

$T_{g,\ DMB}$ seems to decrease with an increasing fraction of butadiene units (from 22.4 °C at m_1/m_2 = 62/38 to 18.8 °C at m_1/m_2 = 19/81). This is possibly due to the presence of some butadiene units in the PDMB block. One would expect that as the butadiene content increases, the DMB "block" may contain a higher proportion of butadiene units, which would push down the $T_{g,\ DMB}$. However, the calculation of T_g is also subject to human errors (e.g. establishing the limits of the transition) and the differences between the $T_{g,\ DMB}$ at different copolymer compositions are rather small (ΔT_g less than 4 °C) and perhaps not significant. Comparing the enthalpy of melting (ΔH) for $T_{m\ DMB}$, which is proportional to the degree of crystallinity, one would expect that the value would decreased as the mole fraction of DMB decreased in the copolymer. This seems to be the case with experiments 3.8 (0.50 J/g), 3.10 (0.27 J/g) and 3.12 (0.15 J/g). However, experiment 3.9 (0.21 J/g) and especially experiment 3.11 (0.02 J/g) are out of the expected trend. As mentioned in *Chapter 2*, the T_m observed in PDMB are weak and broad compared to T_m observed in typical semi-crystalline polymers such as PE or PET. Therefore, the calculation of ΔH will be inevitably challenging and subject to errors related to the signal to noise ratio. Additionally, crystallinity and hence, ΔH are also dependant on the thermal history, which might also be responsible for the unexpected values of experiments 3.9 and 3.11. As a qualitative conclusion we can conclude that the PDMB "blocks" retain a degree of inherent crystallinity, but the degree of crystallinity is low.

Table 3.28: *DSC analysis of the resulting high molar mass (M_{target} = 100 kg mol^{-1}) DMB-Bd statistical copolymers synthesized in n-heptane at 300 °C/min.*

Experiment	m_1/m_2	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH (J/g)
3.13	68/32	-78.1	16.7	114.0	8.12
3.14	61/39	-80.8	11.4	110.0	2.17
3.15	53/47	-74.1	18.7	122.5	3.62
3.16	23/77	-78.4	11.9	122.7	2.28
3.17	20/80	-77.8	—[a]	128.4	1.41

a) Transition not clear enough for an accurate calculation.

The copolymers synthesized in *n*-heptane (*Table 3.28*) show rather similar results. However, a few differences can be distinguished. Firstly, $T_{g,\ DMB}$ was found at a lower temperature (4.1-19.4 °C) than the PDMB "block" of the copolymers synthesized in benzene (10.9-25.3 °C). This is a consequence of the higher vinyl content of the copolymers synthesized in benzene (10-14%) compared to the copolymers synthesized in *n*-heptane (3-5%). No apparent change was observed for the polybutadiene "block" as the change of solvent from benzene to *n*-heptane does not affect significantly the vinyl content of the butadiene units. Additionally, it was observed that at low m_1/m_2 (copolymers richer in butadiene) $T_{g,\,DMB}$ appeared less clear and in the case of experiments 3.16 (at 100 °C/min) and 3.17 $T_{g,\,DMB}$ was not observed. In terms of crystallinity, the T_m values are consistent with the T_m obtained for homoPDMB synthesized in *n*-heptane (114-115 °C). A comparison of the T_m of the copolymers prepared in benzene (10-14% 1,2 units) and *n*-heptane (3-4% 1,2 units), reveals that the peaks of the latter appear at higher temperatures (106-108 °C in benzene versus 110-128 °C in *n*-heptane) which is in agreement with Chiang's reported observation that T_m shifts to higher values with the increasing vinyl content of PDMB.[17] The ΔH of the copolymers synthesized in *n*-heptane seems to follow the expected trend mentioned previously (lower degree of crystallinity at lower m_1/m_2) with the only exception being experiment 3.14 (2.17 J/g), which might be the consequence of errors establishing the peak limits or thermal history. Comparing the ΔH values of the samples made in benzene and *n*-heptane, it can be seen that ΔH are significantly higher (one order of magnitude) in PDMB-Bd copolymers synthesized in *n*-heptane (1.41-8.12 J/g) than in the equivalents synthesized in benzene (0.02-0.50 J/g). Therefore, the crystallinity of the PDMB "block" in the copolymers synthesized in benzene (10-14% 1,2 units) is lower than in the resulting copolymers in *n*-heptane (3-4% 1,2 units). This is in agreement with the expectations as a higher vinyl (1,2) content will disrupt the crystallinity, see *Chapter 2*.

3.4.2. Thermal analysis of high molecular weight DMB-Sty statistical copolymers

The DMB-Sty copolymers which, according to the results reported in *Section 3.2.2.2.*and *Section 3.2.2.3.*, have a statistical monomer sequence, were also analysed by DSC. The analysis was carried out as above using three (high) heating rates (100, 200 and 300 °C/min) in order to ensure transitions are clear enough to be observed. In this case, the temperature range was between -50 and 250 °C as it was not expected to see any transition below 0 °C. The reactivity ratios of these copolymers (r_{DMB} = 0.18, r_{Sty} = 0.25 in benzene and r_{DMB} = 0.03, r_{Sty} = 0.02 in *n*-heptane) would suggest that a statistical, almost random and therefore rather uniform distribution of monomer units exists and as such only a single T_g was expected. This T_g was expected to be intermediate between the T_g of PDMB (8-16 °C) and the T_g of PS (*ca.* 100 °C). For comparison, a theoretical T_g for the copolymers, based on their composition and the T_g of the homopolymers, was calculated using the Fox equation (*Equation 3.36*) (see *Table 3.29* and *Table 3.30*).

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{(1-x_1)}{T_{g,2}} \qquad \textbf{Equation 3.36}$$

T_g ≡ predicted glass transition temperature of the copolymer (in K)

$T_{g,1}$ ≡ *glass transition temperature of the homopolymer of monomer 1 (in K)*

$T_{g,2}$ ≡ *glass transition temperature of the homopolymer of monomer 2 (in K)*

x_1 ≡ *weight fraction of monomer 1*

DSC thermograms of typical examples of DMB-Sty statistical copolymers, one prepared in benzene and the other *n*-heptane, can be seen in *Figure 3.24* and *Figure 3.25* respectively. Both examples show just one T_g at approximately 60-70 °C, intermediate between T_g of PDMB and PS. This observation reinforces the earlier hypothesis of the statistical nature of the copolymerization of DMB and styrene in non-polar solvents leading to a nearly random sequence of the co-monomers.

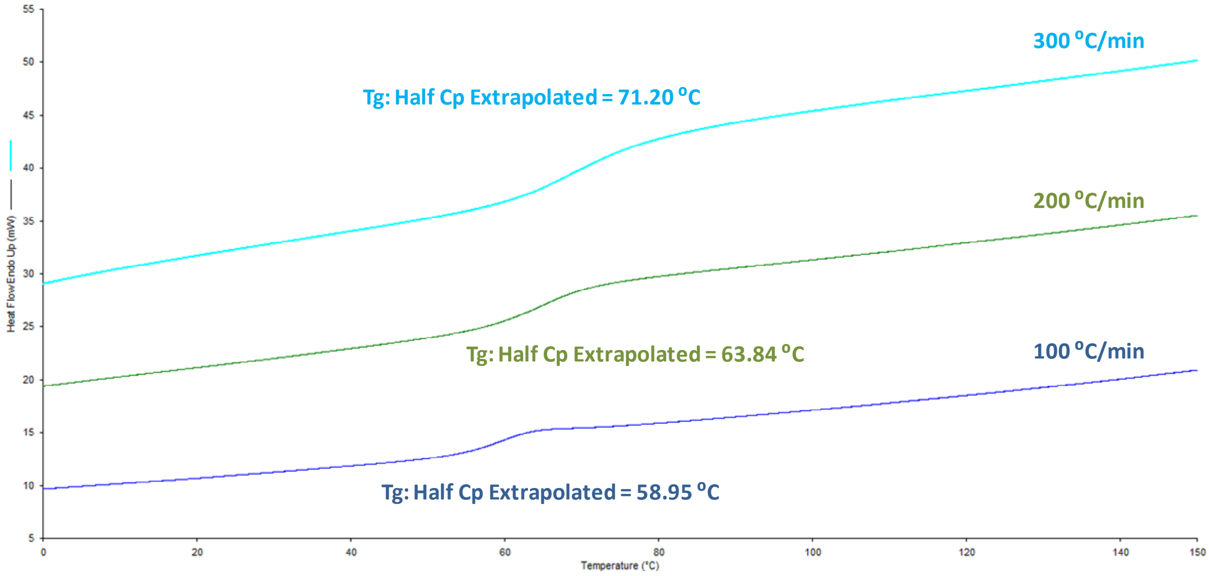


Figure 3.24: *DSC thermogram obtained for experiment 3.27 (poly(DMB-s-Bd)-48/52 synthesized in benzene), showing the T_g observed upon heating at 100 (dark blue line), 200 (green line) and 300 °C/min (light blue line).*

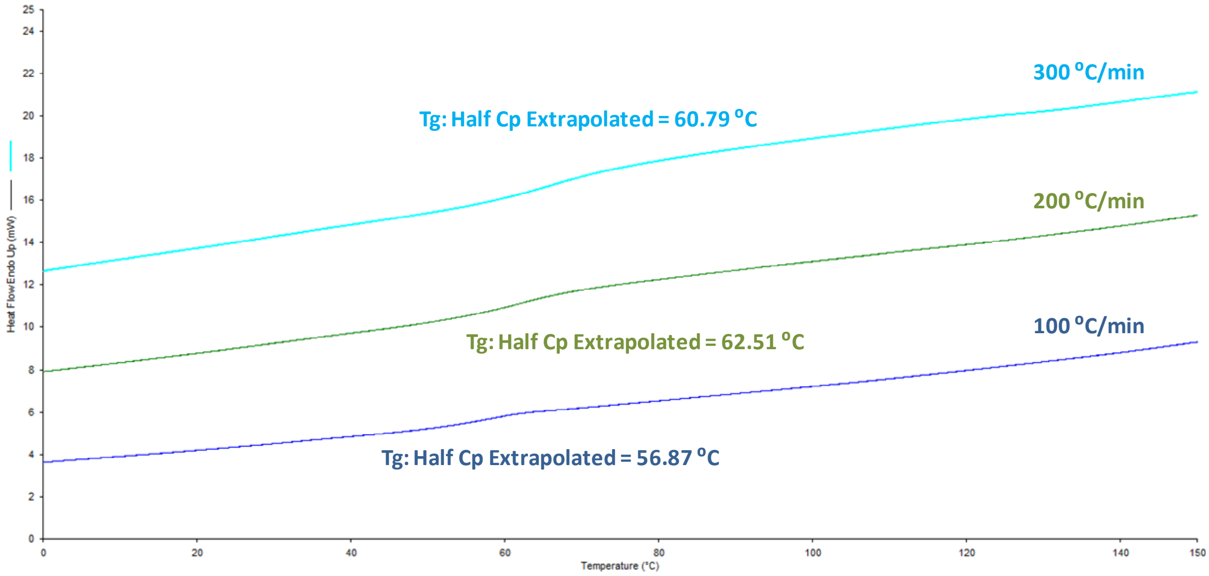


Figure 3.25: *DSC thermogram obtained for experiment 3.32 (poly(DMB-s-Bd)-51/49 synthesized in n-heptane), showing the T_g observed upon heating at 100 (dark blue line), 200 (green line) and 300 °C/min (light blue line).*

Experimental and predicted (calculated by the Fox equation) values of T_g for copolymers synthesized in benzene and *n*-heptane are reported in *Table 3.29* and *Table 3.30* respectively. In this case, T_g at 100 °C/min were reported as transitions were clear enough for calculation and the error due to high heating rate will be lower.

In *Table 3.29* it can be seen that the experimental T_g values are in reasonable agreement with the predicted values when one considers, as explained previously, that the use of higher heating rates results in less accurate data (higher values) due to the thermal lag. Thus, the discrepancy is, at least in part, a consequence of the high heating rates used for ensuring clear transitions.

Table 3.29: *DSC analysis of the resulting high molar mass (M_{target} = 100 kg mol^{-1}) DMB-Sty statistical copolymers synthesized in benzene at 100 °C/min.*

Experiment	**m_1/m_2**	**T_g (°C)**	**Predicted T_g (°C)^a**
3.25	66/34	50.5	41.6
3.26	61/39	60.1	46.0
3.27	48/52	58.9	57.4
3.28	51/49	57.6	54.7
3.29	26/74	87.0	76.8

a) Values predicted by Fox equation.

No melting transition (T_m) was observed which agrees with the expectations considering that styrene and DMB monomer units are randomly distributed, which will disrupt the inherent crystallinity of PDMB.

The higher molar mass DMB-Sty copolymers (M_{target} of 100 kg mol^{-1}) synthesized in *n*-heptane (*Table 3.30*) show a similar trend to that observed for the samples prepared in benzene. The reactivity ratios are very similar in both solvents, which will lead to similar monomer sequences and significant changes in the thermal properties were not expected. The experimental values of T_g are in reasonable agreement with the predicted values and any discrepancies are probably a consequence of the high heating rates and any slight inaccuracy in the calculation of composition. Moreover, as expected the T_g shifted to higher values with the increasing content in styrene units (47.5 °C at m_1/m_2 = 70/30 versus 82.7 °C at m_1/m_2 = 28/72). Again, no peak corresponding to T_m was observed which agrees with the proposed nearly random comonomer sequence.

Table 3.30: *DSC analysis of the resulting high molar mass (M_{target} = 100 kg mol^{-1}) DMB-Sty statistical copolymers synthesized in n-heptane at 100 °C/min.*

Experiment	**m_1/m_2**	**T_g (°C)**	**Predicted T_g (°C)^a**
3.30	70/30	47.5	34.9
3.31	56/44	55.2	47.6
3.32	51/49	56.9	52.2
3.33	40/60	69.5	62.5
3.34	28/72	82.7	73.4

a) Values predicted by Fox equation.

The results for both set of copolymers suggest that the copolymerization of DMB and styrene results in statistical copolymers (in the absence of polar randomizers) whose single T_g could be easily modulated as a function of feed composition, for a specific application.

3.4.3. Thermal analysis of high molecular weight DMB-DPE statistical copolymers

Finally, the DMB-DPE copolymers were also analysed by DSC in order to obtain their T_g. The analysis was carried out as before: namely using three high heating rates of 100, 200 and 300 °C/min (ensuring clear transitions) and the temperature range was between 0 and 250 °C as it was not expected to see any transition below 0 °C. According to the calculated reactivity ratios for the copolymerization of DMB and DPE in benzene (r_{DPE} = 0 and r_{DMB} of 0.33-0.64 depending on the feed ratio), a statistical/alternating copolymer is predicted. Therefore, a single T_g between the T_g of PDMB and a theoretical T_g (229 °C, see below) for PDPE (DPE cannot homopolymerize) was expected. A typical DSC thermogram for a DMB-DPE statistical copolymer is shown in *Figure 3.26* showing a single transition at 103-110 °C, depending on the heating rate, confirming the statistical arrangement of DMB and DPE units along the copolymer chain.

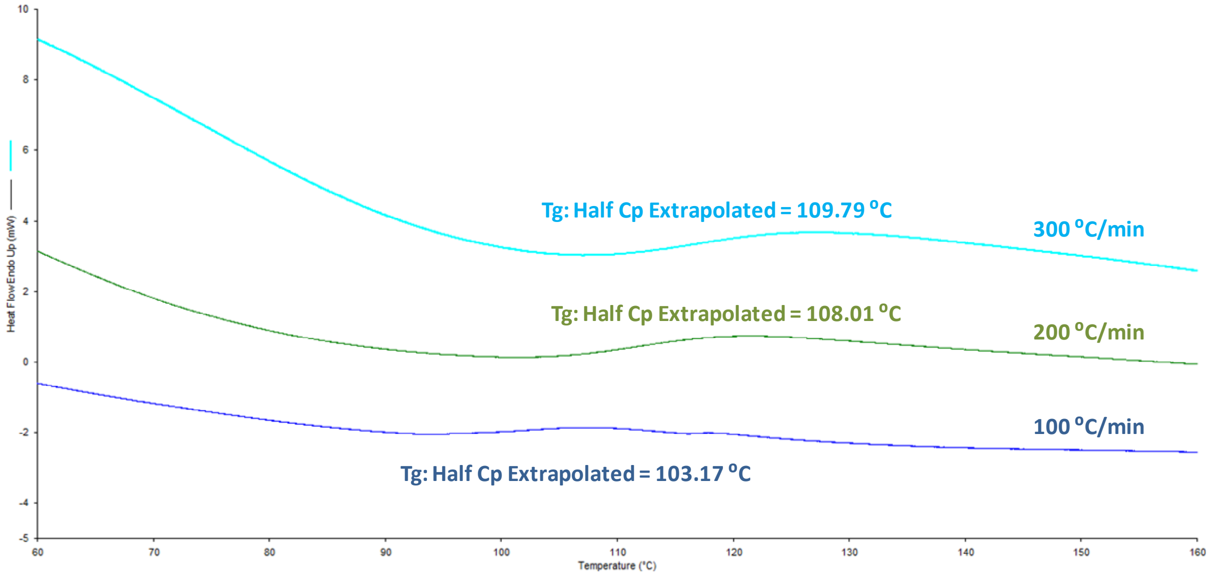


Figure 3.26: *DSC thermogram obtained for experiment 3.35 (poly(DMB-s-DPE)-58/42 synthesized in benzene), showing the T_g observed upon heating at 100 (dark blue line), 200 (green line) and 300 °C/min (light blue line).*

The T_g values for each copolymer were predicted according to the copolymer composition using the Fox equation, *Equation 3.36*, and compared with the experimental T_g. The T_g for PDMB used in the equation was 10.2 °C (corresponding to PDMB synthesized in *n*-heptane) — PDMB synthesized in *n*-heptane showed a vinyl content of 3%, which is very similar to the calculated vinyl content of the DMB-DPE copolymers. The T_g for DPE homopolymer, which cannot be made in practice, was estimated by taking into account previous thermal analysis carried out by Hutchings *et al*. for Bd-DPE copolymers. According to Hutchings, an alternating Bd-DPE copolymer containing a 49 mol-% of DPE showed a T_g of 117 °C.[10] This data was put in Fox equation and a theoretical T_g of 229 °C for PDPE was calculated. Predicted and experimental T_g values at different heating rates for the resulting DMB-DPE copolymers are reported in *Table 3.31*.

As it can be seen in *Table 3.31*, that the experimental T_g values, with the exception of experiment 3.41, are lower than the theoretically predicted value, whereas in previous systems, a high heating rate has always resulted in the experimental value being higher than the predicted value. Thus these discrepancies cannot be ascribed to the high heating rates. This observation may lend some weight to the hypothesis made in *Section 3.3.2.2.*, which suggested that the mole fraction of DPE in the copolymers was overestimated due to the presence of solvent peaks (benzene and chloroform) in the ^{1}H-NMR spectrum. If the mole fraction of DPE in the copolymer is overestimated, then the predicted T_g will also be over-predicted. A further possible source of inaccuracy is the potential presence of unreacted DPE. It is clear that in many cases unreacted DPE monomer remained at the end of the reaction. Any residual monomer would inevitably act as a plasticiser, and lower the glass transition temperature of any contaminated polymer. Only one T_g was observed for each DMB-DPE copolymer which confirms the statistical/alternating arrangements of the polymer sequences for the three compositions. As observed previously, the higher the heating rate, the higher the T_g is. Moreover as expected and predicted by the Fox equation, the higher the content of DPE within the polymer, the higher the T_g. As in case of the DMB-styrene copolymers, the random/close to alternating sequence of the resulting DMB-DPE copolymers will disrupt the inherent crystallinity of PDMB. Therefore, the absence of T_m in the obtained thermograms for DMB-DPE copolymers agrees with the expectations.

Table 3.31: *DSC analysis of the resulting high molar mass (M_{target} = 100 kg mol^{-1}) DMB-DPE statistical copolymers synthesized in benzene at 100 °C/min.*

Experiment	m_1/m_2	T_g (°C)	Predicted T_g (°C)^a
3.37	70/30	70.8	86.1
3.39	58/42	103.2	113.7
3.41	51/49	137.9	129.1

a) Values predicted by Fox equation.

3.5. Summary

The synthesis of copolymers of DMB and butadiene of approximately 10 kg mol^{-1} has been successfully carried out in two non-polar solvents, benzene (ε = 2.27) and *n*-hexane (ε = 1.89). Compositional analysis of the resulting copolymers (from ^{1}H-NMR spectra) showed a compositional drift and a preference for the addition of butadiene in both solvents. However, quantitative conclusions could not be made due the relatively high conversion of the intermediate samples (> 10%) making them unsuitable for the calculation of reactivity ratios. The resulting copolymers were soluble in THF and toluene although the copolymer prepared in *n*-hexane, with a high 1,4 DMB content showed limited solubility in *n*-hexane. This would suggest a blocky structure with a DMB block retaining some of it’s inherent crystallinity.

