The synthesis and characterisation of hyperbranched polyesters

David Parker

How to cite:

Parker, David (2000) The synthesis and characterisation of hyperbranched polyesters. Doctoral thesis, Durham University.

The Synthesis and Characterisation of Hyperbranched Polyesters

David Parker

A thesis submitted for the degree of Doctor of Philosophy

UNIVERSITY OF DURHAM

2000

The Synthesis and Characterisation of Hyperbranched Polyesters

Abstract

A new route to the AB_2 monomer dimethyl 5-(2-hydroxyethoxy) isophthalate and its subsequent polymerisation is reported. Hyperbranched polyesters were prepared by melt condensation polymerisation of the AB_2 monomer and also by copolymerisation with suitable core molecules. Unusual molecular weight growth characteristics were demonstrated. The number average molecular weight (M_n) reached a plateau value after relatively short polymerisation time, whereas the weight average molecular weight (M_w) continued to increase. This limit to the attainable number average molecular weight is thought to be a consequence of intramolecular cyclisation reactions, evidence of which was provided by MALDI-TOF MS. The weight average molecular weight continues to increase after complete cyclisation and it is postulated that this is due to a redistribution of polymer chains by ester interchange reactions. The plausibility of the occurrence of ester exchange processes was demonstrated by the successful incorporation of a dimethyl isophthalate core molecule into a fully cyclised hyperbranched polyester. The amount of branching in the hyperbranched polyesters was in agreement with the theoretical value for a statistical distribution at high conversion, as determined by quantitative ^{13}C NMR spectroscopy. The solution properties of the hyperbranched polyesters were studied and revealed these materials to be soluble in common organic solvents. Solutions of the hyperbranched polyesters had characteristically low intrinsic viscosities ($[\eta]$) and Mark-Houwink plots showed a linear relationship between log M_w and $\log[\eta]$. The thermal properties of the hyperbranched polyesters were examined by differential scanning calorimetry, which showed the polymers to be amorphous materials exhibiting a glass transition temperature (T_g) but no melting point. The T_g varied with molecular weight, was proportional to $1/M_w$ and reached a limiting value of 86 ^0C at high conversion.

Memorandum

The work described in this thesis was carried out in the Interdisciplinary Research Centre in Polymer Science and Technology, the University of Durham, between January 1996 and December 1999. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

Aspects of this work have been presented by the author at the Royal Society of Chemistry Annual Conference, UMIST, Manchester, April 2000.

Some parts of chapters 3 and 5, along with related material, have also been published as a joint publication. (Feast, W.J., Keeney, A.J., Kenwright, A.M., Parker, D., *J. Chem. Soc. Chem. Commun.*, 1997, 1749)

Statement of Copyright

Acknowledgments

Many years ago, in the acknowledgements to my M.Sc. thesis, I had occasion to thank my supervisor Professor W.J. Feast for 'his support and persistent browbeating without which I would not have taken on this project'. I would like to take this opportunity to once again express my thanks for the 'persuasion' required to encourage me to take on this current project and, of course, the support needed to carry it out.

I am grateful to my colleagues both in the IRC and the Chemistry Department for their friendship and good humour. Special thanks go to members of the 'Hyperbranched Polymers Group', Dr. L.J. Hobson, Dr. A.J. Keeney and Mr. I.C. Anderson, for many helpful discussions and much humorous banter. I would like to thank Mr. W.D. Carswell for recording SEC and DSC data, for the loan of a PC and, more importantly, the occasional pint of ale. I would especially like to express my gratitude to the technical staff of both the Chemistry Department and the IRC, particularly the participants of the tea break quizzes and card games. Last but not least I would like to thank my partner Rachel for her support and acknowledge the role of my son Alexander (age 3 months) in some much needed relief of stress!

Contents

Chapter One: Dendritic Macromolecules

Chapter Two: Synthesis and Polymerisation of Dimethyl 5-(2-hydroxyethoxy) isophthalate

Chapter Three: Determination of the Molecular Weight of Hyperbranched Polyesters

Chapter Four: Core Terminated Hyperbranched Polymers

Chapter Five: Branching in Hyperbranched Polymers

Chapter Six: Thermal Analysis of Hyperbranched Polyesters

Chapter Seven: Conclusions and Suggestions for Further Work

Chapter One

Dendritic Macromolecules

1.1 Introduction.

The synthesis of macromolecules with new architectures and the determination and control of polymeric structure are themes driven by the desire for materials with new and / or improved properties.[1] The properties of polymers can be strongly affected by branching and even relatively small fractions of long-chain branched molecules may result in properties very different from those of a purely linear polymer.[2] Consequently the elucidation of branching and the correlation of polymer properties with macromolecular architecture is a subject of continuing research. In the last two decades of the twentieth century research aimed at the investigation of polymers with highly branched topologies, in particular dendritic macromolecules, has become an important theme in polymer science.[3]

Dendritic macromolecules can be conveniently divided into two types, which have been termed dendrimers and hyperbranched polymers.[4] Dendrimers, which are well-defined monodisperse structures in which all branch points are utilised, were first successfully synthesised in the early 1980s.[5] Hyperbranched polymers may be considered as irregular analogues of dendrimers. These are polydisperse systems with varying degrees of branching and are consequently less well-defined structures than dendrimers.[4] As early as 1952, Flory reported a statistical treatment of hyperbranched polymers as a special case of his general treatment of network formation.[6] Despite this early theoretical interest, actual examples of hyperbranched polymers did not become widely available until the late 1980s when the term hyperbranched polymer appears to have originated with workers at Du Pont.[7] Recent advances in dendrimer research have engendered the current interest in the synthesis and properties of hyperbranched polymers. The synthesis of polymers that possess the unique properties associated with dendritic architectures, but at the same time are made by relatively straightforward single-step reactions, is an attractive target for research.

Although the work reported in this thesis deals specifically with the synthesis and characterisation of hyperbranched polymers it is useful to consider this in the wider context of the field of dendritic macromolecules. Hyperbranched polymers share many features with dendrimers and hence a description of the structure and properties of these well-defined materials is a useful starting point, which provides essential background information for the following discussion. After a brief description of the synthesis and properties of dendrimers, the theoretical and practical aspects of hyperbranched polymer synthesis will be described in some detail. Finally the background and aims of this project, together with a brief description of hyperbranched polyesters, will be described.

1.2 Dendrimers.

Dendrimers are highly branched polymers with tree like structures in which each repeat unit contains a branch junction, all non terminal units are fully branched and the molecule possesses a large number of identical chain ends.[3c] The principal features of a dendrimer are illustrated in the two-dimensional representation below (Figure 1.1).

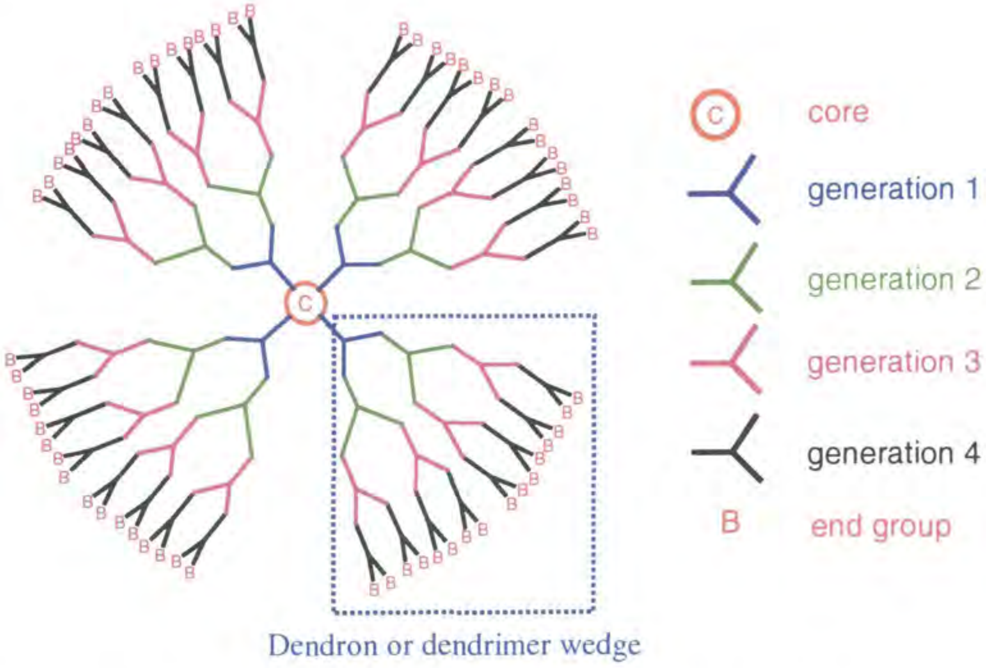


Figure 1.1 Schematic representation of a four-directional dendrimer assembled from AB_2 monomers plus a B_4 core.

A dendrimer molecule possesses a number of arms, often termed dendrons[3c] (or dendrimer 'wedges'),[3b] that branch out from a central core. The number of dendrons in a particular dendrimer molecule depends upon the functionality of the core molecule and is often described by the concept of *directionality.*[3b] A core with four reaction sites will grow in four directions, whereas a core or starting monomer with a single reactive site will grow in only one direction. The core moiety of a uni-directional dendrimer or the tip of a dendrimer 'wedge' or dendron is often termed the focal point group.[3c]

The structural units of a dendrimer are arrayed in a number of layers, termed generations, which are related to the number of iterations required to build the dendrimer. Each terminal group of the outermost generation possesses unreacted functionalities that give the dendrimer its characteristically large number of end groups.

Vögtle first reported the preparation and characterisation of structures with branched topologies via an iterative methodology subsequently termed cascade synthesis (Figure1.2).[8] Dendritic polyamines were prepared by Michael addition of an amine to acrylonitrile, which resulted in the attachment of two branches to each amine group. Subsequent reduction of the nitrile moities reintroduced amine functionalities into the structure and allowed the process to be repeated.

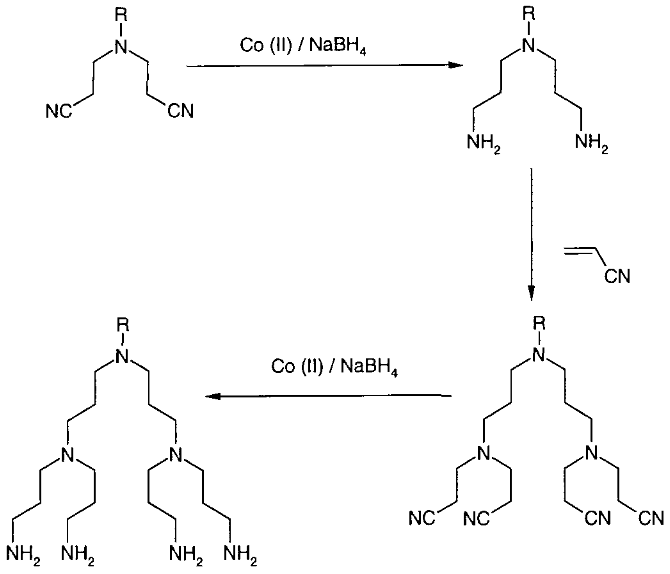


Figure 1.2 Preparation of dendritic polyamines via cascade synthesis.

The growth of this particular cascade molecule was originally limited due to problems associated with the nitrile reduction and the successful synthesis of a regular dendritic structure was not published until the mid 1980s when Tomalia reported the synthesis of dendritic poly(amidoamines) (PAMAMs). These were termed *starburst dendrimers* due to their branched (*dendritic*; Greek for tree-like) as well as oligomeric nature.[9]

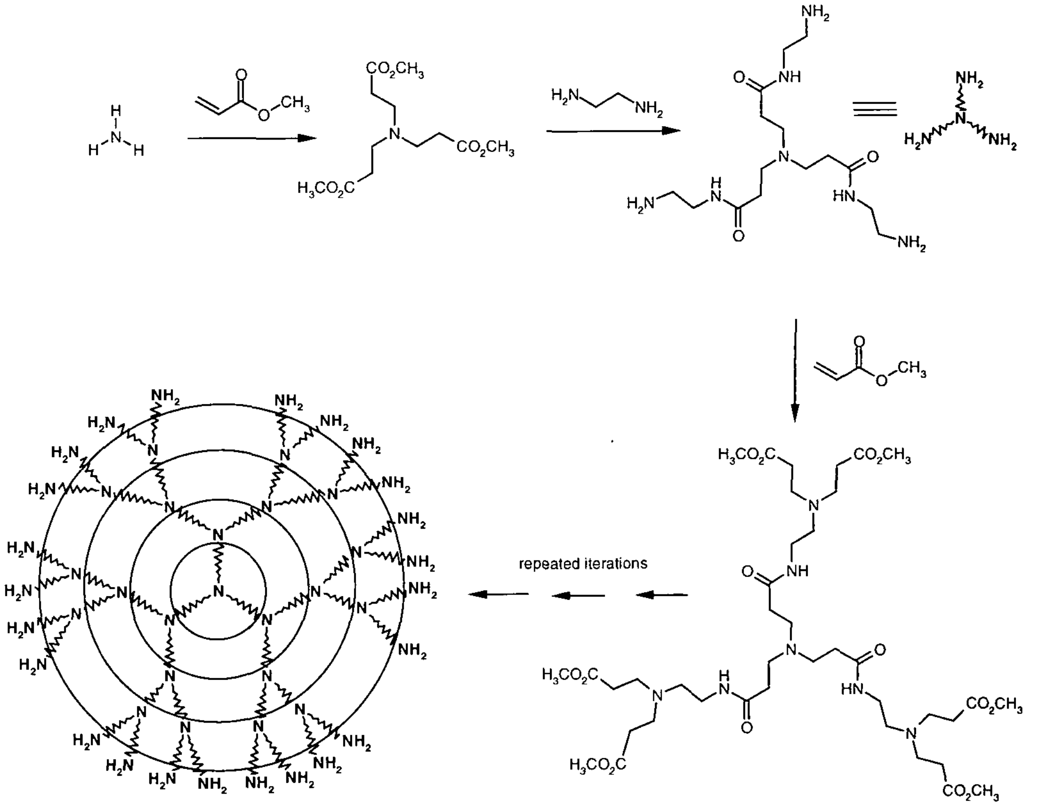


Figure 1.3 Synthesis of poly(amidoamine) starburst dendrimers.

This first successful approach was similar to Vögtle's cascade synthesis and employed a Michael addition of an amine to methyl acrylate as the means of introducing branching. Reintroducing the amine functionalities by amidation of the resulting esters with 1,2-diaminoethane circumvented the problems associated with a reduction step (Figure 1.3). Concurrent with this report Newkome and co-workers reported the synthesis of a series of dendritic poly(ether amides) terminated with hydroxymethyl groups. These highly branched alcohol bearing molecules were termed *arborols* (*arbor*: Latin for tree).[10]

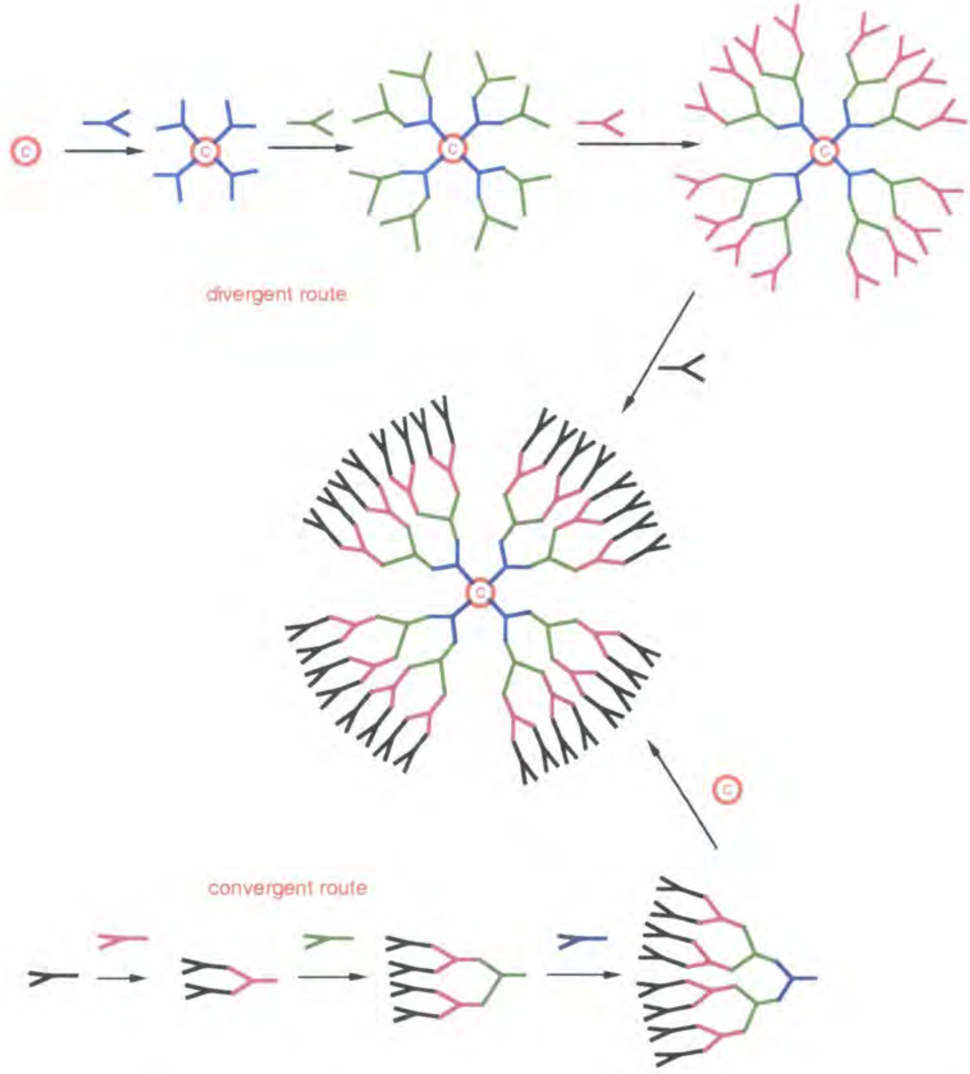


Figure 1.4 Divergent and convergent approaches to dendrimer synthesis.

The above syntheses of cascades, dendrimers and arborols are all examples of the *divergent* approach to the preparation of dendritic macromolecules. In this approach the dendrimer is grown outwards from a core molecule by successive additions of generations using iterative reaction sequences. An alternative approach is the *convergent* method, which involves creation of preformed dendrons. The convergent growth process begins at what will ultimately become the outer generation of the dendron, and growth proceeds inwards towards a focal group. Coupling of preformed dendrons to an appropriate core produces the target dendrimer (Figure 1.4). Fréchet and Hawker reported the first convergent synthesis based upon the pre-construction of polyether dendrons using 3,5-dihydroxybenzyl alcohol as the monomer unit (Figure 1.5).[11]

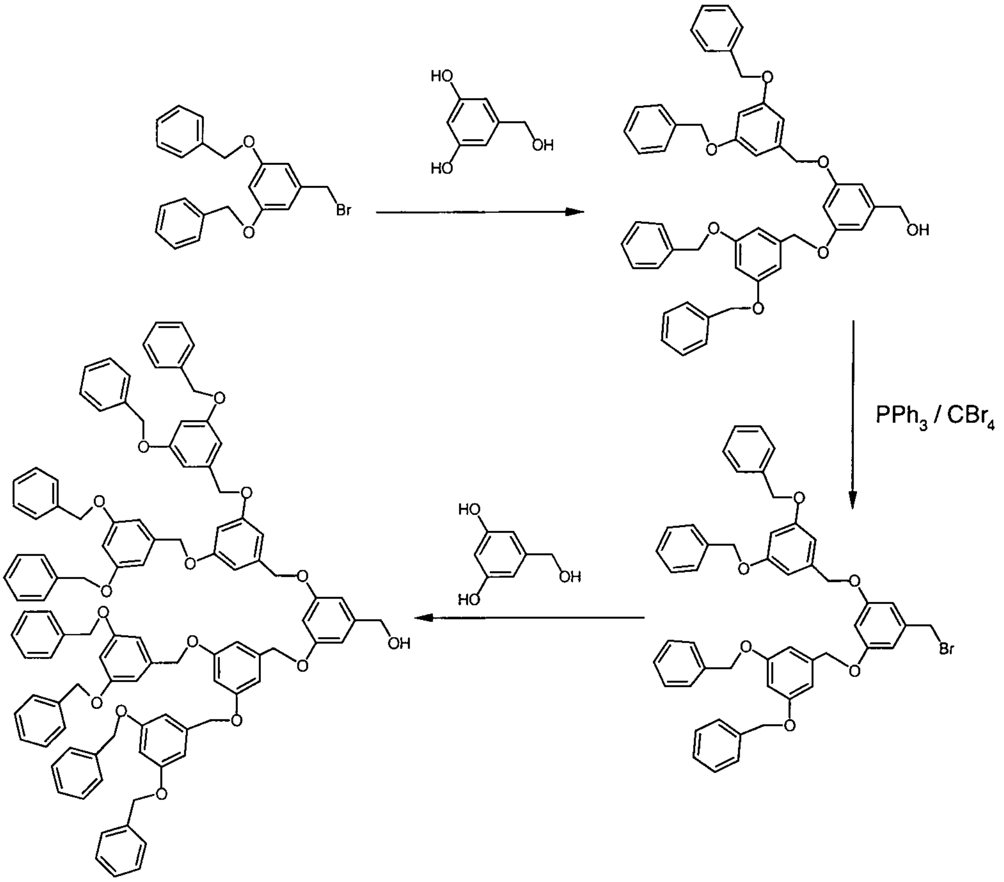


Figure 1.5 Convergent synthesis of polyether dendrons.

Preparation of the first generation dendron was started from the surface functional group, in this case a benzylic ether, by a selective Williamson ether synthesis involving reaction of a benzyl bromide with the phenolic groups of the monomer. The resulting hydroxymethyl focal group was then converted to a benzylic bromide, which was reacted with more monomer. Further dendron growth was continued by repetition of this two step alkylation / bromination procedure.

Since the early reports of Tomalia and Newkome a multitude of different dendrimer types have been presented in the literature including polyamidoamine,[12] poly(propylene imine),[13] aromatic polyethers[11] and polyesters[14], aliphatic polyethers[15] and polyesters[16], polyalkanes,[17] polyphenylene,[18] polysilane[19] and phosphorous dendrimers.[20]

1.3 Dendrimer properties.

Although the synthesis of dendritic macromolecules is well established the properties of these materials are not so well understood. Nevertheless, this is an active area of research and the number of studies examining the physical properties of dendrimers is increasing steadily. It is expected that the unique shape and chain end functionality of dendrimers will result in properties very different from those of classical linear polymers.[3c] An example of how the topology of dendrimers affects their properties is afforded by the concepts of starburst dense packing and topological trapping by shell molecules. Maciejewski discussed this in a theoretical paper as early as 1982, before synthetic examples of dendritic macromolecules were widely available.[21] The concept is based upon the premise that the number of monomer units in a dendrimer increases exponentially as a function of generation, while the volume of the sphere conformationally available to them only increases with the cube of generation. Beyond a certain generation the dendrimer cannot grow due to lack of available space and the steric crowding of branches at the surface of the molecule causes the dendrimer to adopt a globular shape.[3d] The branch ends may lie on the surface of the dendrimer or be distributed in the interior depending upon such factors as the dendrimer's constitution and the nature of the solvent. Modelling studies suggest that when the branch ends are located at the surface the dendrimer contains channels and cavities which may be used to entrap guest molecules.[22] The ability to act as a host for guest molecules has been demonstrated for a number of dendrimers that have been termed unimolecular micelles.[23] Meijer and co-workers reported an elegant demonstration of dendritic host-guest behaviour utilising the concept of the dendritic box.[24] A dense hydrogen bonded shell consisting of L-phenylalanine derivatives was added to the outermost generation of a flexible poly(propylene imine) dendrimer bearing 64 amine end groups. By adding the shell in the presence of a potential guest molecule, such as the dye Bengal Rose, the guest molecule became trapped inside the cavities of the host dendrimer. Host-guest behaviour has also been reported for hyperbranched polyphenylenes (hyperbranched polymers are described in detail in a later section).[25]

The solution properties of dendrimers have been studied in the greatest detail. A characteristic of dendrimers is their enhanced solubility when compared to analogous linear polymers, which has been attributed to both the branched architecture and the contribution of the many solubilising end groups.[3c] For example, Miller and Neenan reported the solubility of a dendritic poly(phenylene) composed of 46 benzene units as 190 g/L in toluene, which is many orders of magnitude greater than the solubility of the linear oligomer *p*-quinqaphenyl at <0.005g/L.[26]

Dendritic macromolecules generally have low solution viscosities and the relationship between molecular weight and intrinsic viscosity has been identified as a characteristic feature of some dendritic polymers.

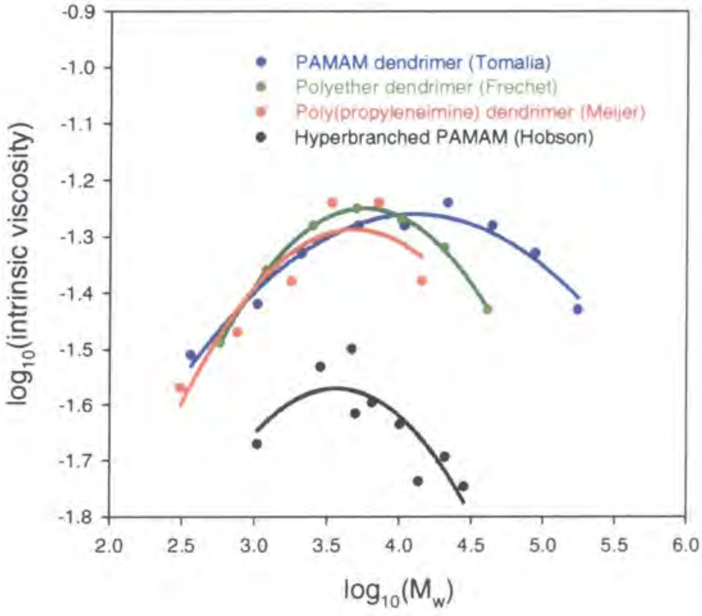


Figure 1.6 Characteristic solution vicosity behaviour of some dendritic polymers.

Dendrimers have been shown to exhibit a maximum of intrinsic viscosity ([η]) as a function of molecular weight. This has been demonstrated for PAMAMs,[27] polyethers,[28] and poly(propyleneimine)s[29] (Figure 1.6). This is in contrast to linear polymers which exhibit increasing intrinsic viscosities as a function of molecular weight (intrinsic viscosity is discussed in chapter 3). Although this behaviour has been said to be a characteristic signature of dendrimers, hyperbranched PAMAMs have been shown to exhibit decreasing viscosity as a function of molecular weight and core terminated hyperbranched PAMAMs also exhibit a maximum in the viscosity profile similar to dendrimers.[30]

1.4 Accelerated syntheses.

Although the unusual properties of dendrimers make them attractive targets for synthesis their production on a large scale has proved problematic. Dendrimer syntheses are iterative processes and often involve protection / deprotection strategies. Many reactions and associated purification steps are required to obtain high generation dendrimers resulting in labour intensive, low yield processes.[3c] Consequently relatively few dendrimers have been made on a commercial scale. Astramol™ [poly(propyleneimine)] dendrimers are marketed by DSM and are produced on an industrial scale using an improved method based upon Vögtle's original cascade synthesis. Starburst™ poly(amidoamine)s are marketed by Dendritech and dendritic polyols are sold by Perstorp under the trade name Boltorn®.

Several methodologies have been developed to decrease the number of isolation and purification steps in dendrimer syntheses with the aim of accelerating dendrimer growth. Fréchet and co-workers reported a double-stage convergent synthesis, which uses the concept of a hypercore.[31] This technique employs a dendrimer as a core to which preformed dendrons are coupled in order to access higher generation dendrimers (Figure 1.7).

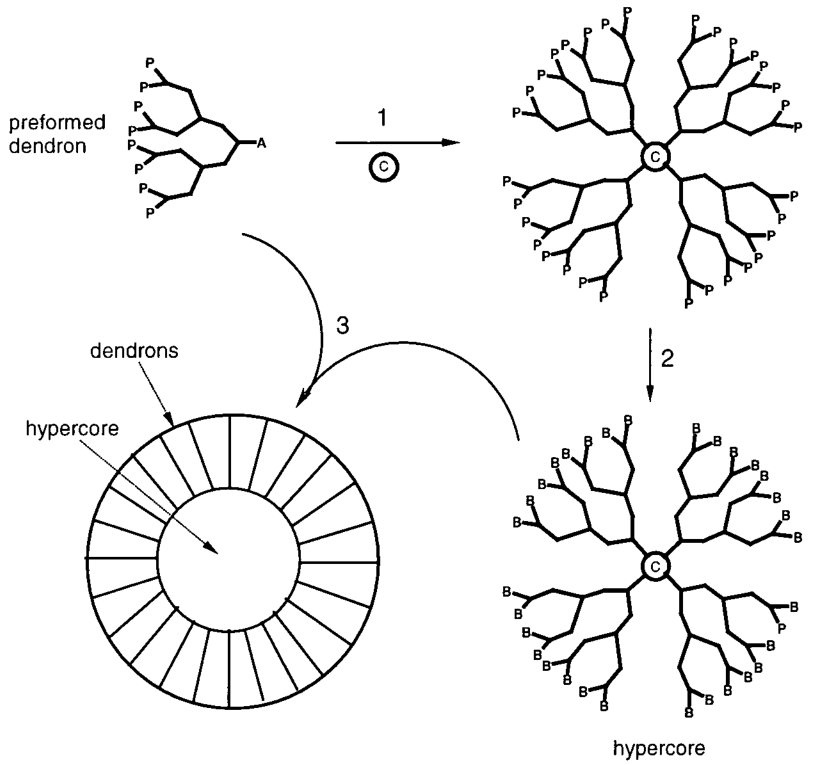


Figure 1.7 Schematic representation of double-stage convergent synthesis.

Preformed branched monomers or hypermonomers have also been used in the synthesis of dendrimers.[32] In this concept the simplest repeating unit or fractal component used in the convergent growth approach is replaced by a larger fractal component of the next generation. For example, an AB_2 monomer is replaced by the next generation AB_4 monomer enabling the generation number to be increased by two in a single coupling step (Figure 1.8).

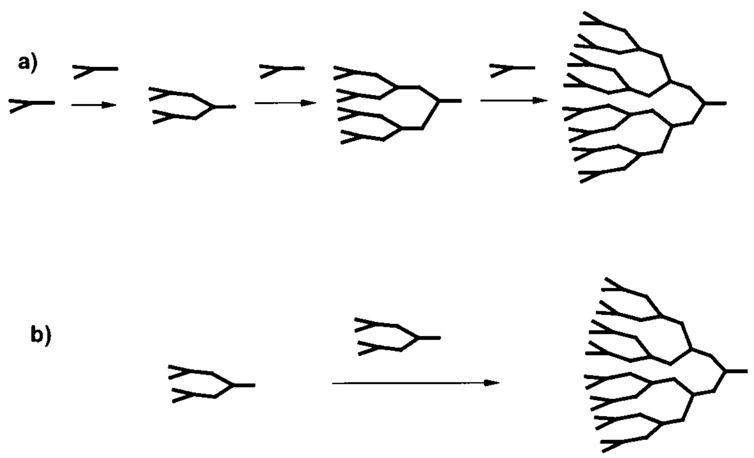
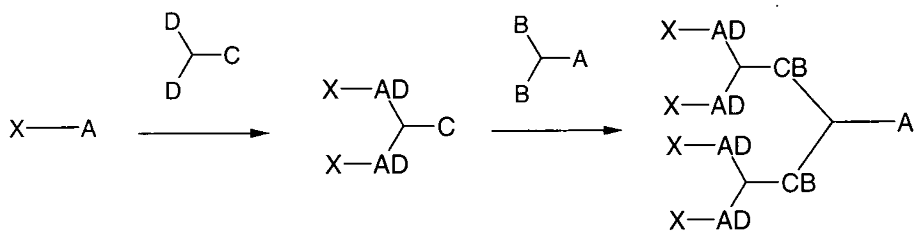


Figure 1.8 Schematic representation of dendron synthesis using a) convergent approach and b) a hypermonomer.

A novel 'two-step' approach to dendrimer synthesis was reported by Spindler and Fréchet[33] and subsequently termed orthoganol coupling by Zimmerman.[34] This method eliminates the need for activation or protection between growth steps by the sequential use of two different monomers. The two monomers are of AB_2 and CD_2 type, where A and D react together to form a bond under conditions where B and C are stable, and B and C react to form a bond under conditions where A and D are stable (Figure 1.9).



X is a surface group. A, B, C and D are reactive functional groups. A and D groups react together as do C and B groups.

Figure 1.9 Schematic representation of convergent synthesis using orthogonal coupling.

A further example of accelerated growth methods is the concept of double exponential growth.[35] This technique uses an AB_2 monomer in which the functional groups A and B are both protected. The monomer is selectively deprotected, in separate reactions, to give a convergent type monomer with a reactive focal group (A) but protected surface groups (B) plus a divergent type monomer with a protected focal group and reactive surface groups. The two types of monomer are reacted together to give an orthogonally protected trimer which may be used to repeat the process (Figure 1.10).

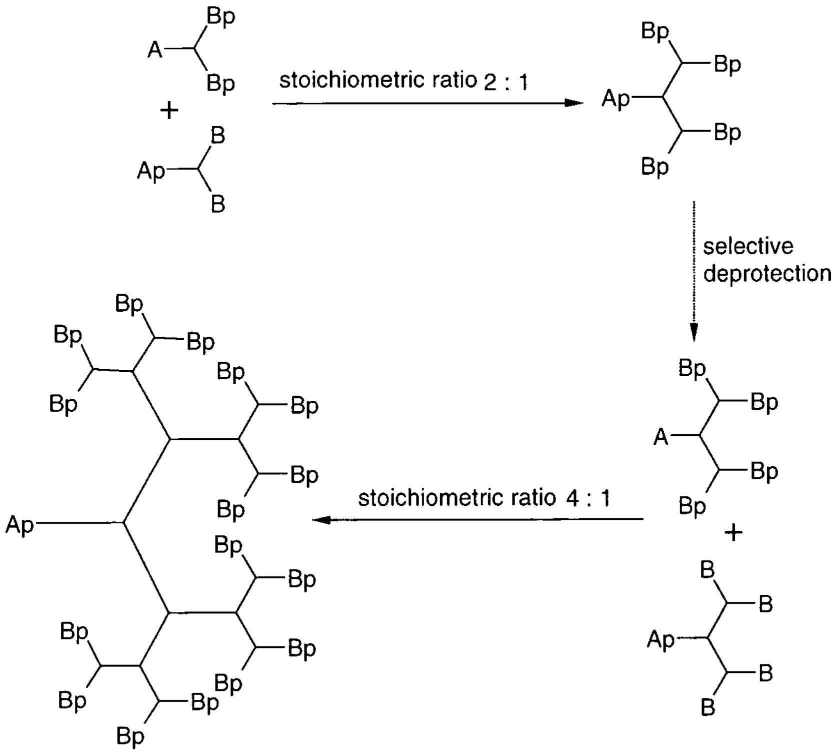


Figure 1.10 Schematic representation of double exponential growth.

In this methodology the growing dendron is used as both the starting dendron and monomer for the next generation. Conventional dendrimer synthesis, in which generations are added layer by layer, gives an exponential increase in the degree of polymerisation (dp) with increasing generation number (Equation 1.1). The accelerated growth technique outlined above results in a much faster increase in dp, which can be described as double exponential (Equation 1.2).

Equation 1.1

(Conventional dendrimer growth - exponential).

$$dp = 2^{(g+1)} - 1$$

Equation 1.2

(Double exponential growth.)

$$dp = 2^{2^{g}} - 1$$

Growth of AB_2 based dendrimers, where dp is the degree of polymerisation and g the generation number.

Although the various accelerated growth techniques are potentially powerful tools for dendrimer synthesis they are all multi-step processes, with all the disadvantages that such a method entails. Much recent interest has focussed upon the synthesis of dendritic macromolecules via single step one-pot reactions. Dendritic macromolecules produced by such a method are known as hyperbranched polymers.

1.5 Hyperbranched polymers.

Since the early 1990s there has been an increasing number of reports concerning the synthesis of hyperbranched polymers, motivated by the interest in dendritic macromolecules and their properties. These are polymers constructed from AB_x monomers, as are dendrimers, but polymerised in one-pot reactions without recourse to the iterative reaction schemes associated with dendrimer synthesis. These polymers have many similarities to dendrimers, such as high degrees of branching and large numbers of end groups, but are irregular polydisperse systems (Figure 1.11).

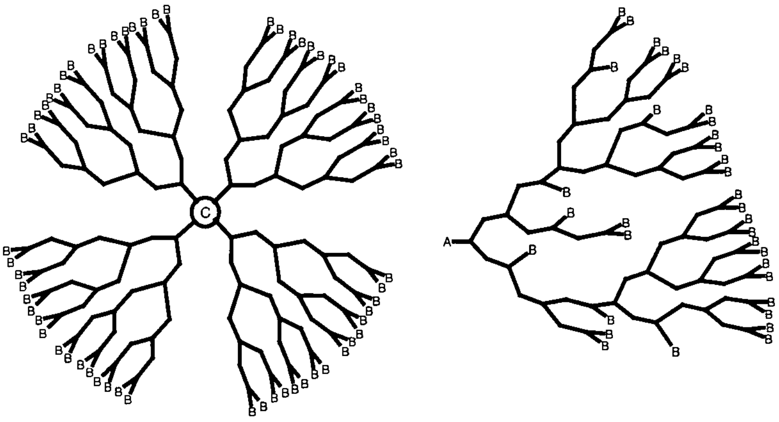


Figure 1.11 A comparison of dendritic and hyperbranched structures.

Early examples of polymers prepared from AB_x type monomers predate the interest in dendrimer synthesis, for example the polymerisation of 9,10-dihydroxystearic acid was reported in 1960, however systematic studies of hyperbranched polymers did not appear until much later.[36] The term hyperbranched polymer appears to have originated with research carried out by workers at Dupont,[7] which led to the report of the first concerted attempt to produce dendritic macromolecules, via a one-pot polymerisation of AB_x monomers, by Kim and Webster.[25, 37] This involved a palladium catalysed coupling of 3,5-dibromophenylboronic acid to give hyperbranched polyphenylenes (Figure 1.12).

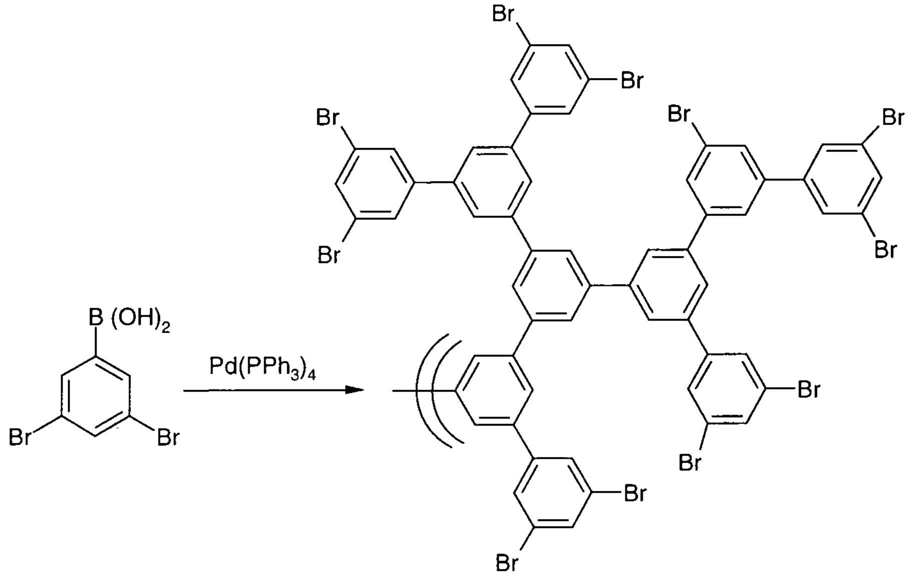


Figure 1.12 Synthesis of hyperbranched polyphenylenes.

A large number of publications concerning the synthesis of hyperbranched polymers have appeared since these initial reports and cover a large variety of different polymer systems. A detailed survey of hyperbranched polymers is outside the scope of this work and the reader is directed to several comprehensive reviews.[3c, 5, 25] However, a detailed description of hyperbranched polyesters will be presented in a later section together with the background to this project. In lieu of a more comprehensive review a survey of the synthesis of hyperbranched polymers, categorised by polymerisation type, is presented below.

Carothers originally classified polymers, in 1929, into condensation and addition polymers on the basis of the compositional difference between the polymer and the monomer from which it was synthesised.[38] Condensation polymers were defined as those formed from polyfunctional monomers by reactions involving the loss of a small molecule, such as water, at each step. Conversely addition polymers were those formed without such a loss. Since then polymers have been classified, according to the mechanism of the polymerisation reaction, as step-growth or chain-growth. Replacing the term condensation by step-growth allows the inclusion of polymers such as polyurethanes, which grow by a step mechanism without elimination of a small molecule (Figure 1.13).[39]

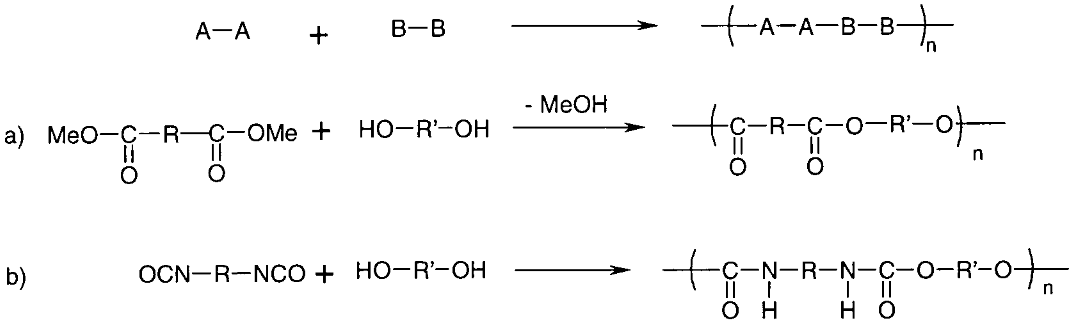


Figure 1.13 Step-growth polymerisation: a) formation of polyester with loss of methanol, b) formation of polyurethane without loss of condensate.

Step polymerisations proceed by the stepwise reaction of monomers with either other monomers or higher oligomers and also reactions between the various oligomeric species.

Addition or chain growth polymerisation requires an initiator from which is produced an initiator species R* with a reactive centre which may be a free radical, cation or anion. Polymerisation occurs by the propagation of the reactive centre by the successive addition of monomer molecules in a chain reaction. Monomer can only react with the propagating species and not other monomer units. The growth of the polymer chain ceases when the reactive centre is destroyed by one of a number of possible termination reactions. The most common example of chain growth polymerisations is the polymerisation of vinyl monomers (Figure 1.14).

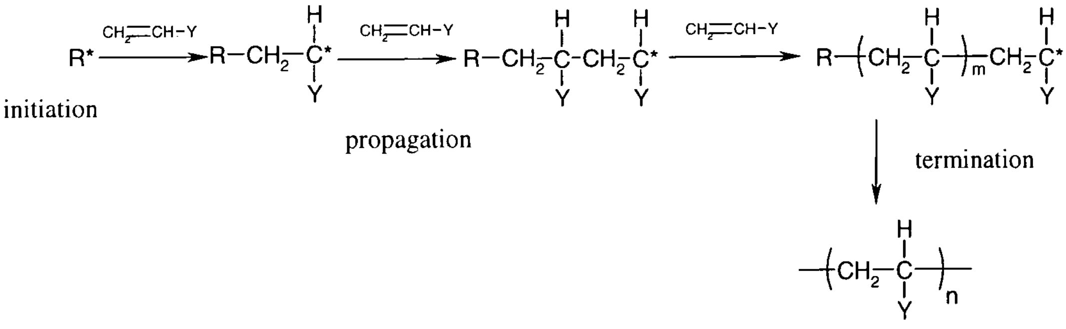
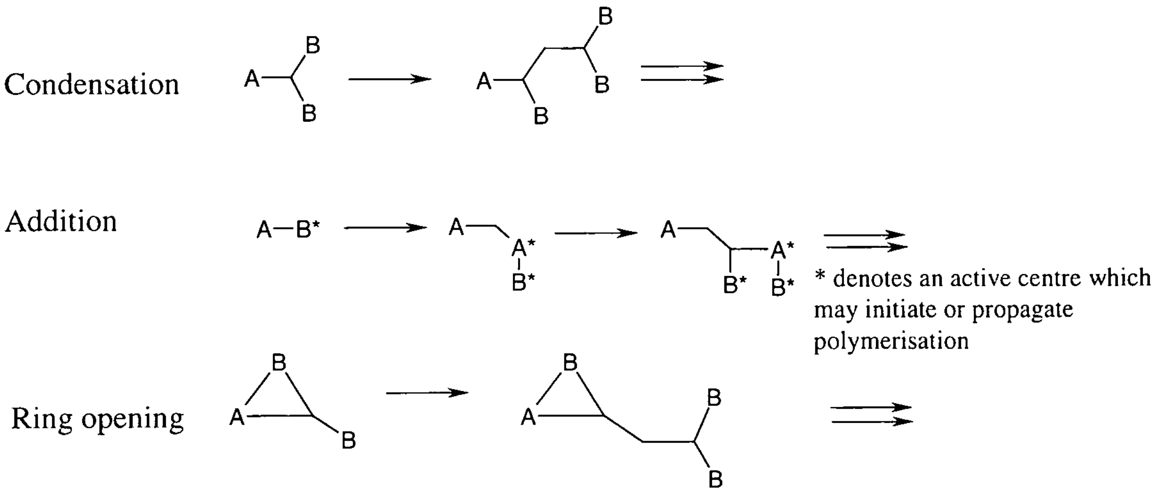


Figure 1.14 Chain-growth polymerisation of vinyl monomers.

Hyperbranched polymers are made via step-growth polymerisations although self condensing vinyl polymerisation, which is described more fully below, is a special case featuring some of the characteristics of both step-growth and addition polymerisation.

There are currently three strategies commonly employed for the synthesis of hyperbranched polymers. These have been categorised as condensation, addition and ring opening polymerisation and are illustrated schematically below (Figure 1.15).[7]



* denotes an active centre which may initiate or propagate polymerisation

Figure 1.15 Comparison of different routes to hyperbranched polymers.

To date the majority of hyperbranched polymers have been made using step growth polycondensation reactions. These employ monomers of AB_x type, where A and B represent two different functional groups and x is the number of B groups in the monomer. Polymerisation proceeds by the reaction of an A unit with a B group from a different molecule. A prerequisite of this type of reaction is that the A and B groups only react in the polymerisation reaction, often facilitated by the action of a catalyst or the application of a suitable activation step (e.g. thermal activation).

A typical example of an AB_x type condensation reaction is the preparation of hyperbranched polyethers using Williamson ether synthesis (Figure 1.16).[40] This is analogous to the polyether dendrimer synthesis described earlier and employs a benzylic bromide as the A group and phenolic B groups. The reaction is carried out in the presence of K_2CO_3 and a crown ether and proceeds with the loss of HBr.

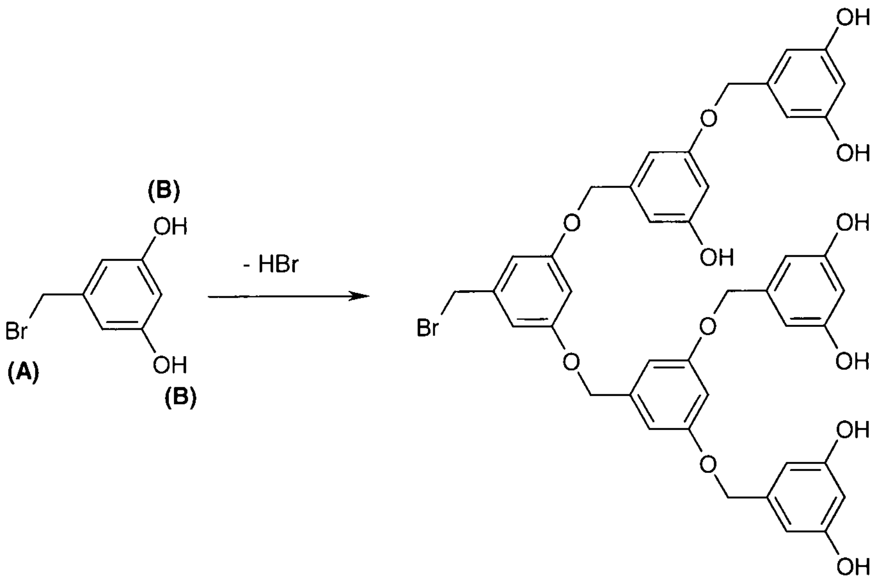


Figure 1.16 Synthesis of hyperbranched polyethers via polycondensation.

An example of a step-growth polymerisation of an AB_2 monomer, without concomitant loss of condensate, is the synthesis of a hyperbranched poly(amidoamine) from N-acryloyl-1,2-diaminoethane hydrochloride (Figure 1.17).[30b] The polymerisation proceeds via a Michael addition in which the A group is the acrylamide double bond and the B groups are the N-H bonds of the terminal amine. The resulting polymer is a hyperbranched equivalent of Tomalia's PAMAM dendrimers.

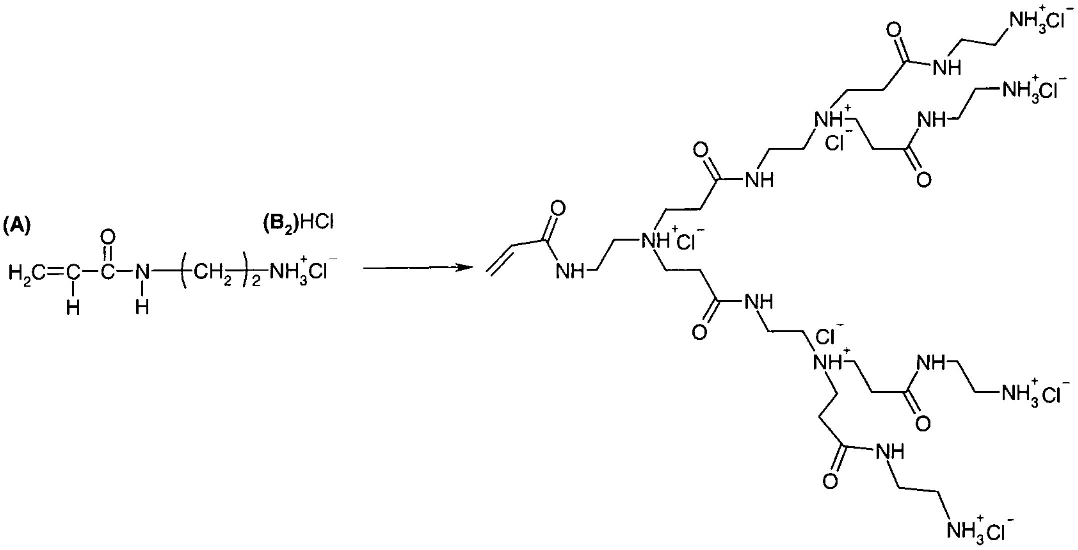


Figure 1.17 Synthesis of hyperbranched PAMAM by a step-growth mechanism without loss of condensate (Michael addition).

A wide variety of hyperbranched polymers have been prepared by step-growth polycondensation and include polyphenylenes[37], polyesters[59-69], poly(ester-amides) [41], polyamides[42], polycarbonates[43], polyurethanes[44], poly(siloxysilanes)[45a,45b] and polycarbosilanes[45b].

The majority of hyperbranched polymers reported are based upon AB$_2$ monomers. These are conceptually the simplest monomer types to yield hyperbranched polymers, although there are an increasing number of reports describing the polymerisation of higher functionality monomers. Hyperbranched polyesteramides, for example, have been synthesised from an AB$_4$ monomer.[41] A variety of AB$_x$ systems using the hydrosilation reaction have been studied. These employ monomers containing a single alkene functionality plus two or more SiH bonds and examples of AB$_2$, AB$_3$, AB$_4$ and AB$_6$ type have been reported (Figure 1.18).[45]

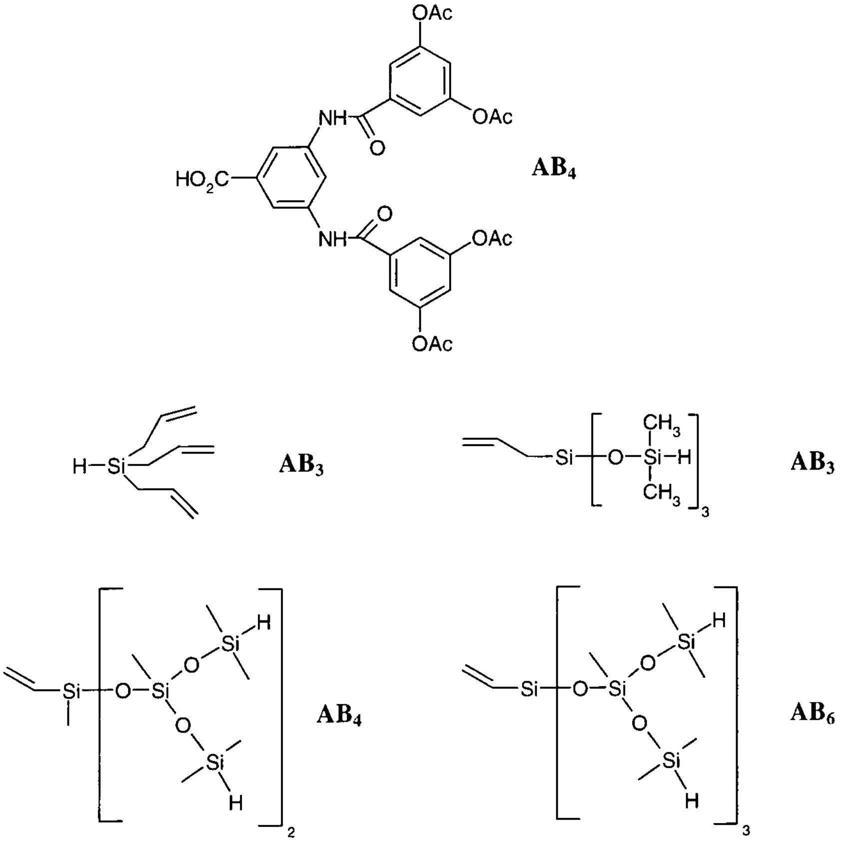


Figure 1.18 Examples of higher functionality AB$_x$ monomers.

Higher functionality monomers (AB_4) have been used as a means of achieving accelerated growth in hyperbranched syntheses and are analogous to the hypermonomers used in dendrimer synthesis discussed earlier. For example, Malmström and co-workers replaced the AB_2 monomer 2,2-dimethylolpropionic acid with its first generation AB_4 equivalent in an attempt to accelerate polymer growth and influence branching (Figure 1.19).[46] A similar technique was employed by Hawker and co-workers in a study of the degree of branching in hyperbranched poly(etherketones) (described in chapter 5).[47]

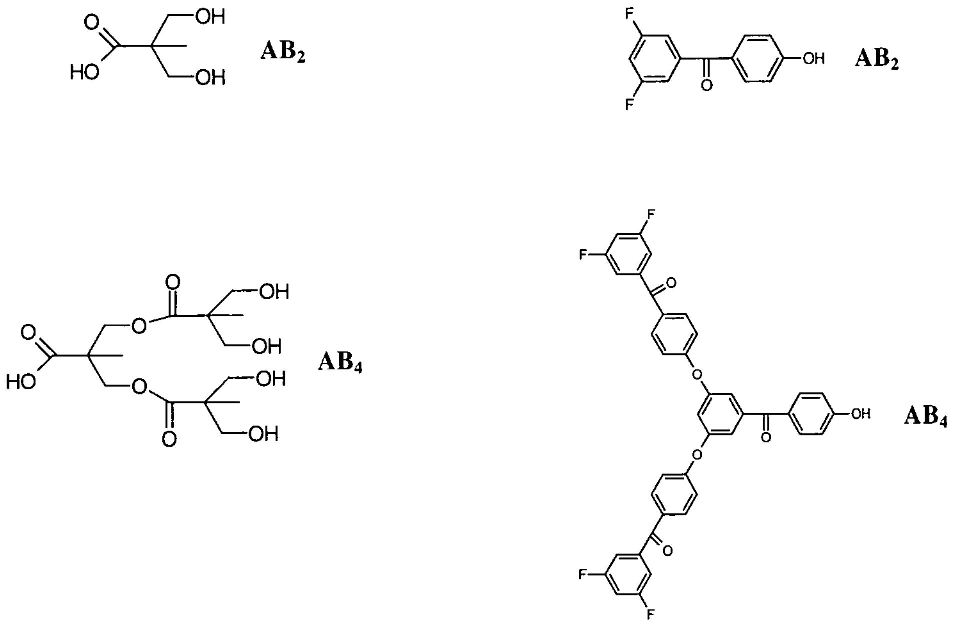


Figure 1.19 Examples of AB_4 hypermonomers used in hyperbranched polymerisations.

Although most hyperbranched polymers have been made using polycondensation, Fréchet and co-workers reported a versatile approach to the synthesis of hyperbranched polymers from vinyl monomers, which they termed self-condensing vinyl polymerisation (SCVP).[48] This type of reaction involves an AB vinyl monomer in which the A group is the double bond and the B group a species that may be converted by some means to give an activated species (B*) which itself is capable of initiating the polymerisation of a vinyl monomer. Molecules of this type that simultaneously act as a monomer and initiator have been termed *inimers*.[49] The polymerisation process is initiated by reaction of one initiating B* group with the A group (double bond) of another AB* monomer unit thereby creating a dimer with a new reactive centre capable of propagation. The dimer is effectively an AB_2 type monomer as it possesses one polymerisable double bond, one initiating centre and one propagating centre (Figure 1.20). Subsequent additions give oligomeric species that may react with other oligomers or more monomer to give a hyperbranched polymer.

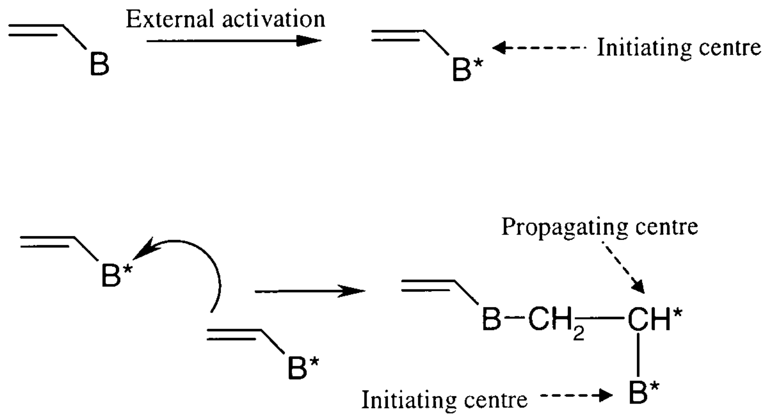


Figure 1.20 Schematic representation of self-condensing vinyl polymerisation.

The polymerisation is a hybrid of classical polycondensation and vinyl polymerisation as it operates by the repeated stepwise coupling of monomer and oligomers using steps typically observed in vinyl polymerisations. The technique of SCVP was first demonstrated by the $SnCl_4$ activated cationic polymerisation of 3-(1-chloroethyl)ethenylbenzene (Figure 1.21).[48]

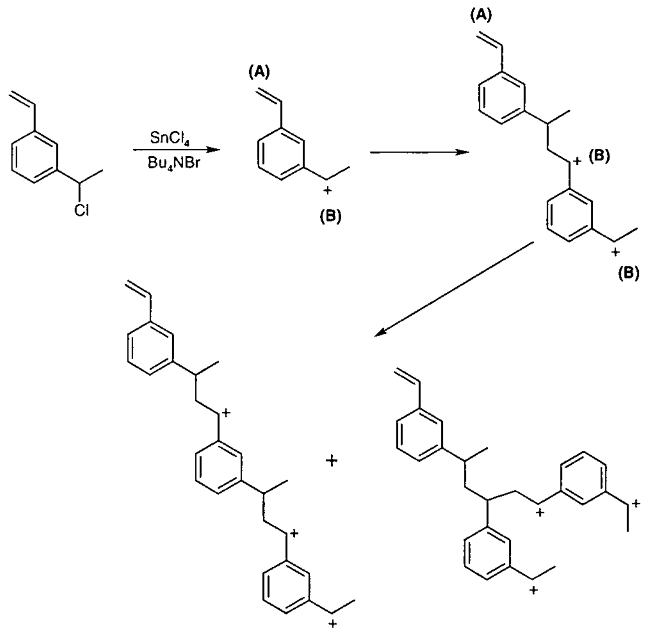


Figure 1.21 Self-condensing vinyl polymerisation (SCVP) of 3-(1-chloroethyl)-ethenylbenzene.

Subsequently, the method has been extended by the application of techniques associated with the field of 'living' free radical polymerisation. Hawker and co-workers reported the use of (2,2,6,6-tetramethylpiperidinyloxy)-based initiators (TEMPO) in the synthesis of hyperbranched polymers by a SCVP route.[50] The mechanism of such a nitroxide mediated 'living' free radical polymerisation is shown below (Figure 1.22). The carbon-oxygen bond of the alkoxyamine undergoes thermal fragmentation to give a stable nitroxide and a polymeric radical. The polymeric radical undergoes monomer insertion and chain extension to give a polymeric radical in which the degree of polymerisation has increased. The nitroxide free radical does not initiate the growth of further polymer chains but does react with carbon centred radicals so that recombination with the polymeric radical yields an inactive chain end. Polymerisation proceeds by the repeated cycle of homolysis, monomer addition and recombination. A consequence of the presence of significant amounts of inactive chain ends is that the concentration of radicals is decreased leading to a lower occurrence of unwanted side reactions such as termination, disproportionation or combination. This enables the polymer to grow in a controlled living-like process.

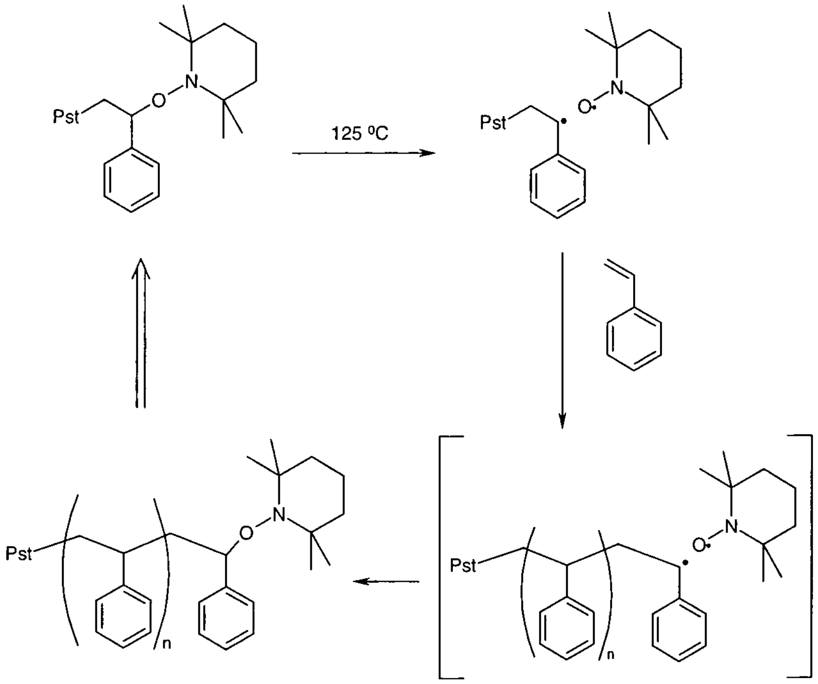


Figure 1.22 The mechanism of TEMPO mediated vinyl polymerisation.

When applied to the synthesis of hyperbranched polymers by SCVP the monomer includes both a polymerisable styrene group and an initiating / propagating moiety in the form of a nitroxide linked to a benzylic carbon atom (Figure 1.23). Thermolysis of the monomer leads to a propagating benzylic radical that can add to the vinyl group of another monomer unit. After recombination with a nitroxide radical the newly created dimer is essentially an AB_2 unit containing one double bond and two initiating / propagating sites. Further additions of monomer or oligomer leads to the formation of hyperbranched polymer.

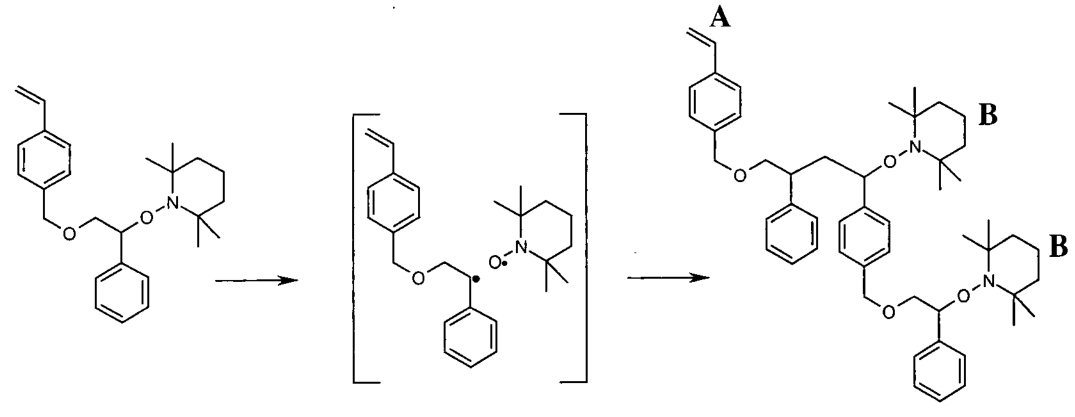


Figure 1.23 The formation of an AB_2 monomer in TEMPO mediated self-condensing vinyl polymerisation.

Other research groups have used the technique of atom transfer radical polymerisation (ATRP) in self-condensing vinyl type systems to give hyperbranched polystyrenes,[51] polyacrylates[52] and polyacrylamides.[53] The method typically employs the reversible reaction of a soluble Cu(I) complex with a benzylic halide to form a Cu(II) halide and a benzyl radical capable of initiating vinyl polymerisation.

Relatively few examples of hyperbranched polymers made via ring opening polymerisation have been reported. Suzuki and co-workers used the ring opening of cyclic carbamates to synthesise hyperbranched polyamines, which they termed multibranching polymerisation.[54] More recently, Frey and co-workers used ring opening multi-branching polymerisation (ROMBP) to prepare hyperbranched polyglycerols from glycidol (Figure 1.24).[55]

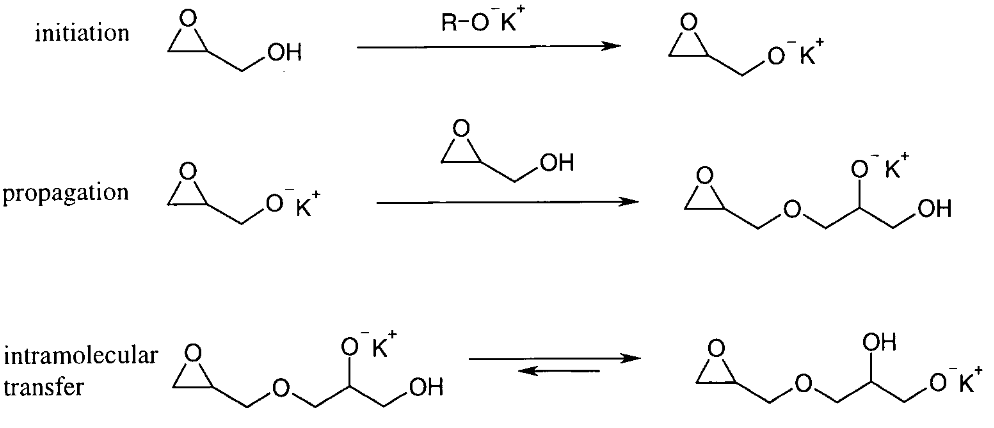


Figure 1.24 Mechanism of ring opening multibranching polymerisation (ROMBP) of glycidol.

This was an anionic polymerisation using an alkoxide initiator. The alkoxide deprotonates the hydroxyl group of a glycidol molecule to give the propagating alkoxide. This reacts with the epoxide ring of another glycidol molecule yielding a secondary alkoxide. The newly formed alkoxide can interchange with the primary alcohol to give two possible propagation sites and so introduce branching.

Voit and co-workers have reported a nucleophilic ROMBP of a 2-oxazoline derivative, which yields a hyperbranched poly(ether amide)[56], whilst Hult and co-workers have reported the cationic ROMBP of 3-ethyl-3(hydroxymethyl)oxetane, which yields a hydroxy terminated hyperbranched polyether.[57]

1.6 Hyperbranched polymers – theoretical aspects.

Structurally hyperbranched polymers have many similarities to dendrimers. Both classes of dendritic macromolecule are based upon AB_x type monomers, are highly branched and possess many end groups. However, hyperbranched polymers also have some important differences from dendrimers that may be expected to be manifest as a difference in polymer properties. A perfect dendrimer, based upon an AB_x monomer and synthesised using a divergent methodology, has a regular branched structure consisting of generations of fully branched units assembled around a central core and terminating in a layer of unreacted B groups. In contrast, the analogous hyperbranched polymer has an irregular structure that may contain some linear units that possess unreacted B functionalities (Figure 1.25). A dendrimer, by definition, is fully branched but the amount of branching in hyperbranched polymers varies between polymer systems (a detailed discussion of branching will be included in chapter 5).

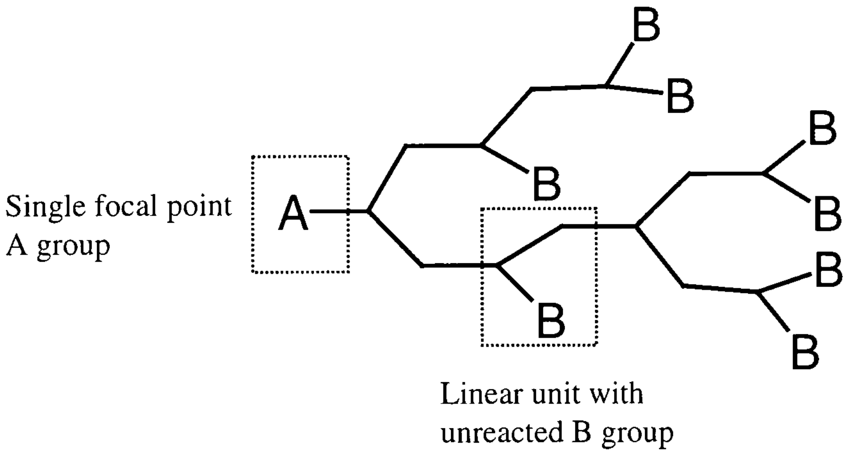


Figure 1.25 Schematic representation of a hyperbranched *7-mer*, based upon AB_2 units.

A hyperbranched polymer is similar to a dendrimer wedge or dendron in that, if intramolecular reactions are excluded from the polymerisation process, it possesses a single unreacted focal point A group. If an intramolecular reaction occurs between the A group and one of the many B groups in the same molecule then a cyclic species is produced and the molecule has no unreacted A groups remaining. Another important feature of hyperbranched polymers is that, unlike dendrimers, they are polydisperse systems. Hyperbranched polymers not only have broad molecular weight distributions, in common with conventional step growth polymerisations, but are also expected to have a distribution in size and shape for molecules of the same degree of polymerisation. This is an inevitable consequence of the many different ways in which a particular oligomer may be assembled from AB_x units. For example a tetramer may be assembled in 7 different ways from AB_2 units, if the B groups are regarded as indistinguishable, as represented below (Figure 1.26).

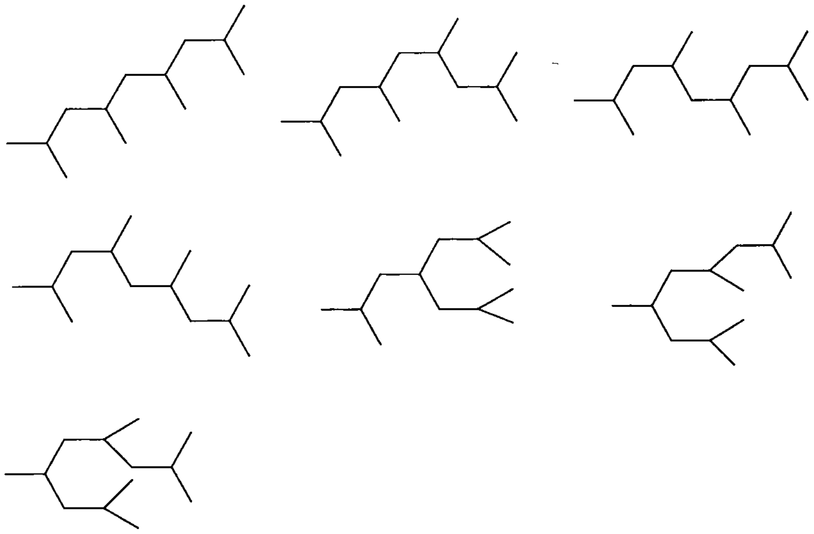


Figure 1.26 Structural possibilities for assembling a *tetramer* from AB_2 units (Note there are actually 14 ways to assemble a *tetramer* if the B groups are considered distinguishable as defined by Flory and described below).

Although interest in hyperbranched polymers is a relatively recent phenomenon, molecular distributions in polyfunctional condensations were first studied by Flory in the 1950s.[58] This was an aside to Flory's study of network formation and was considered as a special case of random branching without network formation. Flory considered the condensation of f-functional monomers of AB_{f-1} type, where A may condense with B but reactions between like functional groups and intramolecular reactions are forbidden. Furthermore, the reactivity of a given B group was considered to be independent of its position in the molecule. A given oligomer or x-meric species contains $(f-2)x + 1$ unreacted B groups and a single unreacted A group. The branching probability, α, was defined as the fraction of B groups reacted, p_B. If the extent of reaction (fraction of A groups reacted) is represented by p, then $\alpha = p/(f-1)$. If N is the number of molecules remaining at a given polymerisation time and N_0 is the number of monomer molecules at the start of the reaction, then the number of A groups that have reacted is given by $(N_0 - N)$. The extent of reaction, p, is then given by $(N_0 - N) / N_0$ and hence the total number of molecules is given by $N = N_0(1-p)$. The average degree of polymerisation, x_n, is defined as the total number of monomer residues divided by the number of molecules and can be related to the branching probability as shown below (Equation 1.3).

Equation 1.3 $$\bar{x}_n = \frac{N_0}{N} = \frac{N_0}{N_0(1-p)} = \frac{1}{(1-p)} = \frac{1}{[1-\alpha(f-1)]}$$

If the (f-1) B groups of the monomer are considered as distinguishable then the probability that an unreacted A group belongs to a specific structure equals the probability that a particular sequence of (x-1) B groups have reacted while the remaining (fx –2x +1) have not. This probability, P_x, is the same for each x-meric configuration and is shown below (Equation 1.4).

Equation 1.4 $$P_x = \alpha^{x-1}(1-\alpha)^{fx-2x+1}$$

The probability that an unreacted A group is attached to an x-mer of any structural configuration is given by the probability of a specific configuration multiplied by the number of possible configurations, ω_x, (Equation 1.5).

Equation 1.5 $$N_x = \omega_x \alpha^{x-1}(1-\alpha)^{fx-2x+1} \qquad \text{Where, } \omega_x = \frac{(fx-x)!}{(fx-2x+1)!x!}$$

Since each molecule bears a single A group, N_x is also the mole fraction of x-mer.

Flory also derived expressions for the weight fraction of x-mer, w_x, and the weight average degree of polymerisation, x_w. The weight fraction of x-mer is given by the weight of the x-mer divide by the weight of all x-mers and is related to the mole fraction of x-mer by the following expression (Equation 1.6).

Equation 1.6 $$w_x = \frac{xN_x}{\Sigma xN_x}$$

Similarly the weight average degree of polymerisation may be related to the mole fraction of x-mers by the following expression (Equation 1.7).

Equation 1.7 $$\bar{x}_w = \frac{\Sigma x^2 N_x}{\Sigma x N_x}$$

From the above expressions Flory derived expressions relating the weight fraction of x-mer and the weight average degree of polymerisation to the branching coefficient, α. Evaluation of the summations required for this is a complex problem and only the final expressions obtained are presented here (Equations 1.8 and 1.9).

Equation 1.8 $$\bar{x}_w = \frac{\sum x^2 N_x}{\sum x N_x} = \frac{\left(1-\alpha^2(f-1)\right)}{\left(1-\alpha(f-1)\right)^2}$$

Equation 1.9 $$w_x = \frac{xN_x}{\Sigma x N_x} = \left[\frac{(1-\alpha)}{\alpha}\right]\left[1-\alpha(f-1)\right]x\omega_x\beta^x$$

Where, ω_x is as defined in Equation 1.5 and $\beta = \alpha(1-\alpha)^{f-2}$

Finally by combining the expressions for number and weight average degree of polymerisation (Equations 1.3 and 1.9) the polydispersity, x_w/x_n, may be expressed as follows (Equation 1.10).

Equation 1.10 $$\frac{\bar{x}_w}{\bar{x}_n} = \frac{\left(1-\alpha^2(f-1)\right)}{\left(1-\alpha(f-1)\right)}$$

The mole fraction distribution and weight fraction distribution, for an AB_{f-1} polymer, may be calculated using equations 1.5 and 1.9 respectively and are shown below for the simple AB_2 case (Figures 1.27 and 1.28).

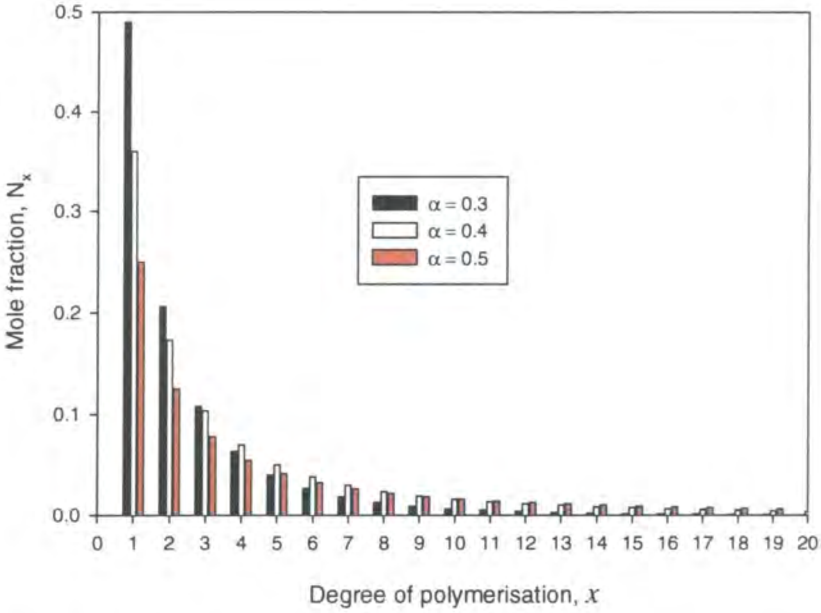


Figure 1.27 Theoretical mole fraction distribution for an AB$_2$ polymer at varying values of α.

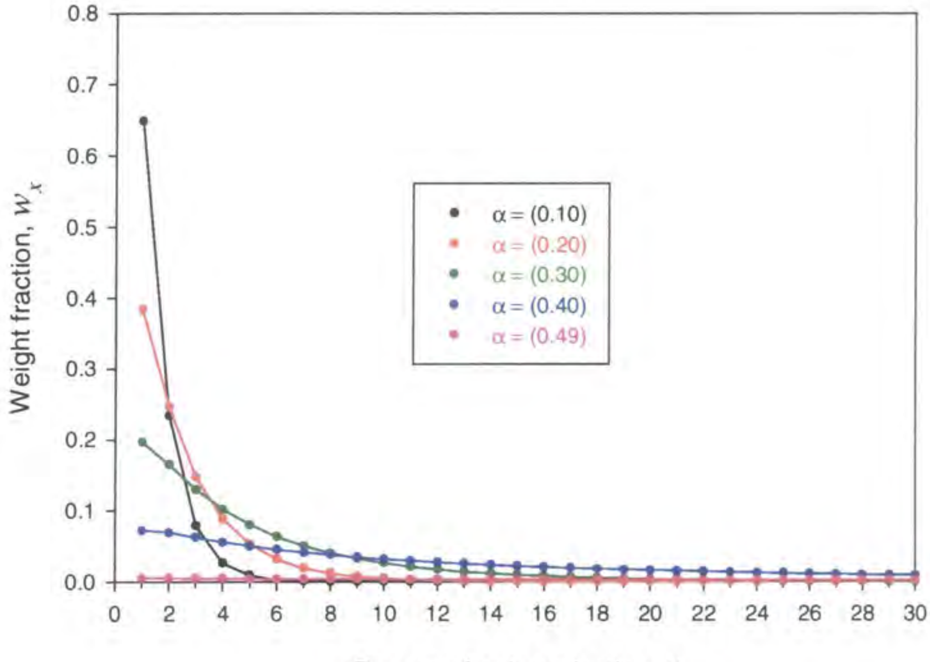


Figure 1.28 Theoretical weight fraction distribution for an AB$_2$ polymer at varying values of α.

It is evident from the mole fraction distribution that at high conversion the most numerous species is unreacted monomer. Broadening of the distribution, with increasing α, is particularly evident in the weight fraction distribution. As α approaches 0.5 (extent of reaction or p approaches unity) the weight fraction of each species approaches zero. Since the area under the curve is unity, it is apparent that as α approaches α_{max} (α_{max} = 0.5 for AB_2 systems), the weight distribution becomes infinitely wide and infinitesimally high. The broadening in the distribution, as the reaction proceeds and α increases, is best illustrated by a consideration of the polydispersity of the system (Figure 1.29).

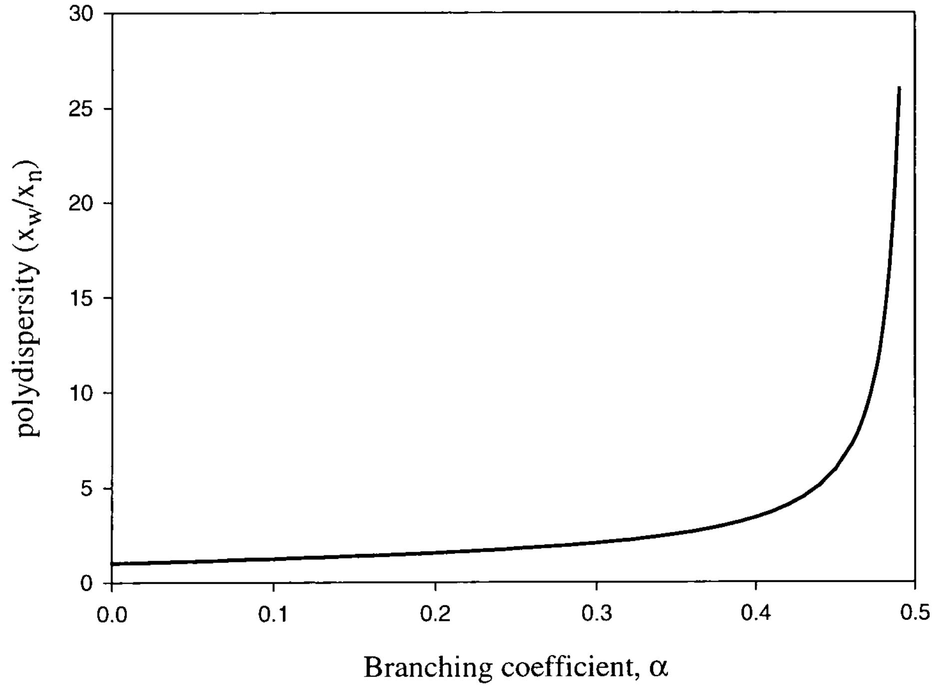


Figure 1.29 Variation of polydispersity as a function of branching coefficient for an AB_2 polymer.

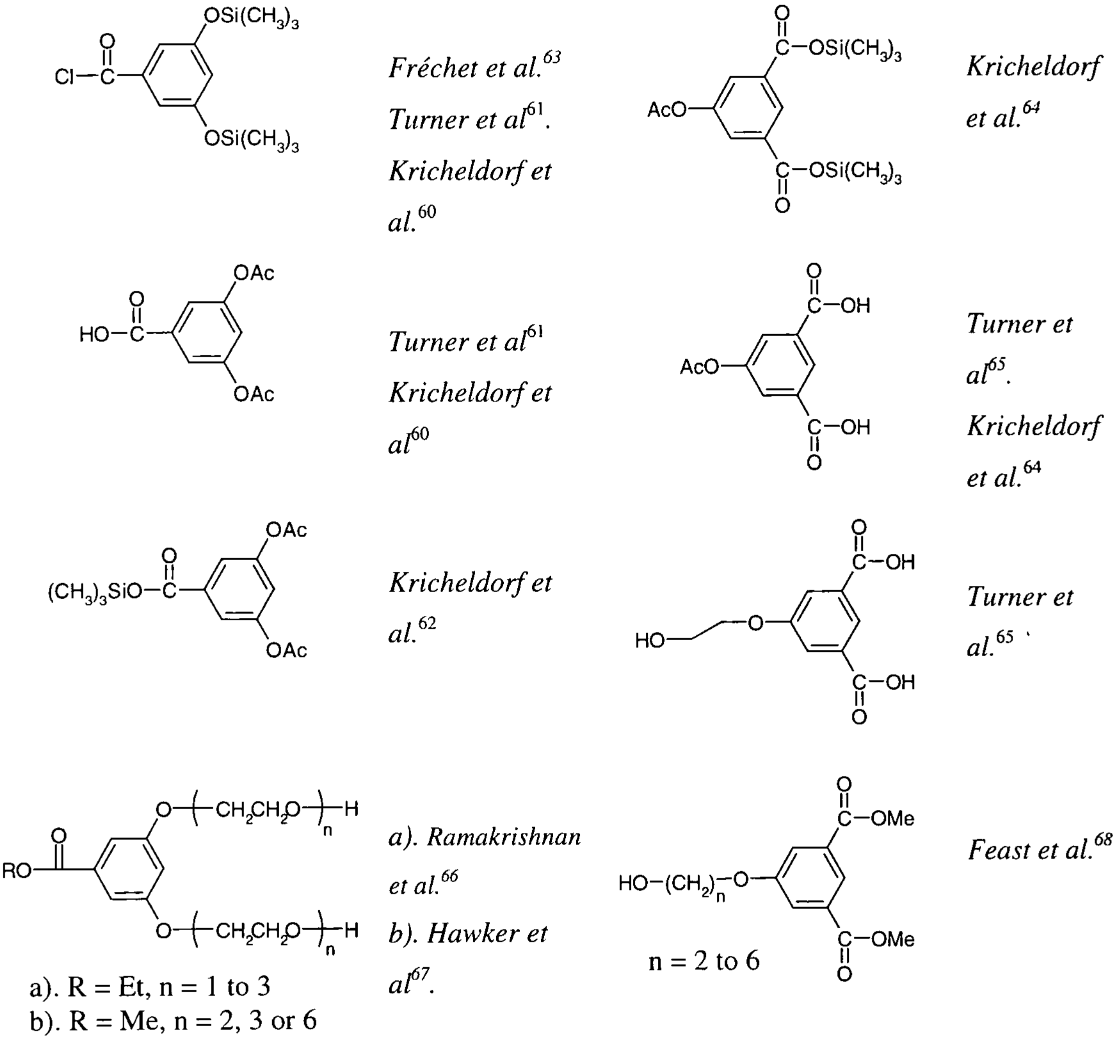
As the reaction proceeds and the branching coefficient, α, approaches 0.5 the polydipersity, x_w/x_n, approaches infinity, hence AB_2 type polymers are expected to have very broad distributions at high conversion. This is in marked contrast to the linear step-growth polymerisation of an AB monomer in which the polydispersity tends to 2 as the extent of reaction p, approaches unity.[39]

1.7 Hyperbranched polyesters.

Polyesters are both an important class of condensation polymer, with many industrial applications, and one of the most studied classes of hyperbranched polymer. The potential for producing hyperbranched analogues of commercial polyesters combined with the availability of suitable hydroxy carboxylic acids make hyperbranched polyesters an attractive target for synthesis. The range of hyperbranched polyesters which have been examined include not only structures which are either fully aliphatic or fully aromatic but also those with mixed aromatic / aliphatic compositions.

There have been relatively few reports concerning the synthesis of aliphatic hyperbranched polyesters. Of these the polymerisation of 2,2-bis(methylol)propionic acid[59] and related aliphatic polyols have been studied the most extensively.(Figure 1.19). Hyperbranched polymers containing aromatic ester linkages have been studied much more widely and, of these, polyesters based upon derivatives of 3,5-dihydroxy benzoic acid or 5-hydroxy isophthalic acid have, perhaps, been studied the most (Figure 1.30).

Derivatives of 3,5-dihydroxy benzoic acid were employed by Kricheldorf and co-workers who used both 3,5-diacetoxybenzoic acid and 3,5-bis(trimethylsiloxy)benzoyl chloride together with their AB analogues, in AB / AB_2 copolymerisations, for the preparation of branched polyesters.[60] Fréchet and co-workers later improved upon this synthesis to produce hyperbranched polyesters from the condensation reaction of 3,5-bis(trimethylsiloxy)benzoyl chloride. Similarly, Turner and co-workers prepared hyperbranched polyesters by melt condensation of 3,5-diacetoxybenzoic acid. These were compared with the analogous polymers from condensation of 3,5-bis(trimethylsiloxy)benzoyl chloride. Both routes gave polymers with phenolic end groups after hydrolysis. [61] In a further variation Kricheldorf and co-workers used the condensation of silylated carboxylic acids and acetyl protected hydroxyls to prepare hyperbranched polyesters from trimethylsilyl 3,5-acetoxybenzoate.[62]



Fréchet et al.[63] *Turner et al*[61]. *Kricheldorf et al.*[60]

Kricheldorf et al.[64]

Turner et al[61] *Kricheldorf et al*[60]

Turner et al[65]. *Kricheldorf et al.*[64]

Kricheldorf et al.[62]

Turner et al.[65]

a). R = Et, n = 1 to 3
b). R = Me, n = 2, 3 or 6

a). Ramakrishnan et al.[66] *b). Hawker et al*[67].

Feast et al.[68]

Monomers based upon 3,5-dihydroxy benzoic acid

Monomers based upon 5-hydroxy isophthalic acid

Figure 1.30 Examples of AB_2 monomers used in the synthesis of hyperbranched aromatic polyesters.

A distinctive feature of hyperbranched macromolecules, first demonstrated with hyperbranched polyesters, is that the choice of the A and B functionalities in the AB_2 monomer are crucial to the polymer properties.[3c] For example, interchange of the A and B functional groups gives an A_2B monomer which, upon polymerisation, yields a polymer with different end groups, and hence properties, from the analogous AB_2 system. If derivatives of 3,5-dihydroxy benzoic acid are regarded as AB_2 monomers then the derivatives of 5-hydroxyisophthalic acid may be considered as their A_2B equivalents. The effect of interchanging the A and B groups has been demonstrated in the polymerisation of the A_2B monomers 5-acetoxyisophthalic acid and trimethylsilyl 5-acetoxyisophthalate.[64, 65] Both of these routes lead to hyperbranched polyesters with carboxylic acid end groups whereas the analogous AB_2 monomers, described earlier, give phenol terminated polymers.[60, 61] The effect of interchanging the A and B groups was manifest in the resulting polymer properties, in particular differences were observed in both the solubility and glass transition temperature.

Several research groups have investigated the effect of introducing flexible aliphatic units into hyperbranched aromatic polyester systems such as those described above. Both Hawker and Ramakrishnan have reported the synthesis of hyperbranched polymers containing aromatic ester units linked by oligo(ethyleneoxy) spacer segments of varying length.[66, 67] The length of the spacer unit was found to influence the glass transition temperature. Turner and co-workers reported the synthesis of polyesters made via the melt condensation of 5-(2-hydroxyethoxy)isophthalic acid.[65] A similar system based upon dimethyl 5-(2-hydroxyethoxy)isophthalate was later reported by Feast and Stainton.[68a]

The work presented in this thesis is a continuation of the work of Stainton who studied the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate as a natural extension to an earlier investigation of aryl ester dendrimers.[69] The molecular weight of the hyperbranched polyester was moderated by the addition of a B_3 comonomer, trimethyl 1,3,5-benzenetricarboxylate (Figure 1.31). The variation of molecular weight with polymerisation time was not reported but the molecular weight was studied as a function of the core : monomer ratio. The molecular weight of the polymer was found to decrease as the amount of B_3 core used in the polymerisation was increased (Figure 1.32).

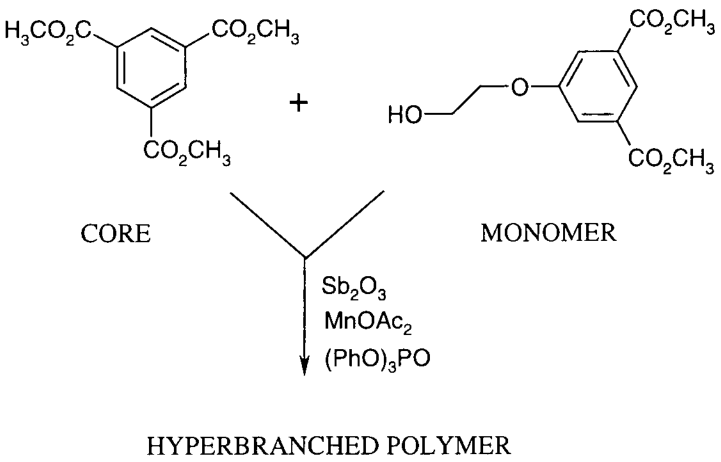


Figure 1.31 Synthesis of core terminated hyperbranched polyesters.

The polydispersity (M_w/M_n) of the hyperbranched polyester was found to approach a value of 3, which is in stark contrast to the infinitely wide distributions predicted by Flory. The aim of this project was to investigate further the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate, in particular the molecular weight distribution and properties of the hyperbranched polymer.

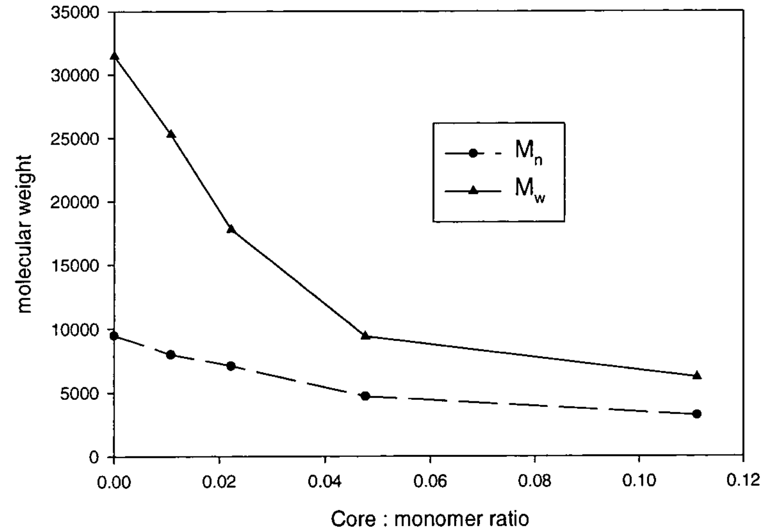


Figure 1.32 Variation of molecular weight with core : monomer ratio for core terminated hyperbranched polyesters.[69]

1.8 References.

---

(1). Kambouris, P., Hawker, C.J., *J. Chem. Soc. Perkin Trans. 1*, 1993, 2717

(2). Roovers, J. 'Branched Polymers' in *Encyclopaedia of Polymer Science and Engineering*, vol. 2, (Eds: Mark, H.F., Bikales, N.M., Overberger, C.G., Menges, G.), 2nd edition, Wiley Interscience, New York, 1985

(3). a) Tomalia, D.A., Naylor, A.M., Goddard, III, W.A., *Angew. Chem. Int. Ed. Engl.* 1990, **29,** 138

b) Moorefield, C.N., Newkome, G.R., 'A Review of Dendritic Macromolecules' in *Advances in Dendritic Macromolecules*, vol. 1, (Ed. Newkome, G.R.), JAI Press, Greenwich, 1994

c) Fréchet, J.M.J., Hawker, C.J., 'Synthesis and Properties of Dendrimers and Hyperbranched Polymers' in *Comprehensive Polymer Science*, 2nd supplement, (Eds: Aggarwal, S.L., Russo, S.,), Pergamon Press, Oxford, 1996

d) Matthews, O.A., Shipway, A.N., Stoddart, J.F., *Prog. Polym. Sci.*, 1998, **23**, 1

(4). Magnusson, H., Malmström, E., Hult, A., *Macromol. Rapid Commun.,* 1999, **20**, 453

(5). Hult, A., Johansson, M., Malmström, E., *Adv. Polym. Sci.*, 1999, **143**, 1

(6). Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953

(7). Kim, Y.H., *J. Polym. Sci.: Part A: Polym. Chem.*, 1998, **36**, 1685

(8). Buhleier, E., Wehner, W., Vögtle, F., *Synthesis*, 1978, 155

(9). Tomalia, D.A., Baker, H., Hall, M., Kallos, G., Martin. S., Roeck, J., Ryder, J., Smith, P., *Macromolecules*, 1986, **19,** 2466

(10). Newkome, G.R., Yao, Z.-Q., Baker, G.R., Gupta, V.K., *J. Org. Chem.*, 1985, **50,** 2003

(11). a) Hawker, C.J., Fréchet, J.M.J., *J. Chem. Soc.,* 1990, 1010

b) Hawker, C.J., Fréchet, J.M.J., *J. Am. Chem. Soc.*, 1990, **112**, 7638

(12). Tomalia, D.A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin. S., Roeck, J., Ryder, J., Smith, P., *Polymer J.*, 1985, **17(1),** 117

(13). de Brabander-van den Berg, E.M.M., Nijenhuis, A., Mure, M., Keulen, J., Reintjens, R., Vandenbooren, F., Bosman, B., de Raat, R., Frijns, T., van den Wal, S., Castelijns, M., Put, J., Meijer, E.W., *Macromol. Symp.,* 1994, **77**, 51

(14). Miller, T.M., Kwock, E.W., Neenan, T.X., *Macromolecules*, 1992, **25**, 3143

(15). Buyle Padias, A., Hall, K., Tomalia, D.A., McConnell, J.R., *J. Org. Chem.*, 1987, **52**, 5305

(16). Ihre, I., Hult, A., Söderlind, E., *J. Am. Chem. Soc.*,1996, **27**, 6388

(17). Newkome, G.R., Moorefield, C.N., Baker, G.R., Johnson, A.L., Behera, R.K., *Angew. Chem.Int. Ed. Engl.*, 1991, **30**, 1176

(18). Miller, T.M., Neenan, T.X., Zayas, R., Bair, H.E., *J. Am. Chem. Soc.*, 1992, **114,** 1018

(19) van der Made, A.W., van Leeuween, P.W.N.M., J. *Chem. Soc. Chem. Commun.* 1992, 1400

(20). Launay, N., Caminade, A.-M., Marjoral, J.-P., *J. Am. Chem. Soc.*, 1995, **117**, 3282

(21). Maciejewski, M., *J. Macromol. Sci. Chem.*, 1982, **A17(4),** 689

(22). Mansfield, M.L., Klushin, L.I., *Macromolecules*, 1993, **26**, 4262

(23). a) Tomalia, D.A., Berry, V., Hall, M., Hedstrand, D.M., *Macromolecules*, 1987, **20**, 1164

b) Newkome, G.R., Moorefield, C.N., Baker, G.R., Saunders, M.J., Grossman, S.H., *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1178

c) Hawker, C.J., Wooley, K.L., Fréchet, J.M.J., *J. Chem. Soc. Perkin Trans. 1*, 1993, 1287

d) Stevelmans, S., van Hest, J.C.M., Jansen, J.F.G.A, van Boxtel, D.A.F.J., de Brabander-van den Berg, E.M.M., Meijer, E.W., *J. Am. Chem. Soc.* 1996, **118,** 7398

(24). a) Jansen, J.F.G.A., de Brabander-van den Berg, E.M.M., Meijer, E.W., *Science,* 1994, **266**, 1226

b) Jansen, J.F.G.A., Meijer, E.W., *J. Am. Chem. Soc.,* 1995, **117**, 4417

(25). Kim, Y.H., Webster, O.W., *J. Am. Chem. Soc.*, 1990, **112**, 4592

(26). Miller, T.M., Neenan, T.X., Zayas, R., Bair, H.E., *J. Am. Chem. Soc.*, 1992, **114,** 1018

(27). Tomalia, D.A., Hedstrand, D.M., Wilson, L.R., 'Dendritic Polymers' in, *Encyclopaedia of Polymer Science and Engineering*, Index volume, (Eds: Mark, H.F., Bikales, N.M., Overberger, C.G., Menges, G.), Wiley Interscience, NewYork, 1990

(28). Mourey, T.H., Turner, S.R., Rubinstein, M., Fréchet, J.M.J., Hawker, CJ., Wooley, K.L., *Macromolecules*, 1992, **25**, 2401

(29). DSM website: http://www.dsm.nl/csc/business_engels/astramol/figure3.htm

(30). a) Hobson, L.J., Feast, W.J., *Chem. Commun.,* 1997, 2067

b) Hobson, L.J., Feast, W.J., *Polymer,* 1999, **40,** 1279

(31). Wooley, K.L., Hawker, C.J., Fréchet, J M.J., *J. Am. Chem. Soc.*, 1991, **113(11),** 4252

(32). Wooley, K.L., Hawker, C.J., Fréchet, J.M.J., *Angew. Chem. Int. Ed. Engl.,* 1994, **33(1),** 82

(33). Spindler, R., Fréchet, J.M.J., *J. Chem. Soc. Perkin Trans. 1*, 1993, 913

(34). Zeng, F., Zimmerman, S.C., *J. Am. Chem. Soc.*, **1996**, 118, 5326

(35). Kawaguchi, T., Walker, K.L., Wilkins, C.L., Moore, J.S., *J. Am. Chem Soc.,* 1995, **117(8),** 2159

(36). Morriss, F.V., Bechtle, G.F., Gadberry, H.M., *J. Am. Oil Chemists' Soc.,* 1960, 37, 475

(37). Kim, Y.H., Webster, O.W., *Macromolecules,* 1992, **25(21)**, 5561

(38). Odian, G., *Principles of Polymerisation,* 2nd edition, Wiley Interscience, New York, 1981

(39). Cowie, J.M.G., *Polymers: Physics and Chemistry of Modern Materials,* 2nd edition, Blackie, London, 1991

(40). Urich, K.E., Hawker, C.J., Fréchet, J.M.J., Turner, S.R., *Macromolecules,* 1992, **25**, 4538

(41). Kricheldorf, H.R., Bolender, O., Stuckenbrock, T., *Macromol. Chem. Phys.,* 1997, **198**, 2651

(42). Kim, Y.H., *J. Am. Chem. Soc.,* 1992, **114**, 4947

(43). Bolton, D.H., Wooley, K.L., *Macromolecules,* 1997, **30**, 1890

(44). Kumar, A., Ramakrishnan, S., *J. Chem. Soc., Chem. Commun.*, 1993, 1453

(45). a) Mathias, L.J., Carothers, T.W., *J. Am. Chem. Soc.,* 1991, **113**, 4043

b) Lach, C., Müller, P., Frey, H., Mülhaupt, R., *Macromol. Rapid Commun.,* 1997, **18**, 253

c) Miravet, J.F., Fréchet, J.M.J., *Macromolecules,* 1998, **31**, 3461

(46). Malmström, E., Trollsås, M., Hawker, C.J., Johansson, M., Hult, A., *Proc. Am. Chem. Soc. Polym. Sci. Eng.*, 1997, **214(2),** 135

(47). Hawker, C.J., Chu, F., *Macromolecules,* 1996, **29**, 4370

(48). Fréchet, J.M.J., Henmi, M., Gitsov, I., Aoshima, S., Leduc, M.R., Grubbs, R.B., *Science,* 1995, **269**, 1080

(49). Müller, A.H.E., Yan, D., Wulkow, M., *Macromolecules,* 1997, **30(23),** 7015

(50). a) Hawker, C.J., Frchet, J.M.J., Grubbs, R.B., Dao, J., *J. Am. Chem. Soc.,* 1995, **117**, 10763

b) Hawker, C.J., *Acc. Chem. Res.*, 1997, **30**, 373

(51). a) Gaynor, S.C., Edelman, S., Matyjaszewski, K., *Macromolecules,* 1996, **29**, 1079

b) Weimer, M.W., Fréchet, J.M.J., Gitsov, I., *J.Polym. Sci. part A Polym. Chem.*, 1998, **36**, 955

(52). Matyjaszewski, K., Gaynor, S.C., Kulfan, A., Podwika, M., *Macromolecules*, 1997, **30**, 5192

(53). Zhang, X., Liu, W., Chen, Y., Gong, A, Chen, C., Xi, F., *Polym. Bull.*, 1999, **43**, 29

(54). Suzuki, M., Ii, A., Saegusa, T., *Macromolecules*, 1992, **25**, 7071

(55). Sunder, A., Hanselmann, R., Frey, H., Mülhaupt, R., *Macromolecules*, **1999**, 32, 4240

(56). Magnusson, H., Malmström, E., Hult, A., *Macromol. Rapid. Commun.*, 1999, **20(8),** 453

(57). Huber, T., Böhme, F., Komber, H., Kronek, J, Luston, J., Voigt, D., Voit, B., *Macromol. Chem., Phys.*, 1999, **200(1)**, 126

(58). Flory, P.J., *J. Am. Chem. Soc.*, 1952, **74**, 2718

(59). Hult, A., Malström, E., Johansson, M., *Macromolecules*, 1995, **28**, 1698

(60). Kricheldorf, H.R., Zang, Q-Z, Schwarz, G., *Polymer*, 1982, **23**, 1821

(61). Turner, S.R., Voit, B.I., Mourey, T.H., *Macromolecules*, 1993, **26**, 4617

(62). Kricheldorf, H.R., Stöber, O., Lübbers, D., *Macromol. Chem. Phys.* 1995, **196**, 3549

(63). Hawker, C.J., Lee, R., Fréchet, J.M.J., *J. Am. Chem. Soc.* , 1991, **113**, 4583

(64). Kricheldorf, H.R., Stöber, O., *Macromol. Rapid Commun.* 1994, **15**, 87

(65).Turner, S.R., Walter, F., Voit, B.I., Mourey, T.H., *Macromolecules*, 1994, **27**, 1611

(66). Kumar, A., Ramakrishnan, S., *Macromolecules*, 1996, **29**, 2524

(67). Hawker, C.J., Chu, F., Pomery, P.J., Hill, D.J.T., *Macromolecules*, 1996, **29**, 3831

(68). a) Feast, W.J., Stainton, N.M., *J. Mater. Chem.*, 1995, **5(3),** 405

b) Feast, W.J., Keeney, A.J., Kenwright, A.M., Parker, D., *J. Chem. Soc. Chem.*

Commun., 1997, 1749

c) Keeney, A.J., *Ph.D. Thesis*, Durham University, 1998

(69). Stainton, N.M., *Ph. D. Thesis*, Durham University, 1994

Chapter Two

Synthesis and Polymerisation of Dimethyl 5-(2-hydroxyethoxy)isophthalate

2.1 Introduction

The work presented here is concerned primarily with the synthesis of hyperbranched polyesters via the melt condensation polymerisation of AB_2 type monomers. In particular this is a continuation of the work of Stainton[1], discussed in chapter one, and focuses on the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate (Figure 2.1)

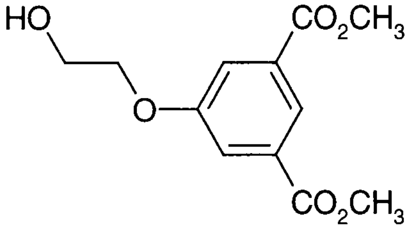


Figure 2.1 Dimethyl 5-(2-hydroxyethoxy)isophthalate

2.2 Established monomer synthesis

The method employed by Stainton used 5-hydroxyisophthalic acid as the starting material and is outlined below (Figure 2.2). The esterification of 5-hydroxyisophthalic acid was achieved by treatment with a commercially available boron trifluoride-methanol complex in methanol solution, to yield dimethyl 5-hydroxyisophthalate. This was followed by coupling of the phenolic diester with 2-bromoethyl acetate, obtained from the reaction of 2-bromoethanol with acetic anhydride, to give dimethyl 5-(2-acetoxyethoxy)isophthalate. It should be noted, however, that the etherification step, carried out by refluxing with a suspension of anhydrous potassium carbonate in acetone, was reported to be a relatively low yield process (37%). The final step in the synthesis involved the hydrolysis of the acetate group, with potassium hydroxide in methanol solution, to yield the required dimethyl 5-(2-hydroxyethoxy)isophthalate. Although this was ultimately a successful route to the desired monomer it suffered from a number of drawbacks. Firstly, the method is a multi step synthesis with all the implications for time, labour and yield inherent in such an approach. Secondly, the procedure uses a relatively expensive reagent in the boron trifluoride-methanol complex. Finally, the route contains a low yield etherification step that affects the overall yield of the complete process adversely. In the light of these limitations, a useful starting point for this project was deemed to be the development of a better monomer synthesis, in terms of the number of steps and overall cost.