Copolymers of DMB and butadiene of approximately 100 kg mol^{-1} were subsequently synthesized in benzene and *n*-heptane and samples collected at lower reaction times in order to obtain the reactivity ratios. The calculation of reactivity ratios was enabled due to the low conversion of the intermediate samples (< 10%) and were calculated by Fineman-Ross and Inverted Fineman-Ross linearization and Kelen-Tudos model to give values of $-0.24 < r_{DMB} < -0.07$ and $25.78 < r_{Bd} < 29.98$ in benzene and $-0.05 < r_{DMB} < 0.18$ and $23.38 < r_{Bd} < 28.53$. The reactivity ratios confirmed that the statistical copolymerization of DMB and butadiene results in a blocky sequence. Although the negative values for r_{DMB} are not possible, these values are very close to 0 and could be positive and still very close to 0 within error.

A blocky sequence of DMB-Bd copolymers was also supported by DSC analysis in which the thermograms showed two distinct glass transitions at approximately -80 °C, corresponding to the polybutadiene “block” and 15 °C, corresponding to the PDMB “block”. Additionally, a weak melting transition at approximately 100-110 °C was observed, arising from some residual crystallinity in the PDMB “block”. The crystallinity of the PDMB “block” was significantly higher in the copolymers synthesized in *n*-heptane as a consequence of the higher content of 1,4 units (96-97%) than the copolymers synthesized in benzene (86-90%).

Compositional analysis of the low molar mass copolymers of DMB and styrene (with M_{target} of 10 kg mol^{-1}), revealed a slight preference for the addition of styrene over the addition of DMB. In contrast to the copolymerization of styrene with butadiene, DMB and styrene seemed to copolymerize in a more random manner. In benzene, the presence of styrene as a co-monomer resulted in a decrease in the vinyl content of DMB (8-10% versus 16% in PDMB) — possibly due to steric hindrance exerted by the bulky phenyl ring of styrene, making 1,2-DMB addition less favoured. However, this effect was not observed for the copolymers prepared in *n*-heptane, where PDMB already has a very low 1,2 content and further decreases in the copolymer were not expected.

Copolymers of DMB and styrene, with a molar mass of approximately 100 kg mol^{-1}, were synthesized in benzene and *n*-heptane to allow the collection of samples at low conversion for calculating reactivity ratio. The calculation of reactivity ratios by Fineman-Ross and Inverted Fineman-Ross linearization and Kelen-Tudos method gave as a result $0.14 < r_{DMB} < 0.27$ and $0.21 < r_{Sty} < 0.38$ in benzene and $0.02 < r_{DMB} < 0.27$ and $0.02 < r_{Sty} < 0.34$ in *n*-heptane. The reactivity ratios confirmed that both, DMB and styrene show a preference for the cross-propagation ($r << 1$) in benzene and *n*-heptane. Thus, the statistical copolymerization of styrene and DMB leads to a high degree of copolymerization and a more random (as opposed to blocky) sequence with a slight preference for the incorporation of styrene ($r_{DMB} < r_{Sty}$).

DSC analysis of the high molecular weight DMB-Sty copolymers showed a single T_g at temperatures intermediate between the T_g of PDMB (10-21 °C) and the T_g of PS (100 °C) reinforcing the conclusion about co-monomer sequence based on the reactivity ratio data. No melting transition was observed since the random sequence distribution will inhibit any crystallinity.

A DMB-DPE copolymer with a feed ratio of 50/50 and a molar mass of approximately 14 kg mol^{-1} was successfully synthesized in benzene and compositional (^{1}H-NMR) analysis suggested a statistical/(nearly) alternating sequence. This contrasts dramatically with the copolymerization of butadiene and DPE, which leads exclusively to a homopolymer of polybutadiene. The reactivity ratios were calculated using an iterative method derived from the Mayo-Lewis equation. The calculated values for the DMB-DPE pair were r_{DMB} = 0.54 (preference for cross-propagation), assuming that r_{DPE} = 0 (DPE cannot homopolymerize). The presence of DPE as a co-monomer caused the vinyl content of DMB to be reduced from 16% for a homopolymer of PDMB (synthesized in benzene) to 3% in the DMB-DPE copolymer, due to the high steric hindrance introduced by the two bulky phenyl side-groups of DPE making the addition of 1,2 DMB very unfavourable.

Finally with the goal of obtaining more information about the copolymer sequence and reactivity ratios, high molar mass DMB-DPE copolymers were synthesized in benzene at different feed ratios (75/25, 50/50 and 25/75). It was observed that DMB-DPE copolymer composition is highly dependent upon the feed ratio, obtaining an almost alternating sequence when DPE is fed in excess ($m_1/m_2 \approx 50/50$ at $[M_1]/[M_2] = 25/75$). The final copolymer of experiment 3.40 showed a composition ratio m_1/m_2 of 49/51. The apparent (slight) molar excess of DPE (not possible as DPE cannot homopolymerize) might be the consequence of errors associated to the calculation from the ^{1}H-NMR spectra, which showed traces of benzene and chloroform solvents. This would result in a slight overestimation of the mole fraction of DPE. The calculated reactivity ratios were in the range of 0.33-0.64. The discrepancies between the reactivity ratios probably arise from the mole fraction of unreacted DPE ($[M_2]$)], which is a key parameter in the calculation of reactivity ratios. The unreacted DPE removed from the reaction in the sampling could not be taken into account, which will inevitably introduce errors.

DSC analysis of the higher molar mas DMB-DPE copolymers (M_{target} = 100 kg mol^{-1}) reinforced the conclusions about monomer sequence distributions and a single T_g was observed at intermediate temperatures between the T_g of PDMB (10-21 °C) and the T_g of a perfectly alternating DMB-DPE copolymer (133 °C, calculated by Fox equation). The experimental T_g values appeared to be generally lower than the predicted value, whereas in previous systems a T_g higher than the predicted value resulted, which reinforces the hypothesis of the overestimation of the DPE mole fraction in the copolymer.

Once again, DMB proved to behave in a dramatically different way to the more commonly used butadiene and isoprene, solely on the basis of one additional methyl group. The copolymerization of DMB with styrene led to statistical/nearly alternating copolymers in both benzene and *n*-heptane, which is in remarkable contrast with the copolymerizations of butadiene-styrene and isoprene-styrene where blocky sequences are obtained in non-polar solvents (benzene and alkanes).[5] Additionally, the copolymerization of DMB-DPE resulted the formation of nearly alternating copolymers while in case of butadiene, the copolymerization with DPE leads to a homopolymer of polybutadiene.

3.6. References

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Chapter 4

Synthesis of Randomly Branched Poly(dimethylbutadiene) via Anionic Chain Transfer Polymerization

Chapter 4: Synthesis of Randomly Branched Poly(dimethylbutadiene) via Anionic Chain Transfer Polymerization

It is commonly known that branched polymers show different physical and mechanical properties compared to their linear counterparts. One interesting property of branched polymers is their significantly different rheology properties (both in the melt and solution) in comparison with linear analogues of the same molecular weight. The controlled inclusion of long branches on a linear backbone reduces polymer hydrodynamic volume in solution — the shape of branched polymers changes to a more compact structure. On the other hand, long-chain branching enhances chain entanglement in the melt, which is a parameter that depends on various parameters such as degree of branching or MW.[1-3] According to Dodds and Hutchings the properties of a polymer melt are affected by the presence of branching.[4] Generally, branched polymers show enhanced melt strength compared to the linear counterparts. However, melt viscosity is also dependant on the shear rate: at low shear rates branched polymers have a higher melt viscosity due to the enhanced chain entanglement, while at high shear rates branched polymers have lower melt viscosity.[3, 4] The degree of branching is an important variable in branched polymers as it affects the intrinsic and melt viscosities (as mentioned above) and the solubility of the resulting polymer. Branched polymers with a very high degree of branching (i.e. hyperbranched and dendrimers) show lower intrinsic and melt viscosities as well as higher solubility in different media than equivalent polymers with lower degree of branching (star-like polymers or long-chain branched polymers for example). The length (i.e. molar mass) of the branches also play an important role in the properties of the resulting polymers. For example, short-chain branches will disrupt the crystallinity of the resulting polymer, even at low degrees of branching, as they will limit effective chain packing. However, a long-chain branched polymer may retain a certain degree of crystallinity (if the linear counterpart had this property) when the degree of branching is low enough to allow packing – e.g. low density polyethylene.[1, 2] As a consequence of this different rheological behaviour promoted by the presence of branching points, branched polymers show enhanced processability.[1, 3-7] Furthermore, branched polymers show exceptional mechanical properties (e.g. initial modulus, compressive moduli or tensile strength) when compared to their linear counterparts.[8, 9]

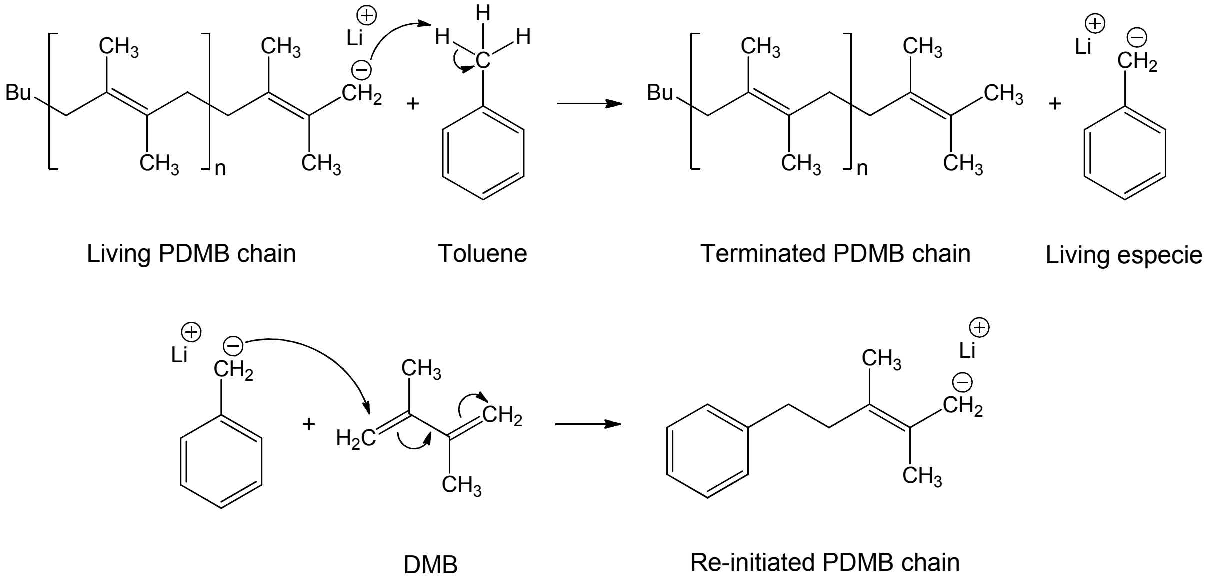
Due to their unique properties, branched polymers have found their way into new fields but also replaced the linear counterparts in some applications where linear polymers cannot fulfil the requirements. One common industrial example is the use of low density polyethylene (LDPE) for the production of carrier bags.[10] As it was explained in *Chapter 1*, polymers can be classified according to their architecture as linear, branched or crosslinked (network). The line separating branched and crosslinked polymers is sometimes very thin. The key distinction between the two types is the degree of connectivity. Branched polymers are discrete molecules, which are soluble and above either T_g or T_m, can be processed as viscous liquids. In crosslinked polymers all the chains are connected either via covalent bonds (crosslinks) or chain entanglement, so they have a molar mass which tends to infinity. As such they are insoluble (although they may swell in a good solvent) and cannot be processed. Crosslinked polymers swollen in a solvent are referred to as gels. Generally the copolymerization of any monomer with a crosslinker as co-monomer can lead to gelation.[11]

Currently, the synthesis of branched polymers via the copolymerization of a difunctional, crosslinking monomer whilst avoiding gelation (excess of crosslinking) is a challenge. In this chapter the synthesis of randomly branched copolymers of DMB and divinylbenzene (DVB) is explored where DVB acts as branching agent. Particular care will be given to develop reaction conditions such that DVB leads to branching but not to gelation.

4.1. Branched copolymers by Strathclyde route

In an attempt to synthesise randomly branched DMB via copolymerization with a difunctional monomer (branching agent), a modified version of the so called “Strathclyde route” was investigated. This process was first developed by Sherrington and co-workers in 2000 and used a radical polymerization mechanism. This route consists of a one-step copolymerization in the presence of a difunctional co-monomer to introduce branch points, and a chain transfer agent to inhibit gelation. In their proof of concept study, Sherrington's group polymerized methyl methacrylate (MMA) with but-2-en-1,4-diacrylate (BDA) as branching agent and 1-dodecanethiol (DDT) as the chain transfer agent.[12]

The addition of the chain transfer agent in the process is a crucial element of the Strathclyde route. Chain transfer reactions involve the premature termination of some active growing chains. These active species transfer their radical (or electric charge in case of ionic polymerization) to a molecule of solvent or monomer, thereby generating a new active species that is capable of initiating other chains to continue the polymerization process. Although chains are terminated, there is no overall loss of activity. For every chain deactivated, a new chain is created. If the transfer is to a solvent molecule, the reaction is called chain transfer to solvent (*Scheme 4.1*), and if it is to a molecule of monomer instead, it is referred to as chain transfer to monomer. As a consequence, polymers with lower molecular weights than the target and high Đ values are obtained. During the synthesis of branched polymers via the Strathclyde approach, both crosslinking and chain transfer process take place simultaneously during the polymerization and balancing the contribution of each is important.



Scheme 4.1: *Example of chain transfer reaction from PDMB to toluene.*

This synthetic strategy was the inspiration for the work carried out in this chapter. Professor Sherrington's method for the synthesis of branched polymers via free-radical polymerization, was adapted for the synthesis of randomly branched polymers of DMB via anionic chain transfer polymerization. In this case, divinylbenzene (DVB), which was selected because of its ready availability and low cost, was used as branching agent, toluene acted as both solvent and chain transfer agent and both, sodium and potassium *tert*-butoxide were used as chain transfer promoter (*Figure 4.1*).

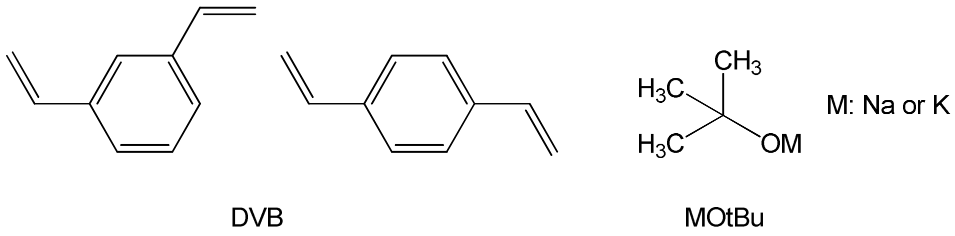


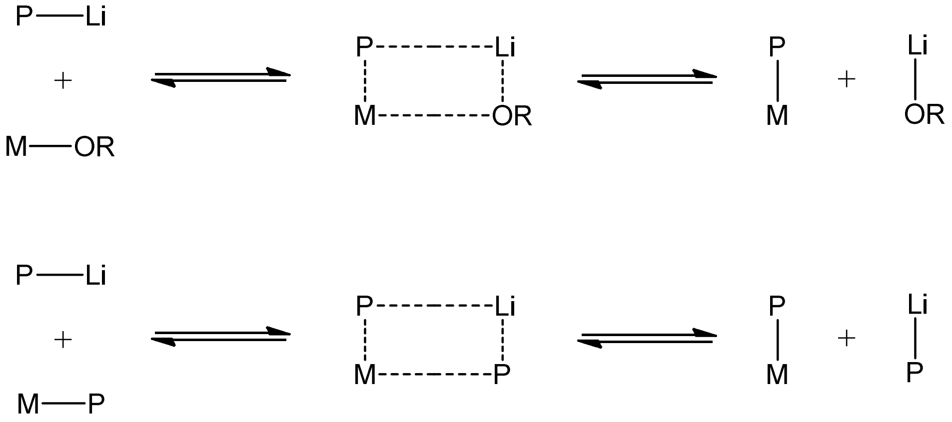
Figure 4.1: *Chemical structures of divinylbenzene (meta- and para- isomers) used as branching agent and sodium/potassium tert-butoxide used as chain transfer promoter.*

Different ratios of DVB/BuLi and butoxide/BuLi were investigated in order to balance crosslinking and chain transfer effects during the polymerization. A high ratio of DVB to initiator will lead initially to chain branching but if the ratio of DVB to initiator is too high, DVB can, and will, lead to gelation. On the other hand, if the butoxide to initiator ratio is too high, undesirable low molecular weight polymers with extremely high Đ values will result.

Theoretically if the ratios of DVB/BuLi and butoxide/BuLi are optimised such that the two effects (branching and chain transfer) are balanced, the synthesis of randomly branched copolymers will be possible.

4.2. The impact of chain transfer on the anionic polymerization of DMB

The anionic polymerization of butadiene and isoprene in toluene, in the presence of Lewis bases such as Group I metal butoxides or TMEDA, is known to undergo chain transfer to solvent.[13] However, to the best of our knowledge, no previous data about chain transfer reactions during the anionic polymerization of DMB have been reported and given the fact that DMB behaves very differently to butadiene and isoprene in many ways, as described in the previous chapters, it would be wrong to simply assume that DMB would undergo chain transfer to solvent under the same conditions. Therefore, before attempting the synthesis of the branched copolymers of DMB, it was decided to establish whether the selected *tert*-butoxide promoted chain transfer reactions to toluene during the anionic polymerization of DMB. Chain transfer reactions of living polybutadiene to toluene (*Scheme 4.1*) can occur even in the absence of butoxide. However, the rate of transfer is very low in the absence of butoxide. The initiation of dienes with a mixture of alkyl lithium and metal alkoxide compounds leads to the formation of new polymer-metal (P—M) species according to the equilibria shown in *Scheme 4.2*.



Scheme 4.2: *Illustration showing the dynamic equilibrium produced in the anionic polymerization of dienes initiated by a mixture of alkyl lithium and metal alkoxides compounds. For the sake of simplicity polymer-lithium growing centres, polymer-metal growing centres and metal alkoxydes are represented by P—Li, P—M and M—OR respectively.*[14]

As mentioned in *Chapter 2*, the polymer-lithium (P—Li) active species tend to aggregate in non-polar solvents and to dissociate in polar media. The presence of dissociated growing species (more reactive) has an impact on both, microstructure (higher 1,2 microstructure contents) and polymerization rate (higher rates). The P—M propagating centres behave in a different way and have tendency to be more dissociated than the P—Li species. Therefore, the presence of metal alkoxides, even when present in small amounts comparable to the concentration of initiator, can increase significantly the concentration of dissociated (more reactive) propagating centres and hence, increase the rate of transfer, polymerization rate and the vinyl content of the resulting polymers.[13, 14]

Two experiments were carried out under the same experimental conditions as described in *Chapter 2* for the synthesis of linear PDMB; i.e. 10% solution concentration of monomer in toluene or cyclohexane as solvents, *sec*-BuLi as initiator and a reaction temperature of 40 °C. The only difference to the previous reactions was the presence of KOtBu for promoting chain transfer reactions during polymerization. The KOtBu/BuLi ratio is expected to be a key parameter as it can increase or decrease the rate of the chain transfer reactions significantly, when this ratio is higher or lower as mentioned above. The ratio of KOtBu/BuLi was kept low (approximately 0.20) as the chain transfer promoter is also known to increase significantly the propagation rate of the polymerization of butadiene, due to the presence of dissociated growing chains (see *Scheme 4.2*) and hence, the reaction temperature could rise dramatically (exothermic reaction) making the process unsafe.[14] Toluene was selected as it is susceptible to chain transfer reactions, as shown in *Scheme 4.1*. In order to check if the mixture of KOtBu and BuLi (very basic) was also able to deprotonate the monomer leading to chain transfer to monomer, an analogous reaction was carried out in cyclohexane, which is a solvent that would not be expected to be susceptible to chain transfer. Thus, if in the experiment in cyclohexane, the $M_n << M_{target}$ and the Đ value is higher than 1.10, this would suggest that chain transfer to monomer may also be occurring during the polymerization. Otherwise, only chain transfer to solvent will take place.

The SEC data for the resulting polymers was obtained as explained previously in *Chapter 2* (triple detection, *dn*/*dc* = 0.130 mL/g of polyisoprene) for the DMB homopolymers. Therefore, the molar mass will be subjected to the same error. The results were compared with experiment 2.1 (polymerization in toluene in the absence of KOtBu) in order to confirm the effect of KOtBu on the molar mass of the resulting PDMB— see *Table 4.1*.