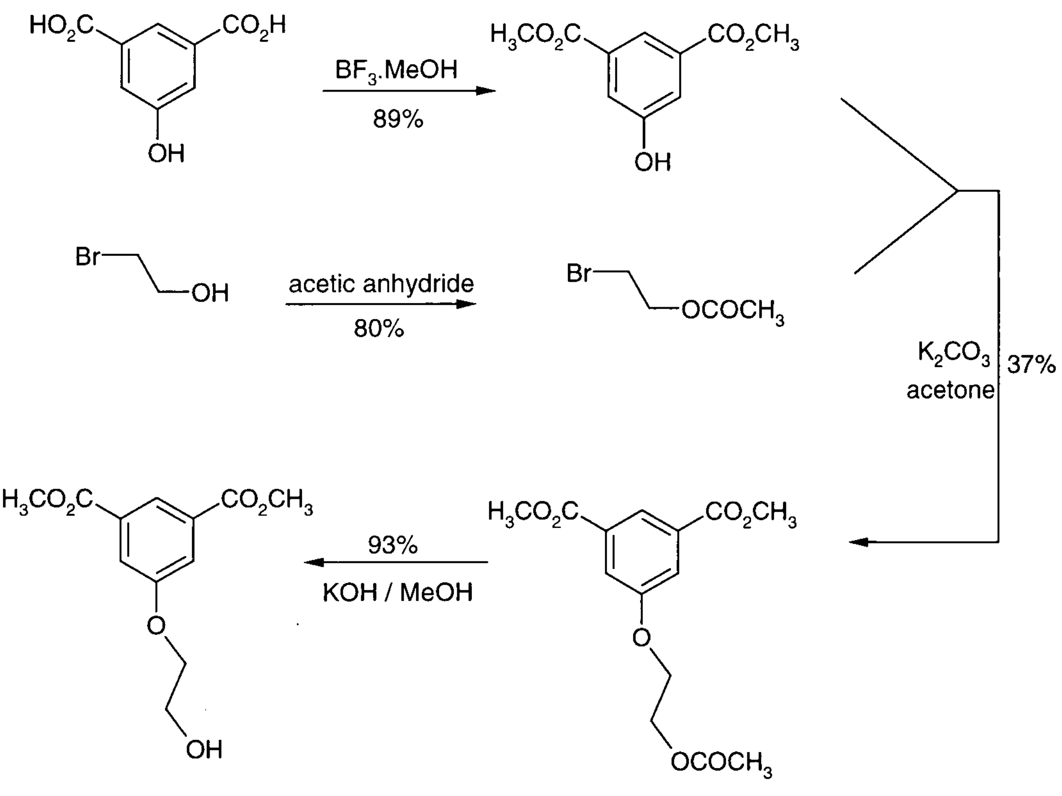


Figure 2.2 Synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate

2.3 An improved monomer synthesis

The synthesis of the AB_2 monomer dimethyl 5-(2-hydroxyethoxy)isophthalate, in a two step reaction from 5-hydroxyisophthalic acid, has been reported by Turner *et al.*[2], although that group apparently employed the monomer in its carboxylic acid form for polycondensation. A modified version of this route has been used successfully in the work reported here and is outlined below (Figure 2.3).

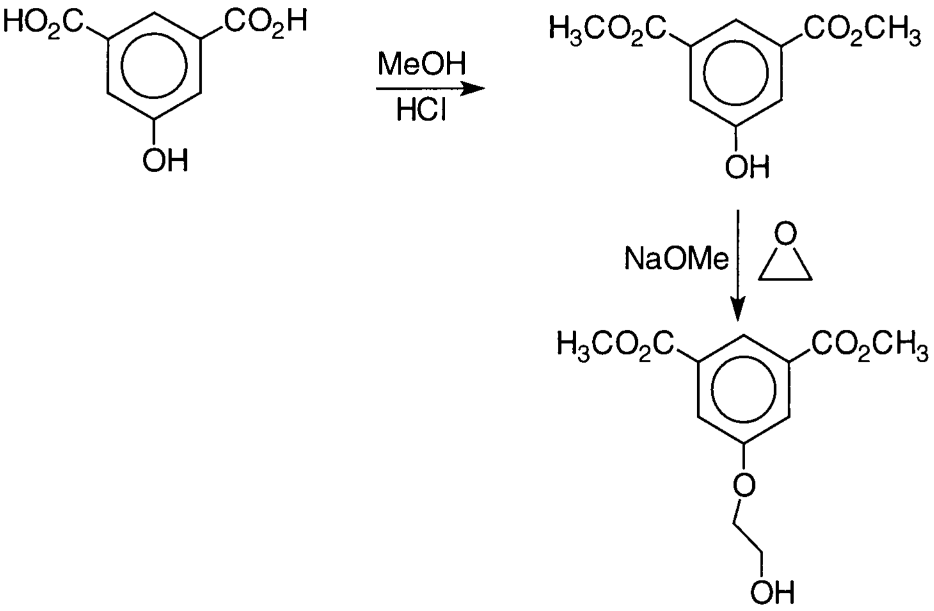


Figure 2.3 Modified synthesis of AB_2 type monomer

The esterification of 5-hydroxyisophthalic acid was accomplished on a moderately large-scale (275g) by refluxing the substrate in an excess of acidic methanol. The product dimethyl 5-hydroxyisophthalate was recovered easily and recrystallised from methanol in good yield (typically in the region of 80 %) as a white solid.

The next stage in the synthetic sequence described by Turner *et al.* involved a nucleophilic addition of dimethyl 5-hydroxyisophthalate to ethylene oxide to yield the required monomer, dimethyl 5-(2-hydroxyethoxy)isophthalate. Unfortunately, this reaction was found to be unrepeatable using the conditions reported. This step was purportedly carried out with a threefold excess of ethylene oxide in isopropanol, the whole system being pressurised with 75 psi of nitrogen and heated at 95 ^{0}C for 4 hours. Purification was reported to be effected by column chromatography to give a 64% yield of a product showing evidence of partial hydrolysis. Numerous attempts were made to repeat the above reaction using the stated conditions but, invariably, this resulted in recovery of unreacted starting materials.

Although ethylene oxide is known to react with phenols at elevated temperatures it has long been known that the reaction proceeds more rapidly in the presence of alkali.[3] As a consequence the reaction was repeated using the reported conditions but utilising a small amount of sodium as a base catalyst. Unfortunately this revised procedure resulted in the formation of viscous brown oil which analysis by ^1H NMR revealed to be a complex mixture of carboxylic acids and their methyl and isopropyl esters. The reaction conditions were altered to utilise methanol as solvent and sodium methoxide as the base catalyst, thereby avoiding the problem of mixed ester production. This procedure gave high yields of the required product. Purification by recrystallisation from methanol / water gave a crystalline white solid (78% yield).

2.4 Polymerisation

The polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate is in many ways analogous to that used for the synthesis of linear polyesters such as poly(ethylene terephthalate) (PET). In the latter case, polymerisation is often via a route involving alcoholysis. In the commercial preparation of PET polymerisation is frequently carried out in two stages[4] (Figure 2.4).

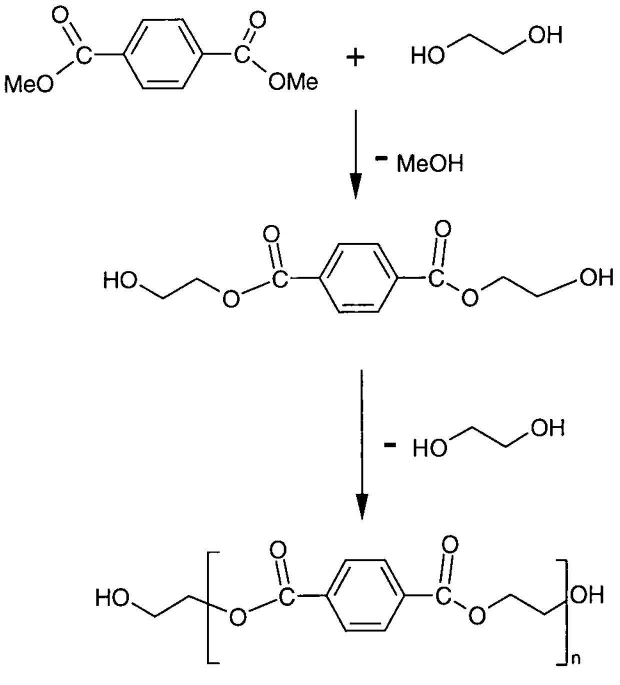


Figure 2.4 Synthesis of poly (ethylene terephthalate)

Firstly dimethyl terephthalate is reacted with ethylene glycol, eliminating methanol, to yield mainly bis-β-hydroxyethyl terephthalate plus higher oligomers.[5] Secondly, the glycolic esters are polymerised via a condensation reaction eliminating ethylene glycol. With pure reagents the alcoholysis reaction proceeds very slowly, even at high temperatures, consequently these reactions are usually catalysed and many catalyst systems have been studied. For the first step of the reaction acetates of lead (II), lead (IV), zinc, manganese, calcium, cobalt and cadmium have been found to be the most useful. The second step is catalysed by oxides such as Sb_2O_3 or GeO_2, whilst titanium alkoxides are known to be effective catalysts for both steps.[6] Often phosphorous containing compounds, such as triphenyl phosphate, are added to inhibit unwanted coloration of the polymer, although such additives have been shown to retard the polymerisation reaction at high concentrations.[7]

The polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate can be thought of as analogous to the first step in the synthesis of PET, condensation proceeding with the production of methanol (Figure 2.5) and as such manganese (II) acetate might be expected to be a suitable catalyst. Stainton demonstrated that the polymerisation could be carried out utilising a combination of manganese (II) acetate and antimony trioxide, with the addition of triphenyl phosphate to suppress thermal degradation.[8] Antimony trioxide is normally only used in the second stage of the commercial production of PET as its activity is dependent upon the concentration of hydroxyl groups, the efficiency of the catalyst actually increasing with degree of polymerisation due to the removal of hydroxyl groups from the system. These differences notwithstanding, polymerisation via the mixed antimony / manganese catalyst system employed by Stainton was considered a practical starting point for the work presented here.

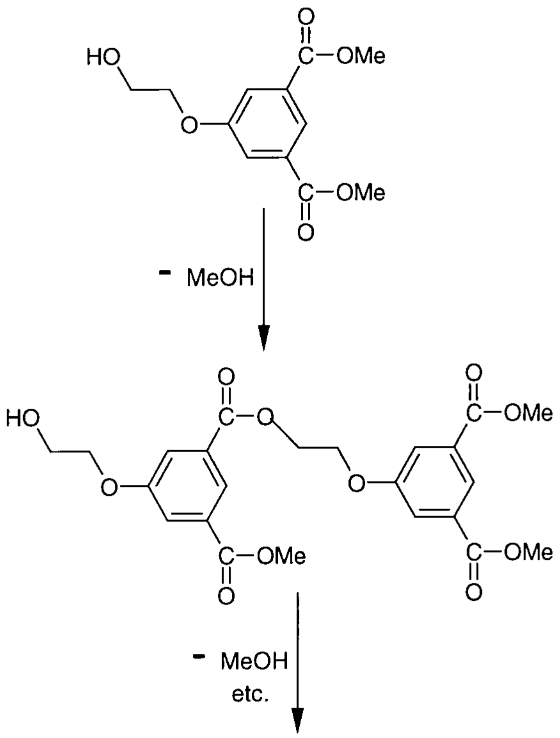


Figure 2.5 Polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate

The polycondensations discussed in this work were carried out in a cylindrical vessel fitted with a flange head which was designed to allow both efficient stirring of the molten polymer and easy removal of the product (Figure 2.6). As the efficiency of stirring was anticipated to be a critical factor in the reproducibility of the polymerisations the reactions were stirred with a close fitting stirrer paddle powered by a high torque motor which allowed a pre-set stirring rate to be employed.

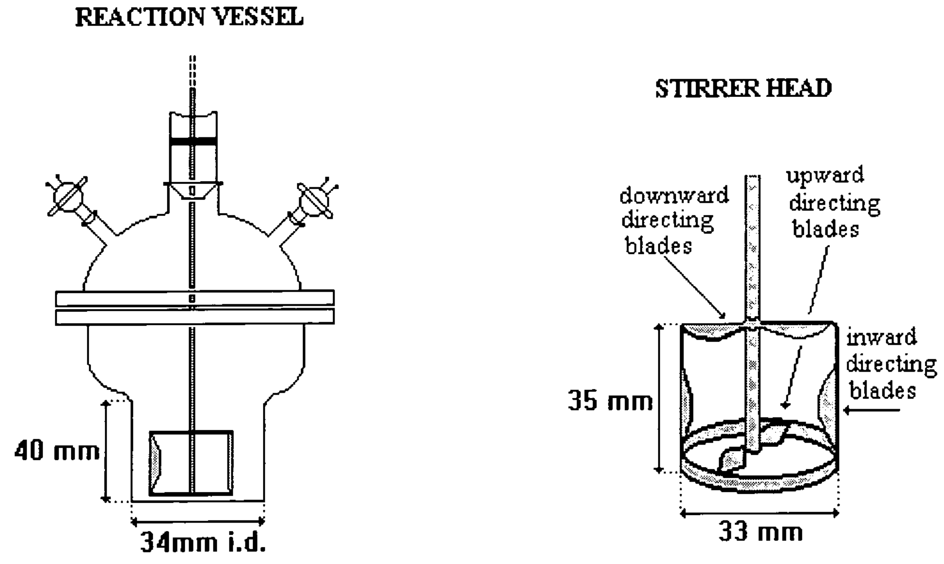


Figure 2.6 Polymerisation vessel and stirrer

The polymerisation set up was designed to allow the employment of a reproducible temperature regime (Figure 2.7). An oil bath, consisting of high temperature silicone oil heated by a 1kW heating band, was employed as the heat source and regulated using a purpose built temperature controller.

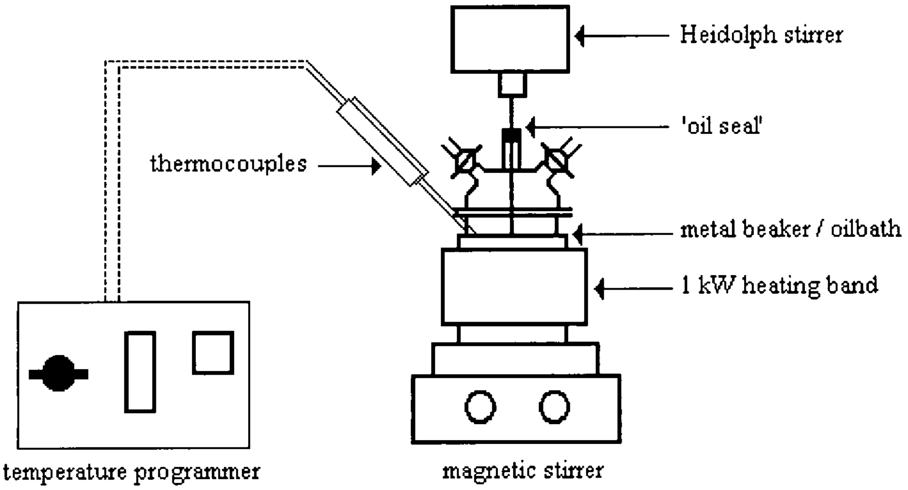


Figure 2.7 Polymerisation set-up

The polymerisations were carried out in the melt at 240 ^{0}C and a stream of nitrogen gas was employed to remove the methanol condensate. A series of polymers were produced in this way by varying the time in the melt. The resulting polymers were obtained as brittle brown glasses that were readily soluble in chloroform. Part of the aim of these experiments was to compare the experimentally obtained molecular weight distributions with the infinitely wide theoretical distributions predicted by Flory. Consequently, the polymers obtained from these reactions were analysed without purification and unintentional fractionation during reprecipitation was avoided.

2.5 Preliminary analyses

Initially the polymers were examined by size exclusion chromatography (SEC) in chloroform solution. As expected, the polymers revealed progressively broader molecular weight distributions with increasing reaction time. In fact the chromatograms resulting from polymers produced after long reaction times were both broad and polymodal in character (Figure 2.8). This was unanticipated but in agreement with similar work reported by Turner *et al.*.[9]

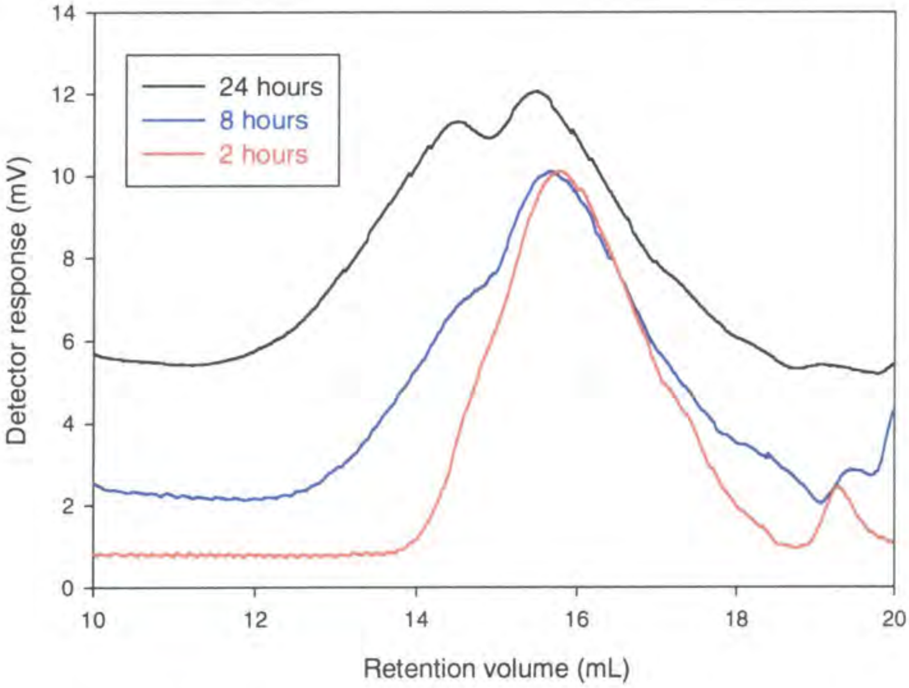


Figure 2.8 Typical SEC traces (RI detector) for AB_2 polyesters

Reaction time (h.)	M_n^*	M_w^*	p.d.i.
1	3100	9800	3.2
2	5500	19700	3.6
3	5300	24700	4.7
4	7200	37900	5.3
6	9100	41400	4.5
8	6400	50300	7.9
12	7500	68400	9.1
16	8800	94300	10.8
24	7400	106900	14.5

* polystyrene equivalents, $CHCl_3$ eluent, see Experimental section for details

Table 2.1 SEC analysis of hyperbranched polyesters

It should be noted at this point, that there is some doubt as to the validity of molecular weight information obtained from SEC for both hyperbranched and dendritic materials.

This point will be discussed in greater depth in a later chapter. For the present purposes the molecular weight data presented is in terms of polystyrene equivalent molecular weights (Table 2.1).

It is apparent from the above data that the polystyrene equivalent molecular weight of the polymers increases steadily with increasing reaction time as expected. Also the weight average molecular weight increases far more rapidly than the number average (Figure 2.9).

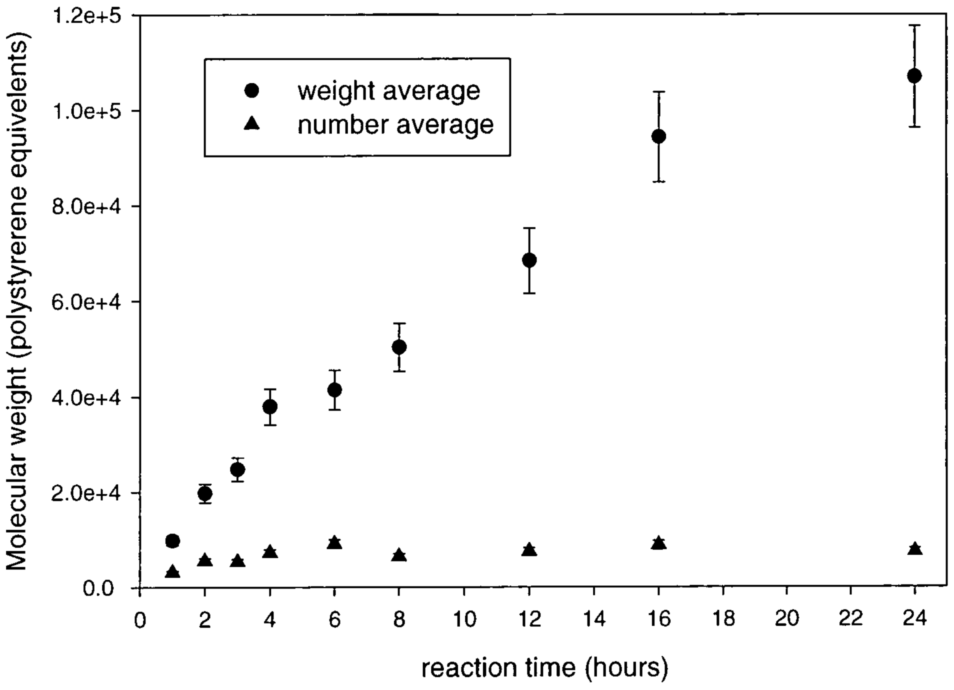


Figure 2.9 Molecular weight determination of hyperbranched polyesters by SEC.

This is most apparent in the increasing value for the polydispersity (M_w/M_n) which increases with reaction time up to a value of 14.5 after 24 hours (Figure 2.10). This is a striking contrast to conventional condensation polymerisation, in which the polydispersity approaches 2 at high extent of reaction but is in accord with the theoretical predictions arising from Flory's statistical treatment. Furthermore, high polydispersities have since been relatively widely reported for other hyperbranched systems, although Stainton reported a value of approximately 3 resulting from early work on this polymer system.[8] It is evident that the low polydispersity reported previously was a consequence of insufficient reaction time and hence lower extents of reaction.

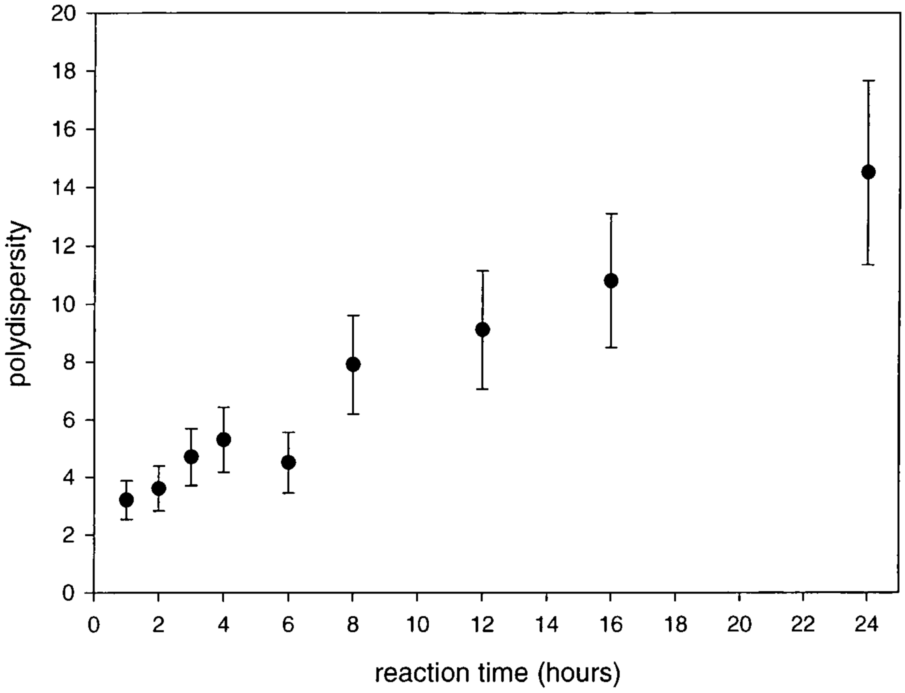


Figure 2.10 Variation of polydispersity

2.6 Summary

A new and improved route to the AB_2 monomer, dimethyl 5-(2-hydroxyethoxy) isophthalate, has been presented here. The monomer has been prepared on moderately high scale and fully characterised. A series of polymerisations have been carried out using a mixed catalyst system based upon antimony trioxide and manganese (II) acetate. By varying the reaction time a series of polymers of differing molecular weight has been synthesised and some preliminary SEC studies carried out. These would seem to be in general agreement with Flory's model of AB_2 condensations. The properties of these polymers plus further, more detailed, characterisation will be presented in later chapters.

2.7 Experimental

All reagents, except where noted below, were purchased from Aldrich Chemicals and used without further purification. Melting points were obtained using an Electrothermal IA9200 series digital melting point apparatus. Elemental analyses were obtained using an Exeter Analytical Elemental Analyser CE-440. Infrared spectra were obtained on a Perkin Elmer 1720X FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on either a Varian Unity 300 spectrometer at 299.91 MHz (^{1}H) and 75.41 MHz (^{13}C) or a Varian Inova 500 at 500.14 MHz (^{1}H) and 12.5.77 MHz (^{13}C). Mass Spectra were recorded on a Micromass AutoSpec instrument. Molecular weight distributions were obtained using size exclusion chromatography in chloroform using three 5μm columns of PLgel beads with pore sizes of 100, 10^3 and 10^5 Å, calibrated against polystyrene standards and utilising an ERC 7515A refractive index detector.

2.7.1 Synthesis of dimethyl 5-hydroxyisophthalate

Anhydrous hydrogen chloride (38.5g, 1.04mol) was bubbled through a stirred mixture of 5-hydroxyisophthalic acid (275.0g, 1.51mol) and methanol (1300cm^3) to form a clear solution. The solution was heated under reflux for 4hours and on cooling to room temperature the crude product crystallised from the methanol solution as a white solid. The solid was recovered by filtration, washed with cold water and recrystallised from methanol to yield dimethyl 5-hydroxyisophthalate, (258.0g, 1.23mol, 81%), as fine colourless needles (m.pt. 158 ^{0}C, lit.[10] 158 - 159 ^{0}C). Analysis by thin-layer chromatography (silica gel / ethyl acetate) showed a pure compound (single spot, R_f = 0.73)

Elemental analysis calculated for $C_{10}H_{10}O_5$: C, 57.14%; H, 4.80%. Found: C, 56.84%; H, 4.78%.

FTIR (KBr disc): 3363cm^{-1} (br, H-bonded O-H stretch), 3011cm^{-1} (w, aromatic C-H stretch), 2961cm^{-1} (w, methyl C-H stretch), 1703cm^{-1} (s, aromatic ester C=O stretch), 1599cm^{-1} (s, aromatic C-C stretch), 756cm^{-1} (s, aromatic C-H out of plane vibration). (Appendix 1.1)

^{1}H NMR (acetone-d^6, 300 MHz): δ3.91 (s, 6H, OC$\underline{H}_3$), δ7.67 (d, 2H, Ar$\underline{H}$). δ8.08 (t, 1H, Ar$\underline{H}$). (Appendix 1.3)

^{13}C NMR (acetone-d^6, 75 MHz): δ52.01 ($\underline{C}H_3$), δ120.42, 121.33 (aromatic $\underline{C}$-H), δ132.18 (aromatic $\underline{C}$-R), δ158.02 (aromatic $\underline{C}$-O), δ165.80 ($\underline{C}$=O). (Appendix 1.5)

MS (EI+): 210 (M), 179 (M- OCH_3), 151 (- CO_2CH_3), 136 (M - CH_3, - CO_2CH_3). (Appendix 1.7)

These spectral data were consistent with those reported.[10]

2.7.2 Synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate

A 2 litre Parr pressure reactor (Figure 2.11) was charged with dimethyl 5-hydroxyisophthalate (100.0g, 0.48mol), sodium methoxide (6.0g, 0.17mol) and methanol (600cm^3). The reactor system was purged with nitrogen gas, immersed in liquid air, evacuated and ethylene oxide (Fluka) (44.0g, 1.00mol) condensed into it. The vessel was allowed to reach room temperature and then pressurised with 100psi of nitrogen and the solution stirred at 95 ^{0}C for 6 hours. The product, obtained as a white solid, was recovered by filtration, washed with water, recrystallised from a mixture of methanol and water (50 % v/v) and dried in a vacuum oven. (Yield 95.2g, 0.37mol, 78 %) m.pt. 109.8 -110.2 ^{0}C, lit[8] 112.0-112.5°C). Single spot in TLC analysis (silica gel 60, ethyl acetate $R_f = 0.55$)

Calculated for $C_{12}H_{14}O_6$: C, 56.69%; H, 5.55%. Found: C, 56.62%; H, 5.56%.

FTIR (KBr disc), 3312cm^{-1} (br, H-bonded O-H stretch), 3010cm^{-1} (w, aromatic C-H stretch), 2951cm^{-1} (w, methyl C-H stretch), 1727cm^{-1} (s, aromatic ester C=O stretch), 1596cm^{-1} (s, aromatic C-C stretch), 754cm^{-1} (s, aromatic C-H out of plane vibration). (Appendix 1.2)

^1H NMR ($CDCl_3$, 300 MHz), δ2.38 (s, 1H, O<u>H</u>), δ3.94 (s, 6H, OC<u>H</u>$_3$), δ4.01 (t, 2H, C<u>H</u>$_2$), δ4.18 (t, 2H, C<u>H</u>$_2$), δ7.76 (d, 2H, Ar<u>H</u>). δ8.28 (t, 1H, Ar<u>H</u>). (Appendix 1.4)

^{13}C NMR ($CDCl_3$, 75 MHz), δ52.70 (<u>C</u>H$_3$), δ61.42, δ70.04 (aliphatic <u>C</u>H$_2$), δ120.05, δ123.51 (aromatic <u>C</u>-H), δ132.00 (aromatic <u>C</u>-R), δ158.93 (aromatic <u>C</u>-O), δ166.26 (<u>C</u>=O). (Appendix 1.6)

MS (EI+): 254 (M), 223 (M- OCH_3), 211 (M – CH_2CH_2OH), 210 (M – CH_2=CHOH), 179 (M – CH_2=CHOH, - OCH_3), 151 (- CO_2CH_3), 136 (M - CH_3, - CO_2CH_3). (Appendix 1.8)

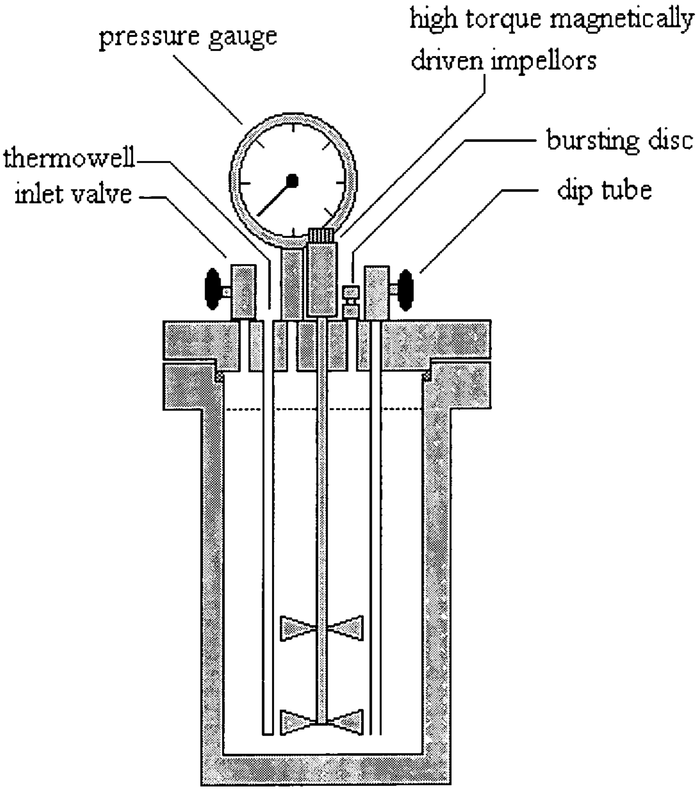


Figure 2.11 Parr 2 litre stirred pressure reactor system

2.7.3 Representative polymerisation procedure

Dimethyl 5-(2-hydroxyethoxy)isophthalate (5.0 g, 19.69 mmol.) was placed into the lower section of the polymerisation flask and the catalyst components added ($Mn(OAc)_2$: 3.2mg, 0.018 mmol. Sb_2O_3: 2.1 mg, 0.007 mmol. $(PhO)_3PO$: 2.7 mg, 0.008 mmol.). The flask was subjected to a nitrogen purge and placed in a high temperature oil bath, controlled by means of a 1 kW heating band / temperature programmer combination. The oil bath was heated at a rate of 10 ^{0}C / min. to 240 ^{0}C and held at that temperature for a period of 4 hours. The mixture was stirred continually at a rate of 125 r.p.m. by means of a stainless steel stirrer paddle (Figure 2.6) powered by a Heidolph stirrer motor. After cooling the polymer was obtained as a clear brown brittle glass (3.5g) which was chipped from the bottom of the flask and stirrer paddle. No purification of the polymer was carried out at this stage.

SEC ($CHCl_3$, polystyrene equivalents), M_w 37900, M_n 720, M_w/M_n 5.3

^{1}H NMR ($CDCl_3$, 500 MHz), δ3.89 (br s, $OC\underline{H}_3$), δ4.39, δ4.70 (br s, $C\underline{H}_2$), δ7.75 (br s, Ar$\underline{H}$). δ8.24 (br s, Ar$\underline{H}$). (Appendix 1.9)

^{13}C NMR (tetrachloroethane-d2, 125 MHz), δ52.21 (s, $\underline{C}H_3$), δ63.55, δ67.06 (s, aliphatic $\underline{C}H_2$), δ120.44, δ123.77 (m, aromatic $\underline{C}$-H), δ132.24 (m, aromatic $\underline{C}$-R), δ158.90 (s, aromatic $\underline{C}$-O), δ165.48 (m, $\underline{C}$=O). (Appendices 1.10 and 1.11)

2.8 References

(1). Stainton, N.M., *Ph. D. Thesis*, Durham University,1994

(2). Turner, S.R., Walter, F., Voit, B.I., Mourey, T.H., *Macromolecules*, 1994, **27**, 1611

(3). Boyd, D.R., Marle, E.R., *J. Chem. Soc.,* 1914, 2117

(4). Hovenkamp, S.G., *J. Polym. Sci. A1*, 1971, **9**, 3617

(5). Tomita, K., Ida, H., *Polymer*, 1975, **16**, 185

(6). Pilati, F., *Comprehensive Polymer Science*, Pergamon Press, Oxford, 1989, **5**, 275

(7). Gumther, B., Zachmann, H.G., *Polymer* 1983, **24**, 1008

(8). Feast, W.J., Stainton, N.M., *J. Mater. Chem.,* 1995, **5(3)**, 405

(9). Turner, S.R., Voit, B.I., Mourey, T.H., *Macromolecules*, 1993, **26**, 4617

(10). Yoshino, T., Nagata, Y., Itoh, E., Hashimoto, M., Katoh, T., Terashima, S., *Tetrahedron*, 1997, **53(30),** 10239

Chapter Three

Determination of the Molecular Weight of Hyperbranched Polyesters

3.1 Introduction

The molecular weight distribution in a sample of a polymer can have a significant influence upon its properties. Hence the accurate determination of molecular weight and its distribution is essential if the relationship between a polymer's structure and its properties is to be explored.

In this chapter the techniques used to determine the molecular weight of the hyperbranched polyesters described in chapter 2 are discussed. The application of size exclusion chromatography (SEC), dilute solution viscometry and matrix assisted laser desorption / ionisation time of flight mass spectrometry (MALDI-TOF MS) and the results obtained using these techniques with these samples are reported.

3.2 Molecular weight distributions

Before outlining the techniques used to measure the molecular weight of the hyperbranched polymers described in this thesis it is useful to define the molecular weight averages used in the following discussion. A sample of polymer contains polymer chains of different length, which is a consequence of statistical variations in the polymerisation process.[1] Consequently, polymer samples are mixtures of molecules of different molecular weight and are best characterised by a molecular weight distribution (MWD) and its associated molecular weight averages.

The methods used for the measurement of the molecular weight of polymers employ different averaging procedures. Methods that involve counting the total number of polymer molecules present, for example end group counting using nuclear magnetic resonance (NMR) spectroscopy, yield number average molecular weights. The number average molecular weight, M_n, is defined as the total weight, w, of all the molecules in a polymer sample divided by the total number of moles present (Equation 3.1).[1]

Equation 3.1 $$M_n = \frac{w}{\sum N_i} = \frac{\sum N_i M_i}{\sum N_i}$$ Where, N_i is the number of moles of species *i* of weight M_i.

Methods that depend upon the size of the molecules rather than the number present, for example light scattering, yield the weight average molecular weight, M_w (Equation 3.2).[2]

Equation 3.2 $$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$ Where, N_i is the number of moles of species *i* of weight M_i.

More than one average molecular weight is required to reasonably characterise a polymer sample. The ratio of the two average molecular weights, M_w / M_n, is an indication of the breadth of the molecular weight distribution and is termed the polydispersity index (pdi). The value of pdi is unity for a perfectly monodisperse polymer, such as a perfect dendrimer, but greater than unity for most synthetic polymers. As discussed in chapter one, conventional condensation polymerisations theoretically approach a pdi of 2 at high conversion, whereas hyperbranched polycondensations theoretically approach a pdi of infinity.

3.3 Size exclusion chromatography

Size-exclusion chromatography (SEC) is a technique that separates molecules according to their effective size in solution and is widely used in polymer analysis.[3] The method involves the introduction of a polymer solution onto a column filled with a porous packing material. The polymer sample is carried through the column by the solvent and size separation takes place by repeated exchange of the solute molecules between the bulk solvent of the mobile phase and the stationary liquid phase within the pores of the packing. Typical packing materials have a distribution of different pore sizes. The separation process is illustrated below (Figure 3.1).

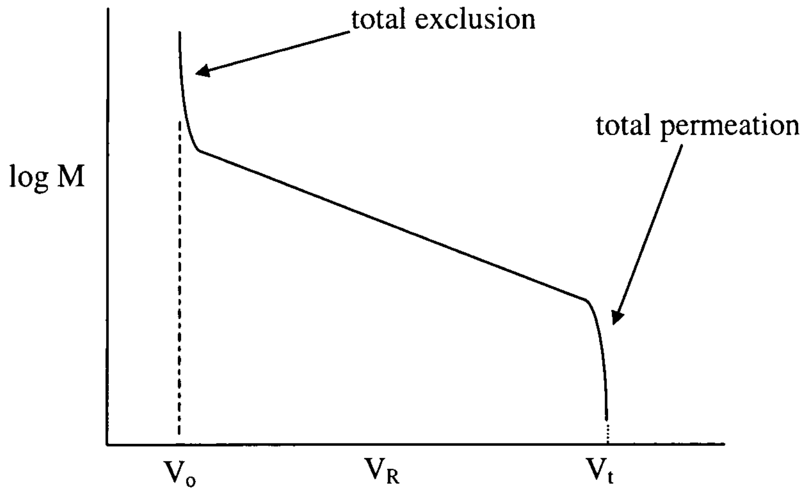


Figure 3.1 Separation profile of a SEC column

In the above diagram V_0 is the interstitial volume between the particles of packing material and represents the minimum amount of solvent that must be eluted in order to move material from the top to the bottom of the column, assuming that it has not entered the pores. Any molecule larger than the particle pores elutes at a volume V_0 which is termed the total exclusion volume. Molecules that are smaller than the smallest pores can permeate all the pores and elute at V_t, which is, termed the total permeation volume. Intermediate sized molecules penetrate some of the pores, spending a fraction of their time within the pores and a fraction within the interstitial volume. This is the region of selective permeation and is responsible for the separation of the solute molecules on the basis of size. The smaller molecules are able to penetrate more pores so they are retained by the column for a greater length of time and elute at larger retention volumes.[4]

The SEC chromatogram itself is a graph of weight fraction of polymer versus elution volume (or time) and to obtain molecular weight information from this a calibration must be established relating retention volume to the molecular weight. Polymers with different chemical structures and the same contour length will usually have different coil dimensions in solution. As the relative sizes of the solute macromolecules and the sizes of the pores in the packing material determine retention time a SEC molecular weight calibration is only valid for that particular polymer-solvent system.

In this study, molecular weights for polymers analysed by this technique are expressed as polystyrene (i.e. the calibrant) equivalent molecular weights. This method gives values for molecular weight that are those for a linear polystyrene standard of an equivalent coil size in solution as the unknown polymer sample. A common procedure to overcome this problem of calibration is to use the universal calibration method.

The universal calibration method uses a measure of the polymer size in solution as the calibration parameter. The most useful parameter in this respect has been shown to be the hydrodynamic volume, which is proportional to the product of intrinsic viscosity $[\eta]$ and molecular weight (M). Benoit and co-workers demonstrated that a plot of $\log[\eta]M$ against elution volume gave a single 'universal' curve for a series of polymers including; linear polymers, block and graft copolymers, star polymers and comb polymers.[5] The use of an in-line viscometer in combination with a concentration detector, in SEC systems, enables the universal calibration method to be applied and has proved effective for many classes of polymer.

Recent advances in SEC techniques have included the use of in-line light scattering detection. Light scattering is an absolute method for molar mass determination in macromolecules.[6] When the electric vector of electromagnetic radiation interacts with a molecule it induces a temporary dipole moment which oscillates in phase with the incident beam. The oscillating electrons of the molecule become a source of new electromagnetic radiation, of the same wavelength as the incident beam, which is known as Rayleigh scattering. Pure solvent also scatters light, so a light scattering experiment measures the excess light scattering intensity above the solvent background. The excess light scattering intensity, caused by the presence of polymer molecules in the sample solution, is directly proportional to the polymer molecular weight and the sample concentration and is related by the following expression (Equation 3.3).[7]

Equation 3.3

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)} + 2A_2c$$

Where R_θ is the Rayleigh ratio, M is the molecular weight, c the concentration, K an optical constant, $P(\theta)$ the particle scattering function and A_2 the second virial coefficient.

The second virial coefficient A_2 is a measure of the thermodynamic quality of the solvent for the given polymer. However, the concentrations employed in SEC are low enough so that the term containing the second virial coefficient, $2A_2c$, becomes insignificant in most cases and may be omitted from the above expression. Large macromolecules may have dimensions comparable to the wavelength of light and are subject to intramolecular interference when light scattered from different points in the same molecule reaches the detector out of phase. Thus the intensity of light scattered by a large particle is smaller than the sum of the intensities of light scattered by all individual mass points of that particle. This phenomenon leads to an angular dependence of scattering intensity,which is described by the particle scattering function, $P(\theta)$. Thus, SEC systems based upon light scattering detectors must also include both a concentration detector and a method of allowing for the angular dependence of the scattering intensity.

Three types of laser light scattering detector are commonly employed in SEC and differ mainly in the angle of observation employed, which may be low angle (LALLS), multi-angle (MALLS) or right angle (RALLS). The LALLS detector is the earliest light scattering detector used for SEC and works on the principle that at small forward scattering angles (typically 5 – 7 degrees for LALLS) the particle scattering function, $P(\theta)$, may be approximated to unity. The MALLS detector uses a number of angles of observation and relies on an extrapolation to zero angle to eliminate the effects of intramolecular interference. The technique also provides a measurement of the angular dependency of the light scattering, which allows the calculation of molecular size. The RALLS detector is the most recent type of commercial light scattering detector and must be used in combination with an in-line viscometer to allow for the angular dependency of the light scattering intensity. The Viscotek TRISEC system used in this study utilises the viscometer output to estimate the radius of gyration, which is then used in the Debye equation to obtain the particle scattering function (a detailed description is included in Appendix 3).

3.4 Dilute solution viscometry

A characteristic feature of a dilute polymer solution is its marked increase in viscosity, relative to the pure solvent, arising from the large difference in size between polymer and solvent molecules. Dilute solution viscometry, which involves the quantitative measurement of this increase in viscosity, allows determination of the intrinsic ability of polymer to increase the viscosity of a particular solvent at a given temperature. The measurement of intrinsic viscosity is often used as a means of estimating the molecular weight of a polymer.[8] Experimentally, intrinsic viscosity, $[\eta]$, is related to molecular weight by the empirical relationship most commonly known as the Mark-Houwink equation (Equation 3.4).[9]

Equation 3.4

$$[\eta]=KM_v^a$$

Where Mv is the viscosity average molecular weight. K and *a* are constants for a given polymer /solvent / temperature system.

For many polymer systems there is a linear relationship between log $[\eta]$ and log M and values for K and *a* can be determined by a least squares fit. The constant *a* is related to the conformation of the polymer chains in solution and generally lies between 0.5 and 0.8 for flexible chains, between 0.8 and 1.0 for inherently stiff molecules and between

1.0 and 1.7 for highly extended chains. Values of *a* for branched polymers are commonly below 0.5. Intrinsic viscosity studies involving dendrimers have revealed two very different types of behaviour. The asymmetrically branched, uniformly dense dendrimers of the Denkewalter series exhibit a constant value of [η] for generations 0 - 9.[10] The more common behaviour for dendrimers is that exhibited by the dendritic macromolecules of Tomalia, Fréchet and Meijer, as described in chapter 1.[11] Whilst these dendrimers exhibit linear Mark-Houwink plots at low molecular weight their intrinsic viscosities are reported to reach a maximum, in the region of generation 5, thereafter decreasing in value. Recently, similar behaviour has been reported for the core terminated hyperbranched analogues of PAMAM dendrimers.[12] Furthermore, modelling studies have shown that hyperbranched polymers with high degrees of branching are expected to deviate from linear Mark Houwink plots with curves tending towards dendritic behaviour.[13]

3.5 Matrix assisted laser desorption / ionisation - time of flight mass spectrometry (MALDI-TOF MS)

The basic principle underlying MALDI-TOF MS is similar to that in other types of mass spectrometry. The sample is placed in a vacuum where it is both vaporised and ionised, the ions are then separated and detected on the basis of their respective mass to charge ratios.

In the MALDI technique the analyte is uniformly mixed with a large excess of a matrix, which is usually an organic compound having a strong absorption at the wavelength of the laser light. The mixture is placed in a vacuum chamber where it is subjected to a pulse of laser light that causes rapid heating and vaporisation of the sample molecules. Ions are generated in this process and are commonly of the type $[M + H]^+$ or $[M + \text{cation}]^+$, where M represents the sample molecule. The ions are subjected to a potential difference, between the sample probe and an extraction grid, which is used to accelerate ions to constant energy. The ions then pass into a field free drift region that is crossed with velocities inversely proportional to the square root of their masses. Thus, lighter ions have greater velocities and arrive at the detector sooner than heavier ions. The mass to charge ratio of an ion is related to its time of flight by the following expression (Equation 3.5).

Equation 3.5 $$\frac{m}{z}=\frac{2V_0t^2}{L^2}$$

Where m is the ion mass, z ion charge, t flight time, V_0 potential difference between the sample probe and the extraction grid and L the length of the flight tube.

The above description applies to the simplest time of flight acquisition mode, which has high mass sensitivity but low resolution and is termed the linear method. A further acquisition mode, relevant to the instrument used in this study, uses an energy focussing device known as a reflectron. With this method a deflector repels ions extracted from the ion source and a voltage applied to an ion mirror, termed the reflectron, turns the ions back towards the source (Figure 3.2).

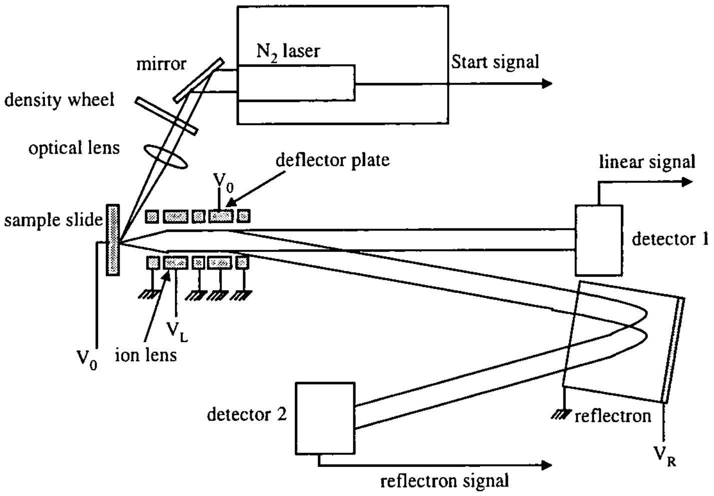


Figure 3.2 Schematic layout of a MALDI-TOF mass spectrometer

By application of an ion reflecting field the distribution in the time of flight, caused by differences in kinetic energy when the ion is created, for ions of the same mass is eliminated and they are 'time focussed'. Ions having a higher energy advance deeper into the reflectron whereas lower energy ions have a longer time of flight through the drift space. Thus, ions with equivalent mass/charge ratios are detected at essentially the same time irrespective of the magnitude of their initial energy. This gives an improved resolution but has a lower mass sensitivity.

The MALDI technique is a relatively recent method, developed in 1987 as a means of measuring high mass ions of biomolecules with m/z in excess of 100kDa.[14] The technique is a soft ionisation process with little fragmentation. The ability to detect high mass ions of intact molecules makes the technique particularly useful for the analysis of polymers. The potential exists for the direct identification of mass resolved oligomers, measurement of molecular weight averages and distributions, and the simultaneous determination of structure and end groups in polymer samples. Most studies have been restricted to the analysis of polymers with low polydispersities and the results are in good agreement with those from conventional methods. However, for polydisperse samples MALDI-TOF fails to give reliable results for the calculation of molecular weight averages.[15]

The well-defined monodisperse nature of dendrimers makes them particularly suitable for this technique. MALDI-TOF MS has been used to confirm the molecular mass of dendrimers[16], identify defects due to incomplete reaction[17] and detect the presence of impurities not discernible by other techniques.[18] Dendritic-linear block copolymers, formed via metal catalysed ‘living’ free radical polymerisation of vinylic monomers using a polyether dendron as initiator, have been characterised using MALDI-TOF MS.[19] The technique has also been employed to confirm the attachment of poly(ethylene glycol) arms to a polyether dendrimer in the synthesis of star like molecules.[20]

There are comparatively few studies involving analysis of hyperbranched macromolecules by MALDI. The broad molecular weight distributions characteristic of many hyperbranched polymers are difficult to analyse by MALDI and reliable molecular weight averages are often inaccessible. Nevertheless, the technique has been successfully employed in the few cases of hyperbranched polymers with low polydispersities. The number average molecular weight of polyglycerols, produced via ring-opening multibranching polymerisation using the method of slow monomer addition, was in good agreement with that obtained by ^{13}C NMR spectroscopy.[21] Despite the problem of obtaining reliable molecular weight averages MALDI-TOF MS is a useful method for investigating other aspects of hyperbranched macromolecules. It has been used to characterise the low molecular weight oligomers present in wider distributions and identify the products of intramolecular cyclisation reactions that compete with polymerisation.[22] MALDI-TOF MS also proved useful in the characterisation of hyperbranched poly(diethyl 3-hydroxyglutarate) where the products of alkoxide exchange between the alkoxide ligands of the polymerisation catalyst and terminal ester groups of the polymer were detected.[23]

3.6 Analysis of hyperbranched polyesters by size exclusion chromatography

The study of the molecular weight dependence of polymer properties requires reliable data for molecular weight averages and distributions. The novel relationship between intrinsic viscosity and molecular weight for dendrimers and some hyperbranched polymers means that the universal calibration method is not necessarily reliable for dendritic macromolecules. The universal calibration relates the hydrodynamic volume of the polymer, which is proportional to the product of intrinsic viscosity and molecular weight, to its retention volume in SEC. However, the occurrence of maxima in the Mark-Houwink plots for dendritic materials is an indication that the relationship between hydrodynamic volume and molecular weight is different from that found in linear polymers. An absolute method of molecular weight determination, such as light scattering, is necessary in these cases. LALLS online detectors have been used successfully in the characterisation of both poly(amidoamine)[11b] and polyether dendrimers.[24] In both cases the results were in good agreement with the theoretical molecular weights for perfect dendrimers. A triple detector system employing a combination of a refractive index detector, a differential viscometer and a LALLS detector has been used for the analysis of hyperbranched polyesters.[25]

The hyperbranched polyesters described in chapter 2 were analysed by SEC, in tetrahydrofuran, using a Viscotek triple detection system (RI-DV-RALLS).

A prerequisite for the use of a light scattering detector is the determination of the specific refractive index increment, dn/dc. This is the slope of the dependence of the refractive index, n, of solution on the solute concentration, c, and is an important characteristic of a particular polymer-solvent system at a given temperature. The light-scattering constant, K, is proportional to the square of the refractive index increment (see Appendix 3 for details). In this work dn/dc was measured using a Brice-Phoenix differential refractometer. This measures small differences in the refractive indices of a solvent and a dilute polymer solution in that solvent.[6, 26] Measurements were made on a series of hyperbranched polyester solutions of differing concentration and at a variety of different wavelengths. A plot of the refractive index difference against concentration gave a linear relationship with the slope yielding dn/dc at that particular wavelength (Figure 3.3). A further plot of dn/dc against $1/\lambda^2$ gave the wavelength dependence from which the refractive index increment at the required wavelength (670 nm for the RALLS detector) was obtained (Figure 3.4).

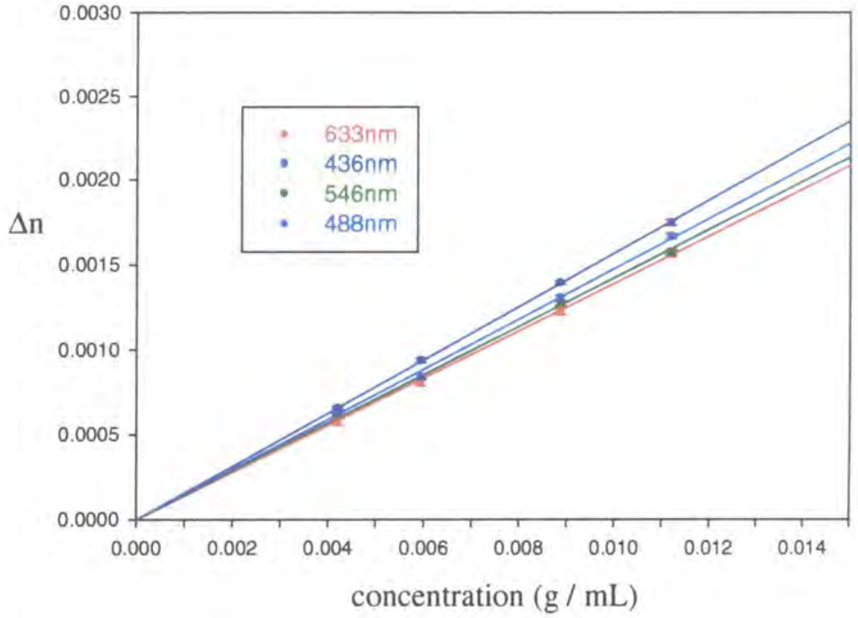


Figure 3.3 The concentration dependence of Δn for hyperbranched polyesters, in THF at 30 ^{0}C.

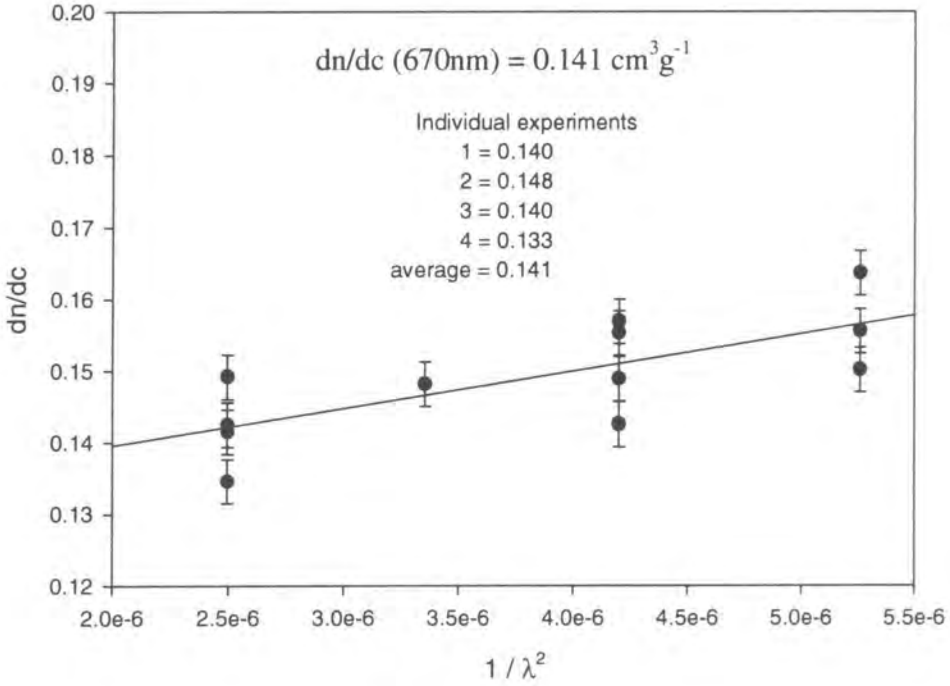


Figure 3.4 The wavelength dependence of dn/dc for hyperbranched polyesters, in THF at 30 ^{0}C.

The refractive index increment was measured in both tetrahydrofuran (dn /dc 0.141 cm^3g^{-1}) and chloroform (dn / dc 0.123 cm^3g^{-1}). The refractive index increment is assumed to be independent of molecular weight, although for linear polymers dn/dc increases with increasing molecular weight until molecular weights in the region of 20,000 to 30,000 are reached. For the hyperbranched polyesters dn/dc was measured, in $CHCl_3$, for polymers of differing molecular weight. No molecular weight dependence was apparent (Figure 3.5).

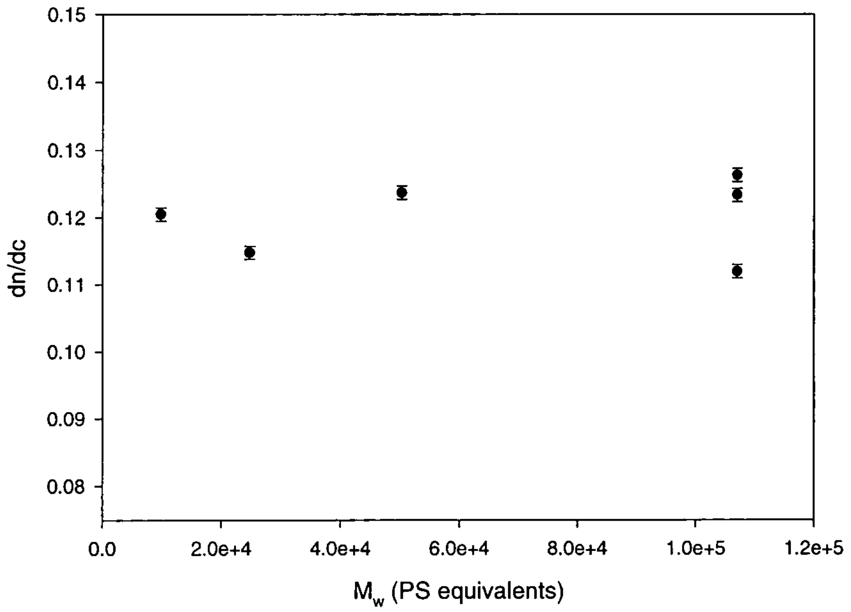


Figure 3.5 The molecular weight dependence of dn/dc for hyperbranched polyesters in chloroform at 30 ^{0}C.

The chromatograms obtained from the refractive index detector showed broad polymodal peaks, which appear to be typical of hyperbranched polymers and have been observed for other aromatic hyperbranched polyesters (for example, see Figure 2.8 in chapter 2).[27] However, the light scattering detector revealed a further set of peaks associated with very high mass species (Figure 3.6). Light scattering detectors emphasise higher molecular weight species and the extra peaks only represent a very small amount of material, which is shown by the concentration detector response (Figure 3.7).

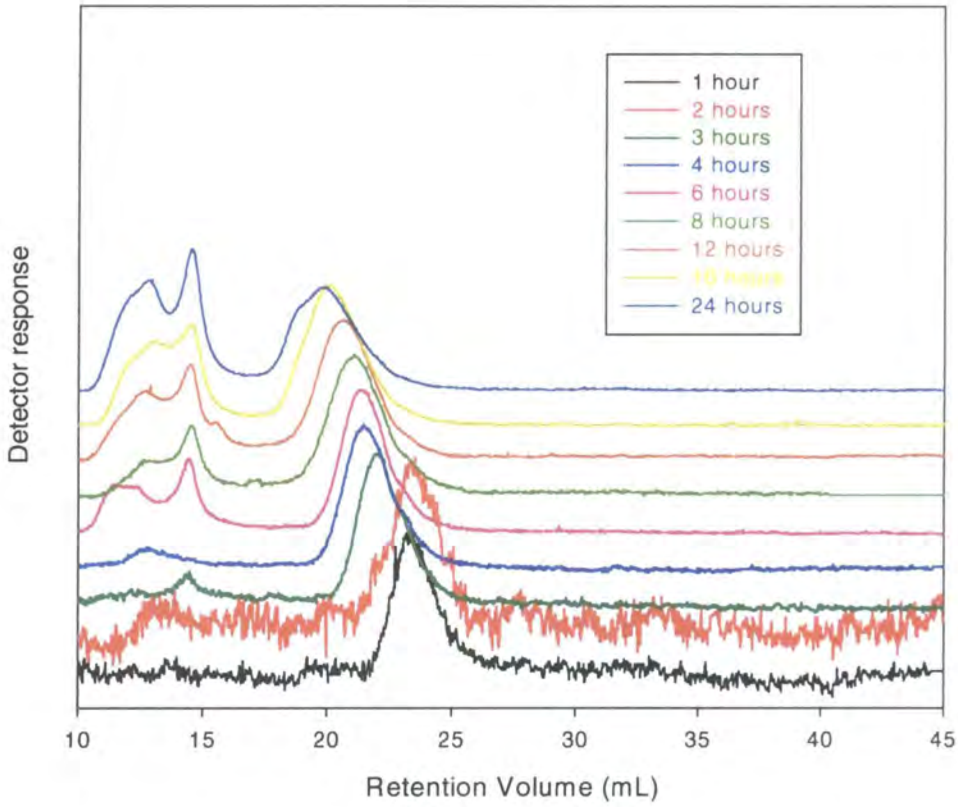


Figure 3.6 SEC traces from the light scattering detector for hyperbranched polyesters at various polymerisation times.

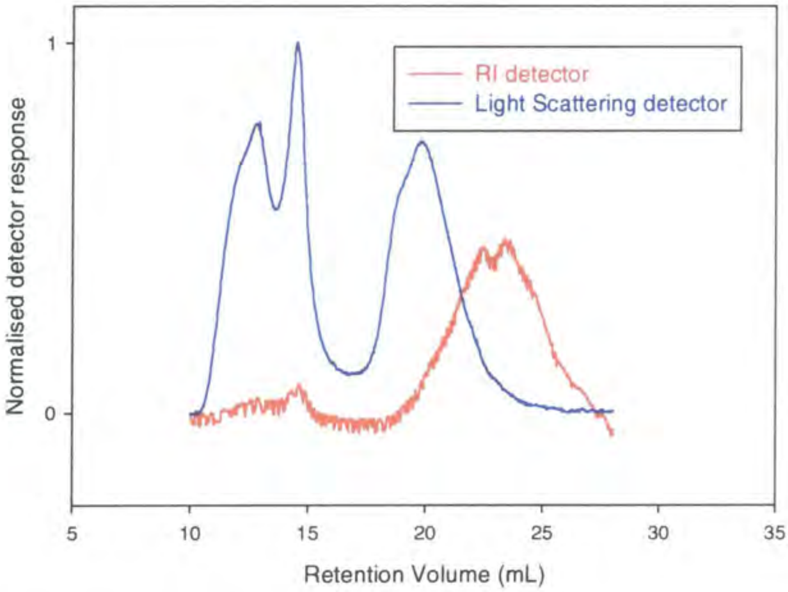


Figure 3.7 Comparison of RI and RALLS detector response for hyperbranched polymer after 24 hours polymerisation

The origin of the high mass peaks is unclear but similar behaviour has been reported in the chromatograms of stiff chain carbohydrate polymers where it has been ascribed to aggregation.[28] For the purposes of this study the extra peaks were deemed to represent only a very minor component and have been omitted from the calculation of average molecular weights. The results from the SEC analysis, using the Viscotek triple detection system, are summarised below (Tables 3.1). In the following table, and subsequent discussion, conventional calibration refers to the results obtained from the refractive index (RI) detector using a calibration that relates the retention volume of the sample to the molecular weight of a linear polystyrene standard. The universal calibration method uses the viscometer detector output, in addition to the RI detector output, to relate retention volume to the hydrodynamic volume of the standards. The data labelled light scattering are obtained by applying the Viscotek proprietary software, which uses the output from the light scattering detector in combination with the RI and viscometer detector outputs (see Appendix 3). A detailed description of SEC calibration techniques is given in the introduction to this chapter (section 3.3).

Polymerisation time (h.)	Conventional calibration			Universal calibration			Light Scattering		
	M_n	M_w	p.d.i.	M_n	M_w	p.d.i.	M_n	M_w	p.d.i
1	1600	7100	4.4	1300	9700	7.5	3100	8200	2.6
2	3000	8200	2.7	5100	22100	4.3	5600	16100	2.9
3	3700	17400	4.7	3100	38200	12.3	3500	38400	11.0
4	4000	23500	5.9	3600	62400	17.3	8300	65000	7.8
6	7100	28400	4.0	7200	75900	10.5	10100	84200	8.3
8	4000	28400	7.1	4400	135400	30.8	5400	109200	20.2
12	6600	45200	6.8	5700	139500	24.5	3400	182900	53.8
16	6100	48900	8.0	4000	221400	55.4	2900	200200	69.0
24	5800	58600	10.1	3500	362000	103.4	4700	279800	59.5

Table 3.1 SEC analysis of hyperbranched polyesters in THF

The results obtained from all three detector sytems show a similar trend of increasing polydispersity with increasing polymerisation time. However, the values for weight average molecular weight, obtained from the light scattering or viscometry detectors, are appreciably higher than the polystyrene equivalent molecular weights obtained from a conventional polystyrene calibration.

In order to circumvent the problem of aggregation the hyperbranched polyesters were re-examined by SEC in chloroform, which is a better solvent for these polymers. No extra peaks were observed in this case and the results are summarised below (Table3.2). Also shown is the result of using the light scattering detector response without any angular correction.

Polymerisation time (h.)	1	2	3	4	6	8	12	16	24
M_w (LS)	11000	34500	49000	86400	74700	104800	144800	253300	475300
M_w LS no correction*	13100	32600	45200	71200	78200	117900	189400	281600	352200
* Values from light scattering without correction for angular dependence of scattering intensity									

Table 3.2 SEC analysis of hyperbranched polyesters in chloroform

The Viscotek TRISEC system uses the viscometer output to estimate the radius of gyration, which in turn is used to obtain the particle scattering function (Appendix 3). Both these quantities are calculated from equations derived for Gaussian coils and hence may not be applicable to hyperbranched materials. By using the light scattering data without allowing for angular dependence a *minimum* value of Mw is obtained.

A comparison of the weight average molecular weights obtained with the different detector systems is shown below (Figure 3.8).

The results obtained using a conventional polystyrene calibration are much lower than either the light scattering or the universal calibration results. The polystyrene equivalent molecular weights obtained in chloroform are generally higher than those obtained in THF. This is consistent with chloroform being the better solvent, as the polymer molecules would be expected to adopt a more extended conformation in a good solvent as polymer solvent interactions become more favourable.

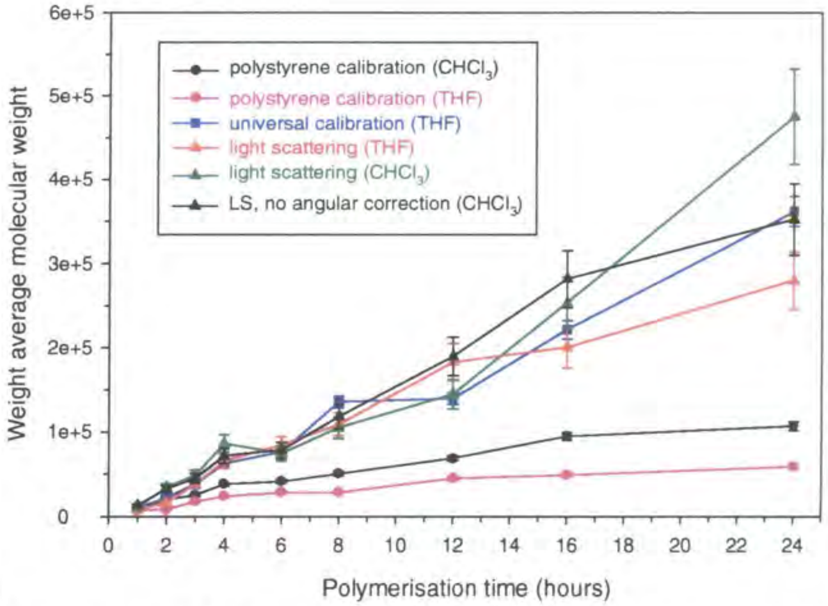


Figure 3.8 Comparison of SEC results for hyperbranched polyesters from different SEC detectors.

The results obtained via the universal calibration are in reasonable agreement with those from the light scattering methods although the difference between the various methods is large for the highest molecular weight polymers. A good agreement between molecular weights obtained by light scattering and universal calibration has been observed in other hyperbranched polyesters.[27, 29]

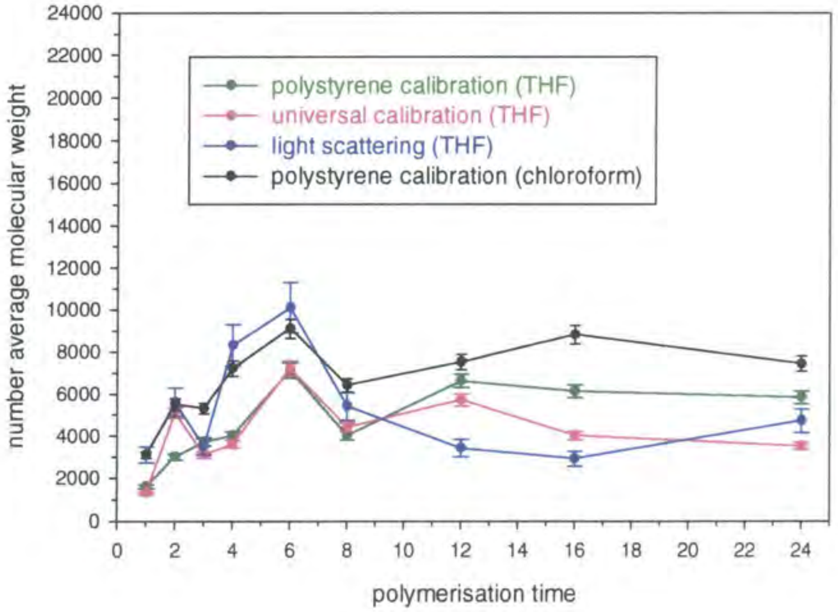


Figure 3.9 Variation of hyperbranched polyester M_n with polymerisation time.

There is a general trend of increasing M_w with increasing reaction time leading to very large values of polydispersity (M_w/M_n). However, the number average molecular weight does not continue to rise but reaches a plateau value after relatively short reaction times (Figure 3.9). This limit to M_n has been observed in other hyperbranched systems and has been ascribed to intramolecular cyclisation, although an associated maximum in M_w is observed in these cases.[30] The relationship between the occurrence of cyclisation and the observed molecular weight averages for the hyperbranched polyesters described in this work will be discussed in a later section.

3.7 Dilute solution viscometry of hyperbranched polyesters

Viscosity measurements were made using the SEC differential viscometer and by conventional capillary viscometry. In the latter case measurements were made on chloroform solutions of the hyperbranched polyesters using an Ubbelhode capillary viscometer. In this method the flow rate of a polymer solution through a capillary tube is compared to the flow rate of the pure solvent. The relative viscosity, η_r, is the ratio of the polymer solution viscosity to the viscosity of the solvent, η_0 (Equation 3.6).

Equation 3.6

$$\eta_r = \frac{\eta}{\eta_0}$$

When the solvent and solution densities are nearly equal, as is the case for very dilute solutions, the relative viscosity may be approximated to the ratio of flow times, t / t_0. The specific viscosity, η_{sp}, is a measure of the increase in viscosity due to the addition of polymer. Infinitely dilute solutions have relative viscosities approaching unity and the specific viscosity may be defined as the relative viscosity minus one (Equation 3.7).

Equation 3.7

$$\eta_{sp} = \eta_r - 1 = \frac{t - t_0}{t_0}$$

The reduced viscosity, η_{sp}/c, is a measure of the specific capacity of the polymer to increase the relative viscosity and in the limit of infinite dilution is known as the intrinsic viscosity, $[\eta]$ (Equation 3.8).

Equation 3.8 $$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c \to 0}$$

Viscosity measurements yield data at finite concentrations and are commonly extrapolated to zero concentration to give the intrinsic viscosity, which simplifies the interpretation of experimental data by eliminating the effects of intermolecular polymer-polymer interactions. The two most common ways of achieving this are by application of either the Huggins or the Kraemer equations (Equations 3.9 and 3.10).

Equation 3.9 $$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$ Huggins equation

Equation 3.10 $$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c$$ Kraemer equation

The intrinsic viscosity can be obtained from the intercepts of plots of either η_{sp}/c or $(\ln \eta_r)/c$ versus concentration. The intrinsic viscosity data for the hyperbranched polyesters are shown below (Table 3.3). The viscosity data for hyperbranched polymers in chloroform are in good agreement, although the SEC values for intrinsic viscosity are slightly lower than those obtained by capillary viscometry, which is probably due to the higher temperature used in SEC. As mentioned above, Mark-Houwink plots for conventional linear and lightly branched polymers are linear whilst those for dendrimers and some hyperbranched polymers exhibit maxima. The Mark-Houwink plots for the hyperbranched polyesters do not exhibit maxima and reasonable linear fits are obtained (Figure 3.10).

Weight average molecular weight [a]	Intrinsic viscosity (cm^3g^{-1})		
	VISC ($CHCl_3$) [b]	SEC ($CHCl_3$) [c]	SEC (THF) [d]
11000	7.7	8.6	4.9
34500	13.4	13.1	6.5
49000	17.3	13.2	7.9
74700	18.7	16.0	8.7
86400	17.7 17.9	15.8	9.6
104800	19.9	17.4	8.8
144800	23.4	18.3	10.1
253300	26.1	24.6	9.3
475300	30.7 30.7	28.9	10.9

a) M_w from SEC in $CHCl_3$ solution, light scattering detector.
b) Ubbelhode viscometer, $CHCl_3$ at 25 ^0C
c) SEC viscometer, $CHCl_3$ at 30 ^0C
d) SEC viscometer, THF at 30 ^0C

Table 3.3 Viscosity data for hyperbranched polyesters

The Mark-Houwink plot, based upon of viscosities measured by SEC in $CHCl_3$, gave a good straight line fit (correlation coefficient r^2 = 0.99) which allowed the Mark-Houwink parameters to be determined as a = 0.3 and K = 0.4 cm^3g^{-1}. On first inspection the corresponding data from capillary measurements appears to give a curved plot. However, there is an anomalous point for the lowest molecular weight sample that has a lower intrinsic viscosity than the equivalent, higher temperature, SEC measurement. This point has been omitted from the regression analysis and a reasonable straight line fit obtained (r^2 = 0.96), which yielded Mark-Houwink parameters of a = 0.3 and K = 0.6 cm^3g^{-1}. The relationship between log[η] and log (molecular weight), across the whole molecular weight distribution, was obtained directly from the SEC viscometer and was also linear (Figure 3.11).

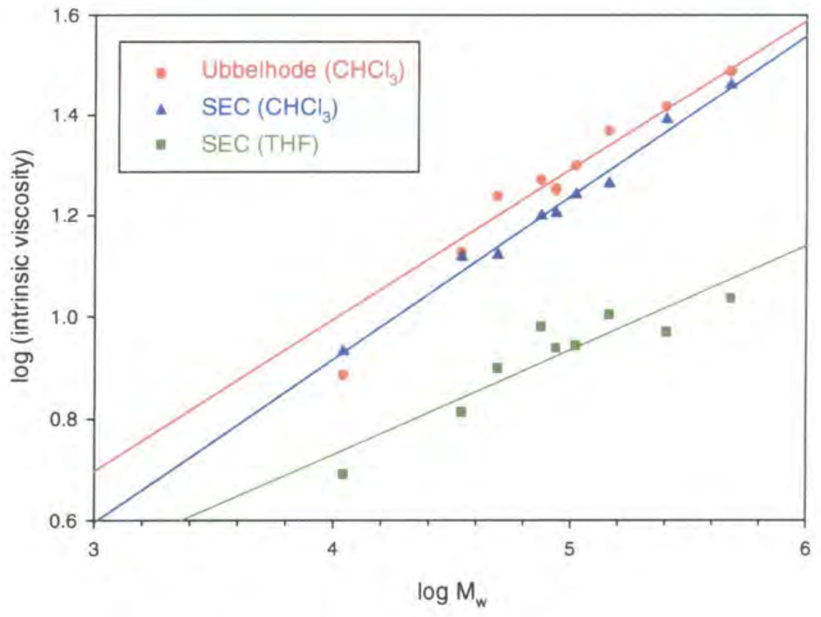


Figure 3.10 Mark-Houwink plots for hyperbranched polyesters

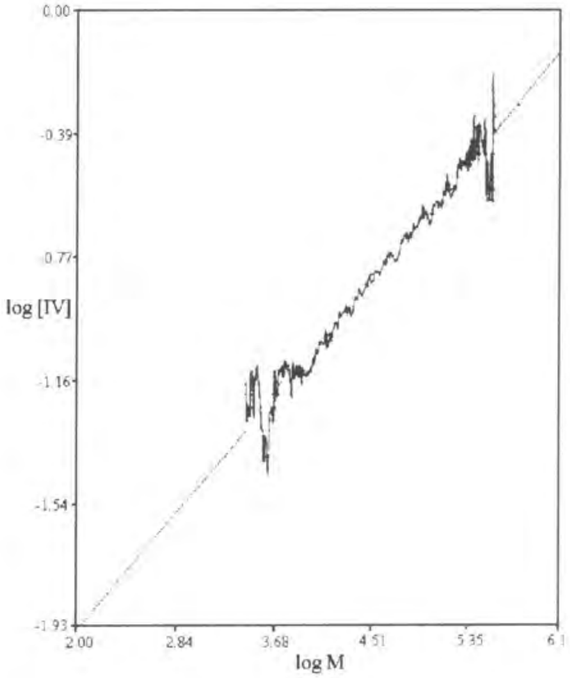


Figure 3.11 Representative Mark-Houwink plot for a hyperbranched polyester (M_w 49 000, $CHCl_3$ @ 30 ^{0}C) from SEC.

The hyperbranched polyesters were less soluble in THF than chloroform, which necessitated using lower concentration sample solutions in the SEC experiment. Consequently, the SEC viscometer response has a lower signal to noise ratio, when using THF solutions, and the measurements are subject to a greater degree of experimental error. Thus the data obtained from THF solutions is more scattered and a poorer linear fit obtained ($r^2 = 0.85$). This gave Mark-Houwink parameters of $a = 0.2$ and $K = 0.8\ cm^3g^{-1}$.

Linear Mark-Houwink plots have been reported for the analogous hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s[31] and hyperbranched polymers derived from 5-acetoxyisophthalic acid or 1,3-diacetoxybenzoic acid.[27, 29] The Mark-Houwink parameters ($a = 0.2 - 0.3$) for the hyperbranched polyesters are consistent with a branched polymer.

3.8 MALDI-TOF analysis of hyperbranched polyesters

In order to investigate further the molecular weight growth of the hyperbranched polyesters dimethyl 5-(2-hydroxyethoxy)isophthalate was polymerised for 65 hours and sampled every 5 hours. The samples were analysed using SEC and MALDI-TOF mass spectroscopy. MALDI-TOF mass spectrometry was carried out using a Kratos Kompact MALDI IV mass spectrometer. All spectra were run in linear mode at a laser power of 125 (ca. 15% transmission) and the data collected over 200 laser shots. Samples were prepared in a 2,5-dihydroxybenzoic acid matrix and were deposited from a THF solution. The spectra were calibrated against a commercial sample of poly(ethyleneoxide) (Polymer Labs PEO 1470). This gave a relatively narrow calibration range but was sufficient for accurate peak assignment in the low molar mass region where peaks were fully resolved. A MALDI-TOF MS spectrum representative of those obtained from the hyperbranched polyesters is shown below (Figure 3.12 and Appendix 2.1).

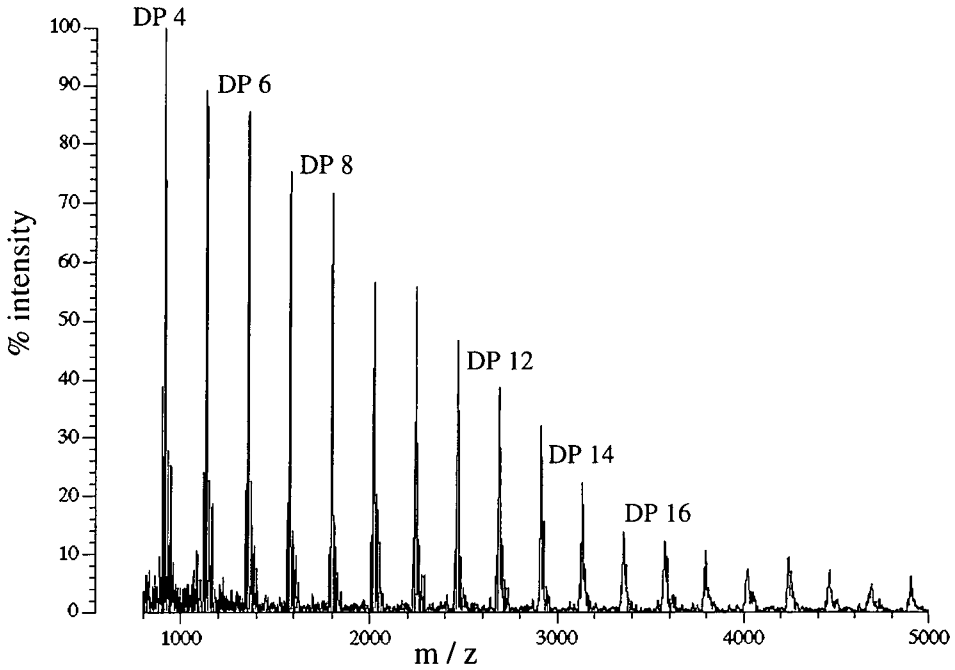
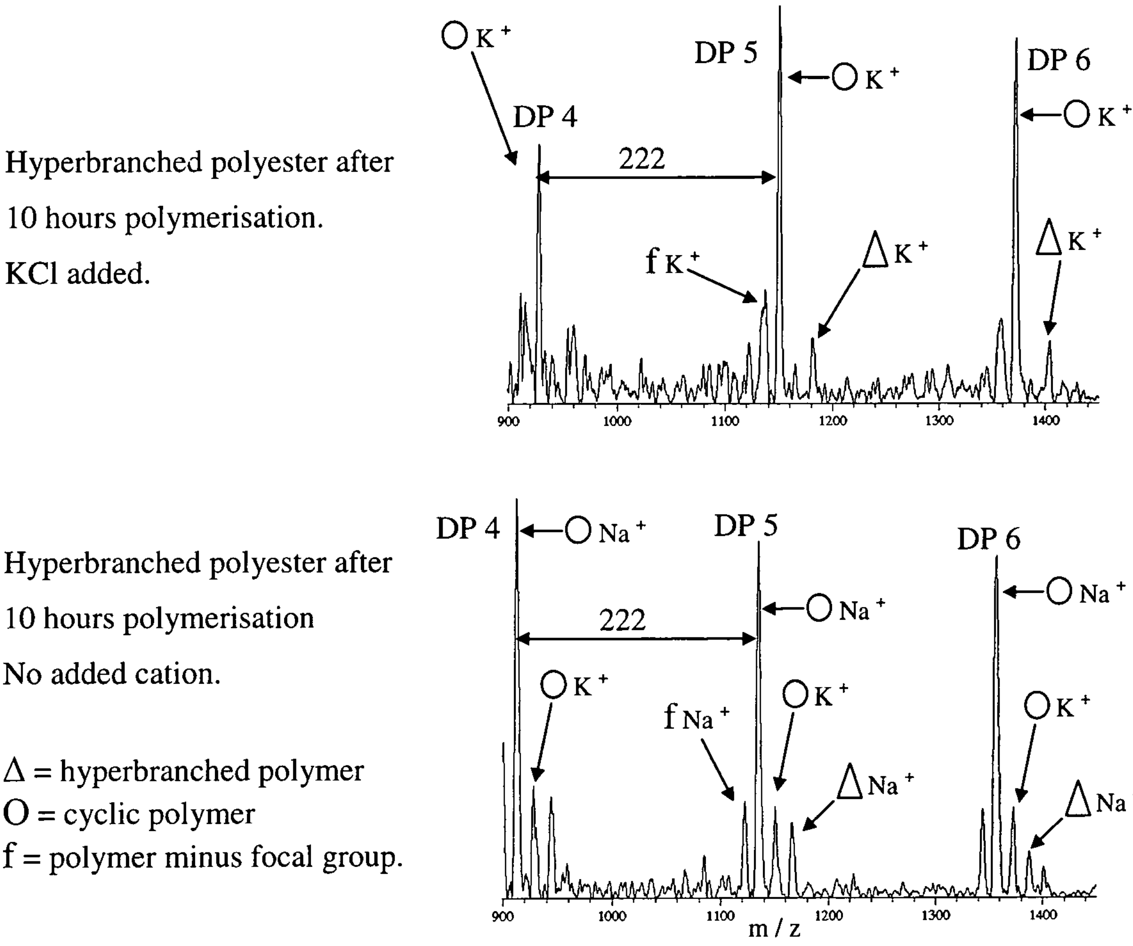


Figure 3.12 MALDI-TOF spectrum of a hyperbranched polyester after 10 hours polymerisation

The MALDI-TOF MS spectrum shows a series of peaks corresponding to a distribution of oligomers with increasing degrees of polymerisation (DP) up to a DP of 22. It is apparent that the high molecular weight region of the spectrum is under represented and molecular weight averages calculated from the MALDI-TOF spectra are much too low. For example, the MALDI-TOF spectrum of the hyperbranched polyester prepared in a 50 hour polymerisation gave a number average molecular weight (M_n) of 2300 and a polydispersity (M_w/M_n) of 1.2. The corresponding values from SEC were M_n 8000 (polystyrene equivalent molecular weight) and M_w/M_n 14.6. The failure of MALDI-TOF MS to give reliable molecular weight averages for polymers with broad molecular weight distributions has been widely reported.[17, 32] It has been shown that in a polydisperse sample the optimum laser power required for the ionisation / desorption process is greater for the high molecular weight species than the low molecular weight oligomers. The greater levels of laser power required for the analysis of high molecular weight species can lead to fragmentation of lower DP components.

Although it was not possible to obtain reliable molecular weight averages for the hyperbranched polyesters by MALDI-TOF MS it was possible to obtain the masses of individual oligomers in the low molecular weight region. The region below a DP of 4 is obscured by matrix and fragmentation peaks whilst peaks corresponding to a DP of greater than 11 are not fully resolved. Hence, the analysis of the MALDI-TOF spectra was restricted to the region associated with DP 4-11 (m/z 900-2600).

Individual species in a MALDI-TOF spectrum are commonly observed as the parent species plus an attached proton $[M + H]^+$ or cation $[M + \text{cation}]^+$. Low levels of impurities containing sodium and potassium ions give rise to substantial cation peaks and sample peaks are observed as $[M + Na]^+$ and $[M + K]^+$ ions.


Hyperbranched polyester after
10 hours polymerisation.
KCl added.

Hyperbranched polyester after
10 hours polymerisation
No added cation.

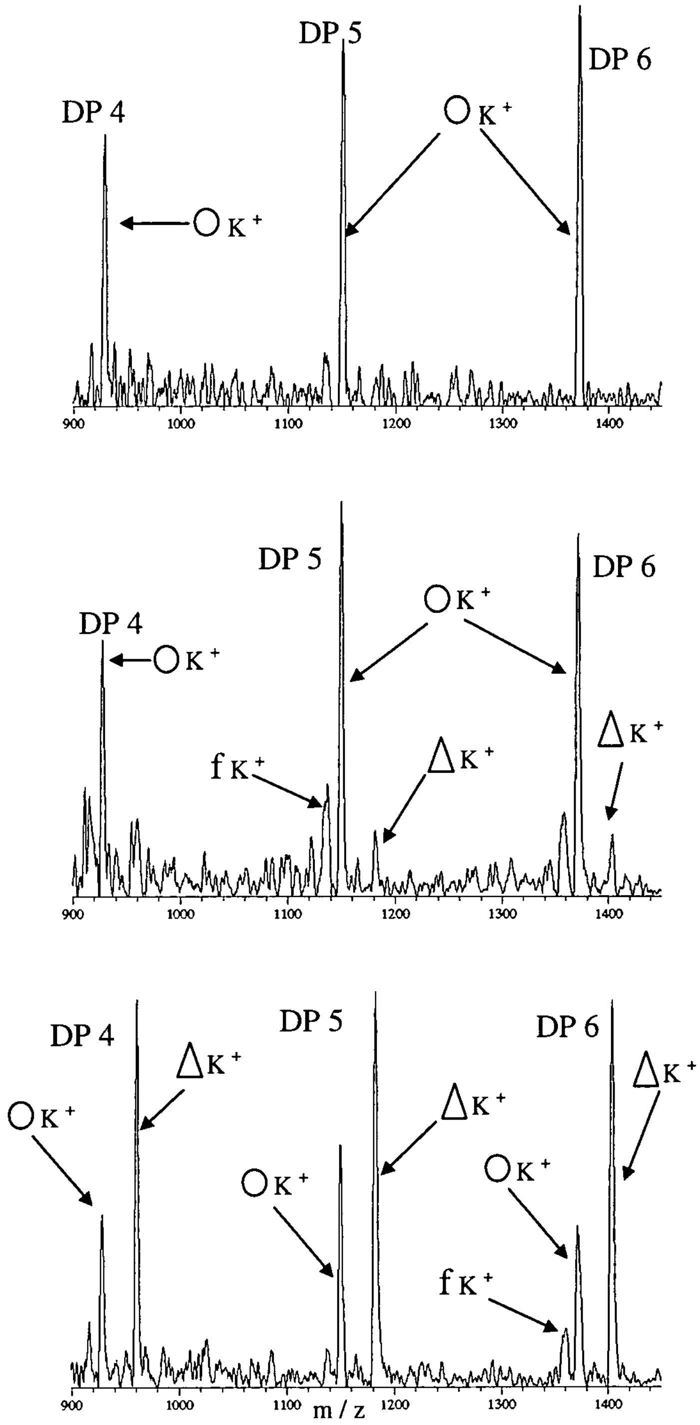
Δ = hyperbranched polymer
O = cyclic polymer
f = polymer minus focal group.

Figure 3.13 MALDI-TOF spectra of hyperbranched polyester after 10 hours polymerisation. Expansion of region corresponding to degree of polymerisation (DP) 4-6, illustrating the effect of potassium doping.

The spectra can often be simplified by the addition of an appropriate salt to the sample or matrix in order to favour a particular cation (Figure 3.13 and Appendix 2.2). The hyperbranched polyesters were examined with the addition of KCl to the matrix.

The mass of a particular polymer molecule may be calculated by a consideration of the polymerisation process. A hyperbranched polymer of n repeat units is the result of (n-1) condensation steps. Each successive condensation is accompanied by the loss of a single methanol moiety. Hence, the mass of an oligomer of n units is [(monomer mass) x (n) - (mass of methanol) x (n-1)]. The main ion series observed for the hyperbranched polymers prepared with short polymerisation times corresponded to oligomers formed by such successive condensation reactions (Figure 3.14).

However, two further ion series were also present. The first of these was observed 32 mass units behind the main series and can be attributed to the loss of a further single methanol moiety to form a cyclic polymer. An alternative interpretation of this series would be hydrolysis of a single methyl ester unit. If this is occurring it seems reasonable to expect that more than one of the many methyl ester units in each molecule would undergo the reaction but there is no evidence for the extra methanol losses required.



40 hours polymerisation.

10 hours polymerisation.

4 hours polymerisation.

Δ = hyperbranched polymer
O = cyclic polymer
f = polymer minus focal group

Figure 3.14 MALDI-TOF spectra of potassium doped hyperbranched polyester at various polymerisation times. Only the region corresponding to degree of polymerisation 4-6 is shown.

The second extra ion series is observed 44 mass units behind the main series. This can be explained by cleavage of the alkyl chain of the focal group at the O-C bond β to the aromatic ring accompanied by a hydrogen migration. This is a common fragmentation of aromatic alkyl ethers in electron impact (EI) mass spectrometry (Figure 3.15).[33] A similar cleavage of the hydroxyalkyl ether from a hyperbranched polyester would result in the formation of a stable acetaldehyde molecule. For example, when R = OH, in Figure 3.15, fragmentation leads to the elimination of $CH_2{=}CHOH$, which is the enol form of $CH_3CH{=}O$ and corresponds to a loss of 44 mass units.

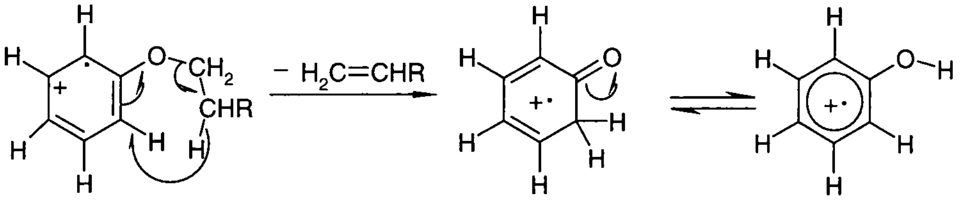


Figure 3.15 Fragmentation of aromatic alkyl ethers in EI mass spectrometry.

The fragmentation of hyperbranched polymers leading to loss of a focal point group has been observed in the MALDI-TOF MS of hyperbranched poly(amidoamines) (Figure 3.16).[34]

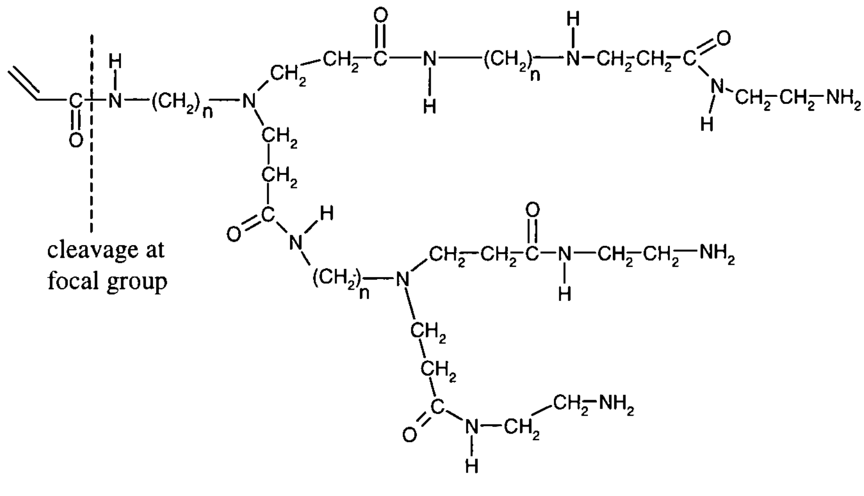


Figure 3.16 Amide cleavage at the focus in a poly(amidoamine) hyperbranched system as observed in MALDI-TOF mass spectrometry.[34]

The relative proportions of the 3 ion series varied with polymerisation time (Figure 3.14). The proportion of oligomers due to cyclised polymer increased with longer reaction times. The disappearance of the series due to hyperbranched polymer minus the focal group, in the spectra of the polymers after long reaction times, supports the notion that the fragmentation occurs in the spectrometer and not during the polymerisation. If occurring during the polymerisation such fragmented species would be expected to be present throughout, whereas if the fragmentation occurs in the spectrometer this can only occur in samples with significant amounts of uncyclised material present. Comparing the peak areas in the MALDI-TOF spectrum gave the relative amount of each type of species, for a given degree of polymerisation. The percentage cyclic content of the oligomers, corresponding to DP 4-11, was constant across the region of the spectrum examined (Figure 3.17).