Table 4.1: *Molecular weight data obtained by SEC of the resulting polymers synthesized by anionic polymerization of DMB in the presence and in the absence of KOtBu. Initiator: sec-BuLi,* M_{target} *= 10 kg* mol^{-1}, *T = 40 °C.*

Experiment	Solvent (ε)	KOtBu/BuLi	M_n (g mol^{-1})	Đ	% yield
2.1	Toluene (2.38)	0.00	13300	1.04	92
4.1	Toluene (2.38)	0.21	1600	1.51	69
4.2	Cyclohexane (2.02)	0.21	15100	1.05	99

As can be seen in *Table 4.1*, experiment 4.1 gave a polymer with a M_n (1.6 kg mol^{-1}) which is significantly lower than the M_{target} (10 kg mol^{-1}) and a Đ value (1.51) which is higher than the expected value for a typical anionic polymerization (Đ > 1.10). It is also noteworthy that the polymer from experiment 4.1 was recovered in a low yield — 69%. This is probably due to the lowest MW chains being lost during precipitation (low MW chains might be soluble in methanol). Additionally, low molar mass PDMB is a viscous liquid, which is difficult to handle, so part of the resulting polymer might be lost during work up. In the case of experiment 4.2, it is observed that the polymerization in cyclohexane (no chain transfer to solvent expected) in the presence of KOtBu (KOtBu/BuLi = 0.21) gave a polymer with M_n (15 kg mol^{-1}) slightly higher than M_{target} (10 kg mol^{-1}) and a Đ value of 1.05.

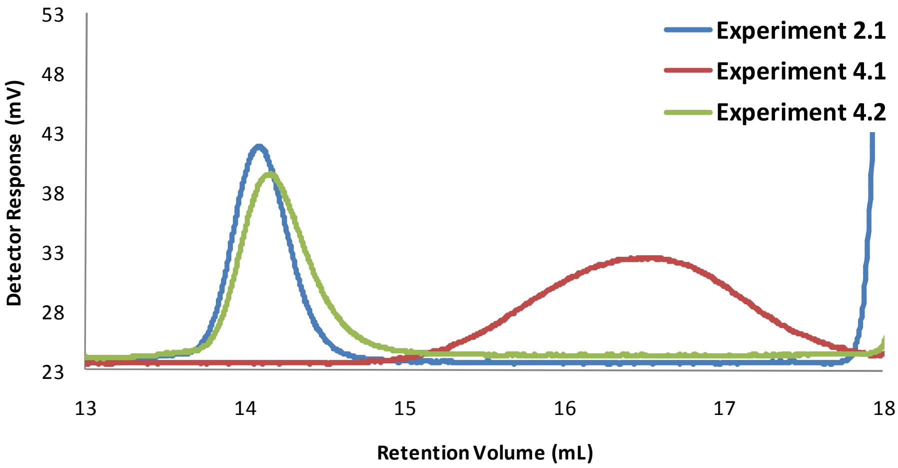


Figure 4.2: *Comparison between SEC chromatograms of experiments 2.1 (blue line), 4.1 (red line) and 4.2 (green line).*

The results of experiments 4.1 (KOtBu/BuLi = 0.21 in toluene) and 4.2 (KOtBu/BuLi = 0.21 in cyclohexane) were also compared with the results obtained previously in experiment 2.1, carried out in toluene but in the absence of any butoxide, a situation that was not expected to lead to any chain transfer. The SEC results are reported in *Table 4.1* and chromatograms in *Figure 4.2*. The chromatogram for experiment 4.1, (red line in *Figure 4.2*) is significantly broader and has a much lower MW distribution (higher retention volume) than the chromatogram for experiments 2.1 (blue line) and 4.2 (green line) in *Figure 4.2*. This confirms that in the presence of KOtBu, chain transfer reactions occur readily during the anionic polymerization of DMB in toluene. On the other hand, experiment 4.2 yielded a polymer with a narrow MW distribution confirmed that cyclohexane is not a solvent susceptible to produce chain transfer to solvent, and also confirming that no chain transfer to monomer takes place under the established conditions. Therefore, only chain transfer to solvent is expected to take place during the polymerization of DMB. Regarding the rate of polymerization, experiment 4.1 (KOtBu/BuLi = 0.21) reached full conversion after 16 h, in contrast with experiment 2.1 (KOtBu/BuLi = 0.00) where 100% conversion was only reached after approximately 48 h. This comparison suggests that the rate of the anionic polymerization of DMB is enhanced by the presence of KOtBu which agrees with expectations in line the discussion above.

Hence, it can be concluded that in common with butadiene and isoprene, the anionic polymerization of DMB in toluene in the presence of KOtBu ($OtBu^-$ anion is a Lewis base) undergoes chain transfer to solvent.

The resulting polymers of experiments 4.1 and 4.2 were also analysed by ^{1}H-NMR in order to ascertain the impact of butoxide on the polymer microstructure. The microstructures were calculated in the same way as described in *Chapter 2,* for the linear polyDMB. Results are reported in *Table 4.2*. Both, experiments 4.1 and 4.2, were compared with the results obtained previously for the polymerizations of DMB in the absence of KOtBu (experiments 2.1 and 2.3).

Table 4.2: *Molecular characteristics of DMB homopolymers synthesized in toluene and cyclohexane in the presence and in the absence of KOtBu. Initiator: sec-BuLi, M_{target} = 10 kg mol^{-1}, T = 40 °C.*

Experiment	Solvent (ε)	KOtBu/BuLi	% 1,2	% *cis*-1,4	% *trans*-1,4
2.1	Toluene (2.38)	0.00	21	24	55
4.1	Toluene (2.38)	0.21	53	23	24
2.3	Cyclohexane (2.02)	0.00	4	30	66
4.2	Cyclohexane (2.02)	0.21	67	20	14

In *Table 4.2* it can be seen that the microstructure of PDMB is clearly affected by the presence of KOtBu. When the experiments in toluene (2.1 and 4.1) are compared, experiment 2.1 (in the absence of KOtBu) showed a vinyl content of 21% while in experiment 4.1 (KOtBu/BuLi = 0.21) the content in 1,2 units increased to 53%. When the reactions carried out in cyclohexane are considered, a similar effect was observed. As explained in *Chapter 2*, experiment 2.3 (in the absence of KOtBu) showed a very low content in 1,2 units of 4%. On the other hand, the presence of KOtBu (KOtBu/BuLi ratio of 0.21) the vinyl content increased from 4% to 67%. This effect is clearly a consequence of the increased dissociation of the growing chains due to the presence of KOtBu (Lewis base) which favours the addition of 1,2 microstructures in polydienes.[13] In *Table 4.2* it can also be seen that the increase in the vinyl content is accompanied by a significant reduction in the content in *trans*-1,4 content. In experiments 2.1 and 4.1 it is observed that the content of *cis*-1,4 units remains unaltered while the vinyl content raises from 21% to 53% and the content in *trans*-1,4 units drops from 55% to 24% when the KOtBu/BuLi ratio passes from 0.00 to 0.21. A similar effect is observed in the experiments in cyclohexane: 1,2 content rises from 4% to 67% while *trans*-1,4 content drops from 66% to 14% and the *cis*-1,4 content only drops from 30% to 20%. This is probably a consequence of the dissociated active centres (promoted by the presence of butoxide) having a preference for the addition of more sterically hindranced microstructures 1,2 and *cis*-1,4 over the addition of *trans*-1,4 microstructures of PDMB.

4.3. DMB-DVB copolymers

Having confirmed that KOtBu successfully promotes chain transfer from polyDMB to solvent, the synthesis of branched copolymers of DMB via anionic chain transfer polymerization was attempted. In order to obtain branched copolymers, divinylbenzene (DVB) was added to the polymerization as a branching agent.

The source of DVB monomer used in this project is a mixture of meta- and para-DVB, meta- and para-ethylvinylbenzene (EVB) and meta- and para-diethylbenzene (DEB), as shown in *Figure 4.3*. Among them, only DVB (both meta- and para- isomers) is able to promote branching as it is the only difunctional monomer.

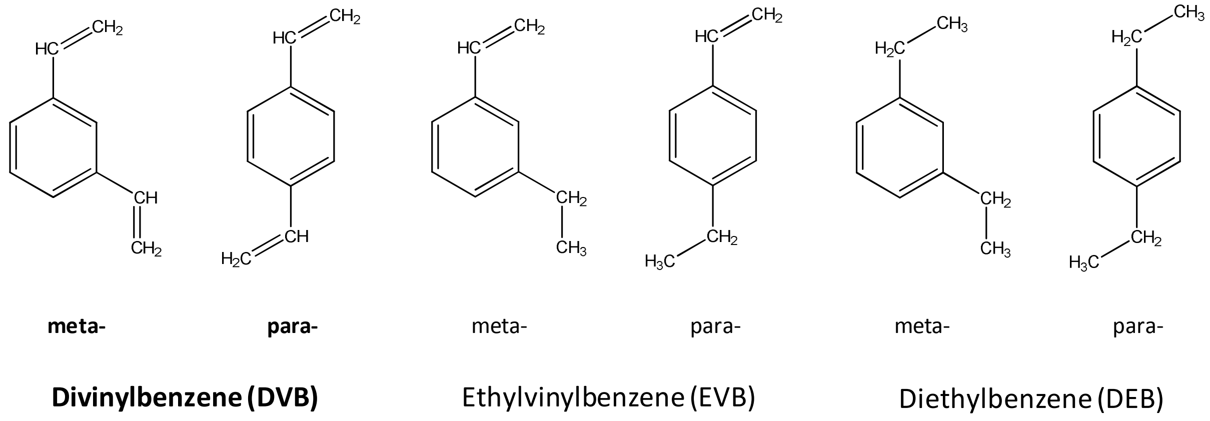


Figure 4.3: *Chemicals present in the DVB monomer stock.*

The composition of the crude DVB was determined by ^{1}H-NMR to be 61.72% meta-DVB, 28.01% para-DVB, 15.95% EVB (meta- and para- isomers) and 0.02% DEB (meta- and para- isomers). However, as the boiling point of EVB and DEB are lower than the boiling point of DVB, the DVB content of the distilled monomer was always lower than the crude material. The ^{1}H-NMR analysis of the distillate revealed a composition of 55.79% meta-DVB, 26.45% para-DVB, 16.53% EVB (meta- and para- isomers) and 1.24% DEB (meta- and para- isomers). As the DVB was prepared freshly for each the polymerizations, it was assumed that the composition of the distillate was the same for all the experiments.

As mentioned above, the synthesis of branched copolymers by the described methodology has associated challenges that may not be obvious at first sight:

Firstly, if the concentration of DVB (crosslinker/branching agent) is too high gelation will occur and any analysis of the resulting polymer (by SEC or ^{1}H-NMR) is not possible as a consequence of the total insolubility of the gel in any solvent (it only can swell in appropriate solvents). On the other hand, at very low concentrations of DVB, the ^{1}H-NMR signals corresponding to DVB might be too low to be distinguished from the baseline and hence, the calculation of the fraction of DVB in the copolymer might be impossible or very inaccurate. Other authors have overcome this issue by using crosslinkers which are more easily detectable (e.g. EGDA, EGDMA, etc.).[12, 15] However, these crosslinkers are methacrylates and acrylates which are unsuitable for copolymerization with butadiene by anionic polymerization due to inability of the (meth)acrylate propagating species to react with butadiene and the possibility of side-reactions involving the carbonyl group of the (meth)acrylate monomer.

As mentioned previously, the presence of KOtBu, is also expected to have an impact on the kinetics of the copolymerization. For example, KOtBu will increase the rate of polymerization and the rate of chain transfer due to the increase in the amount of dissociated active centres promoted by metal alkoxides. Additionally, it is expected that the addition of KOtBu will have a significant impact on the reactivity ratios of copolymerization of DMB and DVB. However, as a consequence of the difficulties in the analysis of the copolymer composition stated above, the calculation of reactivity ratios, which are very useful in order to understand the statistical copolymerization of two co-monomers, for the pair DMB-DVB might not be possible due to the very low content of DVB. The resulting copolymers would show different branching structures depending on the reactivity ratios, as shown in *Figure 4.4*.

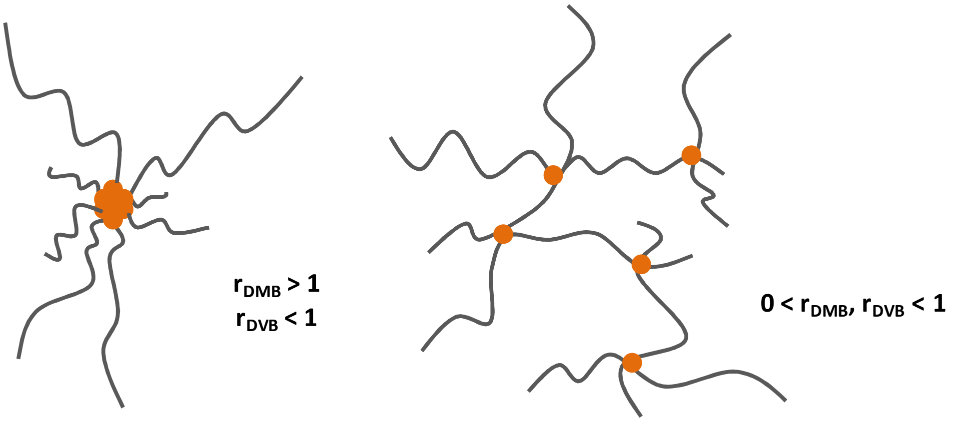


Figure 4.4: *Schematic diagram to illustrate probable architectures for poly(DMB-DVB) synthesized by anionic polymerization depending on the reactivity ratios: (left) star-like copolymer if* $r_{DMB} > 1$ *and* $r_{DVB} < 1$ *and (right) randomly branched copolymer if* $0 < r_{DMB}, r_{DVB} < 1$*. DMB (grey lines) and DVB (orange balls).*

As shown in *Figure 4.4*, if DMB has a strong preference to homopolymerize ($r_{DMB} > 1$) and DVB has a tendency to copolymerize ($r_{DVB} < 1$), then the very small fraction of DVB would likely be excluded from the reaction until most of the DMB has reacted. Hence most of the DVB would be near the chain ends and lead to star coupling. On the other hand, if the co-monomers show a preference for cross-propagation (r between 0 and 1) the result will be DMB units (fed in clear majority over DVB) reacting with other DMB units creating PDMB linear segments that eventually will react with a DVB unit, which will introduce a branching point, coupling with another PDMB linear segment. Thus, a randomly branched copolymer will be obtained. Considering that DVB is a styrene derivative, even it will not behave in exactly the same way as styrene, it is not unreasonable to assume that DVB might behave in a similar fashion to styrene. The results obtained in *Chapter 3* revealed that the anionic statistical copolymerization of DMB with styrene in both, benzene and *n*-heptane, behaves in a random manner ($r_{DMB} \approx r_{Sty}$ and $r_{DMB}, r_{Sty} < 1$, see *Chapter 3*). Considering these results it would be reasonable to assume that the anionic statistical copolymerization of DMB with DVB will proceed in a random or close to random manner. Additionally, Henderson reported that polar Lewis bases such as TMEDA act as randomizers in the copolymerization of DMB with other dienes and styrene.[16] Therefore, it is expected that the presence of butoxide (polar Lewis base) in the DMB-DVB copolymerization will randomise the sequence of the resulting copolymers ($0 < r_{DMB}$, $r_{Sty} < 1$). Thus it is expected that, under the selected reaction conditions, the resulting polymers will have a randomly branched structure as shown in *Figure 4.4 (right)*.

The gelation point, and even whether gelation occurs at all, in the synthesis of branched polymers via copolymerization with a difunctional co-monomer is dependent on many interrelated parameters such as the crosslinker/initiator and butoxide/initiator ratios and reaction temperature. When the ratio of crosslinker/initiator is high enough to cause gelation, gelation can be inhibited by increasing the extent of chain transfer reactions. This promotion of chain transfer can be achieved by increasing the butoxide/initiator ratio or by increasing the reaction temperature. Nevertheless, it is noteworthy that changing one parameter, e.g. ratio of chain transfer promoter to initiator, may require that other parameters are also adjusted in order to maintain a soluble branched structure and to avoid gelation. Therefore, avoiding gelation implies the optimization of many parameters which makes the synthesis of branched copolymers by the Strathclyde approach a challenging process.

All the challenges stated above were considered for planning the strategy to produce branched DMB-DVB copolymers whilst avoiding gelation.

4.3.1. DMB-DVB copolymers at high ratios of DVB to initiator

First, the synthesis of branched polymers of DMB with DVB as branching agent was attempted using DVB/BuLi ratios in the range of 3.50-5.70. The rest of the parameters were those established in *Section 4.2* i.e. an M_{target} of 10 kg mol^{-1}, toluene as solvent, *sec*-BuLi as initiator, 40 °C and KOtBu as chain promoter in a KOtBu/BuLi ratio of approximately 0.20. The reaction mixture turned to dark orange immediately after initiation as a consequence of the (ambitiously) high ratio of DVB/BuLi, implying that a certain proportion of propagating chain ends were DVB, giving a colour similar to living PS. Data for the resulting polymers are reported in *Table 4.3*. In order to investigate the degree of crosslinking using relatively high ratios of DVB, two initial experiments were carried out in the absence of KOtBu. Experiment 4.3 (DVB/BuLi = 5.70) resulted in a significant increase in the viscosity of the reaction mixture after approximately 1 h which was orange-coloured and increasingly opaque (*Figure 4.5b*). Macrogelation appeared to occur after approximately 3 h, as shown in *Figure 4.5*. In the present work, macrogelation is referred to as gelation that traps all the solvent of the reaction, as shown in *Figure 4.5c*. When the DMB-DVB copolymerization was repeated with a lower DVB/BuLi ratio of 3.93, again in the absence of KOtBu (experiment 4.4), the result was partial gelation after approximately 4 h. It is clear that in the absence of butoxide, no chain transfer is occurring and the system is crosslinking. Thus experiment 4.4 was repeated in the presence of KOtBu (experiments 4.5 and 4.6) in order to study if the addition of butoxide could limit the onset of crosslinking by promoting chain transfer. However, it was observed that the presence of KOtBu did not inhibit the gelation, but accelerated it. At a DVB/BuLi ratio of 3.53 and KOtBu/BuLi of 0.20 (experiment 4.5) gelation was observed after 10 min of reaction. When the concentration of KOtBu was doubled (KOtBu/BuLi = 0.40) (experiment 4.6) the gelation was observed 30 sec after initiation.

Table 4.3: *Results for the anionic copolymerization of DMB and DVB in the absence and in the presence of KOtBu. Initiator: sec-BuLi, solvent: toluene,* M_{target} *= 10 kg mol*$^{-1}$*, T = 40 °C.*

Experiment	[DVB] (mol-%)[a]	DVB/BuLi	KOtBu/BuLi	Result
4.3	5.18	5.70	0.00	Macrogelation
4.4	3.27	3.93	0.00	Partial gelation
4.5	3.06	3.53	0.20	Gelation (10 min)
4.6	3.16	3.62	0.40	Gelation (30 sec)

a) Relative to [DMB].

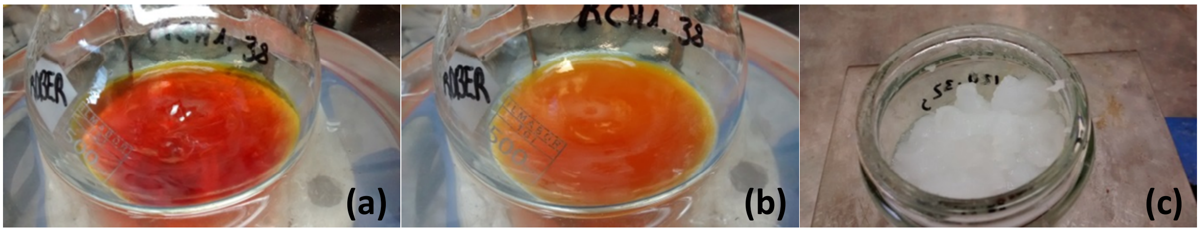


Figure 4.5: *Pictures of experiment 4.3: a) right after initiation, b) 1 h after initiation and c) right after termination without further treatment.*

As a consequence of the insolubility of the resulting gels, further information about molecular weight (SEC analysis) or composition of the copolymers (^{1}H-NMR analysis) was not possible to obtain.

These results suggest that at high DVB/BuLi ratios (*ca.* 3.50-5.70) the crosslinking effect of DVB is far more significant than the chain transfer which is promoted by KOtBu. Thus, the presence of KOtBu cannot inhibit crosslinking and, moreover, as discussed above, the presence of butoxide led to a significantly enhanced rate. Consequently, gelation in experiments 4.5 and 4.6 was observed at much shorter reaction times. It was thus concluded that the synthesis of soluble branched DMB-DVB copolymers at high DVB/BuLi ratios (3.50-5.70) may not be possible unless the contribution of chain transfer is significantly increased. However increasing the ratio of KOtBu to initiator to much higher values could make the reaction dangerously fast. Sherrington and co-workers had predicted that for a controlled radical polymerization (ATRP), in the absence of termination and chain transfer, a ratio of difunctional monomer to initiator of less than 1 should always lead to soluble polymers with a branched architecture whereas when the ratio of difunctional monomer to initiator exceeds 1, the formation of crosslinked gel is almost inevitable.[15] Even though chain transfer was expected to play a role in the reactions described above, it would appear that using a DVB/BuLi ratio far greater than 1 (3.50-5.70), crosslinking is unavoidable.

4.3.2. DMB-DVB copolymers at low ratios of DVB to initiator

It was subsequently decided to reduce drastically the DVB/BuLi ratio to establish conditions where no gelation occurred, and then to increase this DVB/BuLi ratio (if necessary) in small steps, keeping the KOtBu/BuLi ratio at approximately 0.20. A series of reactions were carried out with DVB/BuLi ratios < 1.0 whilst keeping the remainder of the copolymerization parameters were the same as established previously in *Section 4.2.* The resulting copolymers were all soluble and analysed by SEC (*Table 4.4*). Although the resulting samples are DMB-DVB copolymers, we would argue that as a consequence of the very low DVB content (< 1 mol-%), any errors associated with the use of *dn/dc* = 0.130 mL/g (polyisoprene) were expected to be approximately equal to the errors assumed in the SEC analysis of PDMB as discussed in *Chapter 2*.

Table 4.4: *Results for the anionic copolymerization of DMB and DVB in the absence and in the presence of KOtBu. Initiator: sec-BuLi, solvent: toluene, M_{target} = 10 kg mol^{-1}, T = 40 °C.*

Experiment	[DVB] (mol-%)[a]	DVB/BuLi	KOtBu/BuLi	M_n (g mol^{-1})	Đ	Result
4.7	0.27	0.32	0.00	16700	1.57	No observed gelation
4.8	0.26	0.31	0.23	1800	2.59	Soluble polymer
4.9	0.24	0.29	0.19	1300	1.80	Soluble polymer
4.10	0.43	0.52	0.19	2200	2.28	Soluble polymer
4.11[b]	0.74	0.89	0.19	5500	1.43	Soluble polymer
				70900	1.57	

a) Relative to [DMB]; b) Bimodal SEC trace.

Experiment 4.7 was carried out in the absence of KOtBu in order to check the branching effect of DVB at low DVB/BuLi ratio (0.32) and the resulting polymer had an M_n of 16.7 kg mol^{-1}, which was approximately 60% higher than M_{target} (10 kg mol^{-1}). The higher than expected molar mass might be a consequence of a low degree of branching/chain coupling but not enough to lead to crosslinking. The presence of chain coupling is also supported by a Đ value of 1.57, which is much higher than that expected from a simple anionic polymerization in the absence of chain transfer (no butoxide). The SEC trace of experiment 4.7 (*Figure 4.6*) shows a broad peak with some structure: a main peak at a retention volume of 13.85 mL, which corresponds to approximately 30 kg mol^{-1} and a shoulder at 14.50 mL corresponding to approximately 15 kg mol^{-1}.

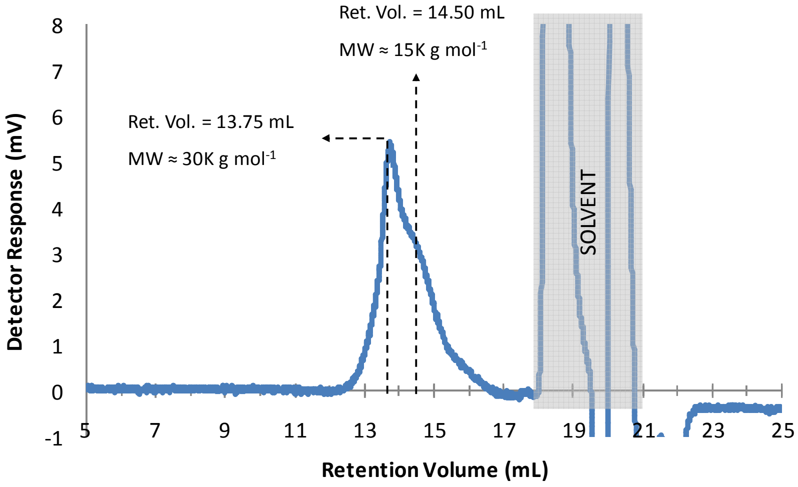


Figure 4.6: *SEC chromatogram of experiment 4.7 (RI).*

A ratio of DVB to initiator of 0.32 implies that there was one molecule of DVB (difunctional co-monomer) per three living chains and when two of the living PDMB chains react with a molecule of DVB they will be coupled together but it is inevitable that other PDMB chains will remain linear and uncoupled. Thus, the shoulder shown in *Figure 4.6* might be reasonably assigned to linear uncoupled PDMB chains with a molecular weight of *ca.* 15 kg mol^{-1}, slightly higher than the M_{target} of 10 kg mol^{-1}, whilst the main peak shown in *Figure 4.6* would correspond to the two PDMB chains linked together via a molecule of DVB with a molecular weight of *ca.* 30 kg mol^{-1} (2 x 15 kg mol^{-1}). Additionally, the SEC trace of experiment 4.7 shows some evidence of a low molecular weight tail which might be the consequence of premature termination of some living chains as a consequence of impurities having leaked into the reaction vessel.

Experiment 4.7 was then repeated (4.8) in the presence of KOtBu (KOtBu/BuLi approximately 0.20). As can be seen in *Table 4.4*, experiments 4.8 (DVB/BuLi = 0.31 and KOtBu/BuLi = 0.23) and 4.9 (DVB/BuLi = 0.26 and KOtBu/BuLi = 0.19) led to copolymers with M_n of 1800 and 1300 g mol^{-1} respectively, significantly lower than M_{target} (10 kg mol^{-1}), and Đ values (1.80-2.59) much higher than that expected from an anionic polymerization. The SEC chromatograms (*Figure 4.7*) for both samples show a long tailing towards the low molecular weight region that in case of experiment 4.9 overlaps the solvent peaks. These results suggest that at those ratios of DVB/BuLi and KOtBu/BuLi, the impact of chain transfer dominates, driving down molar mass, whereas the expected impact of DVB, chain coupling, would be to drive up molar mass.

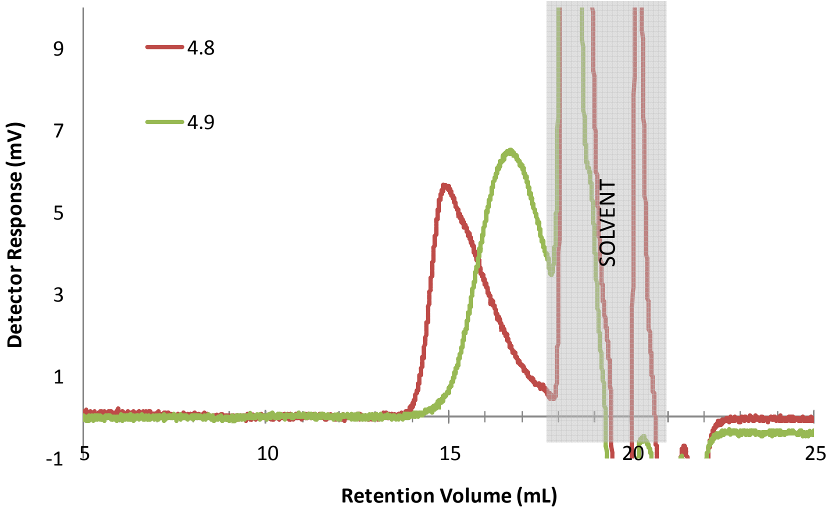


Figure 4.7: *Comparison between SEC chromatograms (RI) of 4.8 (red line) and 4.9 (green line).*

The ratio of DVB to BuLi was then increased in small steps of approximately 0.20 whilst keeping the KOtBu/BuLi ratio unchanged at approximately 0.20, in order to explore the effect of the rising ratio of DVB to initiator on the molar mass of the resulting polymers. At a DVB/BuLi of 0.52 (experiment 4.10) the resulting copolymer was fully soluble with a M_n of 2.2 kg mol^{-1} and a Đ value of 2.28. The M_n of experiment 4.10 is still far lower than M_{target} (10 kg mol^{-1}) which indicates that even at DVB/BuLi of 0.52, chain coupling has much less impact than chain transfer.

In case of experiment 4.11 (DVB/BuLi = 0.89) (*Figure 4.8, green line*) the resulting polymer showed a bimodal SEC trace with main peak at a retention volume of 12.85 mL, corresponding to an M_n of 70900 g mol^{-1}, which is far higher than M_{target} (10000 g mol^{-1}), suggesting a far more significant degree of chain coupling (branching) than in previous experiments (4.7-4.10). The chains formed in the early stages of the reaction possibly have more than one DVB per chain, which leads to a higher degree of branching. A second peak can be observed at a retention volume of 15.00 mL (M_n of 5500 g mol^{-1}) with a Đ value of 1.43. These lower molecular weight chains are probably unbranched and formed during the latter stages of the reaction when all of the DVB has been consumed and only unreacted DMB remains. Thus, the bimodality of the SEC trace might be the consequence of a copolymerization between DMB and DVB which is not completely random and which proceeds with a preference for the addition of DVB ($r_{DVB} > r_{DMB}$).

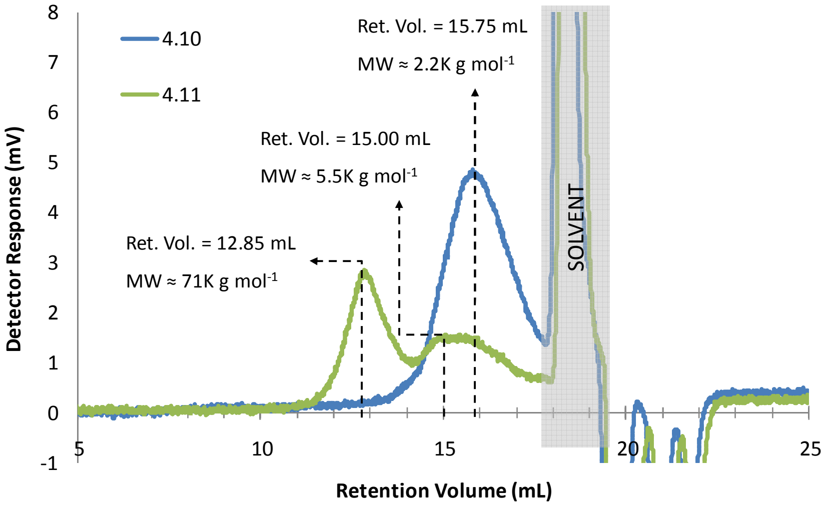


Figure 4.8: *Comparison between SEC chromatograms of experiments 4.10 (blue line), 4.11 (green line).*

During experiment 4.11 the polymer solution appeared to contain small beads floating around the reaction mixture which seemed to be insoluble in the reaction solvent (toluene). However, following the recovery of this sample, these beads of polymer appeared to be fully soluble in THF, in contrast to the gelation observed at high concentrations of DVB (experiments 4.3 to 4.6) where the resulting copolymers were completely insoluble in any solvent. Therefore, since the polymer prepared in experiment 4.11 proved to be fully soluble in THF, it cannot be covalently crosslinked.

Triple detection SEC is able to generate intrinsic viscosity (IV) data as well as molar mass data. Therefore, long-chain branching can be identified qualitatively by the plot of log (IV) vs. log (molecular weight), which is referred to as a Mark-Houwink plot. Compared to a linear counterpart with the same molecular weight, branched polymers show a contraction in the molecular size and hence, the intrinsic viscosity of branched polymers is lower. If the resulting polymer contains a mixture of linear and branched macromolecules, the slope of the plot may vary. Consequently, a deviation from the linear dependency of log (IV) vs. log (MW) would suggest the presence of long-chain branching. The Mark-Houwink plot was obtained for the polymers produced in experiments 4.7 and 4.11 — each of which would appear to have undergone chain branching from the SEC analysis reported above (*Figure 4.9* and *Figure 4.10*).

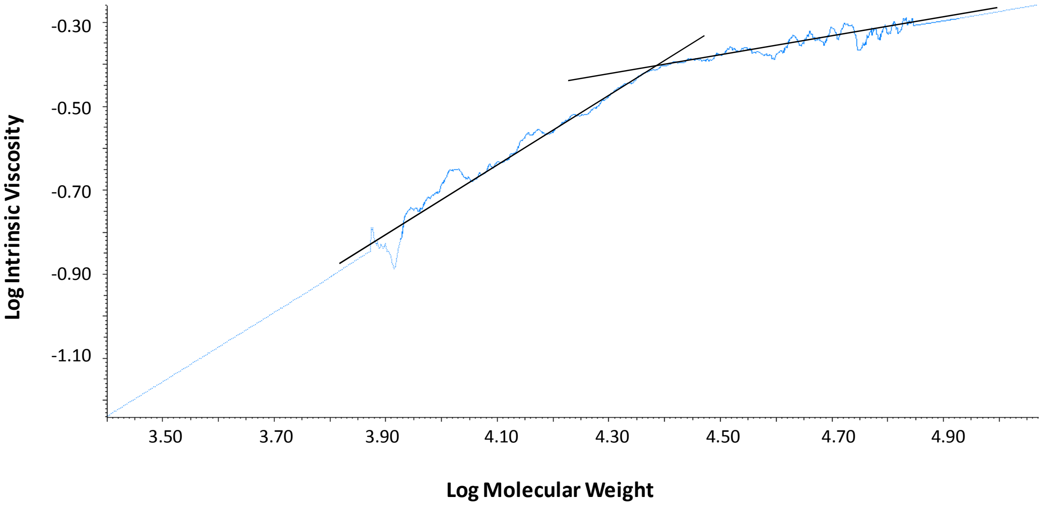


Figure 4.9: *Mark-Houwink plot (log(intrinsic viscosity) vs. log(molecular weight)) of experiment 4.7.*

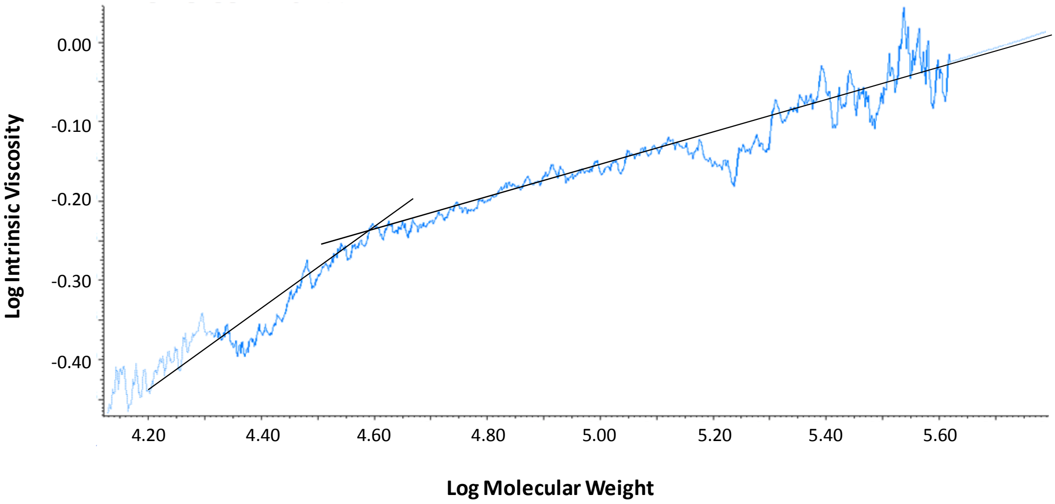


Figure 4.10: *Mark-Houwink plot (log(intrinsic viscosity) vs. log(molecular weight)) of experiment 4.11.*

In case of experiment 4.7 (KOtBu/BuLi = 0.00, DVB/BuLi = 0.32, M_n = 16700 g mol^{-1}) (*Figure 4.9*) a clear deviation from linearity was observed, which suggests a certain degree of long-chain branching. The change in gradient occurs at a log MW value of approximately 4.35, which corresponds to a molar mass of *ca.* 22000 g mol^{-1} which is consistent with the discussion and data in *Figure 4.6* presented above — namely that the peak/shoulder at higher retention volume can be ascribed to linear chains whilst the high molar mass fraction at lower retention volume can be ascribed to branched chains. In *Figure 4.10*, the Mark-Houwink plot for experiment 4.11 (KOtBu/BuLi = 0.19, DVB/BuLi = 0.89, M_{n1} = 5500 g mol^{-1}, M_{n2} = 70900 g mol^{-1}) again shows a deviation from linearity which suggests that the resulting polymer has a certain degree of long-chain branching. This change in the gradient is observed at log MW of approximately 4.5 (MW ≈ 30 kg mol^{-1}) and occurs at a point between the two peaks observed in the SEC trace shown in *Figure 4.8 (green line)*. Thus, in experiment 4.11 the Mark-Houwink plot (*Figure 4.10*) might agree with the explanation above that the high MW peak corresponds to branched polymer and the low MW peak corresponds to linear polymer. It can therefore be concluded that the anionic chain transfer copolymerization of DMB with a DVB to BuLi ratio of around 0.90, in the presence of KOtBu (KOtBu/BuLi ≈ 0.20) results in the formation of soluble branched copolymers with no gelation. However, in order to obtain more wide ranging conclusions and to test the limits of this system, further work should be carried out where the DVB/BuLi ratio is increased up to and beyond 1.00, where gelation is predicted to happen in the absence of chain transfer.[17, 18]

4.4. Influence of butoxide on the microstructure of PDMB

As mentioned in *section 4.2*, the presence of butoxide in the anionic polymerization of dienes promotes dissociation of active centres which in turn tends to result in an increase in the 1,2 microstructure. Therefore, the vinyl content of the polydiene generally increases in the presence of butoxide.[14]

The polymers produced in experiments 4.7 to 4.11 were therefore also analysed by ^{1}H-NMR with the goal of obtaining some information about the impact of butoxide on microstructure. The analysis of microstructure was carried out using ^{1}H-NMR, as described previously for the PDMB homopolymers (*Chapter 2*), using the individual integrals corresponding to the different microstructures (1,2, *cis*- and *trans*-1,4). As mentioned above, due to the very low mole fraction of DVB (< 1 mol-%), the signals corresponding to DVB could not be distinguished in the ^{1}H-NMR spectra and hence, the calculation of the composition of the resulting copolymers was not possible. The microstructure results are reported in *Table 4.5*.

Table 4.5: *Molecular characteristics of DMB-DVB copolymers in the absence and in the presence of KOtBu. Initiator: sec-BuLi, solvent: toluene, M_{target} = 10 kg mol^{-1}, T = 40 °C.*

Experiment	[DVB] (mol-%)[a]	DVB/BuLi	KOtBu/BuLi	% 1,2	% *cis*-1,4	% *trans*-1,4
4.7	0.27	0.32	0.00	18	38	43
4.8	0.26	0.31	0.23	28	23	48
4.9	0.24	0.29	0.19	43	31	26
4.10	0.43	0.52	0.19	43	30	27
4.11	0.74	0.89	0.19	45	30	25

a) Relative to [DMB].

As can be seen from the data reported in *Table 4.5*, the experiment carried out in the absence of KOtBu, experiment 4.7, gave a microstructure comprising of 18% 1,2 (vinyl) which is similar to result for the linear PDMB synthesized in toluene which had a vinyl content of 21% see *Chapter 2*. This observation agrees with the expectations as experiments 2.1 and 4.7 were carried out under the same experimental conditions (M_{target} = 10 kg mol^{-1}, toluene, 40 °C) with the exception of the presence of DVB. As the concentration of DVB is very low, it was not expected to have any impact on the resulting microstructure. However, the presence of KOtBu in experiments 4.8 (KOtBu/BuLi = 0.23) and 4.9 (KOtBu/BuLi = 0.19) changes the resulting microstructure significantly and the DMB vinyl content of the resulting copolymers was 28% and 43% respectively. Considering that the use of a higher ratio of KOtBu should result in a higher vinyl content the result of experiment 4.8 (28% 1,2 microstructure) was considered suspicious. One possible explanation might be that the amount of butoxide added to the reaction vessel was less than planned (KOtBu/BuLi < 0.23). Experiments 4.10 and 4.11 showed a microstructure similar to the microstructure of experiment 4.9 with 43% 1,2 microstructure, which is in good agreement with the expectations as the KOtBu/BuLi ratio is 0.19 in the three cases.