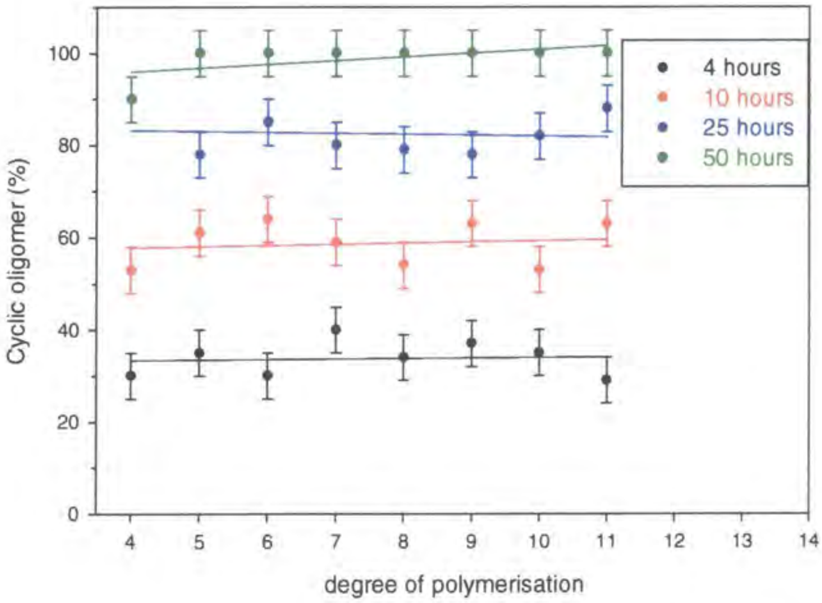


Figure 3.17 Variation of cyclic content of hyperbranched polyester oligomers with polymerisation time.

Polymerisation time (hours)	SEC[a]		MALDI-TOF
	M_n	M_w	Cyclic content[b] (%)
4	3800	13000	35
10	4700	26600	60
15	7300	31500	65
20	6900	33500	80
25	7000	35500	85
30	6700	40700	80
35	7900	53000	90
40	8500	86400	95
45	7900	108400	100
50	8000	116900	100
55	7800	135700	-
60	7700	172900	-
65	7500	215500	100

[a] Calibrated against polystyrene standards

[b] Average cyclic content of oligomers for DP 4 - 11

Table 3.4 Variation of average cyclic content with polymerisation time for hyperbranched polyesters.

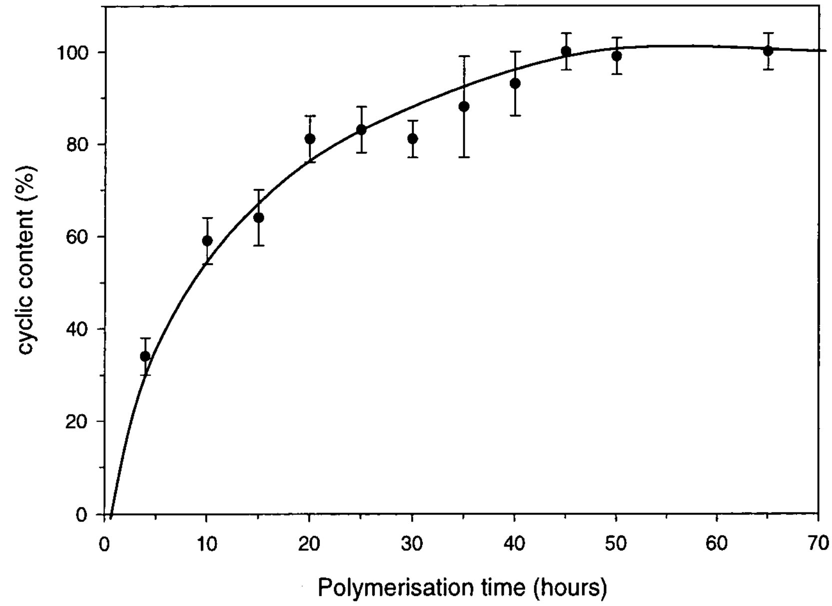


Figure 3.18 Variation of average cyclic content of hyperbranched polyesters, in the range DP 4 to 11, with polymerisation time.

The average cyclic content of the hyperbranched polyesters is shown above (Table 3.4 and Figure 3.18). The proportion of cyclic polymer increases with increasing polymerisation time until all the oligomers, between DP 4 and 11, are fully cyclised after 45 hours reaction.

The number of monomer residues in the cyclic portion of a given oligomer cannot be determined by MALDI-TOF MS. However, oligomers as low as DP 4 contain a cyclic part and the ring size in these species must necessarily be small. Oligomers lower than DP 4 cannot be identified with any certainty in the MALDI-TOF spectrum but cyclic oligomers as small as DP 2 are feasible (Figure 3.19). Similarly, it is unknown whether oligomers of DP >> 11 contain cycles but the nature of step growth polymerisation would suggest this is likely. Higher oligomers are created by oligomer / oligomer or oligomer / monomer condensation reactions.

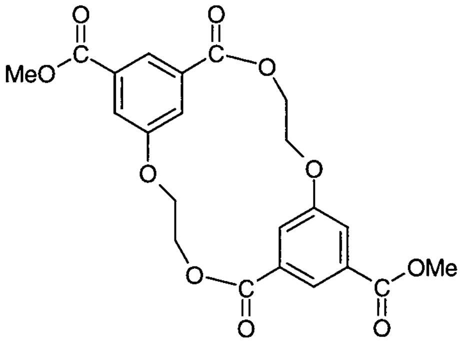
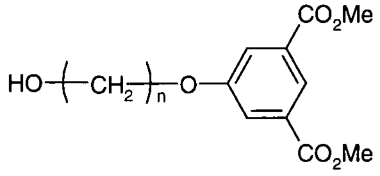


Figure 3.19 A cyclic dimer of dimethyl 5-(2-hydroxyethoxy)isophthalate.

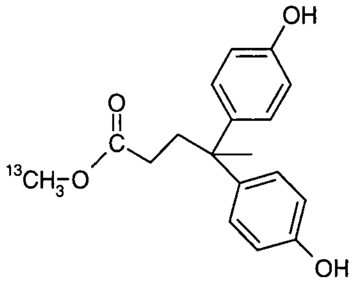
As many of the lower DP oligomers are cyclised then it is probable that the higher molecular weight species are also cyclised. Dušek has reported a kinetic simulation of AB_2 polymerisation, which suggests that if cyclisation occurs, at high extents of reaction, the higher molecular weight oligomers are all cyclised.[35]

Relatively few of the many synthetic examples of hyperbranched polymers have been examined for the presence of cyclisation. Establishing the presence (or absence) of the single unique focal point group in a hyperbranched polymer can prove problematic. Hawker and co-workers reported the use of an isotopically labelled (^{13}C) methyl ester A group to monitor the disappearance of the focal group during polymerisation.[36] Another approach, adopted for some hyperbranched condensation polymers, is to examine the loss of the condensate molecule by the technique of soft ionisation mass spectroscopy. (Figure 3.20).[31, 34, 35, 38, 39] Examples of those hyperbranched polymers that have been examined for the presence of cyclisation are shown below (Figure 3.20).

It can be concluded from the examples shown below that the occurrence of cyclisation in hyperbranched polymerisations is extremely system specific. Modelling studies suggest that cyclisation is the likely outcome of hyperbranched polymerisations.[35, 37] The reasons why some hyperbranched polymers show little evidence of cyclisation may vary between systems but it is possible that the occurrence of cyclisation is related to the conformational mobility of both the monomer and oligomers.



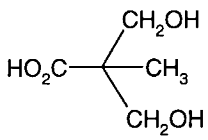
Keeney[31]
n=3,4,6
100%
cyclised
(MALDI
TOF MS)



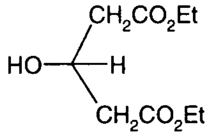
Hawker *et al.*[36]

cyclisation < 5%

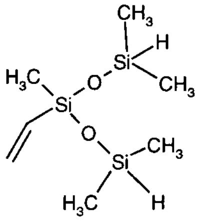
(^{13}C NMR)



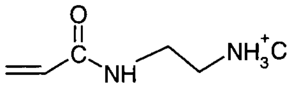
Dušek *et al.*[35]
cyclised
(ESI / FT MS)



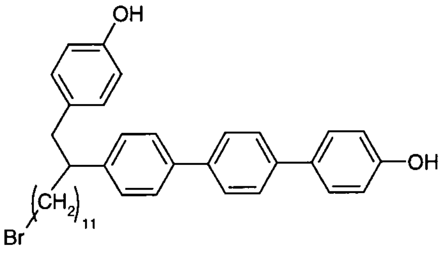
Feast *et al.*[38]
no cyclisation
detected
MALDI TOF MS



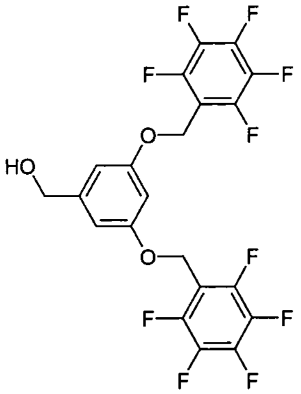
Fréchet, *et al.*[30b]
cyclised
(^{1}H NMR)



Feast *et al.*[34]
no cyclisation
detected
(MALDI TOF MS)



Percec *et al.*[39]
56%
cyclised
(^{1}H NMR)



Wooley *et al.*[40]
50% cyclised
(MALDI TOF
MS)

Figure 3.20 Examples of AB$_2$ systems examined for the presence of cyclisation.

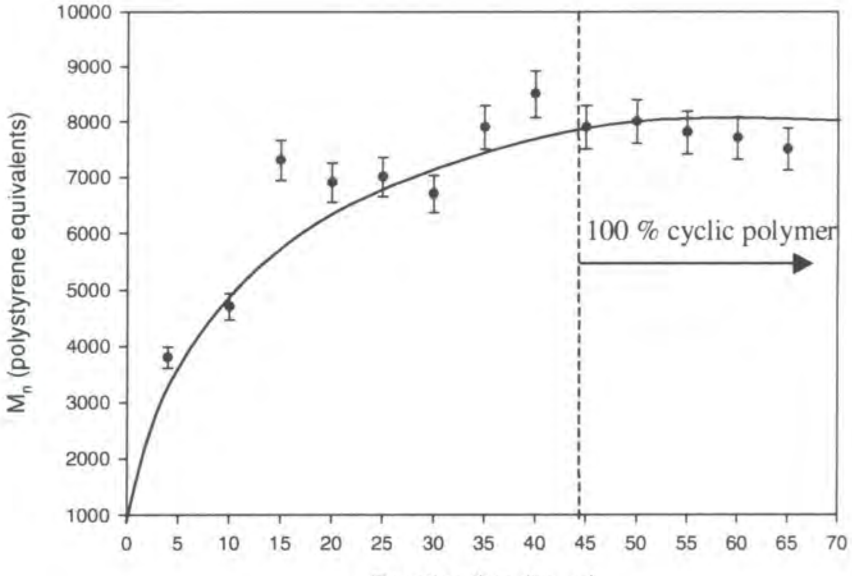


Figure 3.21 Variation of M_n with polymerisation time for hyperbranched polyesters.

The point at which those oligomers measurable by MALDI-TOF MS are fully cyclised corresponds to the observed limit in the number average molecular weight (Figure 3.21). A fully cyclised AB_2 polymer has no remaining A groups left to undergo condensation reactions and hence further growth is not possible by this mechanism.

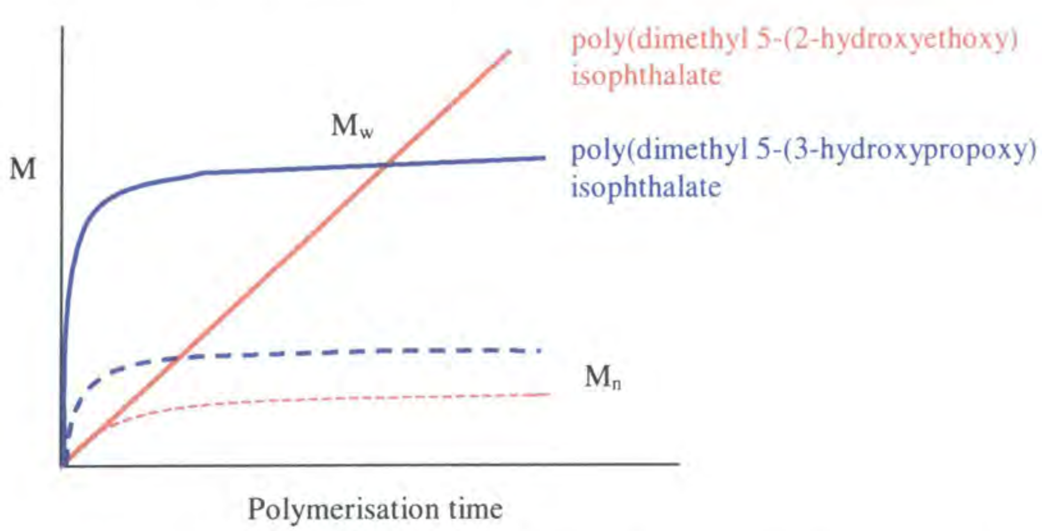


Figure 3.22 Schematic representation of molecular weight growth for AB_2 polyesters.

Cyclisation leading to growth termination has been observed in hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s[30a, 31] and hyperbranched poly (siloxysilane)s.[30b] In both these cases the limit to the maximum attainable M_n was also accompanied by a maximum in the value of M_w (Figure 3.22).

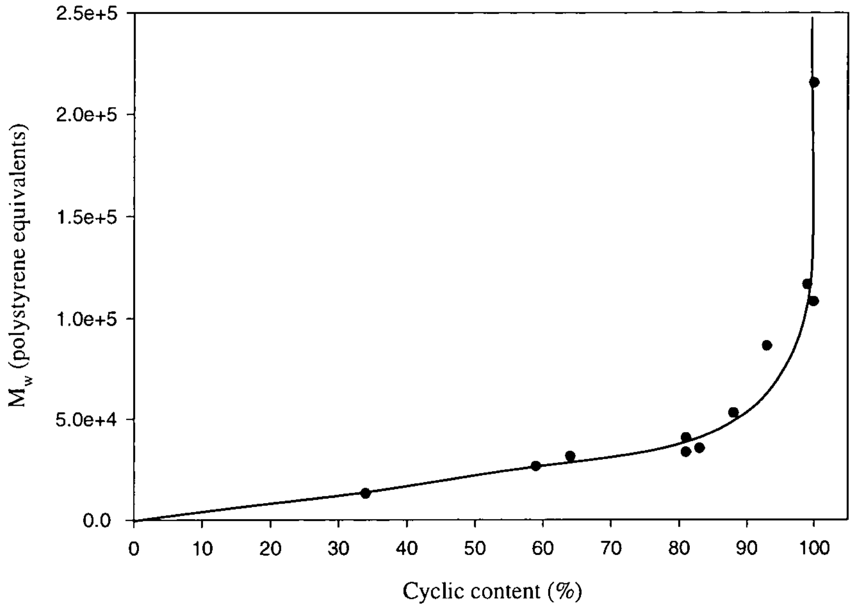


Figure 3.23 Variation of M_w with cyclic content for hyperbranched polyesters.

Surprisingly, this is not the case with the hyperbranched polyesters described here as the weight average molecular weight continues to increase after complete cyclisation (Figure 3.23). Clearly such continued growth must be via an alternative mechanism to simple condensation polymerisation.

Molten polyesters readily undergo interchange reactions in which the polymer chains undergo the scission and recombination reactions collectively referred to as transesterification.[41] Three types of interchange reaction may be identified and are termed alcoholysis, acidolysis and esterolysis or ester interchange (Figure 3.24).[42] Interchange reactions, in the absence of catalysts, are very slow in comparison to the direct esterification reaction between a carboxylic acid and an alcohol.[43] Of the three types of transesterification reaction, alcoholysis is believed to be the faster process and esterolysis the slower.[44]

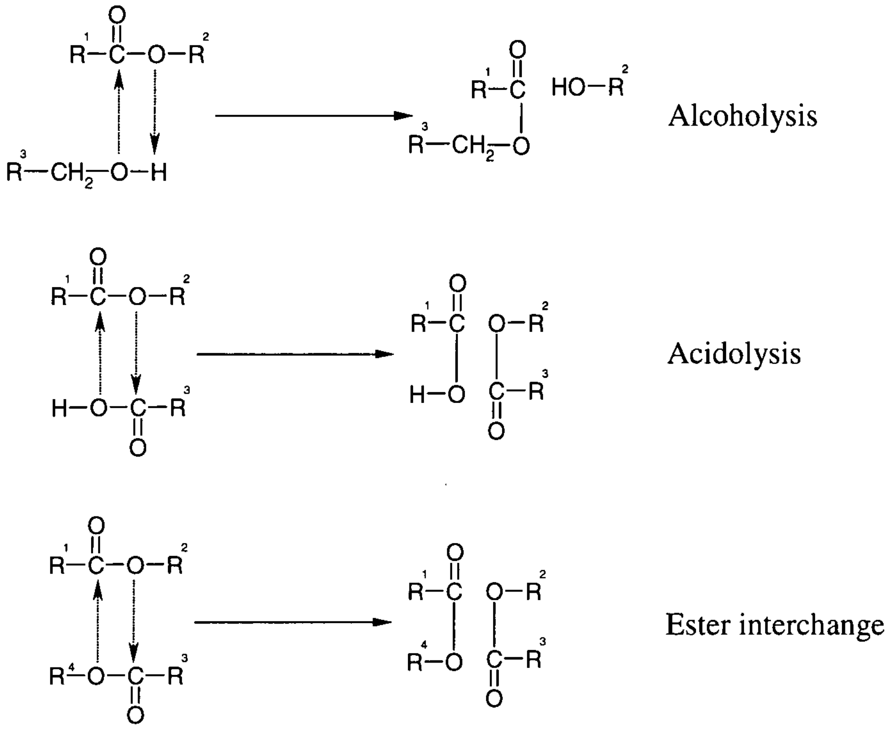


Figure 3.24 Possible interchange reactions in polyesters.

There have been comparatively few studies concerning ester interchange reactions. The difficulty in separating the contribution of esterolysis reactions from those of other ester exchange processes makes its study problematic unless end-capped chains are used.[43] Richards and co-workers have shown that transesterification is slower in blends of poly (ethylene terephthalate) and poly(ethylene napthalene-2,6-dicarboxylate) when the free hydroxyl chain ends are removed by end capping.[41]

In the case of the hyperbranched polyesters, the alcoholysis reaction is the reaction responsible for polycondensation and cannot take place after all the hydroxyl A groups are consumed by polycondensation and / or cyclisation reactions. Within the limits of our analytical techniques, no acid groups are detectable in this system and hence, it is likely that, acidolysis can be disregarded as a potential interchange reaction. However, ester interchange reactions are possible for hyperbranched polyesters and may be the cause of the changes in the molecular weight distribution.

In a linear polymer an interchange reaction between an x-mer and a y-mer yields an (x - z)-mer and a (y + z)-mer. There is no net change in the number of molecules and the number average molecular weight is unaffected. However, the distribution of species may be altered and changes in the distribution produce corresponding changes in the weight average molecular weight.[45] Flory has shown that the ultimate distribution is determined by the equilibria between the various polymer species and the equilibrium distribution is the same as the most probable distribution obtained by statistical considerations for a given extent of reaction. For a linear polymer with an extent of reaction of one the polydispersity index (M_w/M_n), for the most probable distribution, is equal to two.[2] The analogous case for an AB_2 polymer produced via a step growth mechanism has a polydispersity index of infinity.[46] It is possible that as the hyperbranched polyesters undergo interchange reactions along with the consequent redistribution of chain lengths the molecular weight distributions are moving towards the most probable distribution. However, it should be noted that Flory's statistical treatment of AB_2 step growth polymerisation is not strictly applicable in these cases as intramolecular cyclisation reactions are explicitly excluded from the theory.

The reaction between two average size polymer molecules to produce one much larger and one correspondingly smaller molecule will contribute towards an increase in the weight average molecular weight. Conversely the reaction between one large and one small molecule to produce two intermediate size molecules will contribute to a decrease in the weight average molecular weight. If the weight average molecular weight of the bulk sample is to increase then the contribution of reactions producing different size molecules must outweigh the contribution from reactions producing similar size molecules. It is unclear why this should be the case for the hyperbranched polyesters. One possibility is that interchange reactions are more likely to occur at the more accessible chain ends of the branched macromolecule (Figure 3.25).

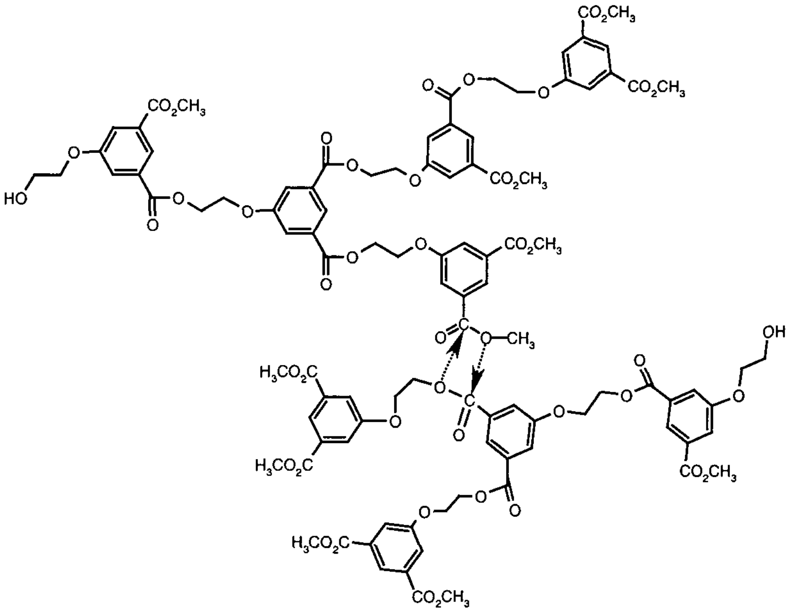
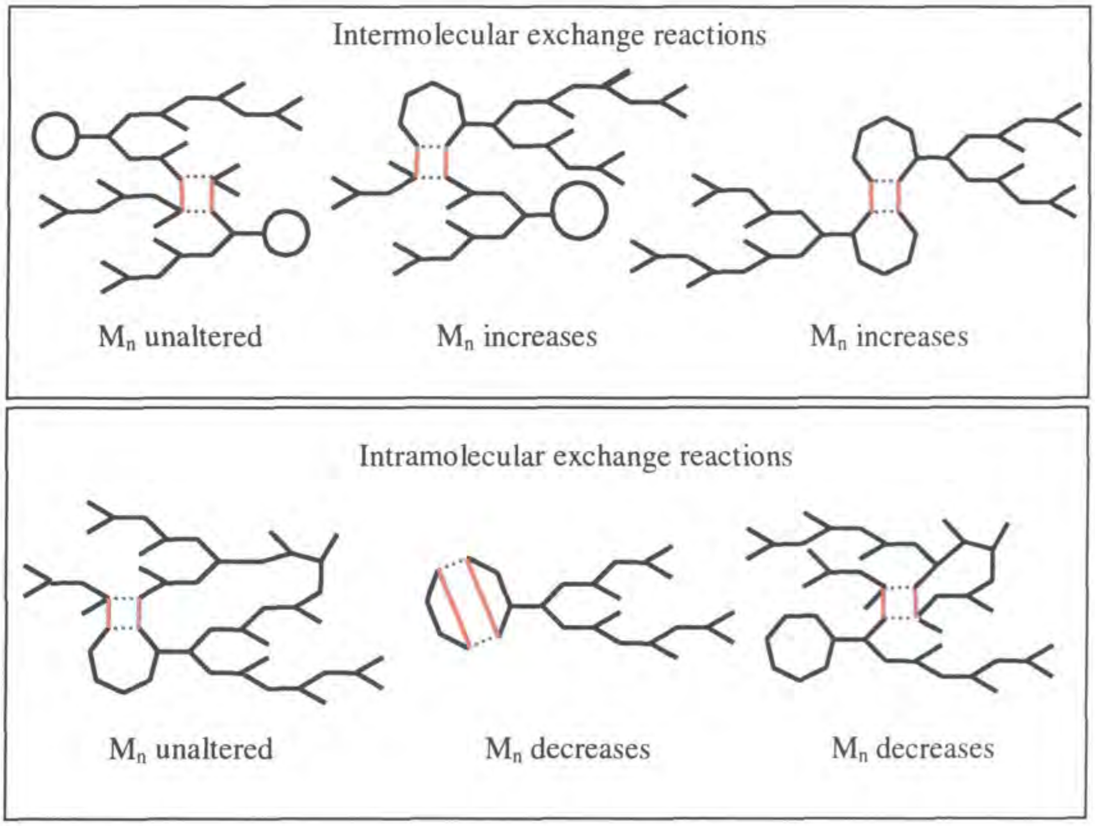


Figure 3.25 Ester interchange reaction between hyperbranched polyesters.

Interchange reactions between the methyl ester B groups of different hyperbranched polymer molecules are possible but do not result in a net change in the mass distribution. However, the interchange of a methyl ester end group in one polyester molecule with a main chain ester linkage in another does result in a change in the mass distribution. The molecule originally bearing the methyl ester is increased in mass as the ester end group is converted into a main chain ester. If the weight average molecular weight is to increase, due to the reaction between a large hyperbranched polyester molecule and a smaller macromolecule, it must be the larger molecule that increases in size. The larger hyperbranched molecules have more methyl ester end groups and hence this type of interchange favours the growth of the larger molecules.

In a linear polymer the number average molecular weight is unaffected by intermolecular interchange reactions as there is no net change in the number of molecules. The situation is much more complicated for a cyclised hyperbranched molecule as both intermolecular and intramolecular reactions are possible and may involve the cyclised and / or the branched part of the molecule (Figure 3.26).


Intermolecular exchange reactions

Intramolecular exchange reactions

Figure 3.26 Schematic representation of the effect upon M_n of potential ester interchange reactions in a fully cyclised hyperbranched polyester (original ester bonds shown with dotted lines, new bonds in red).

An intermolecular interchange reaction between the branched parts of two hyperbranched macromolecules does not change the number of molecules present and hence does not alter the number average molecular weight. However, intermolecular interchange reactions involving a cyclic part of either or both molecules results in ring opening, a reduction in the number of molecules and an increase in M_n. Similarly, intramolecular interchange within either a branched or cyclic part of the same molecule increases the number of molecules present and decreases the number average molecular weight. Interchange between a cyclic and branched part of the same molecule has no effect upon M_n. None of the possible interchange reactions produce uncyclised material but the creation of new cyclic species is possible and ester interchange reactions have been suggested as the source of cyclic oligomers in poly(ethylene terephthalate).[47] If the interchange reactions, described above, occur with equal probability then there would be no net change in the number average molecular weight as there are an equal number of ways to increase M_n as there are to decrease it. However, this seems unlikely as interchange reactions involving a cycle are expected to be subject to greater steric constraints. This is particularly true if the cycle is small as is suggested by the MALDI-TOF MS results. If the most likely interchange reaction is an intermolecular reaction involving the methyl ester end groups, as was suggested in the discussion of M_w, the number of molecules remains the same and the number average molecular weight is unaffected.

3.9 Conclusions

The data presented here has shown that the use of an in-line light scattering detector in SEC provides molecular weight information that is in reasonable agreement with that obtained via universal calibration. Mark-Houwink plots show a linear relationship between log M and log $[\eta]$. There is no evidence of the curved viscosity plots indicative of dendritic behaviour. MALDI-TOF MS provided evidence of cyclisation in hyperbranched polyesters, which is thought to limit the attainable number average molecular weight. The weight average molecular weight continues to increase after complete cyclisation and it is postulated that this is due to a redistribution of polymer chains via ester interchange reactions. This is very different behaviour to that observed in the analogous hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy) isophthalate)s where both M_n and M_w are limited by cyclisation. This has been attributed to the greater flexibility of the longer alkylene chains in these systems which can prevent alignment of the ester groups in the interchange reaction due to steric hindrance.[31]

3.10 Experimental

Size exclusion chromatography was carried out using both chloroform and tetrahydrofuran as solvent. SEC in chloroform utilised three 5μm columns of PLgel with pore size 100, 10^3 and 10^5 Å, calibrated against polystyrene standards and used an ERC 7515A refractive index detector. SEC in THF employed PL gel columns (3 x 300 mm, polystyrene divinyl benzene copolymer beads, mixed pore sizes) maintained at 30 ^{0}C. A Viscotek differential refractometer, viscometer detector, right-angle laser light scattering (RALLS) detector and data capture unit (DM 400) were used in conjunction with TriSEC GPC software (version 3.0). Mass Spectra were recorded on a Kratos MALDI IV instrument, using 2,5-dihydroxybenzoic acid as the matrix and collecting data over 200 laser shots in linear, high mode with laser powers typically in the region of 125 (ca. 15% transmission). Dilute solution viscometry measurements were made with a Schott-Gerate automated viscometer system utilising a Schotte-Gerate Ubbelohde viscometer tube (bore size 0.46mm), immersed in a constant temperature water bath at 25°C. The refractive index increment was determined in both chloroform and THF using a Brice-Phoenix differential refractometer.

3.10.1 Preparation and sampling of poly (dimethyl-5-(2-hydroxyethoxy) isophthalate)

Dimethyl-5-(2-hydroxyethoxy)isophthalate (7.0g, 27.57 mmol.) was placed into the lower section of the reaction flask and the catalyst components added ($Mn(OAc)_2$: 3.3 mg, 0.019mmol. Sb_2O_3 : 1.7 mg, 0.006 mmol. $(PhO)_3PO$: 2.5 mg, 0.007 mmol.). The flask was subjected to a nitrogen purge and placed in a high temperature oil bath, controlled by means of a 1 kW heating band / temperature programmer combination. The oil bath was heated at a rate of 10 ^{0}C / min. to 240 ^{0}C and held at that temperature for a period of 4 hours. The mixture was stirred at a rate of 125 r.p.m. by means of a stainless steel stirrer paddle powered by a Heidolph stirrer motor. The oil bath was lowered and a small sample of the polymer (ca. 100 mg.) removed whilst the polymer was still mobile. The reaction mixture was allowed to cool in a nitrogen atmosphere overnight and the whole procedure repeated for a total cumulative reaction time of 65 h., with the polymer sampled every 5 h.

3.11 References

---

(1). Odian, G., *Principles of Polymerisation*, 2nd edition, Wiley Interscience, New York, 1981

(2). Cowie, J.M.G., *Polymers: Chemistry & Physics of Modern Materials,* Blackie, London 1991

(3). Scouten, W.H. 'Chromatography' in *Encyclopaedia of Polymer Science and Engineering,* vol. 3, (Eds: Mark, H.F, Bikales, N. M., Overberger, C.G., Menges, G.), Wiley Interscience, New York, 1987

(4). Hunt, B.J., Holding, S. R., *Size Exclusion Chromatography* Blackie, Glasgow, 1989

(5). Grubisic, Z., Rempp, P., Benoit , H., *J. Polym. Sci.* B5 1967, 753

(6). Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier , Amsterdam, 1987

(7). Viscotek model 600 RALLS detector manual

(8). Lovell, P.A., 'Dilute Solution Viscometry' in *Comprehensive Polymer Science,* vol. 1, (Eds: Allen, G., Bevington, J.C.), Pergamon Press, Oxford, 1989.

(9). Mays, J.W., Hadjichristidis, N., 'Polymer Characterisation Using Dilute Solution Viscometry' in *Modern Methods of Polymer Characterisation,* (Eds: Barth, H.G., Mays, J.W.), Wiley Interscience, New York, 1991

(10). Aharoni, S. M., Crosby III, C.R., Walsh, E.K., *Macromolecules,* 1982, **15**, 1093

(11). a). Tomalia, D.A., Baker, H., Dewald, J., Hall, M., Kalloss, G., Martin, S., Roeck, J., Ryder, J., Smith, P., *Polymer Journal,* 1985, **17(1)**, 117

b). Tomalia, D.A., Naylor, A.M., Goddard III, W.A., *Angew. Chem. Int. Engl.* 1990, **29**,138

c). Tomalia, D.A., Hedstrand, D.M., Wilson, L.R., 'Dendritic Polymers' in *Encyclopaedia of Polymer Science and Engineering index volume*, (Eds: Mark, H.F, Bikales, N. M., Overberger, C.G., Menges, G.), Wiley Interscience, New York, 1987

d). Mourey, T.H., Turner, S.R., Rubinstein, M., Frechet, J.M.J., Hawker, C.J., Wooley, K.L., *Macromolecules,* 1992, **25**, 2401

e). Gitsov, I., Frechet, J.M.J., *Macromolecules,* 1993, **26**, 6536

f). de Brabander-van den Berg, E.M.M., Nijenhuis, A., Mure, M., Keulen, J., Reintjens, R., Vandenbooren, F., Bosman, B., de Raat, R., Frijns, T., v.d. Wal, S., Castelijns, M., Put, J., Meijer, E.W., *Macromol. Symp.,* 1994, **77**, 51

g) de Brabander-van den Berg, E.M.M., Meijer, E.W., *Angew. Chem. Int. Engl.* 1993, **32**, 1308

(12). Hobson, L.J., Feast, W.J., *J. Chem. Soc. Chem. Commun.,* 1997, **21**, 2067

(13). a). Widmann, A.H., Davies, G.R., *Comp. and Theor. Polymer Science,* 1998, **8**, 191

b). Aerts, J., *Comp. and Theor. Polymer Science*, 1998, **8**, 49

(14). Cotter, R.J., *Time of Flight Mass Spectrometry*, American Chemical Society, Washington, DC, 1997

(15). Montaudo, G., Garozzo, D., Puglisi, C., Samperi, F., *Macromolecules*, 1995, **28**, 7983

(16). Satoh, H.S., Lloyd, P.M., Yeates, S.G., Derrick, P.J., Taylor, P.C., Haddleton, D.M., *J. Chem. Soc. Chem. Commun.,* 1994, 2445

(17). Kawaguchi, T., Walker, K.L., Wilkins, C.L., Moore, J.S., *J. Am. Chem. Soc.*, 1995, **117**, 2159

(18). Leon, J.W., Frechet, J.M.J., *Polymer Bulletin*, 1995, **35**, 449

(19). Leduc, M.R., Hayes, W., Frechet, J.M.J., *J. Polym. Sci. part A Polym. Chem.*, 1998, **36**, 1

(20). Liu, M., Kono, K., Frechet, J.M.J., *J. Polym. Sci. part A Polym. Chem.*, 1999, **37(17)**, 3492

(21). Sunder, A., Hanselmann, R., Frey, H., Mulhaupt, R., *Macromolecules*, 1999, **32**, 4240

(22). a). Martinez, C.A., Hay, A.S. *J. Polym. Sci. part A Polym Chem.*, 1997, **35**, 2015

b). Gooden, J.K., Gross, M.L., Mueller, A., Stefanescu, A.D., Wooley, K.L. *J. Am. Chem. Soc.*, 1998, **120**, 10180

(23). Feast, W.J., Hamilton, L.M., Hobson, L.J., Rannard, S.P. *J. Mater. Chem.* 1998, **8(5),** 1121

(24). Hawker, C.J., Fréchet, J.M.J., *J. Am. Chem. Soc.*, 1990, **112,** 7638

(25). Turner, S.R., Voit,B.I., Mourey, T.H., *Macromolecules* 1993, **26**, 4617

(26). Brice, B.A., Halwer, M., *J. Optical. Soc. of America* 1951, **41(12)**, 1033

(27).Turner, S.R., Walter, F., Voit, B.I., Mourey, T.H., *Macromolecules* 1994, **27**, 1611

(28). Viscotek SEC Training School notes, 1997

(29).Turner, S.R., Voit, B., Mourey, T.H., *Macromolecules*, 1993, **26,** 4617

(30). a). Feast, W.J., Keeney, A.J., Kenwright, A.M., Parker, D., *J. Chem. Soc. Chem. Commun.*, 1997, 1749

b) Gong, C., Miravet, J., Frechet, J.M.J. *J. Polym. Sci. part A Polym. Chem.*, 1999, **37,** 3193

(31). Keeney, A.J., *Ph.D. Thesis*, Durham University, 1998

(32). Martin, K., Spickermann, J., Räder, H.J., Müllen , K., *Rapid Commun. Mass Spec.*, 1996, **10**, 1471

(33). Silverstein, R.M., Bassler, G.C., Morrill, T.C., *Spectrometric Identification of Organic Compounds* , Wiley, 1991

(34). Hobson, L.J., Feast, W.J, *Polymer*, 1999, **40**, 1279

(35). Dušek, K., Šomvársky, J., Smrčková, M., Simonsick, W.J., Wilczeck, L., *Polymer Bulletin*, 1999, **42**, 489

(36). Chu, F., Hawker, C.J., Pomery, P.J., Hill, D.J.T., *J. Polym. Sci. part A Polym. Chem.,* 1997, **35(9),** 1627

(37). Cameron, C., Fawcett, A.H., Hetherington, C.R., Mee, R.A.W., McBride, F.V., *J. Chem. Soc. Chem. Commun.*, 1997, 1801

(38). Feast, W.J., Hamilton, L.M., Hobson, L.J., Rannard, S.P., *J. Mater. Chem.,* 1998, **8(5),** 1121

(39) Percec, V., Chu, P., Kawasumi, M., *Macromolecules,* 1994, **27**, 4441

(40). Gooden, J.K., Gross. M.L., Mueller, Stefanescu, Wooley, K.L., *J. Am. Chem. Soc.*, 1998, **120**, 10180

(41). Kenwright, A.M., Peace, S.K., Richards, R.W., Bunn, A., MacDonald, W.A., *Polymer,* 1999, **40**, 5851

(42). Montaudo, G., Puglisi, C., Samperi, F., *Macromolecules,* 1998, **31(3),** 650

(43). Pilati, F., 'Polyesters' in *Comprehensive Polymer Science*, Vol. 5, (Eds: Eastmond, G.C., Ledwith, A., Russo, S., Sigwalt, P.) Pergamon Press, Oxford, 1989

(44). Kotliar, A.M., J. *Polym. Sci.: Macromol. Rev.*, 1981, **16,** 367

(45). Flory, P.J., *J. Am. Chem. Soc.,* 1942, **64,** 2205

(46). Flory, P.J., *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, 1953

(47). Goodman, I., Nesbit, B.F., *Polymer,* 1960, **1**, 384

Chapter Four

Core Terminated Hyperbranched Polymers

4.1 Introduction

Most hyperbranched polymers are simple homopolymers produced by the condensation polymerisation of AB_X type monomers, although some research groups have explored the copolymerisation of AB_X monomers with core forming molecules. In this approach, which is related to dendrimer synthesis, the growing hyperbranched molecule is coupled with a multifunctional molecule, of B_X type, analogous to the central core of a dendrimer (Figure 4.1). The reaction of a core molecule with the single A group of a hyperbranched molecule terminates growth from the focal group, hence this class of polymers will be referred to herein as core terminated hyperbranched polymers.

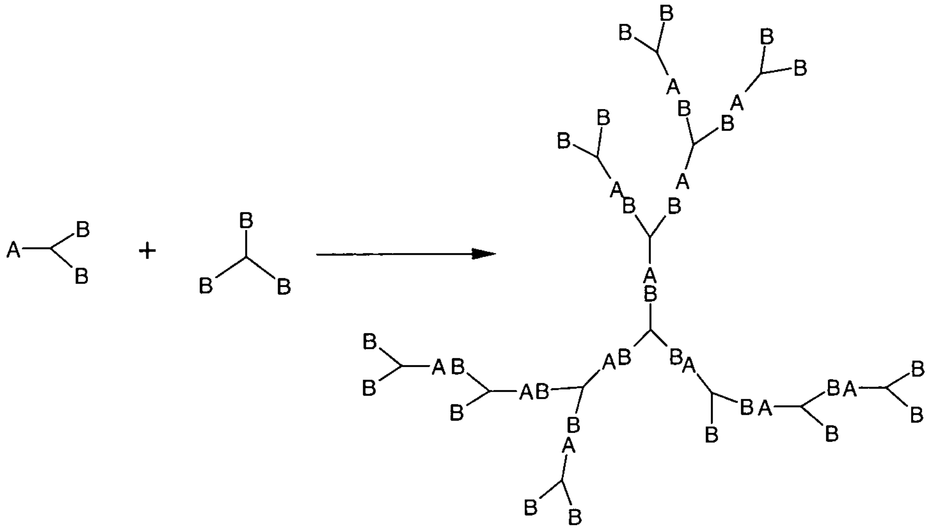


Figure 4.1 An idealised AB_2 core terminated polymer

The copolymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate with trimethyl 1,3,5-benzenetricarboxylate (a B_3 core) was first reported by Feast and Stainton.[1] By varying the ratio of core molecules to monomer molecules some control over the molecular weight of the resulting polymers was achieved. A similar effect has been observed in the copolymerisation of the AB_3 monomer triallyl silane with a monofunctional, B_1, core terminator molecule. Increasing the B_1 content was found to decrease the final molecular weight and narrow the polydispersity considerably.[2]

In a recent theoretical study, Müller has shown that the polydispersity of a hyperbranched polymer can be controlled by a synthesis involving the slow addition of AB_X monomers to a core under dilute conditions.[3] These studies predict that the molecular weight of the core terminated hyperbranched polymer will be lowered and its polydispersity narrowed by increasing the core : monomer ratio used in the polymerisation. The polydispersity of such systems is also predicted to decrease with increasing core functionality. There are, as yet, few examples of this strategy in practice but Frey has demonstrated the technique both by computer simulation[4] and in the ring-opening multibranching polymerisation (ROMBP) of glycidol (see chapter 1, figure 1.24).[5] Using this technique polydispersities of less than 1.25 were obtained in the synthesis of hyperbranched polyglycerols by ROMBP. Hult and co-workers used a method of repeated monomer addition to a core molecule in the synthesis of aliphatic polyesters.[6] In this case the quantity of monomer used in each addition was too large to class the polymerisation as slow addition under dilute conditions but, nevertheless, the use of a core molecule produced relatively narrow polydispersities.

The aim of the work presented in this chapter is to firstly explore the effect of introducing core molecules into the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate and secondly to demonstrate how the incorporation of a core molecule can be used to support the hypothesis that transesterification occurs in these systems.

4.2 Core terminated hyperbranched polyesters

A series of core terminated polymers were prepared using the polycondensation apparatus described in chapter 2. A number of cores of differing functionality were investigated. Dimethyl isophthalate (B_2) and trimethyl 1,3,5-benzenetricarboxylate (B_3) were successfully copolymerised with dimethyl 5-(2-hydroxyethoxy)isophthalate. Attempts to copolymerise a monofunctional core (B_1) using either methyl benzoate or methyl 4-*tert*-butylbenzoate were unsuccessful. In both of the latter cases the core molecules were found to be too volatile at the polymerisation temperature and boiled out of the reaction flask before they could be incorporated into the polymer. As a consequence the present study was restricted to the investigation of B_2 and B_3 cores. A series of core terminated polyesters were synthesised by varying the core : monomer ratio. All polymerisations were of 24 hours duration and the resulting core terminated polyesters were analysed by size exclusion chromatography. The results of the SEC analysis in THF are summarised below (Table 4.1).

		PS calibration			Universal calibration			Light scattering		
core	core : monomer ratio	M_n	M_w	pdi	M_n	M_w	pdi	M_n	M_w	pdi
B_2	0.0108	5600	49400	8.8	5000	163400	32.7	170	2183000	
	0.0222	5700	30400	5.4	3400	74100	21.8	2600	87500	33.7
	0.0467	4300	18000	4.2	2300	38100	16.6	4200	36600	8.7
	0.0811	4100	17000	4.2	3000	32500	10.8	3600	34100	9.6
	0.1105	3000	10900	3.7	1600	16500	10.3	5200	21900	4.2
B_3	0.0103	5300	45500	8.5	3100	128200	41.4	470	609900	
	0.0229	5300	21300	4.1	3700	48500	13.1	6600	45400	6.9
	0.0479	3500	9900	2.8	4100	13500	3.3	3800	16700	4.4
	0.0825	3000	7500	2.5	2200	9300	4.2	2800	11400	4.2
	0.1110	2600	5500	2.2	2300	7000	3.0	2700	9700	3.6

Table 4.1 SEC analysis, in THF, of core terminated hyperbranched polyesters synthesised by the copolymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate and either a B_2 core (dimethyl isophthalate) or a B_3 core (trimethyl 1,3,5-benzenetricarboxylate). Comparison of data obtained using different calibration and / or detector systems as described in chapter 3.

The polystyrene equivalent weight average molecular weights of the core terminated hyperbranched polyesters are much lower than those obtained using either a universal calibration or a light scattering detector (Figure 4.2). The lower values for molecular weight obtained by application of a conventional polystyrene calibration are consistent with the results, discussed previously, for the simple AB_2 hyberbranched polyesters (see chapter 3). The polystyrene equivalent molecular weights obtained from core terminated polyester solutions in chloroform are higher than those obtained in tetrahydrofuran, which is consistent with chloroform being the better solvent for these systems.

Analysis of the SEC traces obtained from the light scattering detector proved problematic as the higher molecular weight samples exhibited extra peaks due to very high molecular weight material, as was discussed for the AB_2 polymers in chapter 3. For example, the light scattering results for copolymers containing 1% core were extremely high for the weight average molecular weight but unrealistically low for the number average molecular weight. Hence, the molecular weights of core terminated polyesters containing 1% core obtained from the light scattering detector have been omitted from the analysis. Nevertheless, with the exception of the 1% core terminated polymers, the results obtained by universal calibration were in reasonable agreement with those from the light scattering detector. Therefore for the purposes of this discussion the results from universal calibration will be used unless otherwise stated.

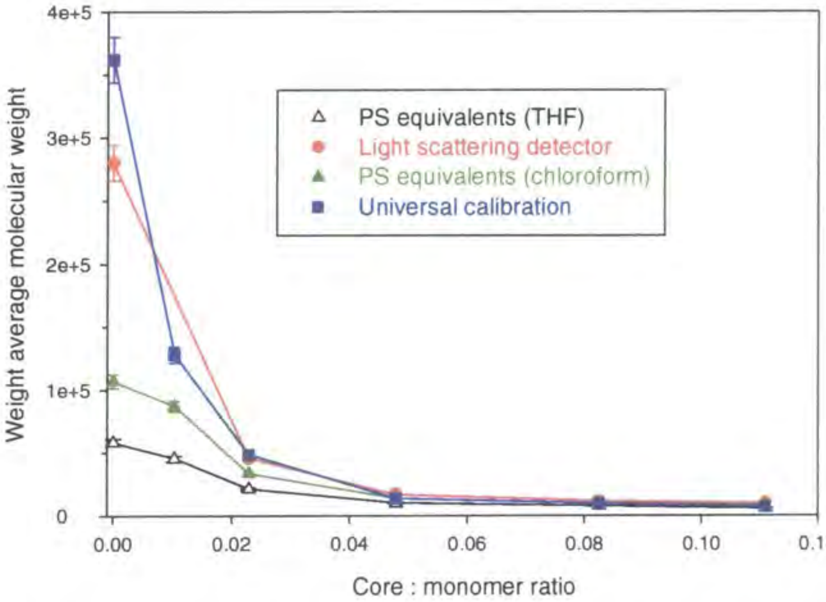


Figure 4.2 Comparison of the results from different SEC techniques for B_3 core terminated hyperbranched polyesters.

In order to compare this data with that presented by Stainton the molecular weights, obtained from a conventional polystyrene calibration, were plotted against the core to monomer ratio used in the polymerisation (Figure 4.3).

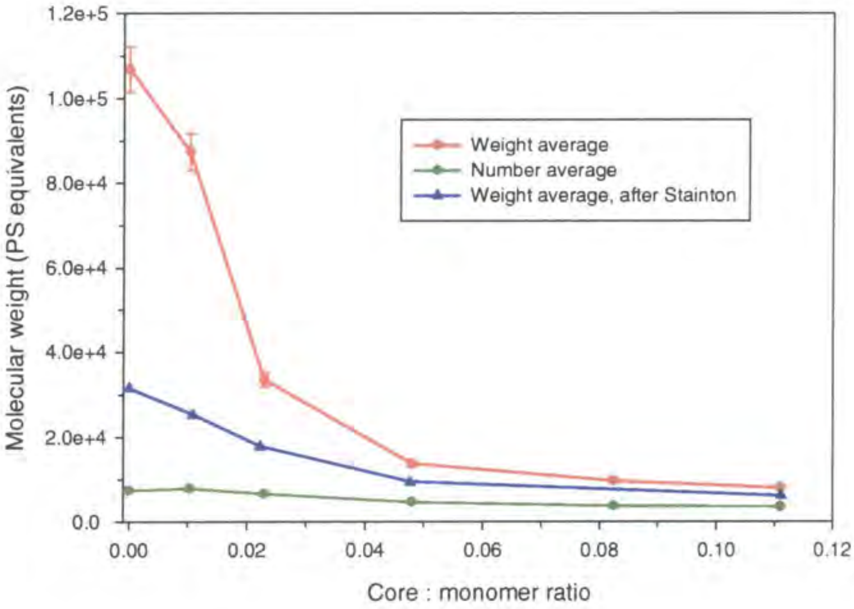


Figure 4.3 Plots of molecular weights of core terminated hyperbranched polyesters versus core : monomer ratio.

The ratio of core to monomer, used in the reaction, had a marked effect upon the eventual molecular weight of the polyesters. As the core content was increased the molecular weight decreased rapidly, which is in good agreement with the reported behaviour of both core terminated polyesters[1] and polyglycerols.[4] The observed reduction in the molecular weight is associated with very low levels of core molecules, for example increasing the B_3 core content from one to two percent reduces M_w (quoted as polystyrene equivalent molecular weights) by a factor of two. Although the variation in molecular weight is similar to that observed by Stainton, for core terminated polyesters after 5 hours polymerisation, the molecular weights of the core terminated polyesters, after 24 hours polymerisation, are markedly higher. This implies that either complete consumption of the A groups has not occurred after 5 hours polymerisation or that further polymerisation proceeds via an alternative mechanism, as suggested in chapter 3.

Theoretically the use of a simple B_1 core could lower the molecular weight of a core terminated hyperbranched polymer and such monofunctional cores have been successfully employed in the synthesis of hyperbranched polyglycerols.[4] Hence it is of some interest to know whether multifunctional cores react at more than one B group or whether they simply act as B_1 core terminators. The use of different core molecules allowed the effects of varying the core functionality to be investigated. Plots of molecular weight against core : monomer ratio, for the B_2 and B_3 core systems, show that the B_3 core has a greater influence on the final molecular weight than the corresponding B_2 core (Figure 4.4).

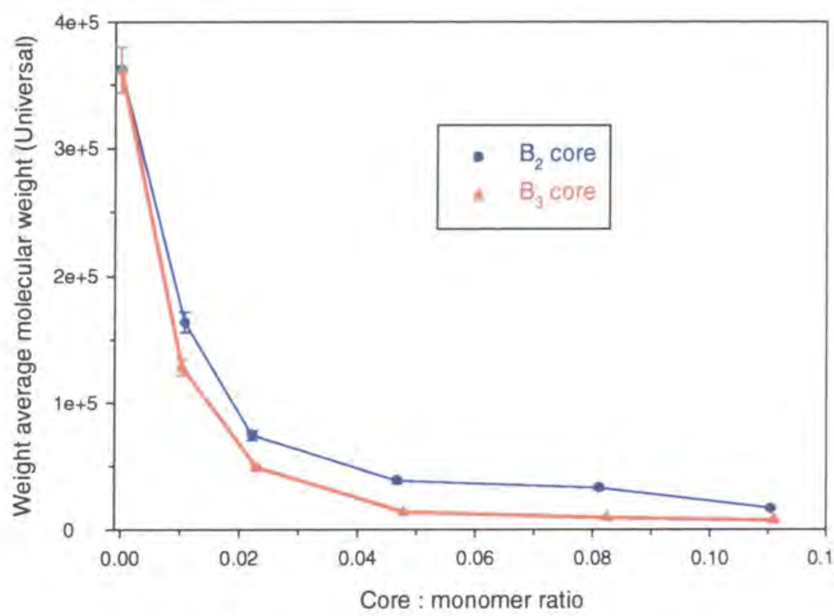


Figure 4.4 Effect of varying the core functionality upon the molecular weight of core terminated hyperbranched polyesters; reaction time 24 hours.