As shown above, the presence of KOtBu in the anionic copolymerization of DMB and DVB led to higher DMB vinyl content (up to 45%). This high vinyl content is not desirable for certain applications. For example, Henderson reported that for PDMB to show stress-induced crystallization, the vinyl content should be less than 20%.[16] Thus, the microstructure of the branched copolymers of DMB and DVB obtained in this chapter are far out of the desired range. With this in mind, the use of alternative Group I metal alkoxides were investigated.

In 1969, Hsieh and Wofford reported that for the anionic polymerization of butadiene in cyclohexane, the resulting microstructure was highly dependent not only on the mole ratio of potassium *tert*-butoxide/BuLi but also nature of the Group I metal *tert*-butoxides (Na, K, Rb and Cs). Moreover, the same authors explored the impact of reaction temperature. Thus at a KOtBu/BuLi ratio of approximately 0.20 (similar to the ratio used in the experiments described above), the resulting polybutadiene showed 35% 1,2 microstructure at 30 °C which decreased to 25% at 50 °C. Additionally, Hsieh and Wofford reported that at 50 °C the use of sodium *tert*-butoxide (NaOtBu) leads to lower polybutadiene vinyl content than KOtBu. Moreover, in the presence of NaOtBu (NaOtBu/BuLi ≈ 0.20), the vinyl content of polybutadiene was reported to be only 15% at 50 °C. However, at 30 °C and the same NaOtBu/BuLi ratio the %1,2 is close to 45%, which is higher than in the presence of KOtBu at 30 °C.[14]

In order to study the effect of both the change from potassium to sodium *tert*-butoxide and the variation of temperature, on the microstructure of PDMB, and with a view to producing branched polyDMB with a lower vinyl content, a new set of experiments was carried out with DMB as the only monomer — in the absence of any DVB. The reaction parameters were the same as previously described in the current chapter i.e. M_{target} of 10 kg mol^{-1}, toluene as solvent and *sec*-BuLi as initiator. Four different temperatures from 30 to 60 °C were tested in the presence of either KOtBu or NaOtBu. As in the previous experiments, the butoxide/BuLi ratio was kept at approximately 0.20 in all cases. The resulting polymers were analysed by ^{1}H-NMR in order to calculate the resulting microstructure. The results are shown in *Table 4.6*.

Table 4.6: *Molecular characteristics of PDMB synthesized by anionic polymerization in the presence of butoxide at different temperatures. Initiator: sec-BuLi, solvent: toluene and* M_{target} *= 10 kg mol*$^{-1}$*.*

Exp.	Butoxide	T (°C)	Butoxide/BuLi	M_n (g mol^{-1})	Đ	% 1,2	% *cis*-1,4	% *trans*-1,4	% yield
4.12	KOtBu	30	0.20	1300	1.62	45	18	37	80
4.13	KOtBu	40	0.20	2100	1.73	54	15	31	88
4.14	KOtBu	50	0.19	1200	1.42	51	19	30	53
4.15	KOtBu	60	0.20	900	1.46	34	30	36	100
4.16	NaOtBu	30	0.20	9400	1.21	73	15	11	100
4.17	NaOtBu	40	0.19	9300	1.28	74	16	10	67
4.18	NaOtBu	50	0.20	7300	1.36	73	18	9	98
4.19	NaOtBu	60	0.20	9200	1.27	60	22	17	100

As it can be seen in *Table 4.6*, the experiments carried out in the presence of KOtBu (experiments 4.12 to 4.15) led to PDMB with a vinyl content ranging from 34% to 54%. The vinyl content of experiment 4.13 (54%) is consistent with the vinyl content calculated previously for experiment 4.1 (53%), which was carried out under the same reaction conditions. The vinyl content of the experiments carried out in the presence of KOtBu seems to decrease with increasing temperature: 54% 1,2 at 40 °C, 51% at 50 °C and 34% at 60 °C (*Figure 4.11*). However, experiment 4.12 carried out at the lowest temperature (30 ^{o}C) does not follow this trend and gave a microstructure of 45% 1,2 units. This might be a consequence of adding an amount of butoxide which was less than planned either as an error in the addition of butoxide or perhaps due to partial hydrolysis of KOtBu, which is a chemical compound that readily hydrolyses yielding butanol. In case of the experiments carried out in the presence of NaOtBu (experiments 4.16 to 4.19) the vinyl content of the resulting PDMB shifts to much higher values (in the range of 60% to 74% 1,2) than the equivalent experiments in the presence of KOtBu (from 34% to 54% 1,2). Therefore, it can be concluded that NaOtBu increases the vinyl content of PDMB more than KOtBu. Moreover, in case of the experiments carried out in the presence of NaOtBu, it is observed that increasing the temperature from 30 to 50 °C has little effect on the microstructure but at 60 °C the %1,2 units drops to 60%. This suggests that variations in temperature play a more significant role in the microstructure of PDMB in the presence of KOtBu than in the presence of NaOtBu. As can be seen in *Table 4.6*, the change of butoxide from KOtBu to NaOtBu proved to be ineffective for obtaining PDMB with a lower vinyl content which is another example where DMB behaves different than butadiene.

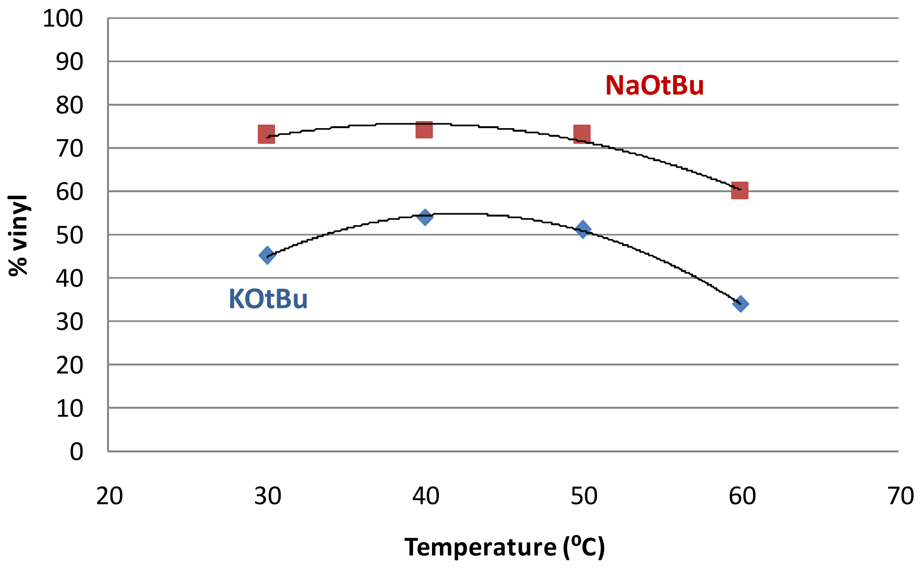


Figure 4.11: *Plot showing the evolution of the vinyl content of PDMB synthesized by anionic polymerization in the presence of butoxide with the reaction temperature.*

Moreover, and perhaps of most significance, the use of NaOtBu resulted in much higher molar masses than expected. Thus PDMB synthesized in the presence of KOtBu (experiments 4.12 to 4.15) had M_n values (900-2100 g mol^{-1}) which were lower than M_{target} (10 kg mol^{-1}) and high Đ values (1.42-1.73), as expected since KOtBu has been shown to be an effective chain transfer promoter. Whereas experiments 4.16 to 4.19 (carried out in the presence of NaOtBu) led to PDMB with M_n values (7300-9400 g mol^{-1}) which were much closer to M_{target} and with lower Đ values (1.21-1.36). It is clear therefore that NaOtBu is a rather ineffective chain transfer promoter for the polymerization of DMB in toluene and is unlikely to be of use in this work.

The results obtained for the anionic polymerization of DMB in the presence of KOtBu and NaOtBu were compared with similar experiments for butadiene described in the literature.[14] A comparison between the synthesis of PDMB carried out at 30 °C (experiments 4.12 and 4.16) and at 50 °C (experiments 4.14 and 4.18) and literature data for the synthesis of polybutadiene at the same temperatures, with butoxide/BuLi ratios of approximately 0.20 in all cases, are shown in *Table 4.7*.

Table 4.7: *Comparison between the vinyl content of PDMB and polybutadiene synthesized by anionic polymerization in the presence of KOtBu and NaOtBu. Butoxide/BuLi ≈ 0.20.*

Polymer	Butoxide	T (°C)	% 1,2	Difference
PDMB	NaOtBu	30	73	0
		50	73	
	KOtBu	30	45	+6
		50	51	
polybutadiene	NaOtBu	30	45	-30
		50	15	
	KOtBu	30	35	-10
		50	25	

As can be seen in *Table 4.7*, in the presence of butoxide, a change in temperature has the opposite effect on the vinyl content of PDMB and polybutadiene. In case of PDMB, in the presence of NaOtBu, the vinyl content remains almost constant when the temperature is raised from 30 °C to 50 °C. However, when the butoxide is changed to KOtBu, the results show that increasing the temperature exerts an increase in the vinyl content. However, as mentioned above, the vinyl content of experiment 4.12 was considered suspiciously low, possibly due to errors in the actual amount of butoxide added. Therefore, between 30 °C and 50 °C, in the presence of KOtBu, the vinyl content of PDMB might remain constant (like in the case of NaOtBu) or might change just slightly. On the other hand, in the case of polybutadiene, an increase in temperature from 30 °C to 50 °C (in the presence of NaOtBu) produces a significant reduction in the vinyl content from 45% to 15% whereas in case of KOtBu, the vinyl content drops from 35% to 25% with increasing temperature. Therefore, once again DMB behaves unexpectedly differently to butadiene when it is polymerized by anionic polymerization, in this case in the presence of butoxides.

4.5. Summary

As is well-known, branched polymers show very different, sometimes advantageous, properties when compared to their linear counterparts. However, the synthesis of branched polymers via the addition of a difunctional comonomer is challenging and may result in crosslinking (gelation). This chapter has focused on the development of synthetic strategies to produce randomly-branched PDMB via anionic chain transfer polymerization, in the presence of low mole fractions (with respect to initiator) of divinylbenzene (DVB), a difunctional monomer. In order to achieve this goal, the so-called Strathclyde route[12] was adapted for the anionic polymerization of DMB. DVB was introduced as a co-monomer in order to promote branching and KOtBu was used to promote chain-transfer to the solvent, toluene, with a view to inhibiting gelation.

In order to confirm the ability of KOtBu to promote chain transfer from DMB to toluene, two experiments were carried out in the presence of KOtBu (KOtBu/BuLi = 0.21); one using toluene and the other cyclohexane — a solvent that is not susceptible to chain transfer. Both experiments were compared with the synthesis of PDMB in toluene in the absence of KOtBu (*Chapter 2*). The experiment in toluene (with butoxide) gave a polymer with a molar mass which is much lower than the M_{target} and a high Đ value — undoubtedly arising due to chain transfer. On the other hand, the experiment in cyclohexane resulted in a polymer with a molar mass which was close to M_{target} and a low dispersity. Therefore, it was concluded that KOtBu promotes chain transfer to solvent during the anionic polymerization of DMB in toluene but does not promote chain transfer to monomer.

The synthesis of branched DMB, using DVB as a branching agent was subsequently attempted in the absence and in the presence of KOtBu to help understand the impact of butoxide/chain transfer on branching/cross-linking. At high ratios of DVB to initiator (3.50-5.70), gelation was observed after 3-4 h of reaction. The presence of KOtBu did not inhibit gelation but accelerated it, with gelation occurring after 10 min (KOtBu/BuLi = 0.20) and after 30 sec when the KOtBu/BuLi ratio was doubled to 0.40. Clearly within that range of DVB/BuLi (3.50-5.70), any chain transfer promoted by butoxide is not enough to overcome the crosslinking effect of DVB and gelation could not be avoided. Although the KOtBu/BuLi could be increased to higher values, to enhance the contribution of chain transfer, it was considered dangerous as the presence of KOtBu also increases the reaction rate.

The mole ratio of DVB to initiator was then reduced drastically to approximately 0.30 and then increased gradually, studying the result after each increase whilst keeping the KOtBu/BuLi ratio constant at approximately 0.20. The polymerization of DMB with a DVB/BuLi ratio of 0.32 in the absence of chain transfer yielded a soluble polymer with M_n equal to 16 kg mol^{-1}, 60% higher than

M_{target} and a Đ value higher than the expected from an anionic polymerization in the absence of chain transfer — suggesting some chain coupling/chain branching. Additionally, the Mark-Houwink plot revealed a change in the gradient at higher molar mass, which is indicative of long-chain branching. It was concluded that the resulting polymer shows some, but only a low degree, of, long-chain branching due to a low DVB/BuLi ratio. When the ratio of DVB/BuLi was raised to between 0.30 and 0.50, KOtBu was shown to promote chain transfer to such an extent that not only was crosslinking inhibited, but the resulting polymers had a molar mass which was far below M_{target}. This suggests under these conditions chain transfer dominates over branching. However, as the DVB/BuLi ratio was increased to 0.90 in the presence of butoxide, a bimodality in the SEC trace was observed with a high molar mass main peak 70900 g mol^{-1}) and a second, lower molar mass peak of 5500 g mol^{-1} — despite the significant increase in the molar mass, gelation was not observed. The Mark-Houwink plot of the resulting polymer showed a clear change in gradient at a log MW value of *ca.* 4.5, corresponding to a molar mass of 30 kg mol^{-1} (between the main and the second peak), suggesting a variation in molecular architecture as a function of molar mass and a certain degree of long chain branching at higher molar mass. With the results described in this chapter it can be concluded that the Strathclyde approach can be successfully adapted to be applied to the synthesis of soluble, branched polyDMB via anionic chain transfer polymerization, using a DVB/BuLi ratio of 0.90 and KOtBu/BuLi ratio of approximately 0.20 at 40 °C. However, the results are preliminary in nature and further work is required to fully explore this system. In particular a wider range of DVB/BuLi ratios should be investigated and of especial interest would be to see if the contribution of chain transfer is sufficient to inhibit gelation when DVB/BuLi ratios of greater than 1.0 are used.

It was also noted that the addition of KOtBu, the chain transfer promoter, caused an increase in the vinyl content of PDMB up to 45%, which is undesirable for some applications and in particular for polymer crystallisation. For this reason, NaOtBu was investigated as an alternative chain transfer promoter, along with the impact of reaction temperature on microstructure. KOtBu proved to be a much more effective chain transfer promoter than NaOtBu whilst the latter also gave PDMB with a higher vinyl content than the equivalent experiments in the presence of KOtBu. The reaction temperature did not seem to play a significant role in influencing the vinyl content of the resulting PDMB when the reaction temperature was between 30 °C and 50 °C, although at 60 °C, the vinyl content decreased somewhat when both KOtBu and NaOtBu were used. These results are (once again) in stark contrast to the results of analogous experiments involving polybutadiene, where a change in temperature from 30 °C to 50 °C in the presence of either chain transfer promoter produces a sharp decrease in the 1,2 content.

It should be noted that the addition of butoxide can have multiple simultaneous impacts on the resulting polymers. Specifically the addition of butoxide can simultaneously promote chain transfer, which can impact on the skeletal structure of the resulting polymer (linear, branched or crosslinked), and promote a higher level of 1,2 vinyl content in the microstructure. How can be assured that branched polymers are actually made and that any changes in physical properties (solubility/gelation) are not due to changes in microstructure. It is true that butoxide increases the proportion of 1,2 vinyl content but it is thought that this is entirely unconnected with any change in solubility or the onset of gelation. The key feature is the presence of divinyl benzene. At high levels of DVB we see crosslinking and gelation, at lower levels of DVB soluble branched/linear polymers are produced. Both the molar mass data and Mark Houwink plots (Figures 4.9 and Figure 4.10) clearly suggest the presence of long chain branching. Moreover, in Chapter 2 (Figure 2.9, page 54) it was seen that solubility actually improves as the 1,2 content increases, so adding butoxide would produce polymers which were more soluble not less.

4.6. References

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Chapter 5

Experimental

Chapter 5: Experimental

5.1. Materials

2,3-dimethyl-1,3-butadiene (DMB) (VWR, 98%), benzene (Aldrich, HPLC grade ≥ 99.9%), cyclohexane (Aldrich, anhydrous, 99.5%), *n*-heptane (Fisher, HPLC grade ≥ 99.9%), *n*-hexane (Fisher, GPR grade), styrene (Aldrich, 99%) and toluene (Fisher, HPLC grade > 99.9%) were dried over calcium hydride, degassed by a series of freeze-pump-thaw cycles and stored under reduced pressure. 1,3-butadiene (Aldrich, +99%) was passed through columns of *Carbosob* (Aldrich) and molecular sieves (Aldrich) to remove any inhibitor and moisture respectively. Diphenylethylene (DPE) (Aldrich, 97%) was degassed by freeze-pump-thaw cycles and purified by dropwise addition of *sec*-butyllithium until a red colour persisted and freshly distilled prior to use. Divinyl benzene (DVB) (Aldrich, technical grade, 80% mixture of isomers) was dried over calcium hydride, degassed by a series of freeze-pump-thaw cycles. The dried and degassed DVB was freshly distilled under reduced pressure into a Young's ampoule that was filled with nitrogen prior injection into the reaction vessel. The composition of the DVB was determined by ^{1}H-NMR (see *section 5.2*). Calcium hydride (Acros Organics, 93%), methanol (Fisher, AR grade), *n*-BuLi (Aldrich, 2.5 M in hexanes), potassium *tert*-butoxide (KOtBu) (Aldrich, 1M in THF), *sec*-BuLi (Aldrich, 1.4 M in cyclohexane), sodium *tert*-butoxide (NaOtBu) (Aldrich, 2M in THF) and 2,6-di-*tert*-butyl-4-methyl phenol (BHT) (Aldrich, 99%) were used as received.

5.2. Measurements

Triple detection size-exclusion chromatography (SEC) was used for the analysis of M_n, M_w and Đ of the prepared polymers, using a *Viscotek* TDA 302 with refractive index (RI), right angle light scattering (RALS) and viscosity detectors and two *PLgel* 5 µL mixed C columns (300 x 75 mm). The eluent used for this analysis was tetrahydrofuran at a low rate of 1.0 mL/min at a temperature of 35 °C. Molecular weights were normally obtained by triple detection SEC. The calibration was carried out with a narrow molecular weight polystyrene standard (*Polymer Laboratories*). A value of 0.130 mL g^{-1}, the *dn/dc* of polyisoprene, was used for the *dn/dc* of the polymers. When the light scattering signal was too weak to allow triple detection analysis, a conventional calibration was used. The conventional calibration was created using the RI detector and a calibration curve constructed using nine reference polystyrene standards (*Polymer Laboratories*, M_p between 580-1112000 g mol^{-1}, Đ ≤ 1.11).

^{1}H-NMR spectra were measured on a *Bruker-400 MHz* spectrometer using $CDCl_3$ as deuterated solvent. Spectra were referenced to the trace of $CHCl_3$ (7.26 ppm) present in $CDCl_3$.

As mentioned previously, the composition of DVB was determined by ^{1}H-NMR according to the peak assignment shown below. The composition of the crude DVB was determined as 61.72% meta-DVB, 28.01% para-DVB, 15.95% EVB (meta- and para- isomers) and 0.02% DEB (meta- and para- isomers) and the distillate 55.79% meta-DVB, 26.45% para-DVB, 16.53% EVB (meta- and para- isomers) and 1.24% DEB (meta- and para- isomers). As the DVB was prepared freshly for each polymerizations, it was assumed that the composition of the distillate was the same for all the experiments.

meta-DVB: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.15 (dd, J = 10.9 Hz, 1Hz, 2H, —CH=C(H)$\mathbf{H}_{cis}$), 5.66(dd, J = 17.6 Hz, 1Hz, 2H, —CH=C(H)$\mathbf{H}_{trans}$), 6.61 (dd, J = 17.6 Hz, 1Hz, 2H, C**H**=CH_2), 6.96-7.34 (m, 4H H_{ar}).

para-DVB: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.14 (dd, J = 10.9 Hz, 1Hz, 2H, —CH=C(H)$\mathbf{H}_{cis}$), 5.64 (dd, J = 17.6 Hz, 1Hz, 2H, —CH=C(H)$\mathbf{H}_{trans}$), 6.59 (dd, J = 17.6 Hz, 1Hz, 2H, C**H**=CH_2), 6.96-7.34 (m, 4H H_{ar}), 7.26 (s, 4H H_{ar}).

meta-EVB and para-EVB: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.14 (t, J = 7.6 Hz, 3H), 2.54 (q, J = 7.6 Hz, 2H), 5.15 (dd, J = 10.9 Hz, 1Hz, 1H, —CH=C(H)$\mathbf{H}_{cis}$), 5.66 (dd, J = 17.6 Hz, 1Hz, 1H, —CH=C(H)$\mathbf{H}_{trans}$), 6.61 (dd, J = 17.6 Hz, 1Hz, 1H, C**H**=CH_2), 6.96-7.34 (m, 4H H_{ar}).

meta-DEB: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.14 (t, 6H, —CH_2—C$\mathbf{H_3}$), 2.54 (q, 4H, —C$\mathbf{H_2}$—CH_3), 6.96-7.34 (m, 4H H_{ar}).

para-DEB: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.14 (t, 6H, —CH_2—C$\mathbf{H_3}$), 2.54 (q, 4H, —C$\mathbf{H_2}$—CH_3), 6.96-7.34 (m, 4H H_{ar}).

Differential Scanning Calorimetry (DSC) analyses were carried out on a *Perkin Elmer DSC 8000* instrument using helium purge gas at 20-50 mL/min. The DSC is controlled by a liquid nitrogen tank enabling the DSC to run from -180 to 300 °C at 0.1 to 300 °C per minute. The analysis software was *Pyris* Version 11.0.2.0468.

5.3. Polymer synthesis

All polymers were synthesized by living anionic polymerizations using standard high vacuum techniques, highly purified (dried and degassed) solvents and monomers and trap to trap distillation. The reaction vessel used for these polymerizations is shown in *Figure 5.1*. Before all the experiments described below were carried out, the reaction vessel was thoroughly cleaned according to the following procedure:

1. The whole reaction vessel (including the side arms) was evacuated under high vacuum for 1 h.

2. The whole reaction vessel was subsequently cleaned with a “living” solution (*c in Figure 5.1*) of oligomeric styrenyl anions in benzene.

3. The whole reaction vessel was evacuated under high vacuum overnight.

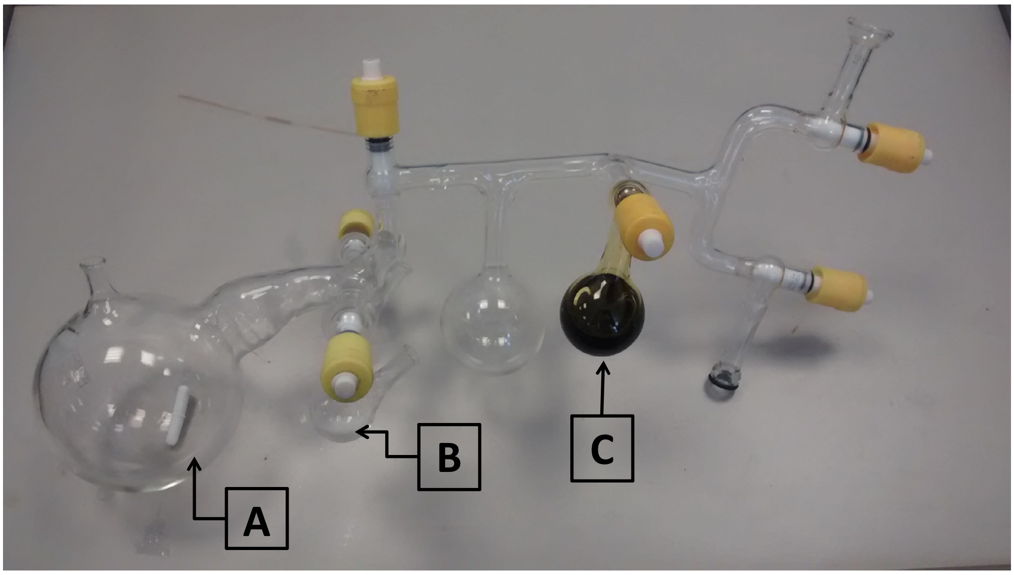

Figure 5.1: *Reaction vessel used for polymerizations, showing (A) main reaction vessel (B) side flask and (C) living polystyrene cleaning solution.*

5.3.1. Synthesis of linear PDMB — Chapter 2

5.3.1.1. Synthesis of 10 kg mol^{-1} PDMB in toluene — Experiment 2.1

The synthesis of linear PDMB was typically carried out according to the following procedure: DMB (9.54 g, 116.14 mmol) was collected by distillation under vacuum, purified bya partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and then distilled under vacuum into the 250 mL reaction flask of the reaction apparatus. Toluene (100 mL) which had previously been dried and degassed over calcium hydride was distilled under vacuum into a Young's ampoule containing a living solution of PS for final purification and then distilled under vacuum into the reaction apparatus. For a M_{target} of 10 kg mol^{-1}, *sec*-BuLi (680 µL of 1.4 M solution, 0.95 mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 48 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. A sample of polymer was also collected after 24 h in the side arms of the reactor. Yield: 92%.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.02 (3H —CH_2—$CC\mathbf{H_3}CCH_3CH_2$—), 1.20 (2H —$C\mathbf{H_2}$—$CCH_3CCH_3CH_2$—), 1.65 (6H —CH_2—$CC\mathbf{H_3}$=$CC\mathbf{H_3}$—CH_2— *cis* isomer), 1.68 (6H —CH_2—$CC\mathbf{H_3}$=$CC\mathbf{H_3}$—CH_2— *trans* isomer), 1.80 (3H —CH_2—$CCH_3CC\mathbf{H_3}CH_2$—), 2.02 (4H —$C\mathbf{H_2}$—CCH_3=CCH_3—$C\mathbf{H_2}$— *trans* isomer), 2.04 (4H —$C\mathbf{H_2}$—CCH_3=CCH_3—$C\mathbf{H_2}$— *cis* isomer), 4.70 (1H —CH_2—$CCH_3CCH_3C\mathbf{H_2}$—), 4.81 (1H —CH_2—$CCH_3CCH_3C\mathbf{H_2}$—).

M_n = 13250 g mol^{-1}, M_w = 13850 g mol^{-1}, Đ = 1.05.

5.3.1.2. Synthesis of 10 kg mol^{-1} PDMB in benzene — Experiment 2.2

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1. sec*-BuLi (870 µL of 1.4 M solution, 1.22 mmol) was injected into the reaction solution of DMB (12.41 g, 150.96 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 120 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 98%.

M_n = 10800 g mol^{-1}, M_w = 11600 g mol^{-1}, Đ = 1.07.

5.3.1.3. Synthesis of 10 kg mol^{-1} PDMB in cyclohexane — Experiment 2.3

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1. sec*-BuLi (740 µL of 1.4 M solution, 1.04 mmol) was injected into the reaction solution of DMB (10.27 g, 125.03 mmol) in cyclohexane (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 96 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 86%.

M_n = 11700 g mol^{-1}, M_w = 12150 g mol^{-1}, Đ = 1.04.

5.3.1.4. Synthesis of 10 kg mol^{-1} PDMB in *n*-hexane — Experiment 2.4

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1.* *sec*-BuLi (800 µL of 1.4 M solution, 1.12 mmol) was injected into the reaction solution of DMB (11.15 g, 135.74 mmol) in *n*-hexane (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 120 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 86%.

M_n = 9200 g mol^{-1}, M_w = 12200 g mol^{-1}, Đ = 1.32.

5.3.1.5. Synthesis of 20 kg mol^{-1} PDMB in *n*-hexane — Experiment 2.5

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1.* *sec*-BuLi (370 µL of 1.4 M solution, 0.52 mmol) was injected into the reaction solution of DMB (10.39 g, 126.49 mmol) in *n*-hexane (100 mL) for a M_{target} of 20 kg mol^{-1}. Reaction was stirred at 40 °C for 24 h and then the reaction was raised to 50 °C, right after the reaction turned to milky white, and stirred for 68 h. Yield: 81%.

M_n = 25700 g mol^{-1}, M_w = 27900 g mol^{-1}, Đ = 1.08.

5.3.1.6. Synthesis of 100 kg mol^{-1} PDMB in benzene — Experiment 2.6

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1.* *sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (12.15 g, 147.92 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 168 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 96%.

M_n = 135900 g mol^{-1}, M_w = 159500 g mol^{-1}, Đ = 1.17.

5.3.1.7. Synthesis of 100 kg mol^{-1} PDMB in *n*-heptane — Experiment 2.7

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1.* *sec*-BuLi (60 µL of 1.4 M solution, 0.08 mmol) was injected into the reaction solution of DMB (8.28 g, 100.80 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 144 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 40%.

M_n = 114800 g mol^{-1}, M_w = 218800 g mol^{-1}, Đ = 1.90.

5.3.1.8. Synthesis of 100 kg mol^{-1} PDMB in *n*-heptane — Experiment 2.8

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1. sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (12.28 g, 149.50 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 144 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 91%.

M_n = 169700 g mol^{-1}, M_w = 216800 g mol^{-1}, Đ = 1.28.

5.3.1.9. Synthesis of 200 kg mol^{-1} PDMB in benzene — Experiment 2.9

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1. sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (22.15 g, 269.66 mmol) in benzene (200 mL) for a M_{target} of 200 kg mol^{-1}. Reaction was stirred at 60 °C for 144 h. Yield: 54%.

M_n = 216700 g mol^{-1}, M_w = 287100 g mol^{-1}, Đ = 1.32.

5.3.1.10. Laboratory scaled-up synthesis of 10 kg mol^{-1} PDMB in toluene — Experiment 2.10

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1.* with the exception of a change of initiator from *sec*-BuLi to *n*-BuLi. *n*-BuLi (2000 µL of 2.5 M solution, 5.01 mmol) was injected into the reaction solution of DMB (50.07 g, 609.57 mmol) in toluene (500 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Yield: 100%.

M_n = 14500 g mol^{-1}, M_w = 16100 g mol^{-1}, Đ = 1.11.

5.3.1.11. Laboratory scaled-up synthesis of 10 kg mol^{-1} PDMB in *n*-heptane — Experiment 2.11

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.1.* with the exception of the change of initiator from *sec*-BuLi to *n*-BuLi. *n*-BuLi (1650 µL of 2.5 M solution, 4.12 mmol) was injected into the reaction solution of DMB (41.17 g, 501.22 mmol) in *n*-heptane (400 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Yield: 100%.

M_n = 18800 g mol^{-1}, M_w = 21400 g mol^{-1}, Đ = 1.14.

5.3.1.12. Industrial scaled-up synthesis of 10 kg mol^{-1} PDMB in toluene — Experiment 2.12

The industrial scale-up synthesis of linear PDMB was typically carried out according to the following procedure: toluene (1000 mL) was charged into the stainless steel reactor and sparged with nitrogen while the temperature was raised to 60 °C. DMB (100 g, 1.22 mol) was charged into the reactor under a flow of nitrogen. For a M_{target} of 10 kg mol^{-1}, *n*-BuLi (3 mL of 3.2 M solution, 9.72 mmol) was added by injection via a septum. The solution was stirred at 60 °C for 5 h before the reaction was terminated by pouring the reaction solution into a vessel containing a mixture of toluene and a protic terminating agent. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Yield: < 20%.

M_n = 4200 g mol^{-1}, M_w = 9700 g mol^{-1}, Đ = 2.30.

5.3.1.13. Industrial scaled-up synthesis of 10 kg mol^{-1} PDMB in toluene — Experiment 2.13

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.12*. *n*-BuLi (3 mL of 3.2 M solution, 9.72 mmol) was injected into the reaction solution of DMB (100 g, 1.22 mol) in toluene (1000 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 60 °C for 5 h. Yield: 62%.

M_n = 8800 g mol^{-1}, M_w = 13600 g mol^{-1}, Đ = 1.55.

5.3.1.14. Industrial scaled-up synthesis of 10 kg mol^{-1} PDMB in *n*-hexane — Experiment 2.14

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.1.12*. *n*-BuLi (3 mL of 3.2 M solution, 9.72 mmol) was injected into the reaction solution of DMB (100 g, 1.22 mol) in *n*-hexane (1000 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 60 °C for 5 h. Yield: 36%.

M_n = 7200 g mol^{-1}, M_w = 9600 g mol^{-1}, Đ = 1.33.

5.3.2. Synthesis of DMB-butadiene statistical copolymers — Chapter 3

5.3.2.1. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-71/29 in benzene — Experiment 3.1

The synthesis of DMB-Bd statistical copolymers was typically carried out according to the following procedure: DMB (11.24 g, 136.84 mmol) was collected by distillation under vacuum, purified by a partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and then distilled under vacuum into the 250 mL reaction flask of the reaction apparatus. Butadiene (3.08 g, 56.94 mmol) was collected by distillation under vacuum, further purified by a partial pre-polymerization with *n*-BuLi (50 µL) for 30 sec and then distilled under vacuum into the 250 mL reaction flask of the reaction apparatus. Benzene (100 mL) was distilled under vacuum into a Young's ampoule containing a living solution of PS for purification and then distilled under vacuum into the reaction apparatus. For a M_{target} of 10 kg mol^{-1}, *sec*-BuLi (1000 µL of 1.4 M solution, 1.40 mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 144 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Two samples were collected at intermediate timesafter 4 hand 8 h in the side arms of the reactor. Yield: 85%.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.02 (3H —CH_2—$CC\mathbf{H_3}CCH_3CH_2$—), 1.20 (2H —$C\mathbf{H_2}$—$CCH_3CCH_3CH_2$—), 1.24 (2H —$C\mathbf{H_2}$—$CCHCCHCH_2$—), 1.65 (6H —CH_2—$CC\mathbf{H_3}$=$CC\mathbf{H_3}$—CH_2— *cis* isomer), 1.68 (6H —CH_2—$CC\mathbf{H_3}$=$CC\mathbf{H_3}$—CH_2— *trans* isomer), 1.80 (3H —CH_2—$CCH_3CC\mathbf{H_3}CH_2$—), 2.03 (4H —$C\mathbf{H_2}$—CCH_3=CCH_3—$C\mathbf{H_2}$— *trans* isomer), 2.04 (4H —$C\mathbf{H_2}$—CCH_3=CCH_3—$C\mathbf{H_2}$— *cis* isomer), 4.70 (1H —CH_2—$CCH_3CCH_3C\mathbf{H_2}$—), 4.81 (1H —CH_2—$CCH_3CCH_3C\mathbf{H_2}$—), 4.95 (2H —CH_2—$CHCHC\mathbf{H_2}$—), 5.38 (2H —CH_2—$CC\mathbf{H}$=$CC\mathbf{H}$—CH_2— *cis* isomer), 5.42 (2H —CH_2—$CC\mathbf{H}$=$CC\mathbf{H}$—CH_2— *trans* isomer), 5.56 (1H —CH_2—$CCHCC\mathbf{H}CH_2$—).

M_n = 16300 g mol^{-1}, M_w = 17400 g mol^{-1}, Đ = 1.07.

5.3.2.2. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-52/48 in benzene — Experiment 3.2

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (1000 µL of 1.4 M solution, 1.40 mmol) was injected into the reaction solution of DMB (9.02 g, 109.81 mmol) and butadiene (5.47 g, 101.13 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 144 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 85%.

M_n = 14700 g mol^{-1}, M_w = 15600 g mol^{-1}, Đ = 1.06.

5.3.2.3. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-25/75 in benzene — Experiment 3.3

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (970 µL of 1.4 M solution, 1.36 mmol) was injected into the reaction solution of DMB (4.55 g, 55.39 mmol) and butadiene (9.06 g, 167.50 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 120 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 91%.

M_n = 11600 g mol^{-1}, M_w = 13000 g mol^{-1}, Đ = 1.06.

5.3.2.4. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-74/26 in *n*-hexane — Experiment 3.4

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (750 µL of 1.4 M solution, 1.05 mmol) was injected into the reaction solution of DMB (8.55 g, 104.09 mmol) and butadiene (1.95 g, 36.05 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 144 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 74%.

M_n = 9600 g mol^{-1}, M_w = 11900 g mol^{-1}, Đ = 1.24.

5.3.2.5. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-51/49 in *n*-hexane — Experiment 3.5

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (770 µL of 1.4 M solution, 1.08 mmol) was injected into the reaction solution of DMB (6.58 g, 80.11 mmol) and butadiene (4.19 g, 77.46 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 164 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 82%.

M_n = 12500 g mol^{-1}, M_w = 13400 g mol^{-1}, Đ = 1.07.

5.3.2.6. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-43/57 in *n*-hexane — Experiment 3.6

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (770 µL of 1.4 M solution, 1.08 mmol) was injected into the reaction solution of DMB (6.58 g, 80.11 mmol) and butadiene (4.19 g, 77.46 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 164 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 82%.

M_n = 12500 g mol^{-1}, M_w = 13400 g mol^{-1}, Đ = 1.07.

5.3.2.7. Synthesis of 10 kg mol^{-1} P(DMB-s-Bd)-24/76 in *n*-hexane — Experiment 3.7

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (790 µL of 1.4 M solution, 1.11 mmol) was injected into the reaction solution of DMB (3.49 g, 42.49 mmol) and butadiene (7.50 g, 138.66 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 167 h. Two samples were collected (after 4 and 8 h) in the side arms of the reactor. Yield: 82%.

M_n = 10000 g mol^{-1}, M_w = 11000 g mol^{-1}, Đ = 1.10.

5.3.2.8. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-63/37 in benzene — Experiment 3.8

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (110 µL of 1.4 M solution, 0.15 mmol) was injected into the reaction solution of DMB (10.60 g, 129.05 mmol) and butadiene (4.12 g, 76.17 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 69%.

M_n = 202200 g mol^{-1}, M_w = 280900 g mol^{-1}, Đ = 1.39.

5.3.2.9. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-57/43 in benzene — Experiment 3.9

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (75 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (6.97 g, 84.86 mmol) and butadiene (3.45 g, 63.88 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 3 and 7 min) in the side arms of the reactor. Yield: 68%.

M_n = 148100 g mol^{-1}, M_w = 181700 g mol^{-1}, Đ = 1.23.

5.3.2.10. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-49/51 in benzene — Experiment 3.10

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (6.47 g, 78.77 mmol) and butadiene (4.49 g, 83.01 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 2 and 5 min) in the side arms of the reactor. Yield: 45%.

M_n = 115900 g mol^{-1}, M_w = 140300 g mol^{-1}, Đ = 1.21.

5.3.2.11. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-38/62 in benzene — Experiment 3.11

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (140 µL of 1.4 M solution, 0.20 mmol) was injected into the reaction solution of DMB (8.97 g, 109.20 mmol) and butadiene (9.51 g, 175.82 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 6 and 9 min) in the side arms of the reactor. Yield: 84%.

M_n = 122000 g mol^{-1}, M_w = 142800 g mol^{-1}, Đ = 1.17.

5.3.2.12. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-25/75 in benzene — Experiment 3.12

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (100 µL of 1.4 M solution, 0.14 mmol) was injected into the reaction solution of DMB (4.71 g, 57.34 mmol) and butadiene (9.51 g, 175.82 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 120 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 69%.

M_n = 204100 g mol^{-1}, M_w = 260700 g mol^{-1}, Đ = 1.28.

5.3.2.13. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-74/27 in *n*-heptane — Experiment 3.13

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (9.51 g, 115.78 mmol) and butadiene (2.30 g, 42.52 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 4 and 8 min) in the side arms of the reactor. Yield: 77%.

M_n = 152200 g mol^{-1}, M_w = 201000 g mol^{-1}, Đ = 1.32.

5.3.2.14. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-58/42 in *n*-heptane — Experiment 3.14

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (120 µL of 1.4 M solution, 0.17 mmol) was injected into the reaction solution of DMB (10.58 g, 128.80 mmol) and butadiene (4.98 g, 92.07 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 5 and 9 min) in the side arms of the reactor. Yield: 75%.

M_n = 109100 g mol^{-1}, M_w = 144700 g mol^{-1}, Đ = 1.33.

5.3.2.15. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-50/50 in *n*-heptane — Experiment 3.15

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (6.78 g, 82.54 mmol) and butadiene (4.41 g, 81.53 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 4 and 8 min) in the side arms of the reactor. Yield: 59%.

M_n = 125200 g mol^{-1}, M_w = 157200 g mol^{-1}, Đ = 1.26.

5.3.2.16. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-37/63 in *n*-heptane — Experiment 3.16

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (5.46 g, 66.47 mmol) and butadiene (6.16 g, 113.98 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 4 and 8 min) in the side arms of the reactor. Yield: 65%.

M_n =119200 g mol^{-1}, M_w = 139400 g mol^{-1}, Đ = 1.17.

5.3.2.17. Synthesis of 100 kg mol^{-1} P(DMB-s-Bd)-23/77 in *n*-heptane — Experiment 3.17

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.2.1.* *sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (3.50 g, 42.61 mmol) and butadiene (7.77 g, 143.75 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 4 and 10 min) in the side arms of the reactor. Yield: 75%.

M_n = 106000 g mol^{-1}, M_w = 124700 g mol^{-1}, Đ = 1.18.