This result is expected as the B_3 system has more core B groups available to undergo condensation reactions. The molecular weight was also examined as a function of the ratio of core B groups to monomer A groups (Figure 4.5). When plotted in this manner there is little difference between the two core systems and it appears that the greater lowering of the molecular weight by the B_3 core is simply a consequence of the greater number of core B groups present. However, this does imply that more than one B group per core molecule can undergo a condensation reaction, otherwise altering the core functionality would be expected to have no observable effect upon the resulting molecular weight.

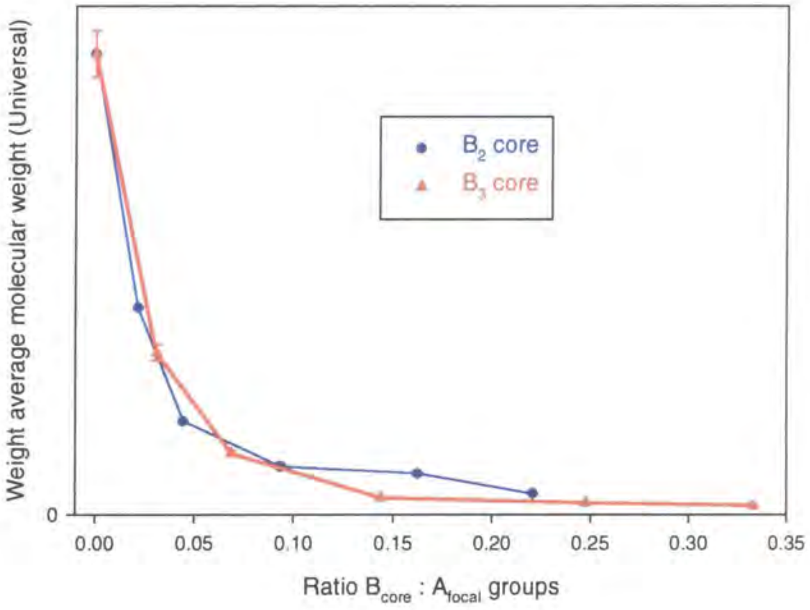


Figure 4.5 Effect upon the molecular weight of core terminated hyperbranched polyesters of varying the B_{core} group concentration.

Although incorporation of a core molecule imparts some degree of control over the final molecular weight of the hyperbranched polyester, there remains the question of whether or not any control can be achieved over the polydispersity. On first inspection there is an apparent lowering of the polydispersity, by copolymerisation with a core molecule, however this may simply be a consequence of the lower molecular weights attained in the core terminated systems. In order to examine this phenomenon more fully, the polydispersities of the core terminated polymers need to be compared to the polydispersities of the analogous AB_2 polymers of the *same molecular weight.* Hence a plot of polydispersity against weight average molecular weight for both the core terminated polyesters and the AB_2 polyesters, examined in chapter 3, is shown below (Figure 4.6).

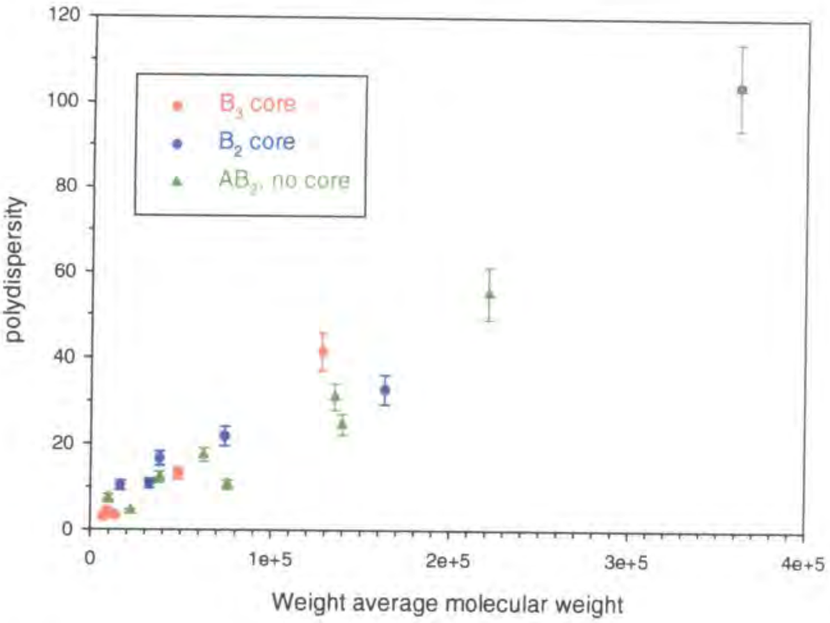


Figure 4.6 Comparison of the polydispersity of core terminated and hyperbranched polyesters of varying molecular weight.

A comparison of the different polymer systems reveals that there is no discernible difference between the polydispersities obtained for polymers of a given molecular weight. In the light of the ester exchange reactions, postulated in chapter 3, this is perhaps to be expected as any control over polydispersdity gained by the introduction of a core molecule will be lost in the following redistribution of polymer chains by ester interchange reactions. In some ways the core terminated polymers are analogous to the cyclised species discussed previously. In both cases growth is limited by the consumption of A groups, through either cyclisation or incorporation of a core molecule, consequently the molecular weight behaviour is expected to be similar in both systems. In order to examine the change in the molecular weight of a core terminated polyester with increasing reaction time, dimethyl 5-(2-hydroxyethoxy)isophalate was copolymerised with dimethyl isophthalate using a fixed core : monomer ratio (0.0844). This polymerisation was sampled at intervals of 5 hours. The change in molecular weight with time, for a given core to monomer ratio, appears to mirror the behaviour of the AB_2 polymers, described previously (Figure 4.7).

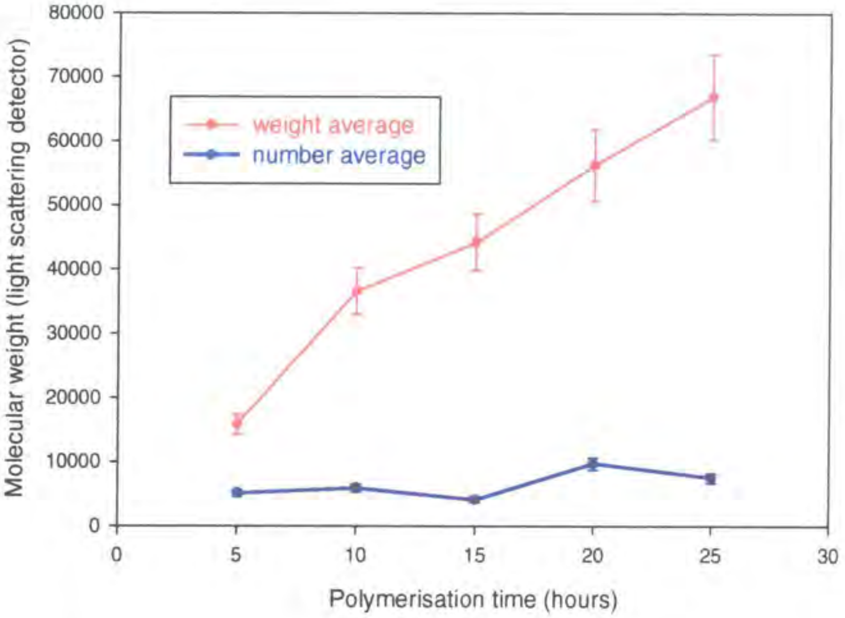


Figure 4.7 Variation of the molecular weight of a B_2 core terminated hyperbranched polyester with reaction time.

4.3 MALDI-TOF analysis of core terminated polymers

As the incorporation of a core molecule prevents further growth from the focal point of the growing oligomer the overall situation is akin to the cyclisation encountered in the AB_2 polymers. At the point of complete core termination, or cyclisation, the polymer can no longer grow via a polycondensation mechanism. Hence, to further understand this system as regards the role of the core molecule it is useful to attempt to evaluate the level of incorporation of core molecules into the polymer. The presence or otherwise of cyclic polymer is also a potentially important factor in the understanding of the core terminated polyesters.

As demonstrated in chapter 3, MALDI-TOF spectra of AB_2 type polyesters show oligomeric series with peaks corresponding to discrete numbers of monomer residues depending upon the degree of polymerisation (DP). A further series of peaks, corresponding to a single extra methanol loss, is often discernible and can be accounted for by the single extra condensation reaction required to create a cyclic polymer. It was anticipated that the presence of either, or both, of these species should be readily identifiable in the MALDI spectrum of the core terminated polymers. Furthermore, core terminated species should be easily recognised by the addition of the extra mass corresponding to the core moiety. However, it should be noted that this technique cannot distinguish between core terminated species in which different numbers of core functionalities have reacted. The addition of an extra monomer unit to a core terminated species results in a change of mass corresponding to the addition of a monomer residue minus the mass of a methanol unit and the consequence for m/z is the same irrespective of whether the reaction is at the core or elsewhere in the oligomer.

The MALDI spectra of core terminated polyesters, after 24 hours polymerisation, showed peaks attributable to cyclic and core terminated oligomers only (a representative spectrum is shown in Appendix 2.3 and more detailed expansion in Figure 4.8).

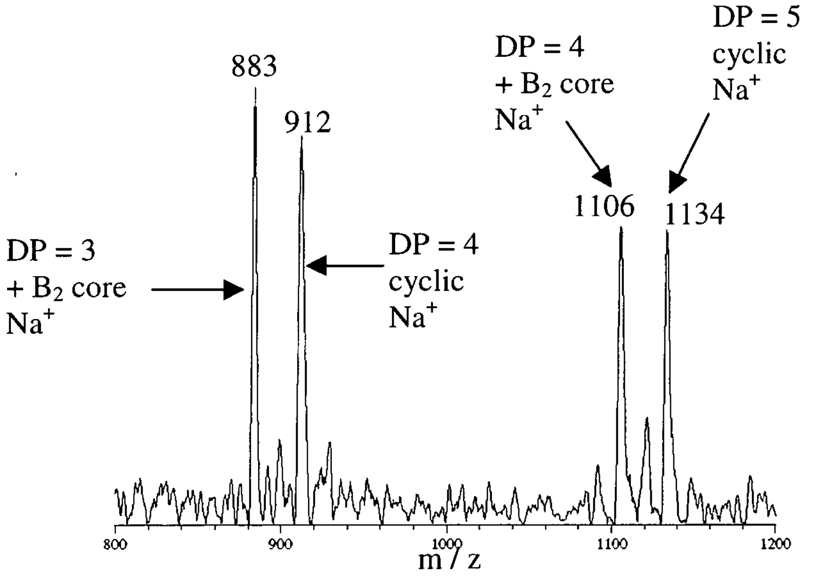


Figure 4.8 Detail of the MALDI spectrum for a B_2 core terminated hyperbranched polyester. Only the region corresponding to DP 3 to 4 is shown.

The relative proportions of cyclic and core terminated species for the various oligomers were assessed by comparing the peak areas in the mass spectrum, as described in chapter 3. The percentage cyclic content of the core terminated polyesters was examined as a function of the core : monomer ratio and is shown below (Figure 4.9).

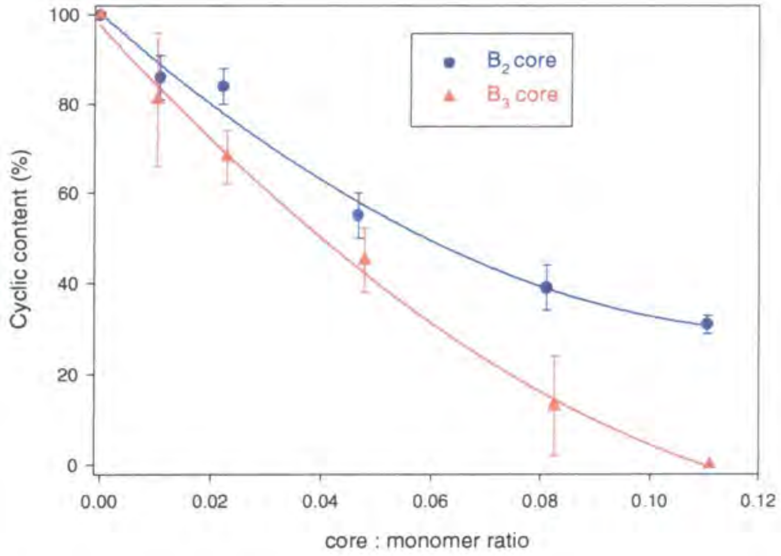


Figure 4.9 Variation of the cyclic content of core terminated hyperbranched polyesters versus the core : monomer ratio.

It appears that the percentage of cyclic polymer obtained is influenced by the relative amounts of core molecule used in the polymerisation. For instance, using 1% of a B_3 core results in virtually fully cyclised polymer. If the core : monomer ratio is increased then the amount of cyclic polymer decreases. The polymers are fully core terminated when the initial core content exceeds about 10%.

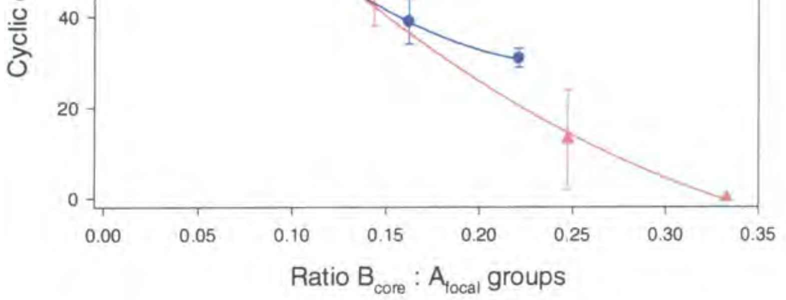


Figure 4.10 The effect upon the cyclic content of core terminated hyperbranched polyesters of varying B_{core} group concentration.

Once again it can be seen that the B_3 core has the greater effect, which is clearly attributable to the greater number of core B groups present (Figure 4.10).

As mentioned above the core terminated polymers effectively have no unreacted A groups as the focal groups have either reacted intramolecularly to form cycles or intermolecularly with other oligomers or core molecules. Thus, as in the case of the AB_2 polymers, there should be no further opportunity for growth via polycondensation reactions. Hence, it is important to establish at what point in the reaction the complete consumption of A groups occurs. This was investigated by examining the MALDI spectra of core terminated polyesters, produced using a fixed monomer : core ratio (0.0844), at different reaction times (Figure 4.11). In this case the MALDI spectra showed the presence of all 3 expected species (hyperbranched, cyclic and core terminated) early in the reaction (5 hours). There were also some minor peaks (labelled with a question mark in Figure 4.11) that could not be identified, however these appear to diminish on increasing the polymerisation time.

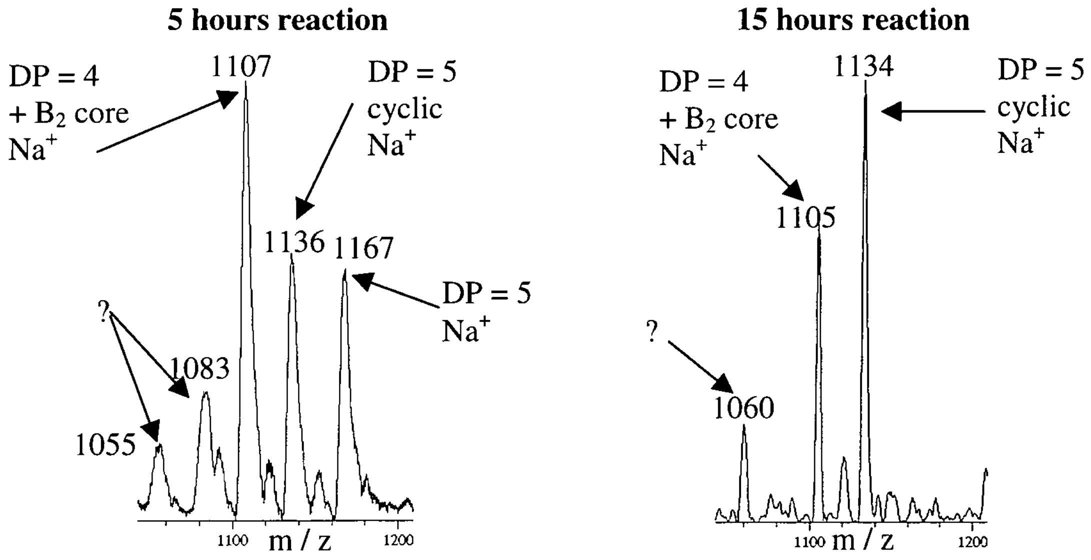


Figure 4.11 Details of MALDI spectra for a core terminated hyperbranched polyester at different reaction times

A plot of the percentage composition against reaction time showed that the A groups were effectively consumed between 5 and 10 hours polymerisation (Figure 4.12). The percentage of cyclic polymer (or core terminated) remains more or less constant at around 50% after this point. This is in good agreement with the results of varying the core to monomer ratio, described above.

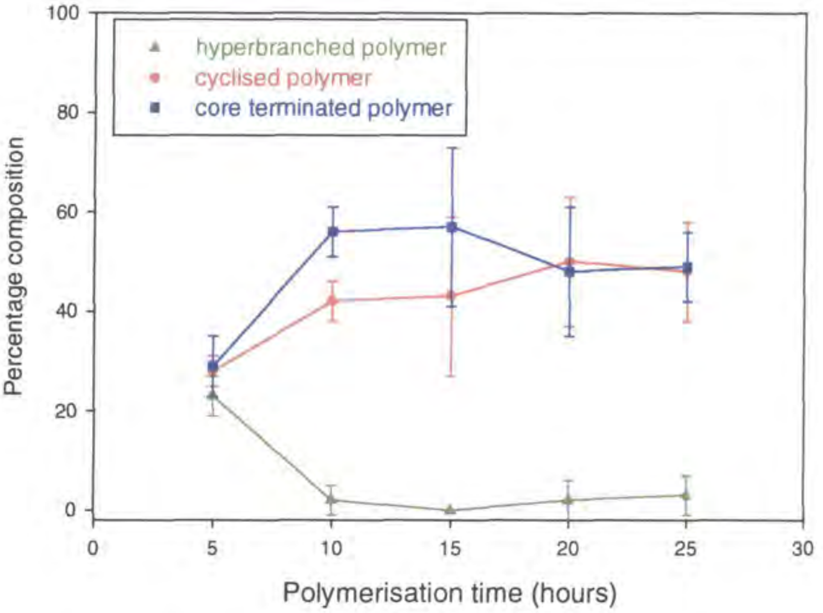


Figure 4.12 Variation of polymer composition with polymerisation time for a core terminated hyperbranched polyester.

A comparison with the SEC data for the same system (Figure 4.7) shows that the weight average molecular weight continues to increase after the point at which the A groups are fully consumed. This is consistent with the results obtained for the analogous AB_2 hyperbranched polyesters.

4.4 Dilute solution viscometry of core terminated polyesters

The core terminated polyesters were studied by dilute solution viscometry in a manner already described for the analogous AB_2 polyesters (chapter 3). Solution viscosities of the various polymer solutions, in chloroform, were measured in an Ubbelohde capillary viscometer tube at 25 ^{0}C. The values for the intrinsic viscosity of the various core terminated polymers, together with their weight average molecular weights, are summarised below (Table 4.2).

core	core : monomer ratio	M_w [a]	$[\eta]$ [b] ($cm^3\ g^{-1}$)
B_2	0.0108	163400	22.4
	0.0222	74100	18.4
	0.0467	38100	13.7
	0.0811	32500	12.9
	0.1105	16500	10.7
B_3	0.0103	128200	18.3
	0.0103	128200	22.1
	0.0229	48500	14.6
	0.0479	13500	9.9
	0.0479	13500	10.5
	0.0825	9300	8.6
	0.0825	9300	9.3
	0.1110	7000	8.2

[a] Weight average molecular weight from SEC using universal calibration.

[b] chloroform solutions @ 25 ^0C

Table 4.2 Intrinsic viscosities of core terminated hyperbranched polyesters, polymerisation time 24 hours.

The Mark-Houwink plots for the core terminated polyesters gave very similar results irrespective of the core functionality (Figure 4.13). Both of the polymers gave reasonable linear plots that allowed the Mark Houwink parameters to be obtained by linear regression. In the case of B_2 core terminated polyesters linear regression (r^2 = 0.99) gave Mark Houwink parameters of $\alpha = 0.3$ and $K = 0.4\ cm^3\ g^{-1}$. Similarly for the B_3 core terminated polyesters linear regression (r^2 = 0.98) gave Mark Houwink parameters of $\alpha = 0.3$ and $K = 0.6\ cm^3\ g^{-1}$. This is in good agreement with the data obtained from the AB_2 polyesters. In fact if the AB_2 and core terminated polymers are assumed to be essentially the same polymer then a reasonable linear fit may be obtained using the combined data (Figure 4.14).

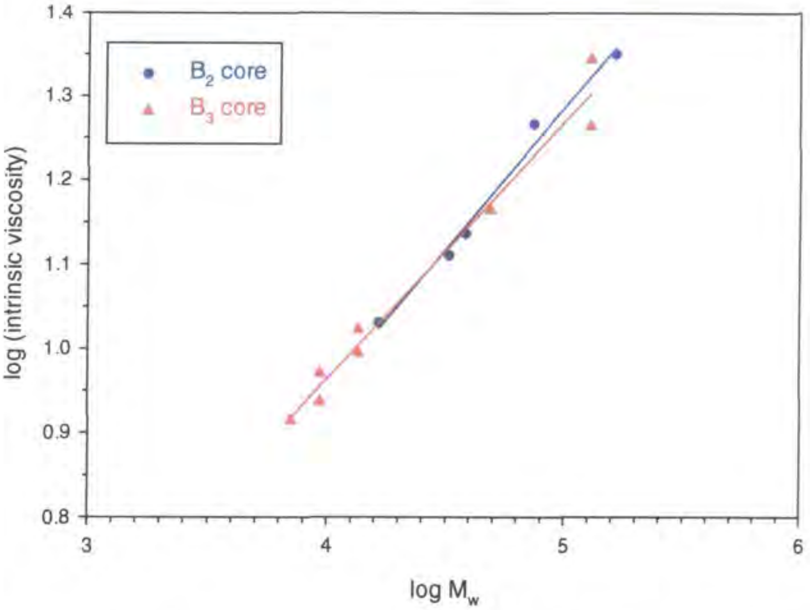


Figure 4.13 Mark Houwink plots for core terminated hyperbranched polyesters.

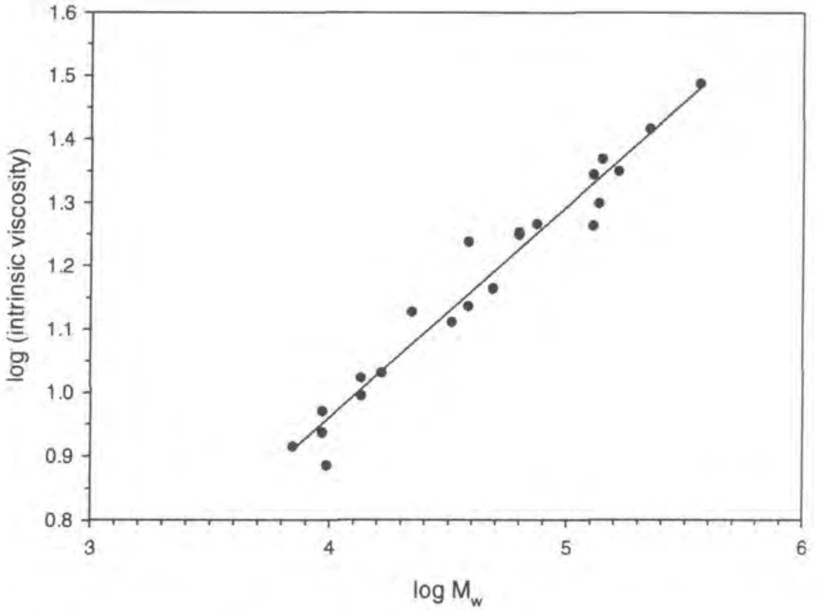


Figure 4.14 Mark Houwink plot for the combined hyperbranched polyester data.

Unsurprisingly, the core terminated polymers have very similar solution viscosity properties to the AB_2 polyesters. Both classes of polyester give linear Mark Houwink plots and do not appear to exhibit any viscosity behaviour characteristic of well defined dendrimers.

4.5 Incorporation of a core molecule into a fully cyclised AB_2 polyester

The ability to distinguish hyperbranched, cyclised and core terminated polymers by MALDI-TOF mass spectroscopy, as demonstrated above, suggested a method of exploring the possibility of ester exchange in these systems. It was postulated that if an AB_2 monomer were to undergo polycondensation until the point at which the resulting polymer was completely cyclised then any further reaction would not be possible by a polycondensation mechanism. If at this point a potential core molecule is introduced then it is possible that the core molecule could be incorporated into the polymer by an ester exchange mechanism. Incorporation of the core is of course not possible by a simple condensation mechanism as there would be no available A groups for this type of reaction. A number of possible reactions of a core molecule with a cyclic polymer were envisaged and are outlined below (Figure 4.15).

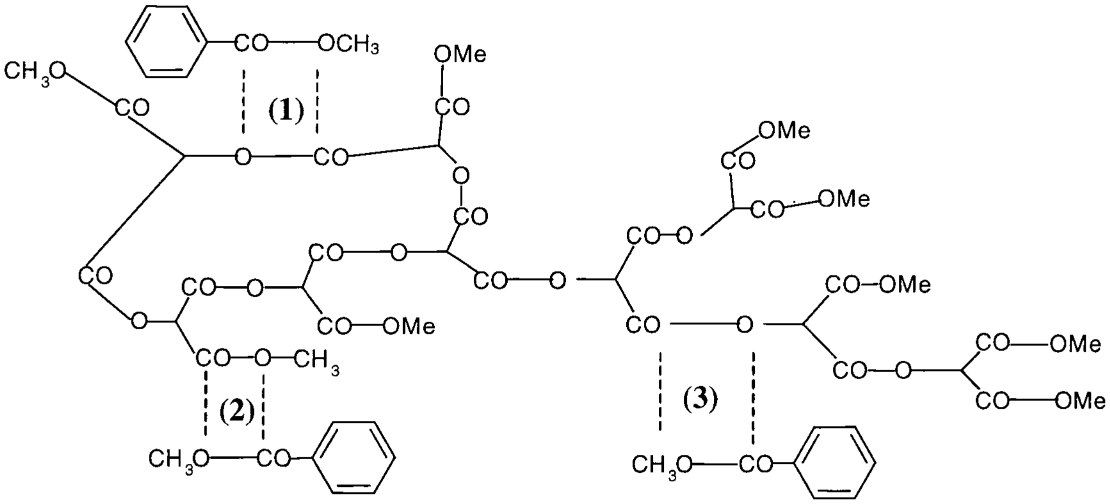


Figure 4.15 Schematic representation of possible interchange reactions between a fully cyclised polyester and a core molecule. (1) Reaction with cyclic part. (2) Reaction with methyl ester end group. (3) Reaction with branched part.

The core molecule could conceivably undergo ester exchange with a methyl ester end group, an ester unit within the cyclic part of the polymer or an ester within one of the many branches. Reaction with an end group would simply result in an exchange of methoxy groups, no net change would be observed and hence this reaction, although plausible, can be ignored for the purposes of the present discussion. In contrast, reaction with the cyclic portion of the polymer would result in ring opening and the net result would be to convert a cyclic polymer into a core terminated polymer. Similarly, a reaction between a core molecule and a branched part of the polymer, not part of the cycle, would result in the cyclic polymer becoming smaller and the creation of a new core terminated species. Hence the appearance of core terminated species in the spectrum of a fully cyclised polymer, after reaction with a core molecule, would provide support for the hypothesis that ester exchange occurs in these systems.

Dimethyl 5-(2-hydroxyethoxy)isophthalate was polymerised in the melt, at 240 ^{0}C, sampling at frequent intervals. The polymerisation was continued until the polymer was completely cyclised, as revealed by MALDI-TOF mass spectrometry. The polymer was ground up and combined with dimethyl isophthalate to give a 50 / 50 mixture (*w/w*), which was reheated, at 220 ^{0}C. The polymerisation was sampled after 6, 12 and 17 hours.

The polymer samples were examined by MALDI mass spectroscopy (a full spectrum of the polymer, after 6 hours, is shown in Appendix 2.4 and a more detailed expansion in Figure 4.16). The MALDI spectrum of the initial polymer sample, before the addition of the dimethyl isophthalate core, showed only the presence of cyclic polymer species. After 6 hours heating signals corresponding to core terminated polymer were evident and with a signal intensity comparable to that for the cyclic polymer species. The intensity of the signals due to core terminated polymer increased with further heating, being the predominant species after 12 hours and the sole species after 17 hours (Figure 4.17). The complete dominance of core terminated species, in the MALDI spectrum, is surprising but may be a result of using a high ratio of core molecule in the reaction.

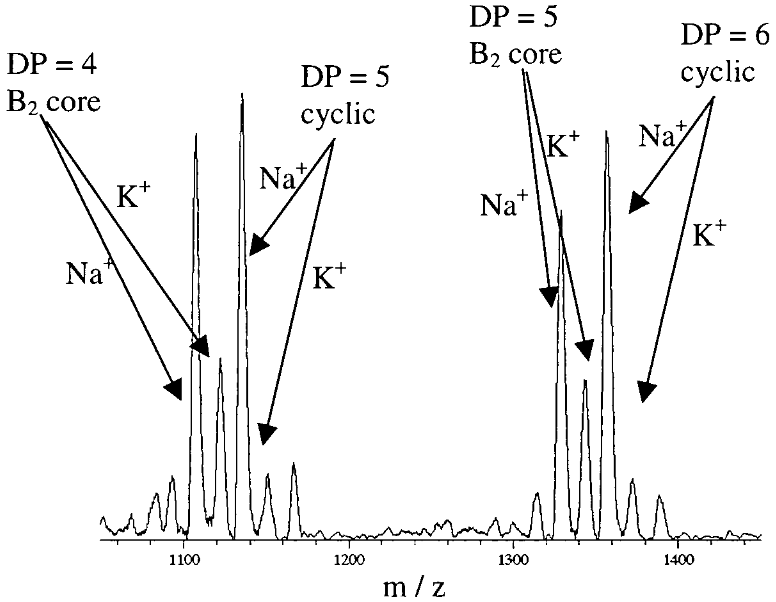
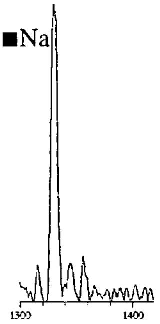


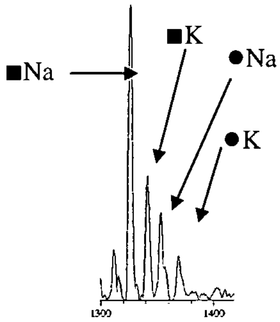
Figure 4.16 MALDI-TOF spectrum of the hyperbranched polyester after 6 hours heating with a B_2 core molecule (dimethyl isophthalate). Only the region corresponding to a degree of polymerisation of 5 is shown.

Nevertheless, only the reaction of a core molecule with the cyclic part of a hyperbranched macromolecule is expected to reduce the amount of cyclic species present. Hence the conversion of a cyclic polymer into a core terminated polymer not only provides support for the concept of ester exchange in these systems but also suggests that the cyclic portion of the polymer may also undergo transesterification.

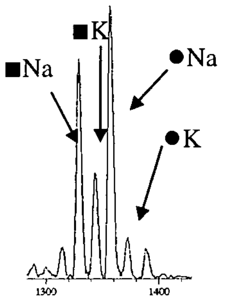
AB$_2$ polyester after 17 hours reaction with a core molecule.



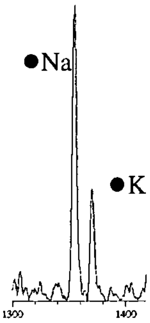
AB$_2$ polyester after 12 hours reaction with a core molecule.



AB$_2$ polyester after 6 hours reaction with a core molecule.



Fully cyclised AB$_2$ polyester before addition of core molecule.



●Na = cyclic polymer + Na$^+$

●K = cyclic polymer + K$^+$

■Na = core terminated + Na$^+$

■K = core terminated + K$^+$

Figure 4.17 Incorporation of dimethyl isophthalate (a B$_2$ core molecule) into the hyperbranched polyester with time, as shown by MALDI TOF mass spectroscopy

4.6 Conclusions

The work presented in this chapter has demonstrated that a limited amount of control over the polymer molecular weight can be achieved by the copolymerisation of a small amount of core molecule with the AB_2 monomer. There would appear to be no significant difference between the core molecules studied here other than that the higher functionality trimethyl 1,3,5-benzenetricarboxylate (B_3 core) provides a greater number of B groups, and hence potential core terminating reactions, than the dimethyl isophthalate (B_2 core). A groups are consumed in the polymerisation by polycondensation, cyclisation or core termination, however the polyester's weight average molecular weight continues to increase even after complete consumption. Hence, there would appear to be no control over the polydispersity, at protracted reaction times, by the introduction of a core. The continued increase in M_w is presumably a result of ester exchange processes, which have been demonstrated by the incorporation of dimethyl isophthalate into a previously fully cyclised polyester.

4.7 Experimental

Size exclusion chromatography was carried out using both chloroform and tetrahydrofuran as solvent. SEC in chloroform utilised three 5μm columns of PLgel with pore size 100, 10^3 and 10^5 Å, calibrated against polystyrene standards and used an ERC 7515A refractive index detector. SEC in THF employed PL gel columns (3 x 300 mm, polystyrene divinyl benzene copolymer beads, mixed pore sizes) maintained at 30 ^{0}C. A Viscotek differential refractometer, viscometer detector, right-angle laser light scattering (RALLS) detector and data capture unit (DM 400) were used in conjunction with TriSEC GPC software (version 3.0). Mass Spectra were recorded on a Kratos MALDI IV instrument, using 2,5-dihydroxybenzoic acid as the matrix and collecting data over 200 laser shots in linear, high mode with laser powers typically in the region of 125 (ca. 15% transmission). Dilute solution viscometry measurements were made with a Schott-Gerate automated viscometer system utilising a Schotte-Gerate Ubbelohde viscometer tube (bore size 0.46mm), immersed in a constant temperature water bath at 25°C.

4.71 Representative polymerisation procedure for core terminated polymers

Dimethyl 5-(2-hydroxyethoxy)isophthalate (4.83 g, 19.06 mmol.) and dimethyl isophthalate (0.172g, 0.89mmol) were placed into the polymerisation flask and the catalyst components added ($Mn(OAc)_2$: 3.8mg, 0.021 mmol. Sb_2O_3: 3.2 mg, 0.011 mmol. $(PhO)_3PO$: 2.0 mg, 0.006 mmol.). The flask was subjected to a nitrogen purge and placed in a high temperature oil bath, controlled by means of a 1 kW heating band / temperature programmer combination. The oilbath was heated at a rate of 10 ^{0}C / min. to 240 ^{0}C and held at that temperature for a period of 24 hours. The reaction mixture was continually stirred, during this period, at a rate of 125 r.p.m. by means of a stainless steel stirrer paddle powered by a Heidolph stirrer motor. After cooling the polymer was obtained as a clear brown brittle glass (3.9g) which needed to be chipped from the bottom of the flask and stirrer paddle.

4.72 Polymerisation procedure for core terminated polymers with varying reaction time

Dimethyl 5-(2-hydroxyethoxy)isophthalate (7.0 g, 27.62 mmol.) and dimethyl isophthalate (0.45g, 2.32mmol) were polymerised at 240 ^{0}C, without the use of a catalyst but otherwise as described previously (section 4.71). The polymerisation was over a period of 25 hours and sampled every 5 hours.

4.73 Polymerisation procedure for reaction of cyclic polymer with a core molecule

Dimethyl 5-(2-hydroxyethoxy)isophthalate (5.0 g, 19.69 mmol.) was polymerised at 240 ^{0}C, without the use of a catalyst but otherwise as described previously (section 2.63). The polymerisation was carried out over a period of 10 hours and the polymer sampled at 5 hourly intervals. The samples were analysed, for cyclic content, by MALDI-TOF mass spectroscopy and the polymerisation discontinued when complete cyclisation had been reached. After cooling the polymer was obtained as a clear brown brittle glass (3.63g) which was subsequently ground into a powder and mixed with dimethyl isophthalate (3.61g). The core / polymer mixture was reheated at 220 ^{0}C and sampled after 6, 12 and 17 hours reaction.

4.8 References

(1). Feast, W.J., Stainton, N.M.S., *J. Mater Chem.*, 1995, **5(3)**, 405

(2). Lach, C., Müller, P., Frey, H, Mülhaupt, R., *Macromol. Rapid Commun.* 1997, **18**, 253

(3). Radke, W., Litvinenko, G., Müller, A.H.E., *Macromolecules*, 1998. **31**, 239

(4). Hanselmann, R., Hölter, D., Frey, H., *Macromolecules*, 1998, **31**, 3790

(5). Sunder, A., Hanselmann, R., Frey, H., Mülhaupt, R., *Macromolecules*, 1999, **32**, 4240

(6). Malmström, E., Johansson, M., Hult, A., *Macromolecules*, 1995, **28**, 1698

Chapter Five

Branching in Hyperbranched Polymers

5.1 Introduction

The properties of polymers can be strongly affected by the presence of branching, particularly those properties related to molecular shape and dimensions. Hence, the correlation of physical properties with molecular architecture is a continuing subject of research and the elucidation of branching an important aspect of this important theme.[1] Hyperbranched polymers, as their name implies, are highly branched materials the study of which offers both challenges in the control of branching and opportunities in the correlation of structure with properties.

The first description of a quantitative measure of branching for hyperbranched polymers was given by Flory in his statistical treatment of network formation.[2] Flory described the copolymerisation of difunctional monomers, A_2 and B_2, with trifunctional branch points of A_3 type. A branching coefficient (α) was defined as the probability of an A group from a trifunctional branch unit being connected via a polymer chain to another branch unit. The polymerisation of monomers of AB_X type was considered as a special case leading to random branching without network formation. Hence, when applied to AB_2 type condensations the branching probability is simply the fraction of B groups that have reacted. Thus the branching coefficient is directly related to the conversion and has a maximum value of 0.5 (Equation 5.1).

Equation 5.1

$$\alpha = p_B = \frac{1}{2} p_A$$

Where α is the branching coefficient and p_A and p_B are the probabilities that an A or B group has reacted.

Since then other workers have endeavoured to derive expressions specific to hyperbranched materials which better describe the branching in these systems.

In this chapter some of these aspects of branching as applied to hyperbranched polymers are discussed and the experimental measurement of the degree of branching in polyesters derived from dimethyl 5-(2-hydroxyethoxy)isophthalate is described.

5.2 Branching in hyperbranched polymers

The branching inherent in a hyperbranched polymer can be described in terms of the structural components that make up that polymer. In an idealised AB_2 type polymer four types of structural unit may be recognised and are termed focal, linear, branched and terminal units (Figure 5.1). If intramolecular reactions are neglected then each individual polymer molecule should contain a single focal group, in which an unreacted A functionality is retained. The focal group may also be further characterised as either linear or branched. Linear units retain an unreacted B group whilst branched or dendritic units have no unreacted B functionalities. Likewise, terminal units are characterised by the retention of both B groups unreacted. Furthermore, in view of its mode of assembly, each polymer molecule should contain one more terminal unit than the number of branched units.

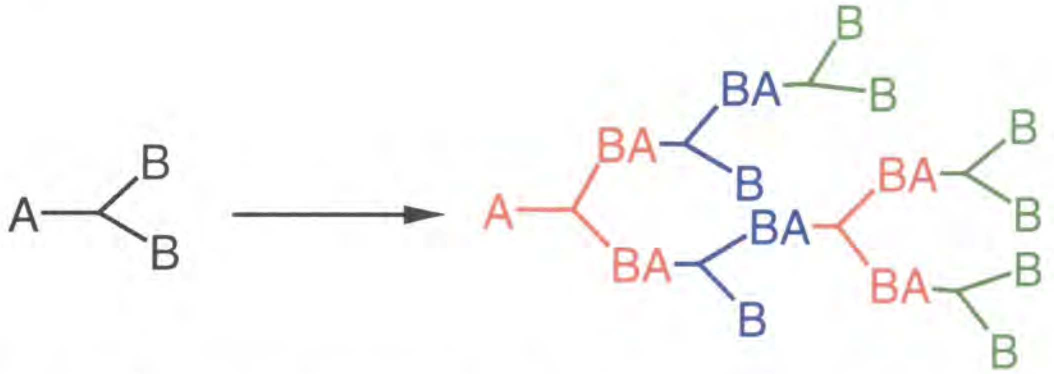


Figure 5.1 The structural components of an AB_2 polymer. The terminal units may be identified by the retention of two unreacted B groups, linear units retain a single unreacted B group whilst branched units contain no unreacted B groups.

The relative proportions of these structural units have been used by some researchers as a means of evaluating the branching content of hyperbranched polymers. Fréchet defined the degree of branching (DB) as the ratio of the sum of branched and terminal units to the total number of repeat units[3] (Equation 5.2), a definition also adopted by Kim[4] but using somewhat different terminology.

Equation 5.2
$$DB = \frac{D+T}{D+T+L}$$

Where L, D and T are the sums of the linear, dendritic and terminal units respectively.

In the above definition DB varies between 0 and 1. A fully branched polymer, such as a dendrimer, has a DB of 1, whereas a linear polymer has a DB of 0 *if terminal units are ignored.* Although this definition gained widespread acceptance, the inclusion of terminal units in the count for branching gives unrealistically high values of DB for small molecules. Both Müller[5] and Frey[6] have suggested alternative definitions, which are universally applicable to low and high molecular weight AB_2 polymers. The definition developed by Frey has the further advantage of being a general expression valid for all AB_X systems, although only the simplified case specific to AB_2 systems will be considered here. This definition of DB is based upon the ratio of actual growth directions to the maximum possible number of growth directions (Equation 5.3).

Equation 5.3
$$DB = \frac{D}{D_{\max}} = \frac{2D}{2D+L}$$

Where L and D are the sums of the linear and dendritic units respectively.

The relationship between the two expressions for the degree of branching, detailed above, can be seen if one considers that the branched and terminal units in an AB_2 oligomer are related by the expression: $t = d + 1$ (where t and d are the sum of the terminal and dendritic units in an individual molecule). For an ensemble of N molecules then $T = D + N$, which upon substituting into the Frey definition of DB (Equation 5.3) gives the following expression (Equation 5.4):

Equation 5.4
$$DB = \frac{D+T-N}{D+T+L-N}$$

Thus, in the case of large hyperbranched molecules where D >> N the Frey and Fréchet expressions become equivalent and, hence, the degree of branching is the same at high conversion no matter which definition is employed.

Whilst the degree of branching is a useful tool for the characterisation of hyperbranched polymers it cannot be used to compare branching between AB_X systems of differing functionality. Paradoxically, statistically branched polymers derived from monomers of higher functionalities actually have lower degrees of branching.[6] This is a consequence of higher functionality monomers having a greater number of possible growth directions. Thus a particular polymer may have more actual branch units than one prepared from a lower functionality monomer, yet may still have a lower proportion of the maximum possible growth directions utilised. In order to compare the 'density of branching' Frey has defined a general parameter based upon the average number of branches (ANB) deviating from the linear direction per non-terminal monomer unit (Equation 5.5).

Equation 5.5

$$ANB = \frac{D}{D+L}$$

Where L and D are the sums of the linear and dendritic units respectively for an AB_2 polymer.

Whilst the evaluation of branching within hyperbranched polymers is clearly desirable, the degree of branching in itself does not provide useful information about the overall topology of hyperbranched polymers. For example, a degree of branching of one does not necessarily imply regular polymer growth, merely the absence of linear sections within the structure. Hence, a dendrimer by definition has a DB of one but the converse is not true and non-dendritic structures, including essentially linear molecules, may also have degrees of branching equal to one. Furthermore, many isomeric structures are possible for a polymer molecule with a given degree of branching (Figure 5.2).

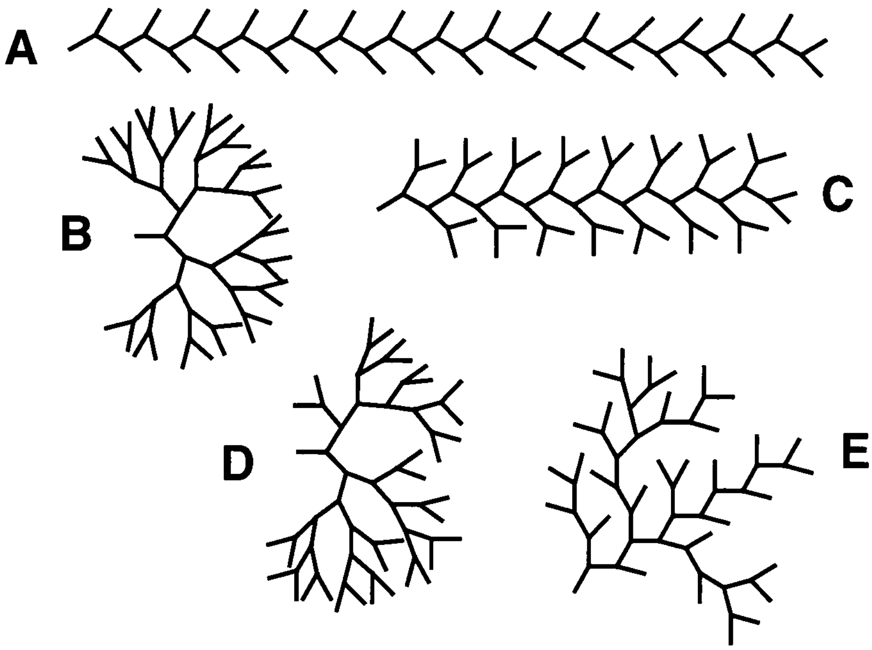


Figure 5.2 AB_2 polymers each of 31 repeat units with various degrees of branching A) Linear polymer, DB = 0; B) Dendritic polymer, perfect branching, regular growth, DB = 1; C) Linear polymer, DB = 1; D) Perfect branching, irregular growth, DB = 1; E) Statistical branching, DB = 0.5

A number of theoretical studies have demonstrated that the degree of branching, as defined by Frey, is proportional to the conversion (p_A), which leads to the conclusion that the maximum DB attainable for a random growth of an AB_2 polymer is 0.5.[7] This is in fact equivalent to Flory's branching coefficient (α) (Equation 5.6).

Equation 5.6

$$DB_{Frey} = \frac{1}{2} p_A = \alpha_{Flory}$$

In an extension of Flory's statistical treatment, Möller has studied the distribution of branching units for AB_2 polycondensates as a function of the conversion of A groups.[8] This study demonstrated that, at a given conversion, the weight fraction of purely linear or purely dendritic structures decreases rapidly with increasing degree of polymerisation. It was also shown that the main contribution to the weight fraction of a particular oligomer arises from isomers containing half the maximum number of branched units (Figure 5.3).

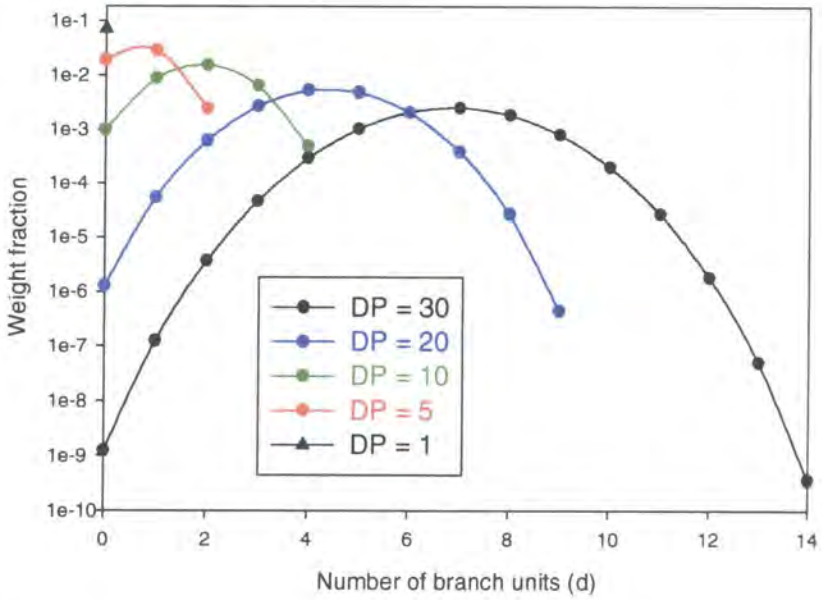


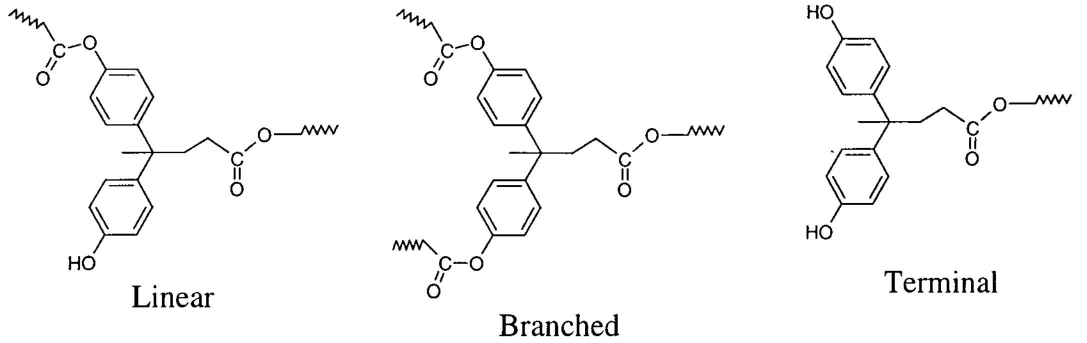
Figure 5.3 Theoretical weight distribution of branching units at a conversion of $\alpha = 0.4$.

5.3 Measurement of the degree of branching

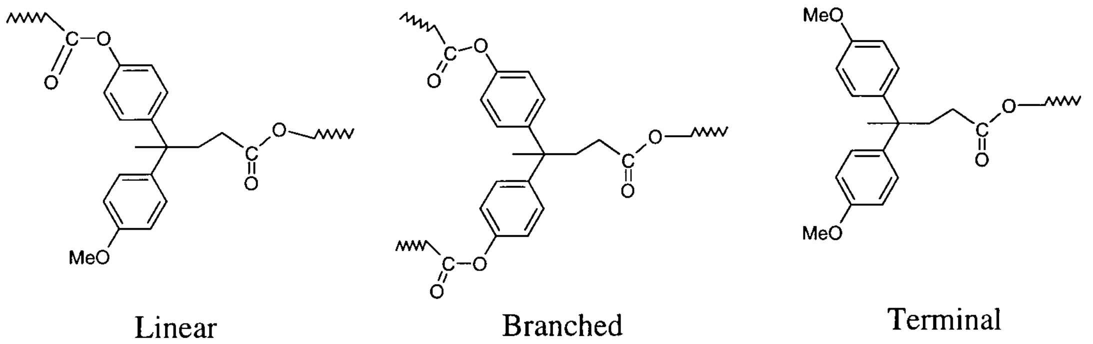
Evaluation of the degree of branching requires a method of quantifying the branched, linear and terminal units in the polymer and for this purpose nuclear magnetic resonance spectroscopy (NMR) has proved invaluable. It is often found that a particular nucleus in a repeat unit has a different chemical shift depending upon whether it is found in a linear, branched or terminal environment and integration of the peak areas allows the relative percentage of each unit to be determined. ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{15}N NMR spectroscopy have all been successfully employed as a means of measuring branching.[9] Low conversion polyester oligomers have been examined, by Voit *et al.*, using ^{13}C NMR, which allowed the conversion dependence of DB to be studied.[10] This was found to fit remarkably well with the theoretical predictions of Frey, for a random polymerisation. Furthermore, six possible diads were identified, depending upon whether a particular repeat unit was next to a branched, linear or terminal unit. The conversion dependence of the diads fitted well with the theoretical distribution and no particular sequence was favoured, once again suggesting a random polymerisation.

Whilst NMR spectroscopy is undeniably a powerful tool for the examination of branching, not all hyperbranched polymers can be studied in this manner. In some cases the method can be thwarted by the absence of significant differences in the chemical shifts of the structural units and an alternative method, based upon chemical degradation, has been employed.

Structural units of a hyperbranched polyester.



Structural units of a hyperbranched polyester after end group modification.



Residues from the modified hyperbranched polyester after hydrolysis.

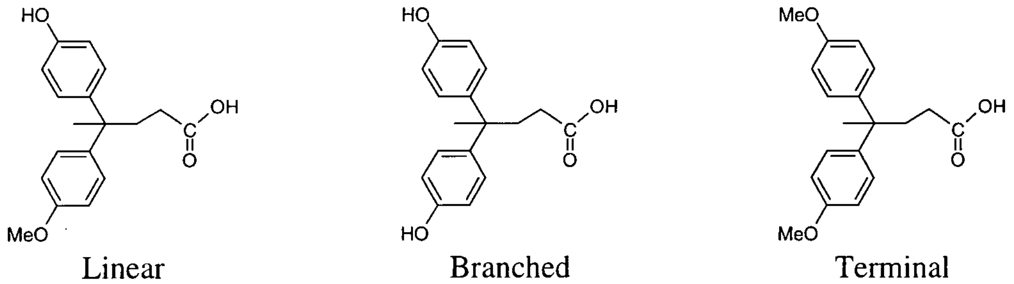


Figure 5.4 Determination of the degree of branching of a hyperbranched polyester by chemical degradation.[11a]

This technique involves the modification of the polymer chain ends followed by a chemical degradation of the polymer linkages but leaving the modified chain ends intact. The origin of the resulting fragments may be ascertained by the number of modified B groups present in each fragment. The relative proportions of each may then be determined by chromatagraphic procedures. Hawker first reported the determination of DB in hyperbranched polyesters by a chemical degradation method and Wooley and co-workers later used a similar approach for the characterisation of hyperbranched polycarbonates.[11] In the former case the hydroxyl groups of a phenoxy terminated hyperbranched polyester were converted to methoxy groups before hydrolytic degradation of the polymer backbone. The number of hydroxyl and methoxy groups present in each fragment indicated the origin of the resulting residues (Figure 5.4).

5.4 Enhancement of branching

A number of studies have been made which have attempted to enhance the degree of branching in hyperbranched polymers by various methods which may be grouped into the following five themes:

i Unequal reactivity of B groups.
ii Polymerisation of preformed dendrons.
iii Criss-cross cyclo-addition.
iv Post synthesis modification.
v Slow addition of monomer to a core molecule.

The first of these approaches is based upon utilising B groups of differing reactivity. A *random* polycondensation of an AB_2 monomer can only occur if the B groups are equally reactive. It is conceivable, however, that the reaction of the first B group, of a particular monomer residue, could deactivate the second B group, for example by steric hindrance. Conversely, the second B group could be activated by reaction of the first. The first of these cases would lead to an increase in the linear content of the polymer, whilst the second would lead to an increase in the branched content. Frey has pointed out that to obtain a DB of above 0.8 the second B group must be at least five times more reactive than the first.[7] Hobson and Feast have reported a hyperbranched poly(amidoamine) with a degree of branching close to one which presumably must fall into this category.[9g]

The second approach to regulating DB involves the polymerisation of AB_X type monomers that already have linear or dendritic segments incorporated. This method has been used by Hawker in the synthesis of poly(ether ketones) (Figure 5.5).[12]

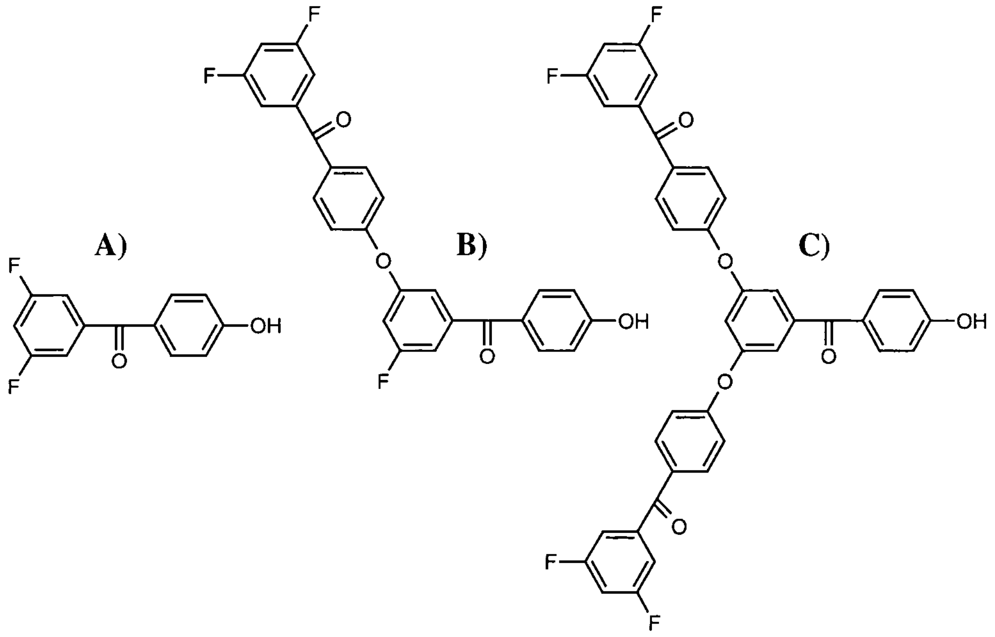


Figure 5.5 Monomers for the synthesis of poly(ether ketones).
A) Random branching B) Diminished branching C) Enhanced branching

Using this approach, polymerisation of the AB_2 monomer (A) gave a polymer with a degree of branching close to the theoretical value (0.49), whilst the corresponding linear AB_3 dendron (B) gave a lower DB (0.38) and the branched AB_4 dendron (C) a higher DB (0.71). This is in good agreement with Frey's theoretical model, which predicts a DB of 0.75 for the AB_4 dendron at full conversion.

The third of the approaches, noted above, uses a monomer that can only react to give fully branched or terminal units. This is based upon an AB_2 monomer with two identical B groups that cannot react independently. If one B group reacts an unstable intermediate is formed *reversibly*. This can then either revert to monomer and terminal units or react

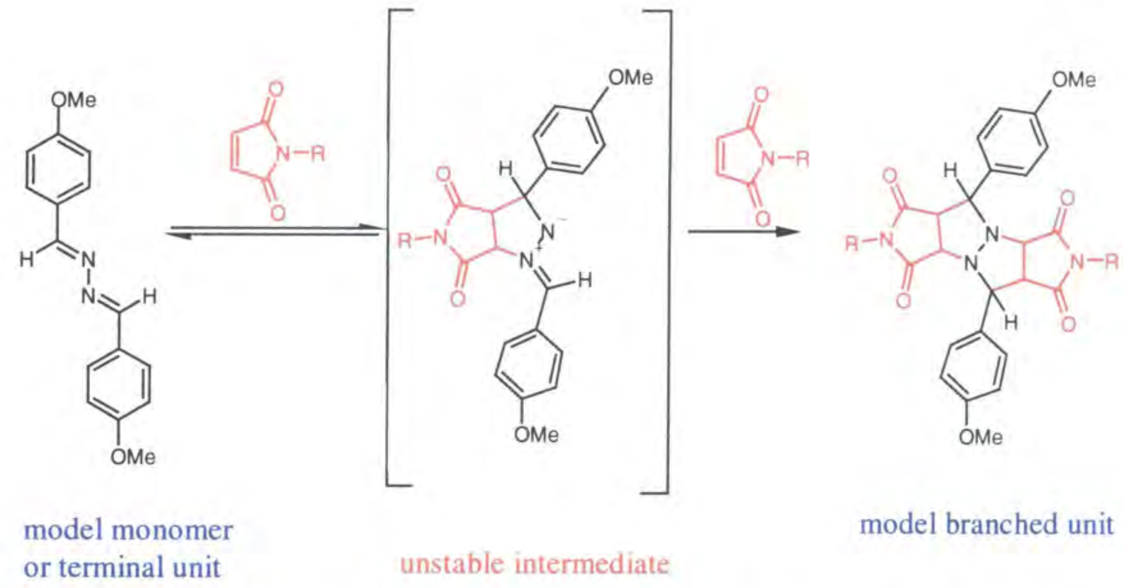


Figure 5.6 Mechanism of 'criss-cross' cycloaddition of a maleimide to an azine. An approach to 100% branching in hyperbranched polymers.

with another A group *irreversibly* to give a branched unit. Hence both B groups react or none at all (Figure 5.6). As yet, the sole example of this method is the 'criss-cross' cycloaddition of an AB_2 monomer using a maleimide as the A group and azine B groups (Figure 5.7).[13]

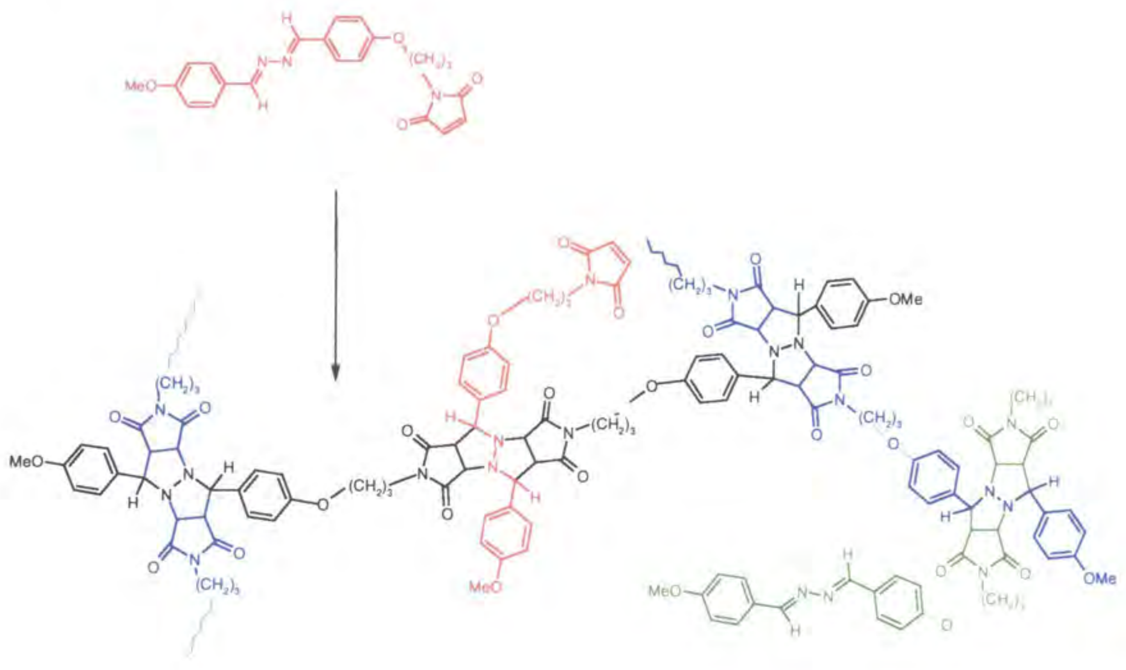


Figure 5.7 Hyperbranched AB_2 polymer from a monomer with a maleimide A group and azine B groups.

The fourth approach, post synthesis modification, involves manipulation of the degree of branching after the polymer has formed. In this method the unused B groups of the polymer are reacted with a monomer in which the B groups are protected. Thus the additional monomer units can only react with the polymer and not with monomeric B groups. The final stage is the deprotection of the added B groups to give a polymer with an enhanced degree of branching (Figure 5.8).

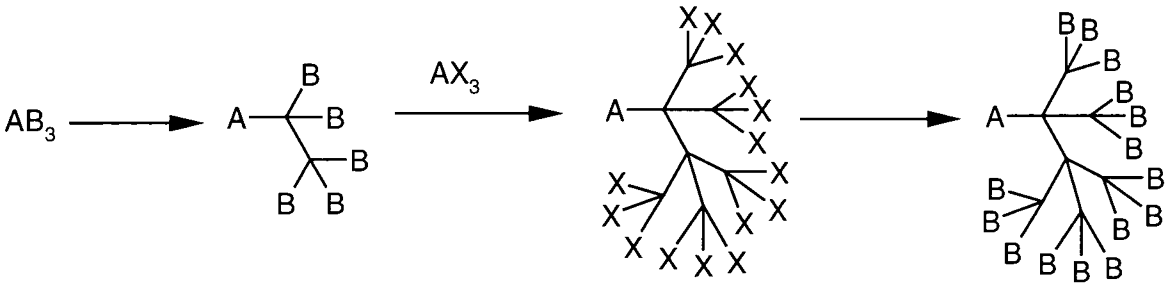


Figure 5.8 Schematic representation of post synthesis modification.

This method has been used in the synthesis of polycarbosilanes from AB_3 type monomers (Figure 5.9). The degree of branching of the intermediate polymer was found to be 0.48, which is close to the theoretical DB of 0.45 for a simple AB_3 random polymerisation. This was increased to 0.92 upon post-synthesis modification.[14]

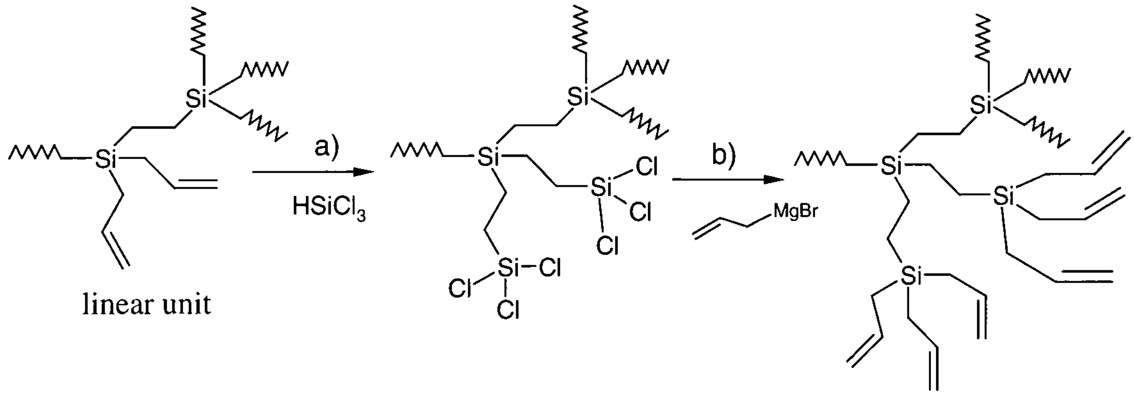


Figure 5.9 Post synthesis modification of a hyperbranched poly(triallylsilane). a) All residual double bonds are hydrosilylated with trichlorosilane. b) Addition of allylmagnesium bromide transforms trichlorosilane groups into terminal units.

The final approach to enhancing the degree of branching uses a multifunctional core molecule, of B_f type, combined with slow monomer addition under dilute conditions.

Although some researchers have attempted to influence branching by the use of a multifunctional core, theoretical calculations have shown that the addition of a core alone should not affect DB at high conversion. By contrast, slow sequential monomer addition to a core, under dilute conditions, will in theory increase the maximum DB to 0.66.[15] The results of recent computer simulations[16] have provided support for this and further corroboration in the form of a controlled synthesis of hyperbranched polyglycerols has been reported.[17] A further point of interest in the slow addition method is that both Frey and Müller have developed models that predict the radial distribution and segment density of hyperbranched polymers made via slow addition. Both models are in agreement and predict the greatest density of branching to be close to the core.[15, 16a]

5.5 Determination of degree of branching in hyperbranched polymers of dimethyl 5-(2-hydroxyethoxy)isophthalate

Determination of the degree of branching for polymers and copolymers derived from dimethyl 5-(2-hydroxyethoxy)isophthalate was first reported by Stainton.[18] Quantitative ^{13}C NMR spectroscopy was used to identify branching environments and degrees of branching of 0.60 - 0.67 were reported. This is greater than the theoretical maximum for a random statistical polymerisation (DB = 0.5), although incorporation of a multifunctional core molecule did not affect the DB which does accord with theory.

The hyperbranched polymers, described in chapter 2, were similarly analysed by ^{13}C NMR spectroscopy with a view to the determination of DB and the various possible branching environments of these polymers are illustrated below (Figure 5.10).

The ^{13}C NMR spectra of polyester solutions in $CDCl_3$ were not sufficiently resolved to allow quantitative analysis, although some fine structure was apparent.

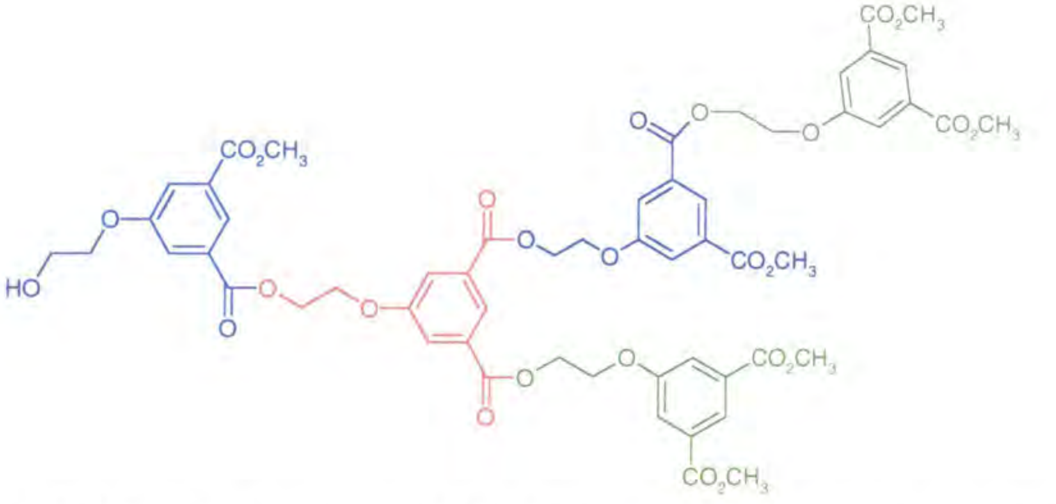


Figure 5.10 Structural components of an AB$_2$ polymer based upon dimethyl 5-(2-hydroxyethoxy)isophthalate. Branched units are shown in red, linear in blue and terminal in green.

The resolution was found to be much improved, however, by acquiring the spectrum at elevated temperature (100 ^{0}C) in tetrachloroethane-d2, even so the signals were seen as partially resolved multiplets rather than separate peaks (Figure 5.11 and Appendices 1.10 to 1.11). Thus, a deconvolution procedure was required to measure the contribution of each of the component parts of the multiplets.

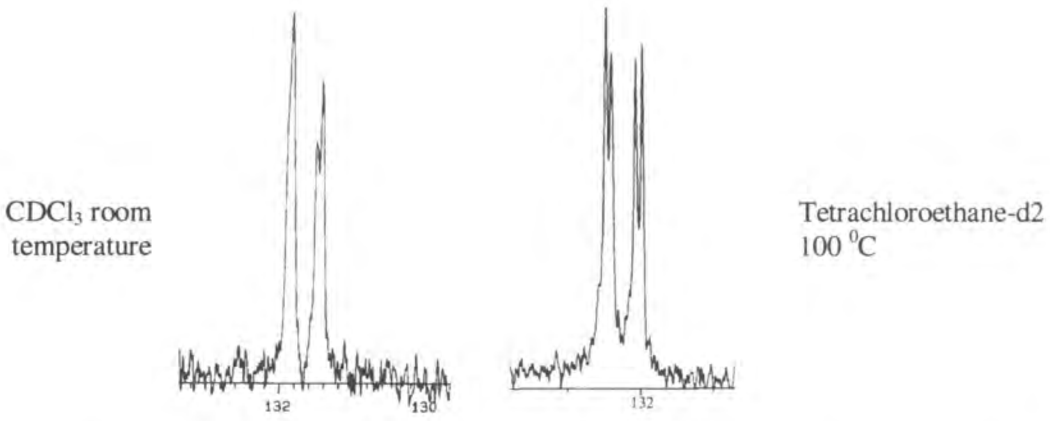
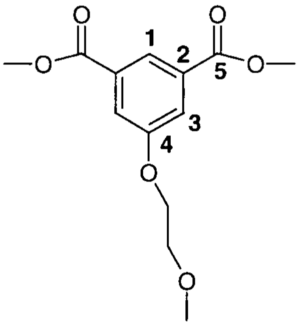


Figure 5.11 The effect of temperature upon the resolution of multiplets in the ^{13}C NMR spectrum of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate).

Even at an elevated temperature of 100 ^{0}C not all signals revealed fine structure, for instance the aliphatic carbons appear not to be influenced by the branching environment. Of the remaining carbons those closest to the branch point displayed the biggest effect with the carbonyl carbon itself exhibiting the most splitting (Figure 5.12). Of the observed multiplets those arising from carbons 2, 3 and 5 are expected to be manifest as 4 signals, attributable to 1 branched, 1 terminal and 2 linear environments (Figure 5.13). In the case of the branched and terminal units, for each multiplet there are contributions from two carbon atoms of the same chemical shift. However, in the linear case there is one contribution from each of two carbon atoms of different chemical shift depending upon whether the carbon nucleus under consideration is close to or distant from the branch point.



Only carbons labelled 1,2,3 and 5 show effects due to branching.

Figure 5.12 Polymer repeat unit showing carbons which are split in the ^{13}C NMR spectrum due to the branching environment.

This splitting pattern was in fact observed for carbons 2 and 5 but carbon 3 was seen as a multiplet of three peaks rather than the expected four (Figure 5.14). Presumably in this case some of the peaks are overlapping and indeed the magnitude of the splitting is less for this multiplet than the better separated carbonyl signals. In the case of carbon 1 only three peaks are seen but as there is only a single carbon contribution no matter whether it is in a branched, linear or terminal environment then this is to be expected.

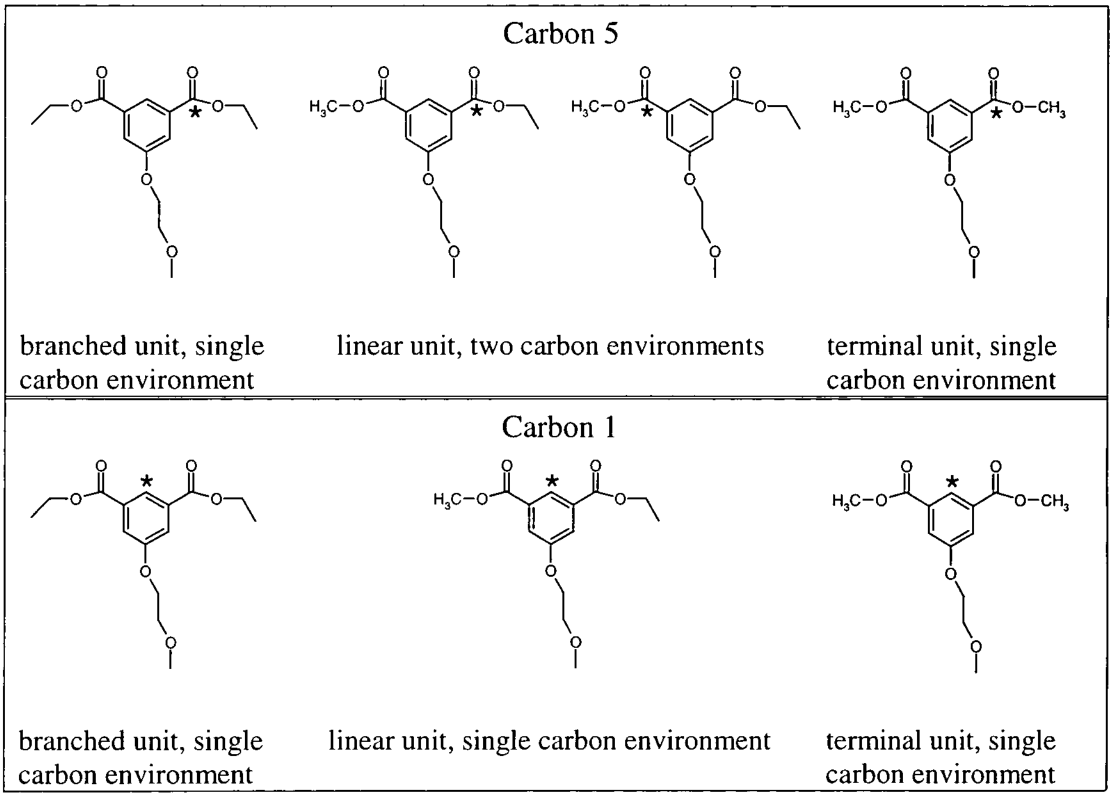


Figure 5.13 Branching, linear and terminal environments for carbons 1 and 5

By assigning the peaks of each multiplet to branched, linear or terminal units the degree of branching can be calculated by comparison of the peak areas. For each multiplet the relative peak areas of its individual components were measured by performing a Lorentzian deconvolution followed by integration. This procedure was carried out for 3 different polymer samples of low, intermediate and high molecular weight (M_w = 9 800, 37 900 and 136 200 PS equivalents respectively) and the results summarised below (Tables 5.1 to 5.3).

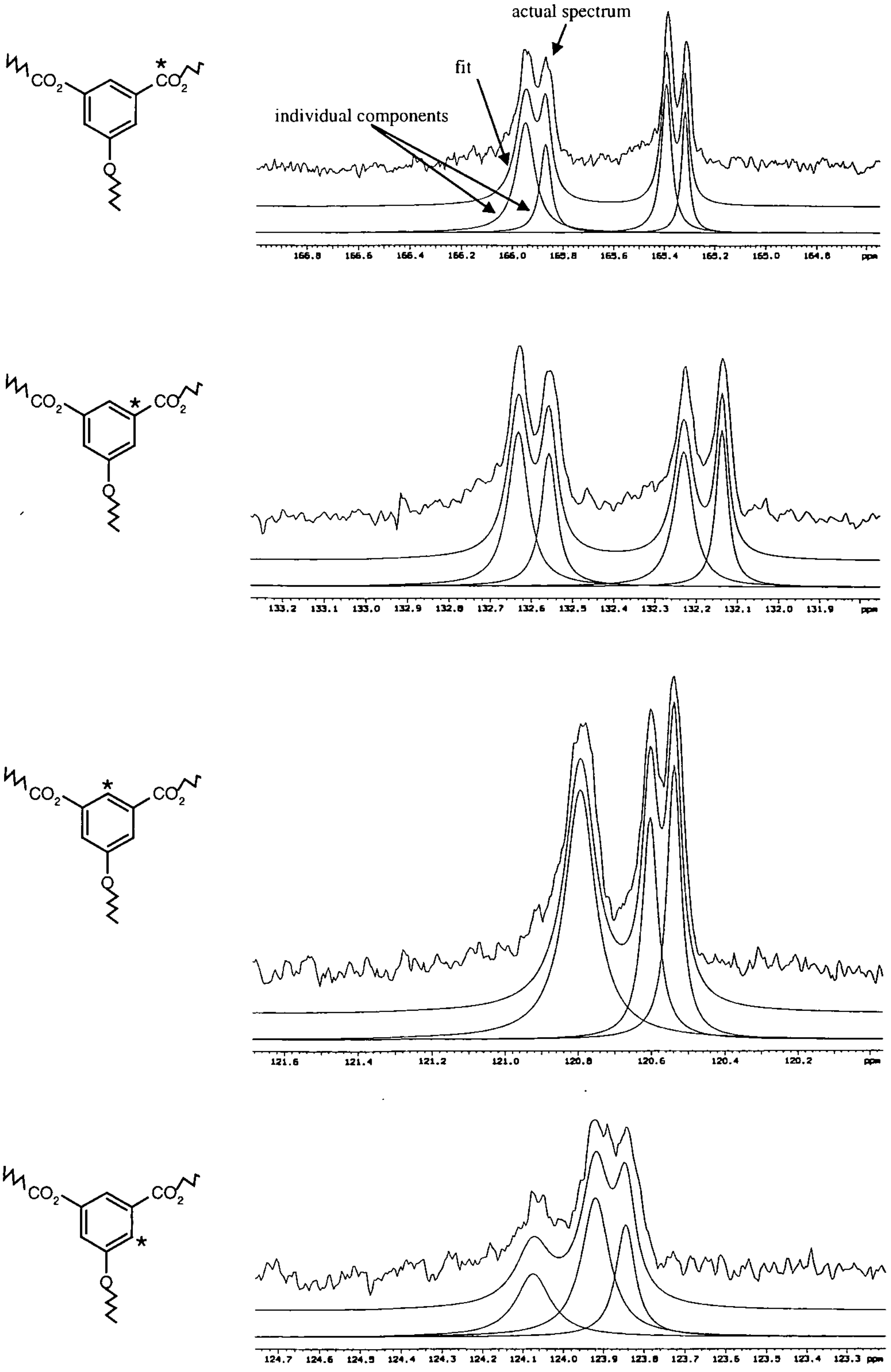


Figure 5.14 ^{13}C **NMR expansions and Lorentzian deconvolution of the multiplets associated with linear, terminal and branched sub-units present in hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate), after 4 hours polymerisation (Mw 9 800 PS equivalents).**

Carbon	Shift (ppm)	Line width (Hz)	Assignment	Integral	$DB_{Frechet}$ $\frac{D+T}{D+T+L}$	DB_{Frey} $\frac{2D}{2D+L}$
1	124.08	9.32	D	109	0.43	0.36
	123.91	10.13	L	385		
	123.84	6.54	T	181		
2	132.62	4.85	D	198	0.51	0.50
	132.54	5.27	L	251		
	132.21	4.41	L	144		
	132.12	4.81	T	216		
3*	120.78	10.26	L	660	0.55	0.51 (0.58)
	120.59	5.29	D (T)	338		
	120.53	5.98	T (D)	457		
5	165.95	10.30	D	318	0.55	0.65
	165387	5.54	L	126		
	165.39	5.73	L	213		
	165.31	3.66	T	98		
Degree of branching averaged across the whole spectrum					0.51	0.51 (0.52)

* Note: carbon 3 signals cannot be unambiguously identified: assignments were made to retain consistency across the whole spectrum.

Shaded areas show cases where D and T integrals are not approximately equal.

Table 5.1 Assignment of branching environments in ^{13}C NMR spectra. Low molecular weight polymer (Mw = 9 800 PS equivalents)

Carbon	Shift (ppm)	Line width (Hz)	Assignment	Integral	DB$_{\text{Frechet}}$ $\frac{D+T}{D+T+L}$	DB$_{\text{Frey}}$ $\frac{2D}{2D+L}$
1	124.07	13.12	D	499	0.53	0.53
	123.92	10.47	L	880		
	123.84	7.22	T	489		
2	132.63	7.44	D	690	0.52	0.56
	132.56	5.75	L	460		
	132.23	6.86	L	557		
	132.14	4.36	T	411		
3*	120.80	12.67	L	1919	0.49	0.47 (0.50)
	120.60	6.33	D (T)	854		
	120.54	5.72	T (D)	954		
5	165.95	10.83	D	719	0.54	0.62
	165.87	6.45	L	344		
	165.39	5.88	L	533		
	165.32	4.35	T	320		
Degree of branching averaged across the whole spectrum					0.52	0.55 (0.55)

* Note: carbon 3 signals cannot be unambiguously identified: assignments were made to retain consistency across the whole spectrum.

Shaded areas show cases where D and T integrals are not approximately equal.

Table 5.2 Assignment of branching environments in ^{13}C NMR spectra. Intermediate molecular weight polymer (Mw = 37 900 PS equivalents)

Carbon	Shift (ppm)	Line width (Hz)	Assignment	Integral	$DB_{Frechet}$ $\frac{D+T}{D+T+L}$	DB_{Frey} $\frac{2D}{2D+L}$
1	124.07	9.46	D	380	0.46	0.43
	123.9	10.00	L	993		
	123.83	5.87	T	471		
2	132.61	4.89	D	153	0.45	0.46
	132.53	7.24	L	222		
	132.21	4.92	L	144		
	132.12	5.14	T	148		
3*	120.78	9.36	L	1984	0.56	0.49 (0.61)
	120.59	5.51	D (T)	939		
	120.53	7.35	T (D)	1540		
5	165.94	7.03	D	138	0.50	0.51
	165.86	7.32	L	159		
	165.38	4.19	L	109		
	165.30	5.35	T	134		
Degree of branching averaged across whole spectrum					0.49	0.47 (0.50)

* Note: carbon 3 signals cannot be unambiguously identified: assignments were made to retain consistency across the whole spectrum.

Shaded areas show cases where D and T integrals are not approximately equal.

Table 5.3 Assignment of branching environments in ^{13}C NMR spectra. High molecular weight polymer (Mw = 136 200 PS equivalents)

Unfortunately, the interpretation of the spectra for these materials proved problematic and completely unambiguous assignments could not be made. In assigning the peaks to the various branching environments recourse was made to the following four criteria:

i Linewidths should reflect the relative mobility of the repeat units within the polymer.

ii Peak integrations should be consistent with the polymer architecture.

iii Chemical shifts of branching environments should be consistent irrespective of polymer molecular weight.

iv The degree of branching should exhibit conformity across the whole spectrum.

The primary method for assigning the individual components of a given multiplet, to the various branching environments, was by a consideration of the relative linewidths of the multiplet's component peaks. This was considered to reflect the relative mobility of the different branching units. A given carbon atom within a branching unit might be expected to have less freedom of movement, and hence a shorter relaxation time leading to broader linewidths, than the same carbon within a more mobile terminal unit. Thus, signals for carbons of fully branched units were expected to have the broadest linewidths, terminal units the narrowest and linear units were expected to be intermediate between the two.

When comparing the relative amounts of the different branching environments certain constraints relating to the polymer architecture must be met. Firstly the number of terminal units in an ensemble of N AB_2 polymer molecules is related to the number of dendritic units by: $T = D + N$ (see Section 5.2). Thus, for large hyperbranched molecules where $D >> N$ the number of dendritic and terminal units are equivalent. Furthermore, for a fully cyclised AB_2 polymer the number of dendritic and terminal units are exactly equal. This can be seen if one considers that to form a cycle an A group can undergo either one of two intramolecular reactions. It can react either with a linear unit to form a single extra dendritic unit or react with a terminal unit to give an extra linear unit but decreasing the number of terminal units by one. Thus it is to be expected that for these polymers the number of dendritic and terminal units, and hence their respective NMR peak areas (i.e. integrals) should be equal.

When the above two considerations, of linewidths and peak areas, have to be reconciled it should also be noted that the chemical shift for a particular carbon in a particular branching environment should be the same, irrespective of its position in the polymer. Hence when comparing polymers of different molecular weights the peak assignments should be consistent between samples. Similarly, a degree of branching obtained by inspection of a particular carbon atom in the molecule should be consistent with the degree of branching obtained by analysis of all the other carbon signals for the same molecule.

Unfortunately not all the above constraints could be reconciled in every case. It is often difficult to distinguish between branched and linear environments when the linewidths are very similar but perhaps the greatest cause for concern is those cases where the integrals do not conform to the expected pattern. The most probable source of this error is in the deconvolution and curve fitting procedure, whereby peak shapes are approximated to Lorentzian curves. Hence errors are likely to be introduced into both the values for linewidth and integration in those cases where the real peak shape does not resemble a Lorentzian curve.

Despite the above caveats a reasonably consistent value for DB was obtained for all three polymer samples, although there must remain some doubt as to the accuracy of the technique in this case.

Degrees of branching (as defined by Frey) averaged for all carbon signals were 0.5, 0.6 and 0.5 ± 0.1, for the low, intermediate and high molecular weight polymers respectively. Although there are certainly difficulties in the calculation of DB by this method it is encouraging that in those cases where assignment by linewidth and integral patterns did in fact coincide a DB of 0.5 was obtained. This is in agreement with the value obtained by averaging across the whole spectrum.

5.6 Conclusions

The data presented here has shown that the measurement of the degree of branching for hyperbranched polyesters is not a trivial process and that in this respect the technique of quantitative ^{13}C NMR spectroscopy is fraught with difficulties. The assignment of the NMR spectra could perhaps be simplified by the synthesis of model compounds but the major complication remains the inconsistency in some of the integral patterns. If this is attributable to the errors introduced by peak deconvolution then a method of improving signal resolution must be sought. Recent work on analogous poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s found that the best resolution was obtained using deuterated toluene at 95 ^0C, although in the present case the choice of high boiling deuterated solvents may be somewhat limiting.[19] A further possibility for the elucidation of DB may be the method of chemical degradation but this is limited by the requirement for highly selective reactions to differentiate between terminal and branching esters.

There was no significant difference between DB values obtained by either the Frechet or the Frey definition but this is to be expected at high polymer conversion.

Nevertheless, the degrees of branching obtained for these polymers are in reasonable agreement with the theoretical value for a statistical distribution at complete conversion (DB = 0.5) but lower than those reported by Stainton (0.66). Furthermore, the effects of redistributing branch units through transesterification might be expected to tend towards statistical branching. Degrees of branching consistent with a statistical distribution have also been reported for the related poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s although again peak assignment proved to be problematic and the author concluded that ^{13}C NMR spectroscopy was unsuitable technique in that instance.[19]

There was no discernible conversion dependence of DB for these polymers as the DB for the 3 different molecular weight polymers were the same, within experimental error. This is perhaps not unexpected as the degree of branching is predicted to approach 0.5 quite rapidly with increasing degree of polymerisation (Figure 5.15). The theoretical DB, for an AB_2 polymerisation, reaches a value of 0.45 at an average degree of polymerisation of only 10, whereas the accuracy of the NMR technique is not sufficient to distinguish degrees of branching at this level.

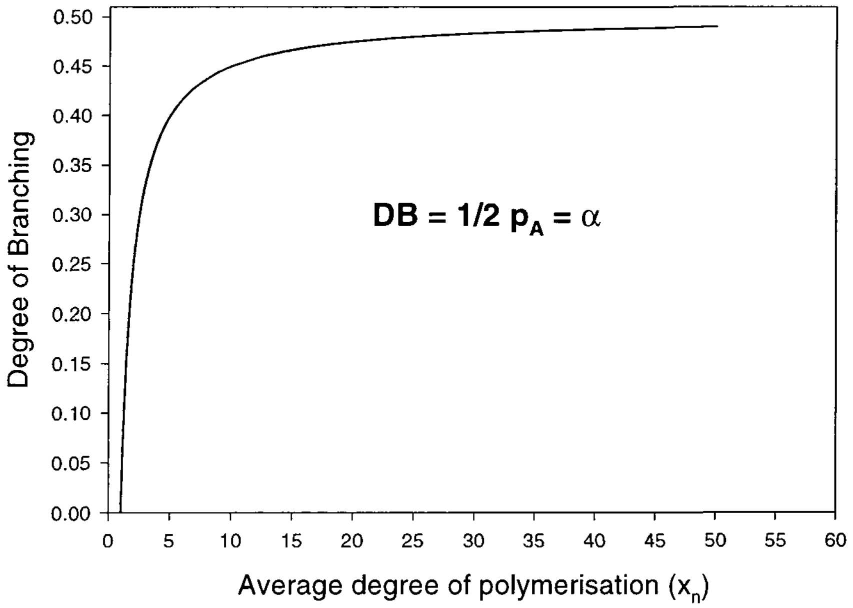


Figure 5.15 Theoretical variation of DB with degree of polymerisation

5.7 Experimental

^{13}C NMR spectra (125.77 MHz) at 100 ^{0}C in tetrachloroethane-d2 were acquired on a Varian Inova 500, using relaxation delays of 2 and 4 seconds. Molecular weight distributions were obtained using size exclusion chromatography in chloroform using three 5μm columns of PLgel with pore size 100, 10^3 and 10^5 Å, calibrated against polystyrene standards and utilising an ERC 7515A refractive index detector.

5.8 References

---

(1). Roovers, J. 'Branched Polymers' in *Encyclopaedia of Polymer Science and Engineering*, vol. 2, (Eds: Mark, H.F., Bikales, N.M., Overberger, C.G., Menges, G.), 2nd edition, Wiley Interscience, New York, 1985

(2). Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953

(3). Hawker, C.J., Lee, R., Fréchet, J.M.J., *J.Am. Chem. Soc.*, 1991, **113**, 4583

(4). Kim, Y. H., Webster, O.W., *Macromolecules*, 1992, **25(21)**, 5561

(5). Yan, D., Müller, A.H.E., Matyjaszewski, K., *Macromolecules*, 1997, **30**, 7024

(6). Hölter, D., Burgath, A., Frey, H., *Acta. Polymer.*, 1997, **48**, 30

(7). Hölter, D., Frey, H., *Acta. Polymer.*, 1997, **48**, 298

(8). Beginn, U., Drohmann, C., Möller, M., *Macromolecules*, 1997, **30**, 4112

(9). a) Shu, C.F., Leu, C.M., *Macromolecules*, 1999, **32**, 100

b) Thompson, D.S., Markoski, L.J., Moore, J.S., *Macromolecules*, 1999, **32**, 4764

c) Kim, Y.H., *Macromol. Symp.*, 1994, **77**, 21

d) Malström, E., Johansson, M., Hult, A., *Macromolecules*, 1995, **28**, 1698

e) Hawker, C.J., Chu, F., *Macromolecules*, 1996, **29**, 4370

f) Lach, C., Müller, P., Frey, H., Mülhaupt, R., *Macromol. Rapid Commun.*, 1997, **18**, 253

g) Hobson, L.J., Feast, W.J., *Polymer,* 1999, **40**, 1279

(10). Schmaljohan, D., Komber, H., Voit, B.I., *Acta. Polymer.*, 1999, **50**, 196

(11). a) Kambouris, P., Hawker, C.J., *J. Chem. Soc. Perkin Trans. 1,* 1993, 2717

b) Bolton, D.H., Wooley, K.R., *Macromolecules*, 1997, **30**, 1890

(12). Hawker, C.J., Chu, F., *Macromolecules*, 1996, **29**, 4370

(13). Maier, G., Zech, C., Voit, B., Komber, H., *Macromol. Chem., Phys.,* 1998, **199**, 2655

(14). Lach, C., Frey, H., *Macromolecules*, 1998, **31**, 2381

(15). Radke, W., Litvinenko, G., Müller, A.H.E., *Macromolecules*, 1998. **31**, 239

(16). a) Hanselmann, R., Hölter, D., Frey, H., *Macromolecules*, 1998, **31**, 3790

b) Widmann, A.H., Davies, G.R., *Comp. and Theor. Polymer Science*, 1998, **8** **(1/2)**, 191

(17). Sunder, A., Hanselmann, R., Frey, H., Mülhaupt, R., *Macromolecules*, 1999, **32**, 4240

(18). Feast, W.J., Stainton, N.M., *J. Mater. Chem.,* 1995, **5(3)**, 405

(19). Keeney, A.J., *Ph.D. Thesis*, Durham University, 1998

Chapter Six

Thermal Analysis of Hyperbranched Polyesters

6.1 Introduction.

For a given polymer the melting temperature (T_m) and the glass transition temperature (T_g) are important parameters which characterise its properties over a wide temperature range.[1] There have been few studies concerning the properties of hyperbranched polymers and the thermal properties of these materials are not understood fully.[2] Hyperbranched polymers are usually amorphous, as their highly branched nature disrupts crystal growth, and these materials exhibit a glass transition but no melting point.[3] In this chapter aspects of the glass transition of hyperbranched polymers are discussed and the thermal analysis of polyesters derived from dimethyl 5-(2-hydroxyethoxy)isophthalate is described.

6.2 The glass transition temperature.

When a polymer, which does not crystallise easily, is cooled from the liquid or rubbery state it becomes much stiffer as it passes through a certain temperature range. This is the glass transition and below this point the polymer is said to be in the glassy state. The transition from a glassy to a rubbery state is accompanied by marked changes in physical properties such as the modulus and specific volume.[4] The glass transition is associated with the onset of long-range co-operative segmental motion in the amorphous phase[5] and the temperature at which it occurs (T_g) is dependent upon the amount of thermal energy required to confer mobility to the polymer chains. This is affected by factors that influence the ease of rotation of the polymer backbone, such as chain flexibility, branching and cross-linking.[6] Stutz has developed a general theoretical treatment, applicable to both linear and crosslinked polymers, in which the glass temperature of a given polymer is described as a function of its end group conversion and degree of branching or crosslinking (Equation 6.1).[7]

Equation 6.1

$$T_g = \left(T_g^{\infty} - K_1(1-p)\right)\left(1 + K_2 \frac{X_c}{1-X_c}\right)$$

Where K_1 and K_2 are constants, X_c is the degree of branching and p is the end group conversion.

In this definition the end group conversion (p) is defined as the number of reacted functional groups (both A and B) divided by the total number of functional groups. The degree of branching (X_c) is defined as the number of branch units divided by the total number of units. The backbone glass temperature (T_g^∞) is used as reference and is defined as the limiting glass temperature of the linear polymer at infinite molecular weight, without end groups or branch points. Unreacted end groups decrease the glass temperature below the reference since they possess greater free volume compared to backbone units (the concept of free volume is discussed more fully at a later stage). Branch points or crosslinks increase the glass temperature since they reduce the mobility of the surrounding chain segments.[7]

It is well established that over certain ranges of molecular weight the value of T_g is a function of the polymer chain length.[4,6,8] At high molar masses the glass transition temperature of a given polymer is constant but decreases as the polymer chain length is shortened. This is a chain end effect and can be described by free volume theory. The free volume is defined as the unoccupied space in a polymer sample arising from the inefficient packing of disordered chains in the amorphous region.[6] This is a measure of the space available for the polymer to undergo rotation and translation and below T_g there is insufficient free volume to allow large scale segmental motion to take place. The free volume increases with temperature and the glass transition is the point at which the free volume is large enough to allow segmental motion. Each chain end contributes a certain amount of free volume to the system and requires more free volume in which to move than a segment in the chain interior. For a polymer of infinite molecular weight the free volume contribution of the chain ends can be neglected and the T_g is dependent upon the free volume of the polymer backbone. The T_g of a polymer of finite molecular weight is lowered due to the free volume contribution of the chain ends. The chain end free volume per unit volume of polymer is given by $2\theta\rho N_A / M_n$ (where θ is the free volume per chain end, ρ is the polymer density, N_A Avogadro's number, M_n the number average molecular weight and the number of end groups per chain is 2). This may be equated to the volume created by expanding the polymer above the glass transition temperature which is equal to $\alpha_f(T_{g\infty} - T_g)$, (where α_f is the free volume expansion coefficient and $T_{g\infty}$ the glass transition temperature of a polymer of infinite molecular weight). This leads to a reciprocal relationship between the glass transition temperature of a polymer and its number average molecular weight (Equation 6.2).[4]

Equation 6.2

$$\alpha_f\left(T_g^{\infty} - T_g\right) = \frac{2\theta\rho N_A}{M_n}$$

Where θ is the free volume of a chain end, ρ density, N_A Avogadro's number and α_f the free volume expansion coefficient.

$$T_g = T_g^{\infty} - K/M_n$$

$K = (2\theta\rho N_A / \alpha_f)$ and is a constant.

6.3 The glass transition temperature of hyperbranched and dendritic polymers

There have been few systematic studies of the glass transition in dendritic polymers and the factors governing the glass temperature are not understood fully. A distinctive feature of dendritic and hyperbranched polymers is that both the number of end groups and branch points increase as the molecular weight is increased. As mentioned above, both the end group conversion and the degree of branching or crosslinking affect the glass temperature of linear polymers but their effect upon the thermal behaviour of dendritic macromolecules is at present unclear.

The flexibility of a hyperbranched polymer's structural units has been shown to have a marked influence upon the glass transition temperature. Ramakrishnan and co-workers have studied the effect of spacer length and backbone flexibility upon the glass transition temperature of hyperbranched aromatic polyesters.[9] The glass transition temperatures were found to decrease upon increasing the length and flexibility of the spacer groups. This is as expected from analogy with the thermal behaviour of linear polymers and has also been observed in hyperbranched polyesters based upon dimethyl 5-(ω-hydroxyalkoxy)isophthalates (Figure 6.1).[10]

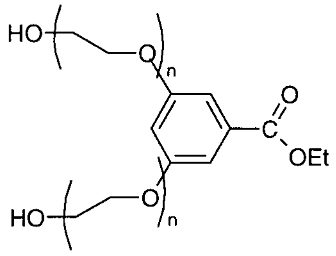
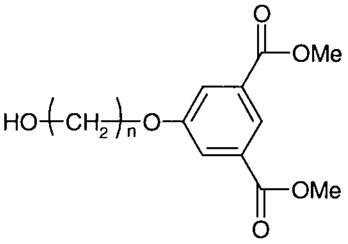
AB_2 monomer	**Spacer length (n)**	**Tg (^{0}C)**
	1 2 3	80 15 -4
	3 4 5 6	61-66 45-51 34-36 24-28

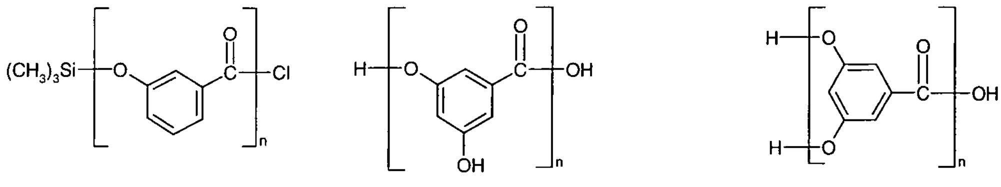
Figure 6.1 Effect of spacer length upon Tg of hyperbranched polyesters

The effect of branching upon the glass temperature is unclear and published examples are contradictory. Kim has shown that the T_g of a hyperbranched polyphenylene is lower than that of a dendritic polyphenylene of comparable molecular weight.[11] This is in agreement with the general theoretical treatment developed by Stutz (Equation 6.1), in which the glass temperature of a dendritic polymer is described as a function of its end group conversion and degree of branching.[12] As hyperbranched and dendritic polymers based upon the same building block and of comparable molecular weight have the same end group conversion it seems reasonable to expect the less branched hyperbranched polymer to have the lower T_g. In contrast Hawker and co-workers have shown that the glass transition temperature of hyperbranched poly(ether ketones) is independent of the degree of branching.[3] Fluoro-terminated poly(ether ketones) with degrees of branching (as defined by Fréchet and described in chapter 5) of 39, 49 and 71% all gave a T_g of 162 ^{0}C. This is unexpected but is in agreement with the work of Fréchet and co-workers who have studied the effect of polymer architecture upon the glass transition temperature.[13] Linear, hyperbranched and fully dendritic systems based upon 3,5-dihydroxybenzoic acid all gave similar value of T_g, irrespective of the degree of branching (Table 6.1).