5.3.3. Synthesis of DMB-styrene statistical copolymers — Chapter 3

5.3.3.1. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-72/28 in benzene — Experiment 3.18

The synthesis of DMB-Sty statistical copolymers was typically carried out according to the following procedure: DMB (7.84 g, 95.45 mmol) was collected by distillation under vacuum, purified by a partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and distilled under vacuum into the 250 mL reaction flask of the reaction apparatus. Styrene (3.102 g, 37.64 mmol) was collected by distillation under vacuum into a Young's ampoule and distilled under vacuum into the 250 mL reaction flask of the reaction apparatus without further purification. Benzene (100 mL) was distilled under vacuum into a Young's ampoule containing a living solution of PS for purification and the distilled under vacuum into the reaction apparatus. For a M_{target} of 10 kg mol^{-1}, *sec*-BuLi (840 µL of 1.4 M solution, 1.18mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 144 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Two samples were collected after 4 hand 8 h in the side arms of the reactor. Yield: 94%.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.03 (3H —CH_2—C$\mathbf{H_3}$CCH_3CH_2—), 1.36-2.52 (15H —C$\mathbf{H_2}$—$CCH_3CCH_3CH_2$—, —CH_2—C$\mathbf{H_3}$=C$\mathbf{H_3}$—CH_2—, —CH_2—CCH_3C$\mathbf{H_3}$$CH_2$— and —C$\mathbf{H_2}$—$CCH_3$=$CCH_3$—C$\mathbf{H_2}$—), 1.36-2.52 (3H —C$\mathbf{H_2}$—C**H**Ph—), 4.71 (1H —$CH_2$—$CCH_3CCH_3C\mathbf{H_2}$—), 4.82 (1H —$CH_2$—$CCH_3CCH_3C\mathbf{H_2}$—), 7.07-7.37 (5H —$CH_2$—CH**Ph**—).

M_n = 12100 g mol^{-1}, M_w = 13200 g mol^{-1}, Đ = 1.09.

5.3.3.2. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-43/57 in benzene — Experiment 3.19

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (1100 µL of 1.4 M solution, 1.54 mmol) was injected into the reaction solution of DMB (5.70 g, 69.39 mmol) and styrene (9.62 g, 92.37 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 142 h. Two samples were collected (after 24 and 40 h) in the side arms of the reactor. Yield: 98%.

M_n = 16400 g mol^{-1}, M_w = 18000 g mol^{-1}, Đ = 1.10.

5.3.3.3. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-24/76 in benzene — Experiment 3.20

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (840 µL of 1.4 M solution, 1.18 mmol) was injected into the reaction solution of DMB (2.29 g, 27.88 mmol) and styrene (9.47 g, 90.93 mmol) in benzene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 72 h. Two samples were collected (after 2 and 4 h) in the side arms of the reactor. Yield: 95%.

M_n = 12800 g mol^{-1}, M_w = 13900 g mol^{-1}, Đ = 1.09.

5.3.3.4. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-70/30 in *n*-hexane — Experiment 3.21

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (580 µL of 1.4 M solution, 0.81 mmol) was injected into the reaction solution of DMB (5.32 g, 64.77 mmol) and styrene (2.83 g, 27.17 mmol) in *n*-hexane (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 120 h. Two samples were collected (after 25 and 48 h) in the side arms of the reactor. Yield: 91%.

M_n = 13000 g mol^{-1}, M_w = 13900 g mol^{-1}, Đ = 1.06.

5.3.3.5. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-49/51 in *n*-hexane — Experiment 3.22

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (750 µL of 1.4 M solution, 1.05 mmol) was injected into the reaction solution of DMB (4.73 g, 57.59 mmol) and styrene (6.09 g, 58.47 mmol) in *n*-hexane (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 144 h. Two samples were collected (after 24 and 48 h) in the side arms of the reactor. Yield: 96%.

M_n = 15500 g mol^{-1}, M_w = 16600 g mol^{-1}, Đ = 1.08.

5.3.3.7. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-49/51 in *n*-hexane — Experiment 3.23

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (870 µL of 1.4 M solution, 1.22 mmol) was injected into the reaction solution of DMB (5.22 g, 63.55 mmol) and styrene (6.98 g, 67.02 mmol) in *n*-hexane (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 72 h. Two samples were collected (after 2 and 4 h) in the side arms of the reactor. Yield: 95%.

M_n = 11400 g mol^{-1}, M_w = 12000 g mol^{-1}, Đ = 1.06.

5.3.3.8. Synthesis of 10 kg mol^{-1} P(DMB-s-Sty)-24/76 in *n*-hexane — Experiment 3.24

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (520 µL of 1.4 M solution, 0.73 mmol) was injected into the reaction solution of DMB (1.43 g, 17.41 mmol) and styrene (5.89 g, 56.55 mmol) in *n*-hexane (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 48 h. A sample was collected (after 24 h) in the side arm of the reactor. Yield: 100%.

M_n = 16700 g mol^{-1}, M_w = 17500 g mol^{-1}, Đ = 1.05.

5.3.3.9. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-70/30 in benzene — Experiment 3.25

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (8.07 g, 98.25 mmol) and styrene (4.32 g, 41.48 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 4 and 7 min) in the side arms of the reactor. Yield: 82%.

M_n = 196100 g mol^{-1}, M_w = 294700 g mol^{-1}, Đ = 1.50.

5.3.3.10. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-62/38 in benzene — Experiment 3.26

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (100 µL of 1.4 M solution, 0.14 mmol) was injected into the reaction solution of DMB (7.44 g, 90.58 mmol) and styrene (5.90 g, 56.65 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 48 h. Two samples were collected (after 3 and 7 min) in the side arms of the reactor. Yield: 74%.

M_n = 143900 g mol^{-1}, M_w = 162300 g mol^{-1}, Đ = 1.13.

5.3.3.11. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-49/51 in benzene — Experiment 3.27

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1.* *sec*-BuLi (100 µL of 1.4 M solution, 0.14 mmol) was injected into the reaction solution of DMB (5.49 g, 66.84 mmol) and styrene (7.34 g, 70.48 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 48 h. Two samples were collected (after 5 and 10 min) in the side arms of the reactor. Yield: 97%.

M_n = 163900 g mol^{-1}, M_w = 187400 g mol^{-1}, Đ = 1.14.

5.3.3.12. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-48/52 in benzene — Experiment 3.28

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (4.74 g, 57.71 mmol) and styrene (6.49 g, 62.31 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 120 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 82%.

M_n = 247600 g mol^{-1}, M_w = 283900 g mol^{-1}, Đ = 1.15.

5.3.3.13. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-25/75 in benzene — Experiment 3.29

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (120 µL of 1.4 M solution, 0.17 mmol) was injected into the reaction solution of DMB (3.54 g, 43.11 mmol) and styrene (13.56 g, 130.20 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 97%.

M_n =219600 g mol^{-1}, M_w = 258200 g mol^{-1}, Đ = 1.18.

5.3.3.14. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-72/28 in *n*-heptane — Experiment 3.30

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (7.54 g, 91.79 mmol) and styrene (3.74 g, 34.95 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 3 and 7 min) in the side arms of the reactor. Yield: 79%.

M_n = 267300 g mol^{-1}, M_w = 341400 g mol^{-1}, Đ = 1.28.

5.3.3.15. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-57/43 in *n*-heptane — Experiment 3.31

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (6.10 g, 74.26 mmol) and styrene (5.81 g, 55.79 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 67%.

M_n = 180700 g mol^{-1}, M_w = 210900 g mol^{-1}, Đ = 1.17.

5.3.3.16. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-50/50 in *n*-heptane — Experiment 3.32

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (5.18 g, 63.06 mmol) and styrene (6.60 g, 63.37 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 72 h. Two samples were collected (after 5 and 10 min) in the side arms of the reactor. Yield: 74%.

M_n = 149300 g mol^{-1}, M_w = 154400 g mol^{-1}, Đ = 1.17.

5.3.3.17. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-40/60 in *n*-heptane — Experiment 3.33

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (100 µL of 1.4 M solution, 0.14 mmol) was injected into the reaction solution of DMB (4.85 g, 59.05 mmol) and styrene (9.04 g, 86.80 mmol)in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 48 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 80%.

M_n = 147100 g mol^{-1}, M_w = 168400 g mol^{-1}, Đ = 1.14.

5.3.3.18. Synthesis of 100 kg mol^{-1} P(DMB-s-Sty)-26/74 in *n*-heptane — Experiment 3.34

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.3.1. sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (2.41 g, 29.34 mmol) and styrene (8.58 g, 82.38 mmol) in *n*-heptane (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 48 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 78%.

M_n = 171900 g mol^{-1}, M_w = 223500 g mol^{-1}, Đ = 1.30.

5.3.4. Synthesis of DMB-DPE statistical copolymers — Chapter 3

5.3.4.1. Synthesis of 10 kg mol^{-1} P(DMB-s-DPE)-50/50 in benzene — Experiment 3.35

The synthesis of DMB-DPE statistical copolymers was typically carried out according to the following procedure: DMB (3.11 g, 37.74 mmol) was collected by distillation under vacuum, purified by a partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and then distilled under vacuum into the 250 mL reaction flask of the reaction apparatus. Benzene (100 mL) was distilled under vacuum into a Young's ampoule containing a living solution of PS for purification and then distilled under vacuum into the reaction apparatus. DPE was purified the dropwise addition of *sec*-butyllithium until a red colour persisted, followed by trap-to-trap (short path) distillation under vacuum using a H-shaped vacuum flask (*Figure 5.2*). The system was raised to atmospheric pressure under dry nitrogen and 6.84 g (37.95 mmol) of purified DPE was collected with a gas-tight syringe and injected into the 250 mL reaction flask of the reaction apparatus via a rubber septum. For a M_{target} of 10 kg mol^{-1}, *sec*-BuLi (710 µL of 1.4 M solution, 0.99 mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 72 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Two samples were collected after 24 hand 48 h in the side arms of the reactor. Yield: 76%.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.37-2.24 (18H $—CH_2—C\mathbf{H_3}CCH_3CH_2—$, $—C\mathbf{H_2}—CCH_3CCH_3CH_2—$, $—CH_2—C\mathbf{H_3}=C\mathbf{H_3}—CH_2—$, $—CH_2—CCH_3C\mathbf{H_3}CH_2—$ and $—C\mathbf{H_2}—CCH_3=CCH_3—C\mathbf{H_2}—$), 2.36-3.08 (2H $—C\mathbf{H_2}—CPh_2—$), 4.59-4.82 (2H $—CH_2—CCH_3CCH_3C\mathbf{H_2}—$), 6.29-7.26 (10H $—CH_2—CH\mathbf{Ph_2}—$).

M_n = 14600 g mol^{-1}, M_w = 16000 g mol^{-1}, Đ = 1.10.

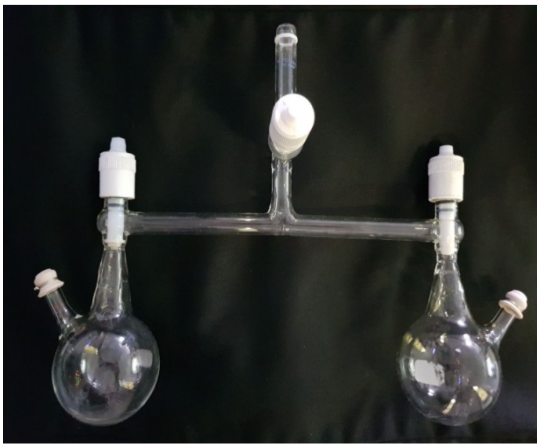

Figure 5.2: *H-shape vacuum flask used for the purification of 1,1-diphenylethylene (DPE).*

5.3.4.2. Synthesis of 100 kg mol^{-1} P(DMB-s-DPE)-75/25 in benzene — Experiment 3.36

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.4.1. sec*-BuLi (70 µL of 1.4 M solution, 0.10 mmol) was injected into the reaction solution of DMB (5.79 g, 70.49 mmol) and DPE (4.28 g, 23.85 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 2 and 5 min) in the side arms of the reactor. Yield: 60%.

M_n = 123200 g mol^{-1}, M_w = 153900 g mol^{-1}, Đ = 1.25.

5.3.4.3. Synthesis of 100 kg mol^{-1} P(DMB-s-DPE)-75/25 in benzene — Experiment 3.37

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.4.1. sec*-BuLi (75 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (5.99 g, 72.92 mmol) and DPE (4.39 g, 24.36 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 144 h. Two samples were collected (after 30 min and 1 h) in the side arms of the reactor. Yield: 17%.

M_n = 49800 g mol^{-1}, M_w = 71900 g mol^{-1}, Đ = 1.44.

5.3.4.4. Synthesis of 100 kg mol^{-1} P(DMB-s-DPE)-50/50 in benzene — Experiment 3.38

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.4.1. sec*-BuLi (90 µL of 1.4 M solution, 0.13 mmol) was injected into the reaction solution of DMB (3.74 g, 44.32 mmol) and DPE (7.96 g, 44.16 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 58%.

M_n = 147800 g mol^{-1}, M_w = 170000 g mol^{-1}, Đ = 1.15.

5.3.4.5. Synthesis of 100 kg mol^{-1} P(DMB-s-DPE)-50/50 in benzene — Experiment 3.39

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.4.1. sec*-BuLi (80 µL of 1.4 M solution, 0.11 mmol) was injected into the reaction solution of DMB (3.59 g, 43.81 mmol) and DPE (7.88 g, 43.82 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 15 and 30 min) in the side arms of the reactor. Yield: 28%.

M_n = 114900 g mol^{-1}, M_w = 149200 g mol^{-1}, Đ = 1.30.

5.3.4.6. Synthesis of 100 kg mol^{-1} P(DMB-s-DPE)-25/75 in benzene — Experiment 3.40

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.4.1.* *sec*-BuLi (100 µL of 1.4 M solution, 0.15 mmol) was injected into the reaction solution of DMB (2.07 g, 25.20 mmol) and DPE (13.73 g, 75.62 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 3 and 6 min) in the side arms of the reactor. Yield: 33%.

M_n = 92100 g mol^{-1}, M_w = 104000 g mol^{-1}, Đ = 1.13.

5.3.4.7. Synthesis of 100 kg mol^{-1} P(DMB-s-DPE)-25/75 in benzene — Experiment 3.41

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.4.1.* *sec*-BuLi (100 µL of 1.4 M solution, 0.15 mmol) was injected into the reaction solution of DMB (1.86 g, 22.64 mmol) and DPE (12.25 g, 67.96 mmol) in benzene (100 mL) for a M_{target} of 100 kg mol^{-1}. Reaction was stirred at 60 °C for 96 h. Two samples were collected (after 30 min and 1 h) in the side arms of the reactor. Yield: 27%.

M_n = 111200 g mol^{-1}, M_w = 142600 g mol^{-1}, Đ = 1.28.

5.3.5. Synthesis of randomly branched copolymers of DMB — Chapter 4

5.3.5.1. Synthesis of 10 kg mol^{-1} PDMB in toluene in the presence of KOtBu — Experiment 4.1

The synthesis of linear PDMB in the presence of KOtBu was typically carried out according to the following procedure: KOtBu (29.40 mg, 0.26 mmol) solution in THF was injected via a rubber septum into the 250 mL reaction flask of the reaction apparatus. The THF was removed by distillation under vacuum for 1 h. DMB (12.45 g, 151.57 mmol) was collected by distillation under vacuum, purified by a partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and distilled under vacuum into the reaction apparatus. Toluene (100 mL) was distilled under vacuum into a Young's ampoule containing a living solution of PS for purification and the distilled under vacuum into the reaction apparatus. For a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.21, *sec*-BuLi (890 µL of 1.4 M solution, 1.25 mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 48 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Two samples were collected (after 16 and 24 h) in the side arms of the reactor. Yield: 69%.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.01 (3H —CH_2—C**H_3**CCH_3CH_2—), 1.20 (2H —C**H_2**—$CCH_3CCH_3CH_2$—), 1.64 (6H —CH_2—C**H_3**=C**H_3**—CH_2— *cis* isomer), 1.67 (6H —CH_2—C**H_3**=C**H_3**—CH_2— *trans* isomer), 1.80 (3H —CH_2—CCH_3C**H_3**CH_2—), 2.02 (4H —C**H_2**—CCH_3=CCH_3—C**H_2**— *trans* isomer), 2.04 (4H —C**H_2**—CCH_3=CCH_3—C**H_2**— *cis* isomer), 4.70 (1H —CH_2—CCH_3CCH_3C**H_2**—), 4.81 (1H —CH_2—CCH_3CCH_3C**H_2**—).

M_n = 1640 g mol^{-1}, M_w = 2500 g mol^{-1}, Đ = 1.51.

5.3.5.2. Synthesis of 10 kg mol^{-1} PDMB in cyclohexane in the presence of KOtBu — Experiment 4.2

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1. sec*-BuLi (710 µL of 1.4 M solution, 0.99 mmol) was injected into the reaction solution of DMB (9.97 g, 121.38 mmol) and KOtBu (23.40 mg, 0.21 mmol) in cyclohexane (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.21. Reaction was stirred at 40 °C for 48 h. Yield: 99%.

M_n = 15100 g mol^{-1}, M_w = 15900 g mol^{-1}, Đ = 1.05.

5.3.5.3. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-95/5 in toluene — Experiment 4.3

The synthesis of branched PDMB by the copolymerization with DVB was typically carried out according to the following procedure: DMB (12.03 g, 146.46 mmol) was collected by distillation under vacuum, purified by a partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and distilled under vacuum into the 250 mL reaction flask of the reaction apparatus. Toluene (100 mL) was distilled under vacuum into a Young's ampoule containing a living solution of PS for purification and the distilled under vacuum into the reaction apparatus. DVB (1.20 g, 9.22 mmol) was purified as described in *section 5.1* and injected into the reaction apparatus via a rubber septum. For a M_{target} of 10 kg mol^{-1}, *sec*-BuLi (950 µL of 1.4 M solution, 1.33 mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 24 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was gel-like and insoluble in any solvent. The polymer was recovered by evaporation of the remaining solvent and dried *in vacuo*. Yield: 63%.

5.3.5.4. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-97/3 in toluene — Experiment 4.4

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.3.* *sec*-BuLi (700 µL of 1.4 M solution, 0.98 mmol) was injected into the reaction solution of DMB (9.73 g, 118.43 mmol) and DVB (0.61 g, 4.69 mmol) in toluene (100 mL) for a $M_{target}$of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 29 h. The polymer was an insoluble gel. Yield: 53%.

5.3.5.5. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-97/3 in toluene in the presence of KOtBu — Experiment 4.5

The synthesis of branched PDMB by copolymerization with DVB in the presence of KOtBu was typically carried out according to the following procedure: KOtBu (24.90 mg, 0.26 mmol) solution in THF was injected via a rubber septum into the 250 mL reaction flask of the reaction apparatus. The THF was removed by distillation under vacuum for 1 h. DMB (10.34 g, 125.88 mmol) was collected by distillation under vacuum, purified by a partial pre-polymerization with *n*-BuLi (500 µL) for 10 min and distilled under vacuum into the reaction apparatus. Toluene (100 mL) was distilled under vacuum into a Young's ampoule containing a living solution of PS for purification and then distilled under vacuum into the reaction apparatus. DVB (0.61 g, 4.69 mmol) was purified as described in *section 5.1* and injected into the reaction apparatus via a rubber septum. For a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.20, *sec*-BuLi (780 µL of 1.4 M solution, 1.09 mmol) was added by injection via a rubber septum. The solution was stirred at 40 °C (pre-heated oil bath) for 24 h before the reaction was terminated by injection of nitrogen-sparged methanol. The polymer was an insoluble gel and was recovered by evaporation of the remaining solvent and dried *in vacuo*. Yield: 61%.

5.3.5.6. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-97/3 in toluene in the presence of KOtBu — Experiment 4.6

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.5.* *sec*-BuLi (760 µL of 1.4 M solution, 1.06 mmol) was injected into the reaction solution of DMB (10.05 g, 122.35 mmol), DVB (0.61 g, 4.69 mmol) and KOtBu (47.70 mg, 0.43 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.40. Reaction was stirred at 40 °C for 24 h. The polymer was an insoluble gel. Yield: 51%.

5.3.5.7. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-99.7/0.3 in toluene — Experiment 4.7

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.3.* *sec*-BuLi (500 µL of 1.4 M solution, 0.70 mmol) was injected into the reaction solution of DMB (7.00 g, 85.22 mmol) and DVB (0.04 g, 0.28 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1}. Reaction was stirred at 40 °C for 28 h. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Two samples were collected (after 5 and 24 h) in the side arms of the reactor. Yield: 60%.

M_n = 16700 g mol^{-1}, M_w = 26400 g mol^{-1}, Đ = 1.06.

5.3.5.8. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-99.7/0.3 in toluene in the presence of KOtBu — Experiment 4.8

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.5.* *sec*-BuLi (670 µL of 1.4 M solution, 0.94 mmol) was injected into the reaction solution of DMB (9.29 g, 113.11 mmol), DVB (0.05 g, 0.35 mmol) and KOtBu (24.10 mg, 0.22 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.23. Reaction was stirred at 40 °C for 21 h. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Yield: 63%.

M_n = 1800 g mol^{-1}, M_w = 4600 g mol^{-1}, Đ = 2.59.

5.3.5.9. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-99.7/0.3 in toluene in the presence of KOtBu — Experiment 4.9

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.5.* *sec*-BuLi (850 µL of 1.4 M solution, 1.19 mmol) was injected into the reaction solution of DMB (11.82 g, 143.100 mmol), DVB (0.05 g, 0.42 mmol) and KOtBu (24.90 mg, 0.22 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.19. Reaction was stirred at 40 °C for 28 h. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Yield: 100%.

M_n = 1300 g mol^{-1}, M_w = 2300 g mol^{-1}, Đ = 1.80.

5.3.5.10. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-99.6/0.4 in toluene in the presence of KOtBu — Experiment 4.10

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.5.* *sec*-BuLi (800 µL of 1.4 M solution, 1.12 mmol) was injected into the reaction solution of DMB (11.15 g, 135.74 mmol), DVB (0.09 g, 0.70 mmol) and KOtBu (23.70 mg, 0.21 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.19. Reaction was stirred at 40 °C for 27 h. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Yield: 88%.

M_n = 2200 g mol^{-1}, M_w = 5000 g mol^{-1}, Đ = 2.28.

5.3.5.11. Synthesis of 10 kg mol^{-1} P(DMB-s-DVB)-99.3/0.7 in toluene in the presence of KOtBu — Experiment 4.11

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.5.* *sec*-BuLi (800 µL of 1.4 M solution, 1.12 mmol) was injected into the reaction solution of DMB (11.10 g, 135.14 mmol), DVB (0.16 g, 1.22 mmol) and KOtBu (23.50 mg, 0.21 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.19. Reaction was stirred at 40 °C for 48 h. The polymer was recovered by precipitation into methanol, collected by filtration and washed with further methanol. The precipitation/collection/washing process was repeated and the isolated polymer was dried *in vacuo*. Yield: 95%.

M_n = 70900 g mol^{-1}, M_w = 136200 g mol^{-1}, Đ = 1.92.

5.3.5.12. Synthesis of 10 kg mol^{-1} PDMB in toluene at 30 ^{o}C in the presence of KOtBu — Experiment 4.12

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* *sec*-BuLi (730 µL of 1.4 M solution, 1.02 mmol) was injected into the reaction solution of DMB (12.28 g, 125.15 mmol) and KOtBu (22.44 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.20. Reaction was stirred at 30 °C for 72 h. Yield: 80%.

M_n = 1300 g mol^{-1}, M_w = 2100 g mol^{-1}, Đ = 1.61.

5.3.5.13. Synthesis of 10 kg mol^{-1} PDMB in toluene at 40 °C in the presence of KOtBu — Experiment 4.13

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* *sec*-BuLi (730 µL of 1.4 M solution, 1.02 mmol) was injected into the reaction solution of DMB (10.16 g, 123.79 mmol) and KOtBu (22.44 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.20. Reaction was stirred at 40 °C for 72 h. Yield: 88%.

M_n = 2100 g mol^{-1}, M_w = 3600 g mol^{-1}, Đ = 1.73.

5.3.5.14. Synthesis of 10 kg mol^{-1} PDMB in toluene at 50 °C in the presence of KOtBu — Experiment 4.14

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* *sec*-BuLi (740 µL of 1.4 M solution, 1.04 mmol) was injected into the reaction solution of DMB (10.43 g, 126.98 mmol) and KOtBu (22.44 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.19. Reaction was stirred at 50 °C for 48 h. Yield: 53%.

M_n = 1200 g mol^{-1}, M_w = 1800 g mol^{-1}, Đ = 1.42.

5.3.5.15. Synthesis of 10 kg mol^{-1} PDMB in toluene at 60 °C in the presence of KOtBu — Experiment 4.15

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* *sec*-BuLi (710 µL of 1.4 M solution, 0.99 mmol) was injected into the reaction solution of DMB (9.97 g, 121.38 mmol) and KOtBu (22.44 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a KOtBu/BuLi of 0.20. Reaction was stirred at 60 °C for 48 h. Yield: 100%.

M_n = 870 g mol^{-1}, M_w = 1300 g mol^{-1}, Đ = 1.46.

5.3.5.16. Synthesis of 10 kg mol^{-1} PDMB in toluene at 30 °C in the presence of NaOtBu — Experiment 4.16

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* with the exception of the change of butoxide from KOtBu to NaOtBu. *sec*-BuLi (700 µL of 1.4 M solution, 0.98 mmol) was injected into the reaction solution of DMB (9.80 g, 119.31 mmol) and NaOtBu (19.22 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a NaOtBu/BuLi of 0.20. Reaction was stirred at 30 °C for 72 h. Yield: 100%.

M_n = 9400 g mol^{-1}, M_w = 11400 g mol^{-1}, Đ = 1.21.

5.3.5.17. Synthesis of 10 kg mol^{-1} PDMB in toluene at 40 °C in the presence of NaOtBu — Experiment 4.17

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* with the exeption of the change of butoxide from KOtBu to NaOtBu. *sec*-BuLi (760 µL of 1.4 M solution, 1.06 mmol) was injected into the reaction solution of DMB (10.66 g, 129.78 mmol) and NaOtBu (19.22 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a NaOtBu/BuLi of 0.19. Reaction was stirred at 40 °C for 120 h. Yield: 67%.

M_n = 9300 g mol^{-1}, M_w = 11900 g mol^{-1}, Đ = 1.28.

5.3.5.18. Synthesis of 10 kg mol^{-1} PDMB in toluene at 50 °C in the presence of NaOtBu — Experiment 4.18

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* with the exeption of the change of butoxide from KOtBu to NaOtBu. *sec*-BuLi (700 µL of 1.4 M solution, 0.98 mmol) was injected into the reaction solution of DMB (9.72 g, 118.34 mmol) and NaOtBu (19.22 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a NaOtBu/BuLi of 0.20. Reaction was stirred at 50 °C for 48 h. Yield: 98%.

M_n = 7300 g mol^{-1}, M_w = 10000 g mol^{-1}, Đ = 1.36.

5.3.5.19. Synthesis of 10 kg mol^{-1} PDMB in toluene at 60 °C in the presence of NaOtBu — Experiment 4.19

The synthesis of this polymer was carried out following the same procedure described above in *section 5.3.5.1.* with the exeption of the change of butoxide from KOtBu to NaOtBu. *sec*-BuLi (720 µL of 1.4 M solution, 1.01 mmol) was injected into the reaction solution of DMB (10.03 g, 122.11 mmol) and NaOtBu (19.22 mg, 0.20 mmol) in toluene (100 mL) for a M_{target} of 10 kg mol^{-1} and a NaOtBu/BuLi of 0.20. Reaction was stirred at 60 °C for 48 h. Yield: 100%.

M_n = 9200 g mol^{-1}, M_w = 11700 g mol^{-1}, Đ = 1.27.

Chapter 6

Concluding Remarks

Chapter 6: Concluding Remarks

6.1. Conclusions

This project has focused on the synthesis and characterization of polymers and copolymers of 2,3-dimethyl-1,3-butadiene (DMB), a monomer which has been largely ignored in recent decades in comparison to the more common diene monomers, butadiene and isoprene, both of which have been extensively researched in the past and continue to attract significant interest both in academia and industry. Therefore, the results reported here are in many cases entirely new and, we believe, will be of significant interest to researchers in both academia and industry. The headline conclusion is that in most respects DMB and the (co)polymers derived from DMB are significantly, and in some cases unexpectedly different from the other dienes, both in terms of the synthesis of the polymers e.g. copolymerization kinetics and the properties of the resulting polymers.

An initial investigation into the synthesis of homopolymers of PDMB, in a range of what might ordinarily be described as “non-polar” solvents, revealed that the resulting microstructure showed surprisingly high degree of sensitivity to the polarity of the reaction solvent. The solvents in question, *n*-hexane, cyclohexane, benzene and toluene, with dielectric constants (ε) in the rather narrow range of $1.89 < \varepsilon < 2.38$, resulted in microstructures comprising of between 3% and 21% 1,2 (vinyl) repeat units. This the first of many examples where DMB behaves very differently to the other dienes, for example the 1,2 content of polybutadiene only varies between 8% and 10% in the same reaction solvents. The microstructure of dienes plays a very large role in determining the physical properties (glass transition temperature, crystallinity etc) and in this respect poly DMB was no different. The physical appearance of poly(DMB) was highly dependent on the microstructure and although all samples were white solids, those prepared in the aromatic solvents, with 16-21% 1,2 repeat units were somewhat rubbery whilst the samples prepared in the aliphatic solvents, with a very low 1,2 content (3-4%) were waxy solids. The origin of those differences in appearance were revealed via differential scanning calorimetry (DCS). The samples with the higher 1,2 content possessed a glass transition temperature (T_g) which was just below room temperature (12-16 °C) and a very weak melting transition (T_m) at 91-106 °C. On the other hand, the samples synthesized in *n*-alkanes, with an astonishingly low 1,2 content, had a slightly lower T_g (8-13 °C) and a more intense T_m peak. We can conclude that the almost total absence of any crystallinity in the samples with *ca.* 20% 1,2 units, is a direct consequence of this higher 1,2 content and the physical (rubbery) appearance arises from a T_g which is just below room temperature. However, a very low 1,2 content enables the polymer samples prepared in aliphatic solvents to undergo partial crystallinity, albeit not to a high degree, and the waxy, more solid-like appearance is a consequence of this low degree of crystallinity. Interestingly, crystallinity is not a property observed in either polybutadiene or polyisoprene samples prepared by anionic polymerization, and both have a T_g which is significantly lower than polyDMB.

An investigation of the anionic copolymerization of DMB with a variety of monomers, specifically butadiene, styrene and diphenylethylene, showed stark differences in terms of the copolymerization kinetics, to analogous copolymerization reactions of either butadiene or isoprene. The differences were quantified by the calculation of the copolymerization reactivity ratios. To the best of our knowledge, no reactivity ratio data for the anionic copolymerization of DMB with butadiene and DMB with styrene has been previously reported. Whilst differences arising from the slight structural difference of DMB were expected, the extent of the differences were significant and most unexpected.

The reactivity ratios for the DMB-butadiene comonomer system, $r_{Bd} > 20$ and $r_{DMB} << 1.0$ and almost zero, suggest that the sequence of the resulting DMB-butadiene copolymers is likely to comprise of a block-like sequence with butadiene initially consumed with a very strong preference. The proposed blocky sequence was supported and evidenced by DSC analysis which showed two glass transitions, at approximately -80 °C, corresponding to the polybutadiene block and 15 °C, corresponding to the PDMB block. Additionally, it was observed that the PDMB block retained its inherent crystallinity with a T_m which was rather weak in the copolymers synthesized in benzene but more pronounced for the copolymers prepared in *n*-heptane. The solubility of the DMB-butadiene copolymers prepared in aliphatic solvents led to some interesting observations during the polymerization. The DMB-butadiene copolymerization carried out in alkane solvents, with a feed ratio of DMB/Bd of approximately 25/75 resulted in an increasingly turbid polymer “solution” as the polymerization proceeded. Based on the earlier observation that polyDMB with a very low 1,2 content (< 4%) was not soluble in *n*-hexane, and the block-like sequence arising from the rather extreme reactivity ratios for this system, we think it is reasonable to conclude that such a copolymerization carried out in a (selective) solvent for the blocky copolymer, results in the formation of micelles, where the PDMB block, being is insoluble in *n*-hexane, forms the core and the polybutadiene block would form the corona. Although further work would be required to prove this beyond any doubt, we believe this may be the first observed example of polymerization induced self-assembly in an anionic polymerization.

The anionic copolymerization of DMB with styrene was shown to proceed in a more random manner. The reactivity ratios in both benzene and *n*-heptane showed a tendency of both monomers to undergo cross-propagation in preference to self-propagation (r_{DMB} and r_{Sty} << 1) leading to copolymers with a nearly random sequence. The reactivity ratios and proposed sequence were supported by DSC analysis which indicated a single T_g at about 50-60 °C (depending on composition) which is almost midway between the T_g's of the two homopolymers. The(nearly) random sequence for DMB-Sty copolymers is another clear example where DMB behaves in stark contrast to butadiene and isoprene in analogous butadiene-styrene and isoprene-styrene statistical anionic copolymerizations, where blocky copolymers are obtained. In order to randomize the butadiene-styrene or isoprene-styrene sequences it is necessary to use polar randomizers (e.g. TMEDA) which not only produce a random sequence but also lead to a significant increase in the vinyl content of the diene, which is undesirable for certain applications.

The anionic copolymerization of DMB and DPE, a monomer which is unable to homopolymerize ($r_{DPE} = 0$) led to copolymers whose composition is highly dependent upon the feed ratio. Thus a nearly alternating sequence is obtained when DPE is fed in excess, which is completely opposite to the observed sequence obtained during the anionic copolymerization of butadiene and DPE, where a homopolymer of butadiene is obtained with DPE being totally excluded from the polymerization. The statistical/alternating sequence of the resulting DMB-DPE copolymers was again supported by the thermal analysis (DSC) which only showed a single T_g for each copolymer with values that ranged between 70 °C and 140 °C depending on the composition.

Finally, an investigation into the viability of adapting the Strathclyde (free radical) route for the synthesis of branched polymers, to allow the synthesis of branched polyDMB via anionic chain-transfer polymerization, led to the conclusion that this is a viable approach. As with butadiene and isoprene, living polyDMB was shown to be susceptible to chain transfer to toluene in the presence of potassium *tert*-butoxide (KOtBu) which promotes chain transfer. In the synthesis of branched polyDMB using divinylbenzene (DVB) as a branching agent, in the absence and in the presence of KOtBu, it was concluded that at high DVB to initiator ratios (3.50-5.70) gelation could not be inhibited by the promotion of chain transfer by KOtBu. On the other hand, at a lower DVB to initiator ratios of between 0.3 and 0.9, soluble polymer was obtained. At the highest DVB to initiator ratio (0.90), significantly levels of chain coupling was observed and the presence of the chain transfer promoter completely inhibited any crosslinking, yielding a soluble (branched) polymer. SEC analysis revealed a bimodal distribution and a Mark-Houwink plot showed a change in the gradient as a function of molar mass, which is agreement with the conclusion that the higher molar mass fraction was comprised of long-chain branched polymer. It was thus concluded that the Strathclyde route can be successfully adapted to the synthesis of branched soluble polyDMB via anionic polymerization using a DVB to initiator ratio of 0.90 in the presence of KOtBu (KOtBu to initiator ratio approximately 0.20) at 40 °C. Nevertheless, the obtained results are preliminary and further work is recommended in order to more widely explore the full scope of this approach, see *Section 6.2*.

In general, DMB has shown to exhibit significantly different behaviour to that shown by butadiene and isoprene both in terms of synthesis and properties. These dramatic differences arise as a result of a relatively minor difference in monomer structure, namely the effect of an extra methyl group on carbon 2. Although it was not possible to complete any tensile testing — to establish whether the resulting polymers undergo stress-induced crystallisation, thermal analysis has shown that both the homopolymers with a high 1,4 content, and even the copolymers with butadiene, show some degree of crystallisation, even under quiescent conditions. Given what is known about natural rubber, it is not unreasonable to conclude that PDMB with a high 1,4 content would show stress-induced crystallisation, making it an interesting material for further studies.

6.2. Future Work

The following experiments and areas of work that were not completed (due to time constraints) during this project are considered topics of interest for future work.

The homopolymerization experiments described in *Chapter 2* explored a relatively narrow range of solvent polarity, with dielectric constants (ε) between 1.89 (*n*-hexane) and 2.38 (toluene). In order to expand the range of solvent polarity, a number of homopolymerizations of DMB could be carried out using suitable solvents for anionic polymerization (or mixtures of solvents) whose dielectric constants are higher than 2.38. For example, diethyl ether (ε = 4.33) or tetrahydrofuran (THF) (ε = 7.58) would be suitable solvents with a higher polarity and may be expected to lead to polymers with a higher vinyl content. Additionally, in order to optimize the scaled-up synthesis of PDMB under industrial conditions (even considering the results obtained were positive) further work on the optimization of the reaction conditions, a specific reactor set-up for DMB and in particular a viable and scalable purification process for the starting materials will be necessary to facilitate large-scale production.

The investigation of the copolymerization of DMB with each of the comonomers studied in this project (butadiene, styrene and DPE) is the biggest part of the current project but this area of work could be significantly expanded with new data. As mentioned in *Chapter 3*, an unexpected trend in reactivity ratios as a function of the feed ratio was observed in the DMB-styrene system. In order to confirm this trend it would be advisable to repeat the experiments taking more intermediate samples and studying composition at different (early) reaction times. The copolymerization kinetics in anionic polymerization are very sensitive to polarity and for example the anionic copolymerization of styrene-butadiene leads to dramatically different monomer sequence distributions in benzene and THF. Therefore, the copolymerization of DMB with butadiene, styrene and DPE could be investigated in more polar solvent such as THF. The number of co-monomers could also be expanded. For example, the statistical copolymerization of DMB with isoprene at different DMB/isoprene mole ratios could be carried out under the same conditions than the DMB-butadiene and DMB-styrene copolymerizations carried out in this work, with the goal of obtaining the reactivity ratios (r_{DMB} and r_{Ip}) for the DMB-isoprene pair.

Another interesting area of work would be the synthesis of terpolymers of DMB, butadiene and styrene (and other co-monomers such as isoprene) with different compositions of each co-monomer. According to the reactivity ratios calculated for DMB-butadiene and DMB-styrene and the reactivity ratios of butadiene-styrene previously reported in the literature, a statistical anionic copolymerization of the three monomers might lead to a terpolymer composed of a first block of polybutadiene followed by a second block of styrene and DMB units statistically distributed. A multi-billion dollar business using anionic polymerization has been built on the use of (mainly) only three monomers, butadiene, isoprene and styrene. However, innovative use of reaction conditions allows these three monomers to be combined in vast number of variants with properties tuned towards particular applications. An clear understanding of how DMB undergoes copolymerization with these common monomers, could expand the pool of commercially viable monomers allowing the synthesis of new/modified copolymers for commercial application.

During the DMB-butadiene copolymerization in *n*-hexane, where butadiene was the major component of the feed ($[M_1]/[M_2] = 24/76$; where M_1 is DMB) it was observed that the reaction solution became slightly turbid. As mentioned in *Chapter 3*, this might be the first example of polymerization induced self-assembly in anionic polymerization, arising from the delayed consumption of DMB and the formation of a blocky sequence with the less soluble DMB-rich block (core) formed after the preferential consumption of butadiene (soluble polybutadiene block forming the corona). In order to confirm this phenomenon it would be necessary to carry out DMB-Bd copolymerizations under the same conditions, testing different feed ratios and collecting several samples starting when the turbid solution appears. The key to confirming that the onset in turbidity arises due to self-assembly in selective solvent for one “block” lies in characterisation. The resulting samples should be analysed for example by dynamic light scattering (DLS), in *n*-hexane, in order to obtain the size distribution profile at different reaction times and check the evolution and growth of the self-assembled particles in solution.

As mentioned in *Chapter 4*, the results obtained for the synthesis of randomly branched PDMB via a modified Strathclyde approach are preliminary in nature. Consequently, the investigation of a wider range of DVB to initiator ratios for the synthesis of branched PDMB via anionic chain transfer polymerization would be necessary in order to obtain more accurate conclusions about the full scope of this approach. Of especial interest would be to see if the contribution of chain transfer is sufficient to inhibit gelation when DVB to initiator ratios of greater than 1.0 are used. This process exploits cheap and commercial available starting materials and (in theory), is viable for scale-up.

As a consequence of time constraints and lack of appropriate equipment, the analysis of the physical (mechanical) properties of the resulting homopolymers and copolymers of DMB could not be carried out. For example, tensile strength, melt and solution rheology and in particular, the ability of the resulting polymers to undergo stress-induced crystallization would be the most relevant properties to analyse. It would be of special interest to crosslink the resulting polymers, possibly by vulcanisation, and look at the tensile properties of the resulting elastomers. Stress-induced crystallisation could also be explored by SAXS.

One further long term aim would be to combine an understanding of the copolymerization kinetics of DMB and butadiene/isoprene and the results of an investigation into the physical properties, to develop a synthetic alternative to natural rubber with a low glass transition temperature and the ability to undergo stress-induced crystallization.