	Glass transition temperature (^{0}C)		
end groups	linear	hyperbranched	dendrimer
phenol	204	197	201
benzyl ether	78	-	73
t-butyldimethylsilyl	102	103	-

Table 6.1 T_g of polymers based upon 3,5-dihydroxybenzoic acid

The linear polymers used in this comparison are derived from the AB_2 monomer 3,5-dihydroxybenzoic acid. Other studies have used linear polymers based upon AB monomers, such as 3-hydroxybenzoic acid, and do not take into account the influence of the numerous unreacted B functionalities that exist in AB_2 based systems.[14] It is apparent that there can be a marked difference in Tg between AB and AB_2 based systems and any attempt to study the effect of polymer architecture upon the glass temperature must take this into account (Figure 6.2).



T_g = 145 ^{0}C [14]

T_g = 204 ^{0}C [13]

T_g = 197 ^{0}C (hyperbranched) [13]
201 ^{0}C (dendritic) [13]
200-225 ^{0}C (hyperbranched) [15]

Figure 6.2 Comparison of the T_g of linear, hyperbranched and dendritic polyesters illustrating the effect of end groups.

The difference in T_g between the AB and AB_2 based linear polyesters in the above example (Figure 6.2) is surprising. Although the AB polymer is expected to have higher end group conversion, less chain end free volume and consequently a higher T_g than the AB_2 based polymer, the Tg of the AB_2 system is higher than is expected by a simple consideration of free volume effects. Similarly, the degree of branching might be expected to influence the glass transition temperature but, as was stated above, the T_g of aromatic polyesters appears to be independent of molecular architecture. This can be rationalised if the glass transition is influenced by the nature of the end group and the effect is large enough to outweigh the influence of branch points and chain end free volume. In linear polymers the end group conversion increases with increasing molecular weight until at high molecular weight the fraction of unreacted end groups is negligible and the glass temperature is determined by the nature of the backbone. Stutz has argued that this is not the case for dendritic systems in which the fraction of unreacted end groups approach a constant value of (1-p). Thus it is to be expected that the nature of the end groups will have a significant effect upon the glass transition temperature, particularly if the end groups are polar or capable of hydrogen bonding. Such an effect has been observed in the study of the influence of chain end composition on the glass temperature of polyether dendrons.[16] When the end groups of a fourth generation polyether dendron were changed from hydrogen to bromo to cyano the T_g increased from 315 to 325 to 349 K. A large change in T_g (128 K) was also observed when benzyl ether terminated dendritic polyesters were compared to the analogous phenolic terminated systems that are capable of hydrogen bonding. Similar behaviour has been observed for a number of different hyperbranched polymers including polyphenylenes[17], aromatic polyethers[18], polyurethanes[19], aromatic polyesters[20] and poly(ether ketones).[3] For example, Hawker and co-workers have demonstrated that large changes in the glass transition temperature of hyperbranched poly(ether ketones) occur on varying the chain end functional group (Table 6.2).

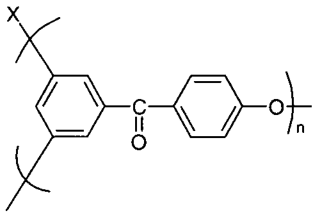
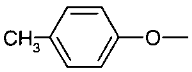
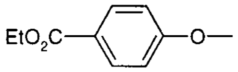
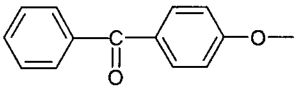
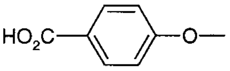
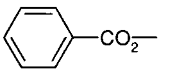
Hyperbranched poly(ether ketone)	
End groups (X)	T_g (^{0}C)
F	162
HO	127
	139
	154
	119
$CH_3(CH_2)_7O$	97
	290
	147
CH_3CO_2	118

Table 6.2 Variation of T_g with end group modification in hyperbranched poly(ether ketone)s

It has been suggested that the T_g of a hyperbranched polymer is strongly dependent on the association of the chain end functional groups with the neighbouring molecule as well as the volume fraction occupied by the terminal groups.[21]

Fréchet and co-workers have studied the relationship between the glass temperature and the molecular weight for a series of polyether dendrons.[16] The T_g of these dendritic polymers was seen to increase with generation number until a maximum was reached after 4 to 5 generations. This is in good agreement with the theoretical predictions of Stutz who has argued that as both the degree of branching (X_c) and end group conversion (p) converge to finite limits, at high generation number, the T_g of a dendritic polymer must also approach a finite value (Figure 6.3).[12]

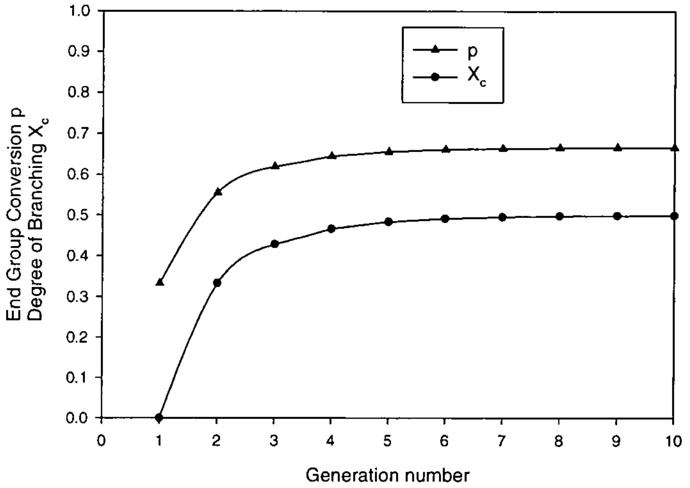


Figure 6.3 Dependence of end group conversion (p) and degree of branching (X_c) upon the generation number for trifunctional dendritic growth.

Fréchet and co-workers have also derived a modified free volume relationship describing the molecular weight dependency of T_g for dendrimers. The well known relationship between molecular weight and the glass transition temperature (Equation 6.2) contains a constant equal to ($2\theta\rho N_A$ / α_f) where the number of chain ends is two. However dendrimers and hyperbranched polymers contain many chain ends and Frechet has proposed a modified expression to account for this (Equation 6.3).

Equation 6.3

$$T_g = T_g^{\infty} - K'\left(\eta_e / M\right)$$

Where K' = ($\theta\rho N_A$ / α_f) and η_e is the number of end groups.

6.4 The glass transition temperature of hyperbranched polyesters

The AB_2 hyperbranched polyesters (described in chapters 2 and 3) and the core terminated polymers (described in chapter 4) were analysed by differential scanning calorimetry (DSC). All samples showed a single glass transition with no evidence of melting or crystallisation peaks. This is consistent with the formation of an amorphous polymer. The lack of crystallinity is to be expected from these highly branched materials and has been observed for many other dendritic and hyperbranched polymers.[3, 17, 23, 24] A typical DSC trace (Figure 6.4) and a summary of the DSC results (Table 6.3) are shown below.

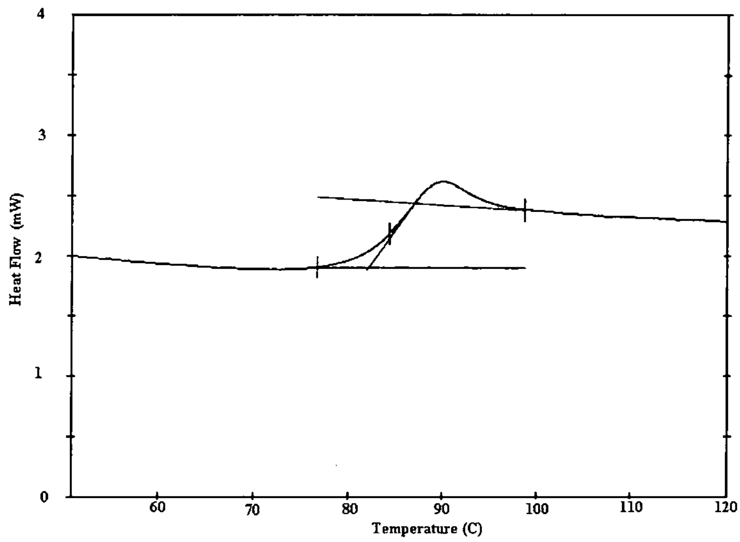


Figure 6.4 A representative DSC trace of a B_2 core terminated hyperbranched polyester (Mw 74100).

The glass temperature varies from 73 to 86 ^{0}C depending upon the molecular weight of the sample. In all three polymer series the T_g tends towards a limiting value of 86 ^{0}C as the molecular weight is increased (Figure 6.5). This tendency of the glass temperature to approach a limiting value is similar to the behaviour of polyether dendrons reported by Fréchet and co-workers.[16]

As described above, Stutz has argued that for dendritic polymers the glass temperature is dependent upon the end group conversion and the degree of branching, both of which approach a limiting value at high generation number. A similar situation is expected of hyperbranched polymers where the theoretical degree of branching has been shown to rapidly approach a finite limit with increasing degree of polymerisation (see Figure 5.15 and accompanying discussion in chapter 5). The theoretical end group conversion for an AB_2 hyperbranched polymer can also be shown to approach a limiting value with increasing degree of polymerisation (Figure 6.6). It follows from this that the glass temperature of a hyperbranched polymer should also approach a limiting value as the molecular weight is increased.

Polymer Type	Molecular weight (M_w)*	Tg (^{0}C)
AB_2	9700	78
	22100	82
	38200	84
	62400	85
	75900	85
	135400	86
	139500	86
	221400	86
	362000	86
B_2 core terminated	16500	76
	32500	79
	38100	81
	74100	84
	163400	85
B_3 core terminated	7000	73
	9300	77
	13500	78
	48500	83
	128200	86

* Values from SEC in THF using universal calibration

Table 6.3 Glass transition temperatures of hyperbranched polyesters

The values for T_g are in good agreement with those previously reported for hyperbranched polyesters based upon dimethyl 5-(2-hydroxyethoxy)isophthalate.[22] These and the glass temperatures for other known hyperbranched and dendritic polyesters are presented below (Table 6.4).

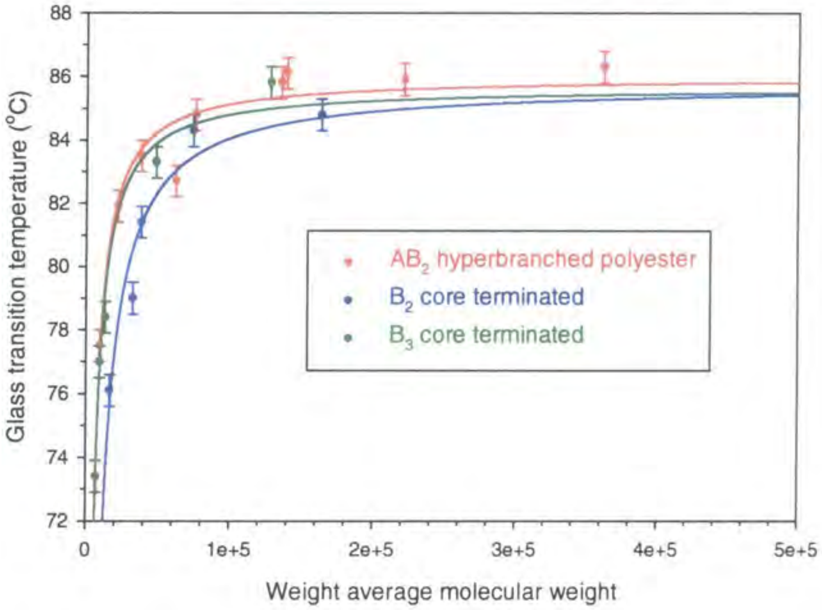


Figure 6.5 Variation of T_g with molecular weight for hyperbranched polyesters.

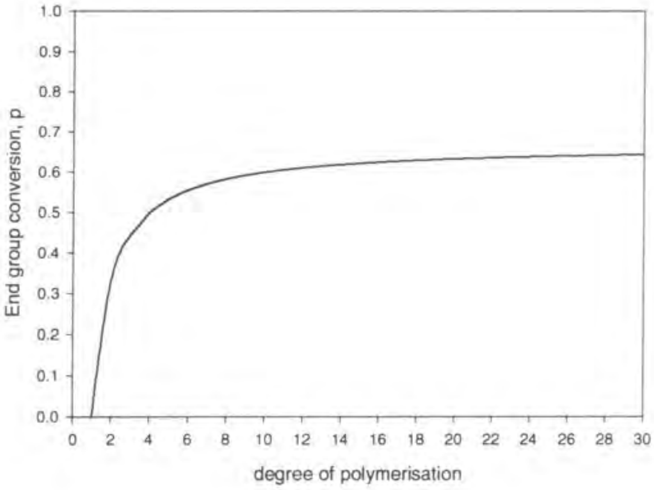


Figure 6.6 Theoretical variation of end group conversion (as defined by Stutz) with degree of polymerisation for an AB_2 hyperbranched polymer.

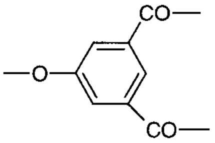
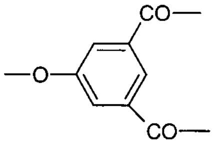
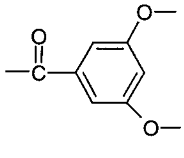
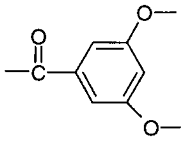
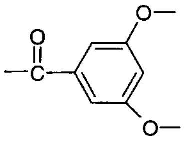
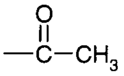
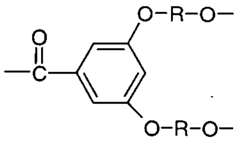
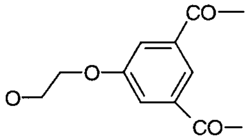
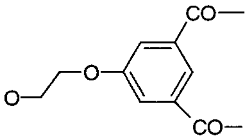
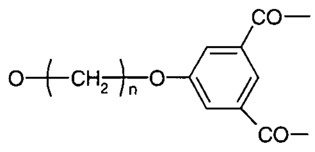
Branch Unit	Terminal Group	T_g (^{0}C)	Ref.
 dendritic	OPh	110 - 141	*Miller et al.*[23]
 hyperbranched	OH	250	*Turner et al.*[24]
 a) linear b) hyperbranched c) dendritic	H	a) 204 b) 190 / 197 c) 201	*Fréchet et al.*[13, 25]
 hyperbranched	H	185 - 217	*Turner et al.*[15]
 hyperbranched	 $-\overset{O}{\overset{\Vert}{C}}-CH_3$	149 - 156	*Turner et al.*[15]
 hyperbranched a) R= $(CH_2)_2$ b) R= $(CH_2)_2O(CH_2)_2$ c) R= $(CH_2)_2O(CH_2)_2O(CH_2)_2$	H	a) 80 b) 15 c) -4	*Ramakrishnan et al.*[9]
 hyperbranched	OH	150	*Turner et al.*[24]
 hyperbranched	OCH_3	71 - 84	*Feast et al.*[22]
 hyperbranched a) n=3 b) n=4 c) n=5 d) n=6	OCH_3	a) 61 - 66 b) 45 - 51 c) 34 - 36 d) 24 - 28	*Keeney*[10]

Table 6.4 Glass transition temperatures of known hyperbranched or dendritic aryl esters

The glass temperatures of the hyperbranched polyesters presented in this work are all higher than those from the analogous dimethyl 5-(ω-hydroxyalkoxy)isophthalate based polymers shown above (Table 6.4). This is a good illustration of the effect of modifying the flexibility of the polymer chain. There is a marked trend towards lower glass temperatures as the alkylene chain length of the hyperbranched polyester repeat unit is increased. This effect can also be observed if the glass temperature is compared to the dendritic polyesters reported by Miller and co-workers.[23] This dendritic system does not include a flexible alkylene spacer and so is expected to have a higher T_g, although differences in the degree of branching may also have an effect upon the glass temperature in this case.

The value of T_g may also be influenced by the nature of the end groups. The glass temperature of the dimethyl 5-(2-hydroxethoxy)isophthalate based polymers is much lower than the analogous 5-(2-hydroxyethoxy)isophthalic acid based hyperbranched polyesters prepared by Turner and co-workers.[24] As these polymers are reported to have similar molecular weights and branching factors, the marked difference in T_g is presumably an effect arising from the difference in end groups. The presence of large numbers of polar end groups with the potential for hydrogen bonding, as is the case for the carboxylic acid terminated system, might be expected to lead to higher values of T_g as the mobility of the polymer chains will be hindered by polar interactions and / or hydrogen bonding.

As discussed in an earlier section, the glass transition temperature of a linear polymer is proportional to $1/M_n$ (Equation 6.2) but Fréchet has asserted that the T_g of a dendrimer is proportional to η_e/M, where η_e is the number of end groups (Equation 6.3). In order to examine whether this holds true for the hyperbranched polyesters, described in this study, the T_g data were plotted against the reciprocal molecular weight (Figure 6.7). Only the weight average molecular weight was used in this analysis as the number average molecular weight reaches an apparent maximum relatively early on in the polymerisation (see chapter 3).

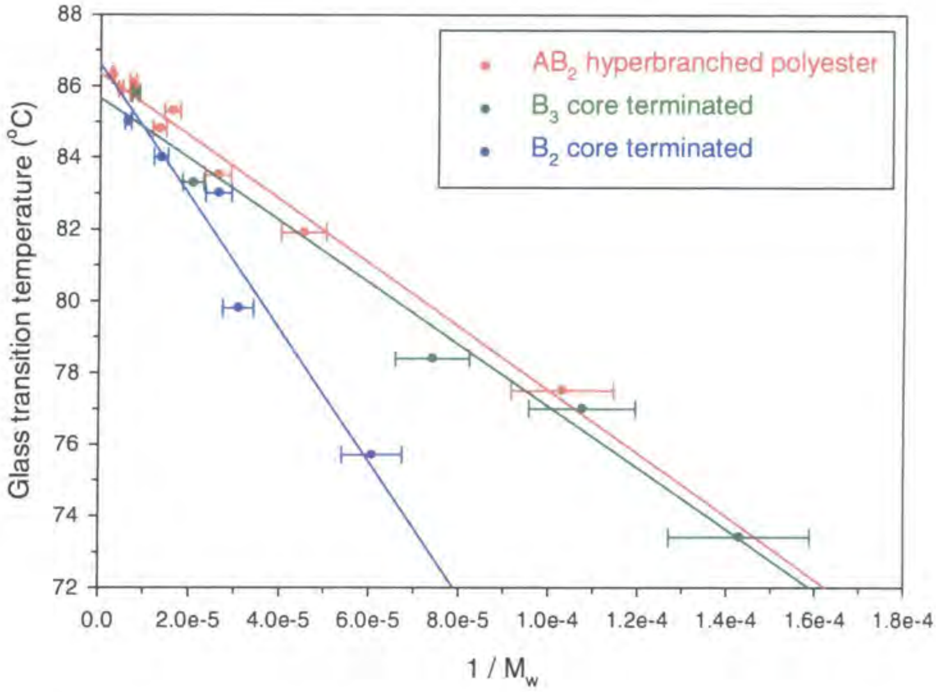


Figure 6.7 The variation of Tg with the reciprocal molecular weight for hyperbranched polyesters.

All three sets of T_g data gave good linear plots with correlation coefficients of 0.98, 0.95 and 0.98 for the AB$_2$, B$_2$ core terminated and B$_3$ core terminated hyperbranched polyesters respectively. All three plots intercept the y-axis (i.e. T_g^∞ in Equation 6.2) at about 86 ^{0}C. This is expected as the polymers of all three series have the same repeat units and hence T_g should tend towards the same limiting glass temperature. However the slopes of the lines are different which is unexpected. The plots for the AB$_2$ and the B$_3$ core terminated systems are very similar but for the B$_2$ core terminated system the values for the glass temperature are lower than expected at high molecular weight. The slope of the line is related to the chain end free volume per unit volume of polymer. The hyperbranched polymers differ only in the type of focal group present, which may result in differences in the chain end free volume between the hyperbranched and core terminated polymers. This seems an unlikely explanation for the differences in the slope as the B_3 core terminated and the AB_2 system give similar results and the B_2 core only differs by a single methyl ester group.

The above analysis does not take into account the fact that the number of chain ends in a hyperbranched polymer increases with molecular weight and Fréchet has argued that, because of this; traditional plots of T_g versus 1/M have little meaning for dendritic systems. If this is true then it is surprising that the hyperbranched polyesters show a linear relationship between T_g and $1/M_w$. However, this line of reasoning does not take into account the fact that the number of end groups in a hyperbranched or dendritic polymer is determined by the degree of polymerisation. Flory has shown that for an AB_2 polymer the number of unreacted B groups in a given x-mer is simply (x+1).[26] For an AB_2 addition polymerisation, for example hyperbranched poly(amidoamines) prepared via Michael addition, the mass of an x-mer is xM_0, where M_0 is the monomer mass. Hence, the ratio of end groups to the polymer mass may be expressed in terms of the masses of polymer and monomer (Equation6.4).

The number of end groups = $\eta_e = (x + 1)$

$$\frac{\eta_e}{M} = \frac{x+1}{M}$$

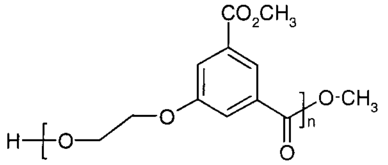
Substituting $x = M / M_0$, *where* M_0 *is the monomer mass*

$$\frac{\eta_e}{M} = \frac{\left(M/M_0 + 1\right)}{M}$$

Equation 6.4

$$\frac{\eta_e}{M} = \frac{1}{M_0} + \frac{1}{M}$$

It is apparent from equation 6.4 that the ratio η_e/M is equal to 1/M plus a constant ($1/M_0$) and hence a plot of Tg versus 1/M might be expected to give linear relationship for AB_2 addition polymers. It can also be shown that for AB_2 condensation polymers η_e/M is again proportional to 1/M. In this case, solely for the purposes of calculating the molecular weight, it is useful to consider the hyperbranched polymer as a number of repeat units linked together in a linear fashion (Figure 6.8). When the polymer is represented in this manner it can clearly be seen that the molecular weight of an x-mer corresponds to the mass of x repeat units plus the mass of the chain end groups (i.e. the mass of a condensate molecule).



$$M = xM_r + M_c$$

Where M_r is the mass of a repeat unit and M_c is the mass of a condensate molecule, in this example methanol.

Figure 6.8 Calculation of molecular weight for an AB_2 condensation polymer.

Using this relationship between the polymer mass and the degree of polymerisation, in Fréchet's expression for the number of chain ends, again leads to a linear relationship between η_e / M and 1/M (Equation 6.5).

The number of end groups = $\eta_e = (x + 1)$

$$\frac{\eta_e}{M} = \frac{x+1}{M}$$

Substituting $x = {(M - M_c)}/{M_r}$, *where* M_r *is the mass of the repeat unit and* M_c *the mass of a condensate molecule.*

$$\frac{\eta_e}{M} = \frac{\left((M - M_c)/M_r\right) + 1}{M}$$

Equation 6.5

$$\frac{\eta_e}{M} = \frac{1}{M_r} + \frac{1}{M}\left(1 - \frac{M_c}{M_r}\right)$$

A linear relationship can be further demonstrated by plotting the theoretical chain end to mass ratio against the calculated reciprocal molecular weight for a hyperbranched polymer derived from dimethyl 5-(2-hydroxyethoxy)isophthalate (Figure 6.9).

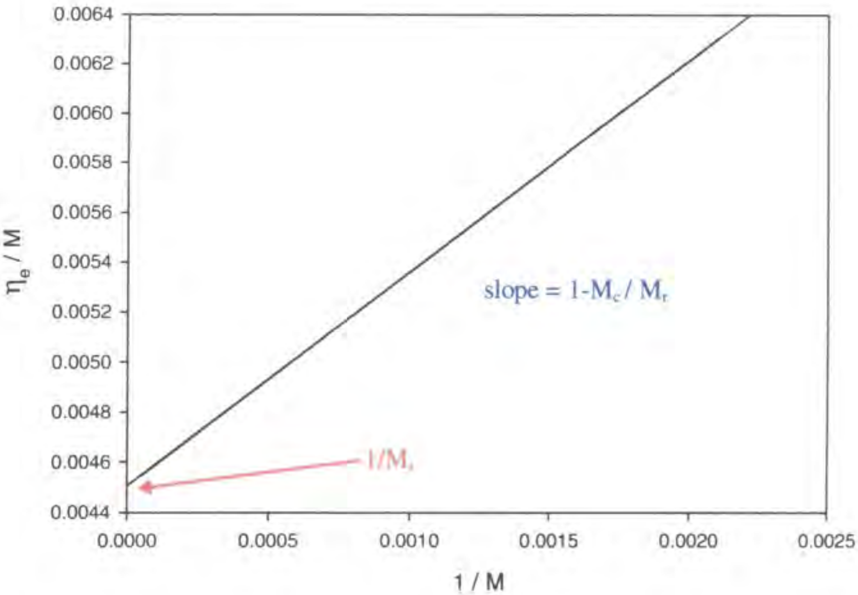


Figure 6.9 Theoretical relationship between η_e/M and 1/M for poly(dimethyl 5-(2-hydroxyethoxy)isophthalate.

A linear relationship is obtained with a y intercept of 4.51 x 10^{-3} (which corresponds to 1/M$_r$) and a slope of 0.86 (which corresponding to 1 - Mc/Mr). Thus for the hyperbranched polyesters described in this work there is a linear relationship between η_e/M and 1/M which explains how it is possible to obtain a linear relationship between T_g and 1/M without taking account of the number of end groups. Fréchet's expression for the molecular weight dependence of T_g , as applied to the hyperbranched polyesters, may then be expressed as: $T_g = T_g^{\infty} - K' (0.86 / M + 4.51 \times 10^{-3})$.

Whilst the above considerations explain the linear dependence of T_g upon the reciprocal molecular weight, the fact that the glass temperature is dependent upon the reciprocal of the *weight average* molecular weight has not been explained. In the treatment of linear polymers M_n is usually used, whilst Fréchet's modified treatment for dendrimers employs the molecular weight of a single dendrimer molecule. In a linear polymer the chain end free volume is dependent upon the number of molecules and hence simply related to the number average molecular weight. However, in the case of a hyperbranched polymer the number of end groups, and hence the chain end free volume, depends not only upon the number of polymer molecules but also their degree of polymerisation. Therefore, it seems reasonable to expect the chain end free volume to be related to the weight average molecular weight.

6.5 Conclusions

The data presented here has shown that the glass transition temperature of hyperbranched polymers based upon dimethyl 5-(2-hydroxyethoxy)isophthalate varies with molecular weight but reaches a limiting value of 86 ^{0}C at high conversions. The thermal properties of the hyperbranched polyesters are in accord with those of similar hyperbranched aryl esters reported in the literature. The glass temperature is higher than those obtained for the analogous polymers based upon dimethyl 5-(ω-hydroxyalkoxy)isophthalate. Higher glass temperatures are obtained for the hyperbranched polyesters with the shorter alkylene spacer groups, which is consistent with the T_g being dependent upon the flexibility of the polymer chain. The nature of the end groups appears to have a marked influence upon T_g with hydrogen bonding or polar groups leading to high glass temperatures. Thus the glass temperature is lower than that obtained from the analogous hyperbranched polyesters derived from 5-(2-hydroxyethoxy)isophthalic acid.

6.6 Experimental

Differential scanning calorimetry (DSC) measurements were recorded using either a Perkin Elmer DSC 7 or a Perkin Elmer Pyris 1. The polymer samples were annealed at 250 ^{0}C and cooled at a rate of 50 ^{0}C min^{-1} to 30 ^{0}C. DSC measurements were made over a temperature range of 30 to 250 ^{0}C using a heating rate of 10 ^{0}C min^{-1}. The value for the glass temperature was taken as the temperature at the midpoint of the observed ΔC_p.

6.7 References

---

(1). Roe, R.-J., 'Glass Transition' in *Encyclopaedia of Polymer Science and Engineering* vol 7, (eds:Mark, H.F, Bikales, N. M., Overberger, C.G., Menges, G.), 2nd edition, Wiley Interscience, New York, 1985

(2). Fréchet, J.M.J., Hawker, C.J., 'Synthesis and Properties of Dendrimers and Hyperbranched Polymers' in *Comprehensive Polymer Science*, 2nd supplement, (eds: Aggarwal, S.L., Russo, S.), Pergamon Press, Oxford, 1996

(3). Hawker, C.J., Chu, F., *Macromolecules,* 1996, **29(12)**, 4370

(4). Bueche, F., *Physical Properties of Polymers*, Interscience, New York, 1962

(5). Chartoff, R.P. 'Thermoplastic Polymers' in *Thermal Characterisation of Polymeric Materials,* vol 1, (ed. Turi, E.A), 2nd edition, Academic Press, San Diego, 1981

(6). Cowie, J.M.G., *Polymers: Chemistry and Physics of Modern Materials*, 2nd edition, Blackie, London, 1991

(7). Stutz, H., Illers, K.H., Mertes, J., *J. Polym. Sci.: Part B: Polym. Phys.*, 1990, **28**, 1483

(8). a). McKenna, G.B., 'Glass Formation and Glassy Behaviour' in *ComprehensivePolymer Science,* Vol. 2. (Eds. Allen, G. and Bevington, J.C.), Pergamon Press, Oxford, 1989.

b). Turner, D.T., *Polymer* 1978, **19**, 789

(9). Kumar, A., Ramakrishnan, S., *Macromolecules*, 1996, **29(7),** 2524

(10). Keeney, A.J., *Ph.D.Thesis*, Durham University, 1998

(11). Kim, Y.H., *J. Polym. Sci.: Part A: Polym. Chem.*, 1998, **36**, 1685

(12). Stutz, H., *J. Polym. Sci.: Part B: Polym. Phy.*, 1995, **33**, 333

(13). Wooley, K.L, Fréchet, J.M.J., Hawker, C.J., *Polymer,* 1994, **35(21)**, 4489

(14). Kricheldorf, H.R., Zang, Q.-Z., Schwarz, G., *Polymer,* 1982, **23**, 1821

(15). Turner, S.R., Voit, B.I., Mourey, T.H., *Macromolecules*, 1993, **26**, 4617

(16). Wooley, K.L., Hawker, C.J., Pochan, J.M., Frechet, J.M.J., *Macromolecules* 1993, **26**, 1514

(17). Kim, Y.H., Webster, O.W. *Macromolecules,* 1992, **25(21)**, 5561

(18). a) Uhrich, K.E., Hawker, C.J., Fréchet, J.M.J., Turner, S.R., *Macromolecules*, 1992, **25**, .4583

b) Miller, T.M., Neenan, T.X., Kwock, E.W., Stein, S.M., *J. Am. Chem. Soc.* 1993, **115**, 357

(19). Spindler, R., Frechet, J.M.J., *Macromolecules*, 1993, **26**, 4809

(20). a) Kricheldorf, H.R., Stober, O., *Macromol Rapid Commun.* 1994, **15**, 87

b) Brenner, A.R., Voit, B.I., *Macromol. Symp.* 1996, **102**, 47

(21). Kim, Y.H., Beckebauer, R., *Macromolecules* 1994, **27**, 1968

(22). Feast, W.J., Stainton, N.M., *J. Mater. Chem.,* 1995, **5(3)**, 405

(23). Miller, T.M., Kwock, E.W.,Neenan, T.X., *Macromolecules.* 1992, **25(12)**, 3143

(24). Turner, S.R., Walter, F., Voit, B.I., Mourey, T.H., *Macromolecules*, 1994, **27**, 1611

(25). Hawker, C.J., Lee,R., Frechet, J.M.J., *J. Am Chem Soc* 1991, **113**, 4583

(26). Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953

Chapter Seven

Conclusions and Suggestions for Further Work

7.1 Conclusions

A new and improved route to the AB_2 monomer dimethyl 5-(2-hydroxyethoxy) isophthalate has been developed and its melt condensation polymerisation investigated. Hyperbranched polyesters were prepared by simple condensation polymerisation jof the AB_2 monomer and also by copolymerisation with suitable core molecules.

Unusual molecular weight growth characteristics were demonstrated. The number average molecular weight (M_n) attained a maximum value after relatively short polymerisation time, whereas the weight average molecular weight (M_w) continued to increase. This limit to the attainable number average molecular weight is thought to be a consequence of intramolecular cyclisation reactions, contributing to the consumption of the remaining A groups. This effectively prevents further growth by a polycondensation mechanism. Evidence of cyclisation in the hyperbranched polyesters was provided by MALDI-TOF MS. The weight average molecular weight continues to increase after complete cyclisation and it is postulated that this is due to a redistribution of polymer chains by ester interchange reactions. It is conjectured that interchange reactions are more likely to occur at the more accessible chain ends of the branched macromolecule, possibly involving reaction of the methyl ester end groups. The larger hyperbranched molecules have more methyl ester end groups and hence this type of interchange favours the growth of the larger molecules. The plausibility of the occurrence of ester exchange processes was demonstrated by the successful incorporation of a dimethyl isophthalate core molecule into a fully cyclised hyperbranched polyester.

The amount of branching in the hyperbranched polyesters was determined by quantitative ^{13}C NMR spectroscopy. The degree of branching obtained (ca. 0.5) was in agreement with the theoretical value for a statistical distribution at high conversion.

The solution properties of the hyperbranched polyesters were studied and revealed these materials to be highly soluble, relative to their linear analogues, in common organic solvents such as chloroform. Solutions of the hyperbranched polyesters had characteristically low intrinsic viscosities ([η]). Mark-Houwink plots showed a linear relationship between log M_w and log [η]. There was no evidence of the curved viscosity plots indicative of dendritic behaviour.

The thermal properties of the hyperbranched polyesters were examined by differential scanning calorimetry, which showed the polymers to be amorphous materials exhibiting a glass transition temperature (T_g) but no melting point. The T_g varied with molecular weight, was proportional to $1/M_w$ and reached a limiting value of 86 ^{0}C at high conversion. The nature of both the polymer backbone and the end groups have a marked influence upon T_g. For example, the glass temperature is lower than that obtained from the analogous hyperbranched polyesters derived from 5-(2-hydroxyethoxy)isophthalic acid but higher than those obtained from dimethyl 5-(ω-hydroxyalkoxy)isophthalates.

In summary, polymers synthesised by the melt condensation of dimethyl 5-(2-hydroxyethoxy) isophthalate have many features typical of other hyperbranched polymer systems. These are amorphous materials with low solution viscosity and degrees of branching consistent with a statistical distribution. However, the molecular weight growth behaviour reported here has not been observed for other hyperbranched polymers. The presence of cyclisation and the consequent restriction of polymer growth have been observed in other systems but the continued increase in weight average molecular weight appears to be unique to the polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate.

7.2 Further work.

The continual increase of weight average molecular weight in hyperbranched polycondensations, after complete cyclisation, has not been reported for other hyperbranched polymers. Although continued growth via an ester exchange mechanism has been tentatively proposed, this aspect requires further investigation. In chapter 3 it was suggested that ester interchange is most likely to occur at the more accessible methyl ester end groups. If this is true, useful information may be obtained by heating blends of hyperbranched polyesters derived from dimethyl 5-(2-hydroxyethoxy) isophthalate and its higher homologues. Fully cyclised hyperbranched polyesters derived from dimethyl 5-(ω-hydroxyalkoxy)isophthalates are thought not to undergo the type of ester exchange necessary to exhibit an increase in M_w, possibly due to steric hindrance from the longer alkylene chain.[1]

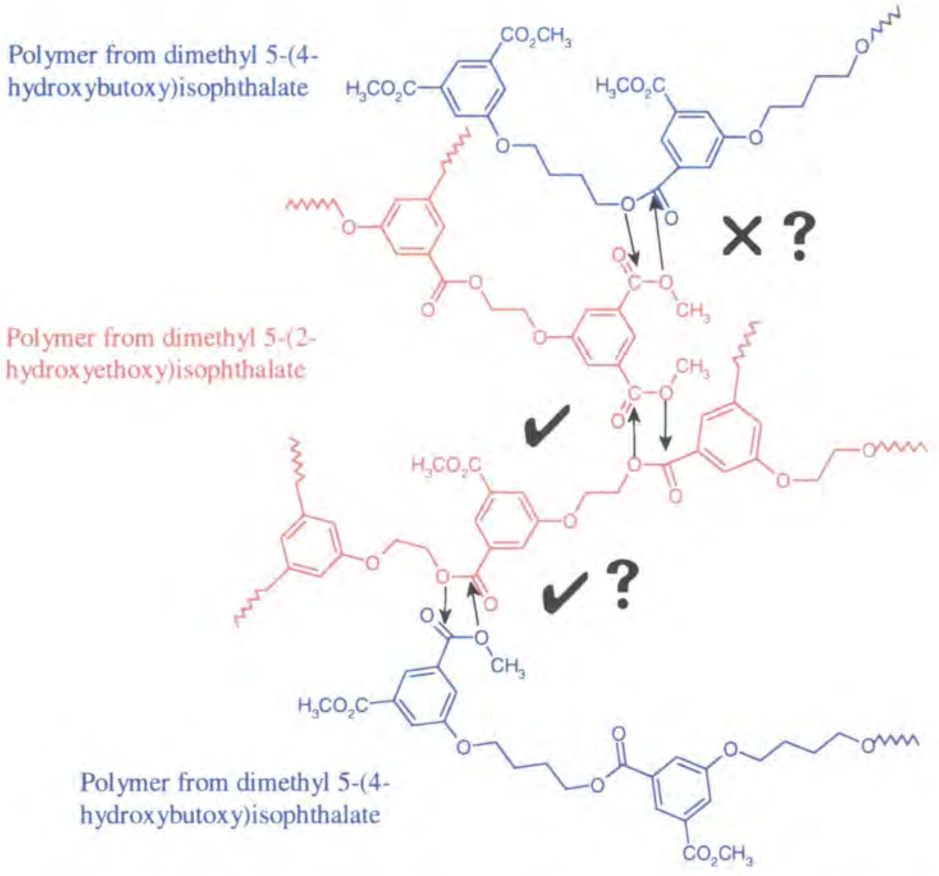


Figure 7.1 Potential ester interchange reactions between hyperbranched polyesters.

For this reason ester exchange is unlikely to take place between the methyl ester groups of poly(dimethyl 5-(2-hydroxyethoxy) isophthalate) and the main chain esters of the poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates) (Figure 7.1). However it is feasible that the surface methyl ester groups of the poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates) could undergo interchange with the less hindered main chain esters of poly(dimethyl 5-(2-hydroxyethoxy) isophthalate). If such an interchange reaction took place then the incorporation of units containing the longer alkylene chain into poly(dimethyl 5-(2-hydroxyethoxy) isophthalate) may be observable by MALDI-TOF MS.

It may also be possible to probe the nature of potential exchange processes by varying the end groups of the hyperbranched polyester. Replacing the methyl esters with bulkier esters such as phenyl or *tert*-butyl esters may reduce the likelihood of ester exchange. Turner and co-workers have successfully modified the end groups of an all-aromatic hyperbranched polyester using a procedure which may be applicable to the polyesters described in this thesis (Figure 7.2).[2]

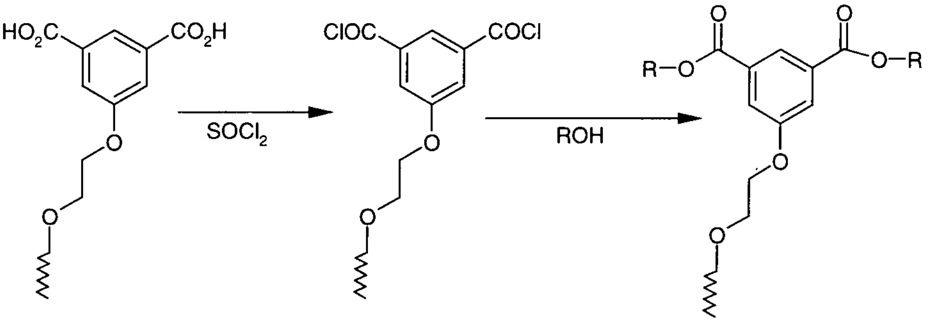


Figure 7.2 End group modification of hyperbranched polyesters.

A further method of modifying the end groups of the hyperbranched polymer is to use an alternative monomer with amidozolide end groups derived from the reaction of a carboxylic acid and 1, 1-carbonyl diimadazole (CDI). CDI is a versatile reagent and has been successfully employed in the synthesis of low molecular weight PET, by direct esterification under mild conditions,[3] as well as in the preparation of both dendrimers[4] and hyperbranched polymers.[5] A potential route to a hyperbranched polyester derived from 5-(2-hydroxyethoxy)isophthalic acid and utilising CDI chemistry is outlined below (Figure 7.3). The adduct of CDI and *tert*-butanol should react selectively with the primary alcohol group of 5-(2-hydroxyethoxy)isophthalic acid to give a t-BOC protected A group. On further addition of CDI the carboxylic acid groups should react to form acid imidazolides B groups. Acid imidazolides undergo condensation reactions with primary alcohols, eliminating imidazole, to give esters.[6] Hence, upon deprotection of the A group a hyperbranched polyester will be formed by a step growth condensation mechanism eliminating imidazole.

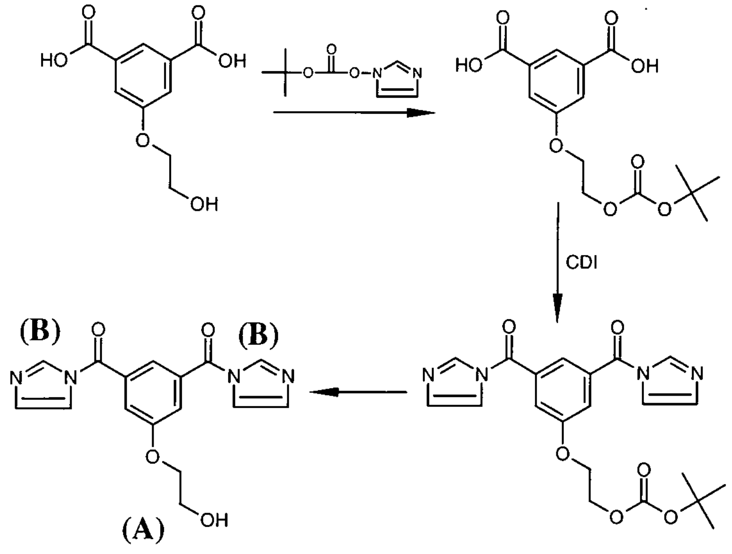


Figure 7.3 Possible route to hyperbranched polyesters using CDI chemistry.

The hyperbranched polyester prepared by the condensation of an alcohol and an acid imidazolide will bear numerous acid imidazolide end groups. The end groups may then be modified by reaction with a number of different primary alcohols to yield a variety of ester end groups. A further potential advantage of using CDI chemistry is that the polymerisation is carried out in solution. This opens up the possibility of using the core-dilution / slow addition technique, described briefly in chapters 4 and 5, which has the potential to increase branching and decrease the polydispersity of the hyperbranched polymer.[7]

The influence of polymer architecture upon the properties of hyperbranched polymers is a theme of great interest. For comparative purposes the synthesis of linear analogues of the hyperbranched polyesters, that have equivalent numbers of unreacted B groups, is an attractive target. Using similar chemistry to that outlined above, such a linear polymer may be accessible from an AB type monomer as shown below (Figure 7.4).

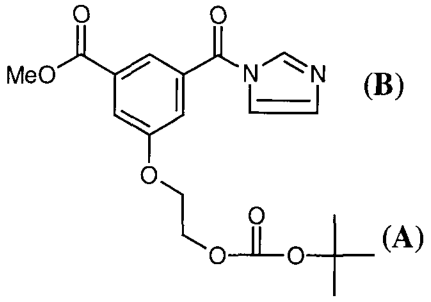


Figure 7.4 Potential AB monomer leading to linear analogue of hyperbranched polyesters.

The use of imidazole derivatives is a potentially versatile method of tailoring the architecture of hyperbranched polyesters. For instance the degree of branching could be lowered by the copolymerisation of the AB and AB_2 monomers shown in figures 7.3 and 7.4. Conversely, it should be possible to synthesise the analogous AB_4 dendron, which would lead to higher degrees of branching upon polycondensation.

7.3 References.

(1). Keeney, A.J., *Ph.D. Thesis*, Durham University, 1998

(2). Turner, S.R., Walter, F., Voit, B.I., Mourey, T.H., *Macromolecules*, 1994, **27**, 1611

(3). Pilati, F., 'Polyesters' in *Comprehensive Polymer Science*, Vol. 5, (Eds: Eastmond, G.C., Ledwith, A., Russo, S., Sigwalt, P.) Pergamon Press, Oxford, 1989

(4). Rannard, S., Davis, N., *Abstracts of Papers of the American Chemical Society*, 1997, **214**, 8-PMSE

(5). Bolton, D.H., Wooley, K.L., *Macromolecules*, 1997, **30**, 1890

(6). Staab, H.A., *Angew. Chem. Int. Edn. Engl.*, 1962, **1(7)**, 351

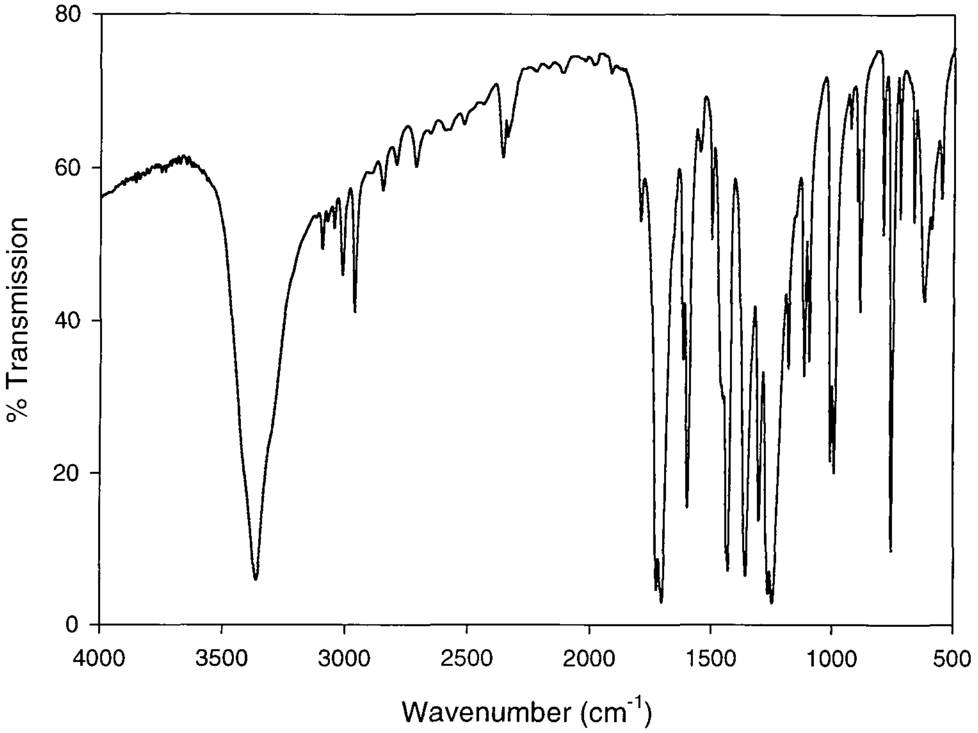
(7). Hanselmann, R., Hölter, D., Frey, H., *Macromolecules*, 1998, **31**, 3790

APPENDICES 1.1 to 1.11

FTIR, NMR and Mass spectra

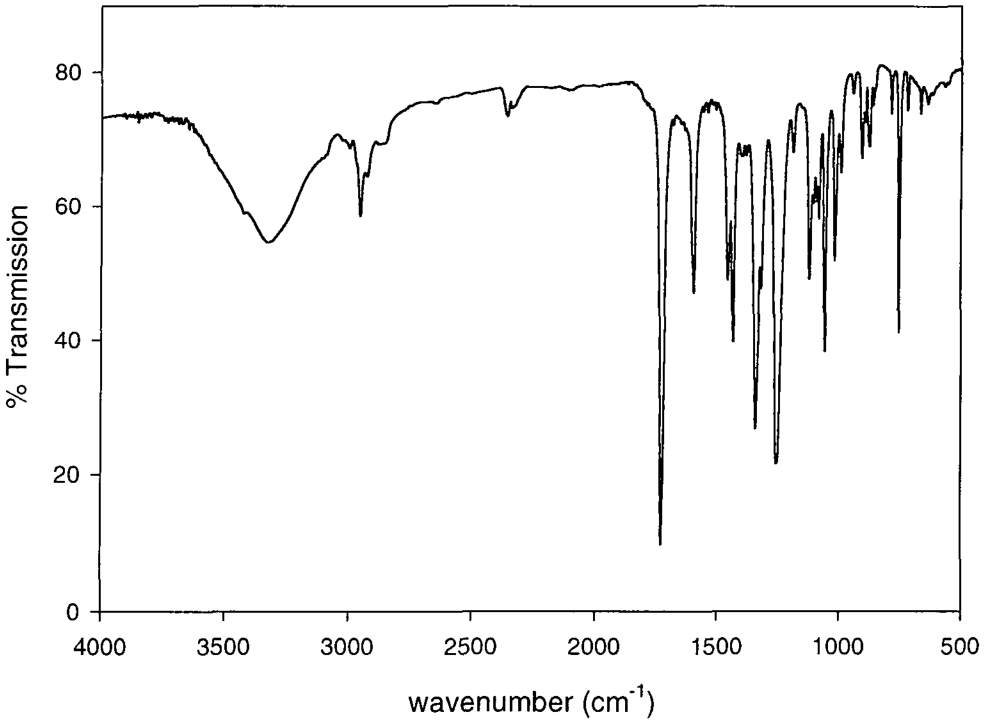
Appendix 1.1

FTIR spectrum of dimethyl 5-hydroxy isophthalate



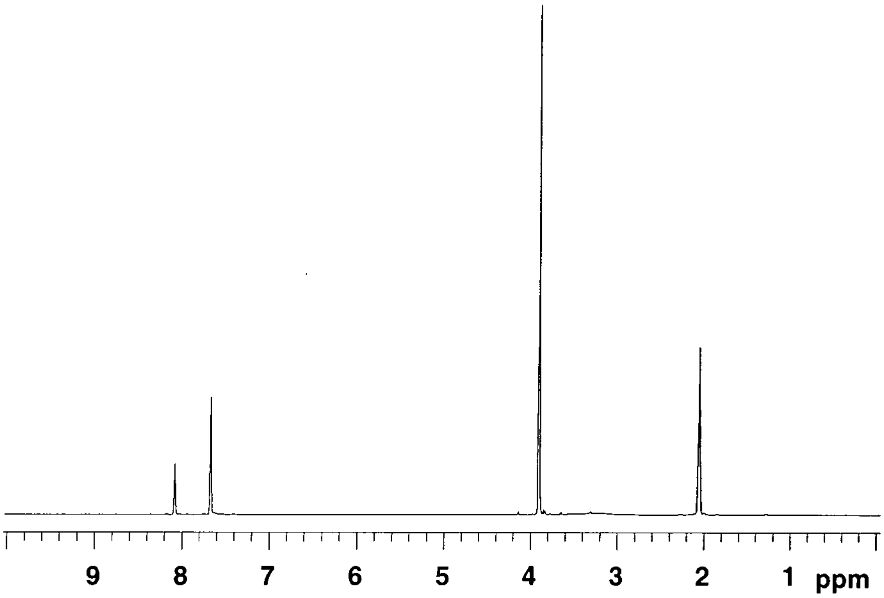
Appendix 1.2

FTIR spectrum of dimethyl 5-(2-hydroxyethoxy)isophthalate



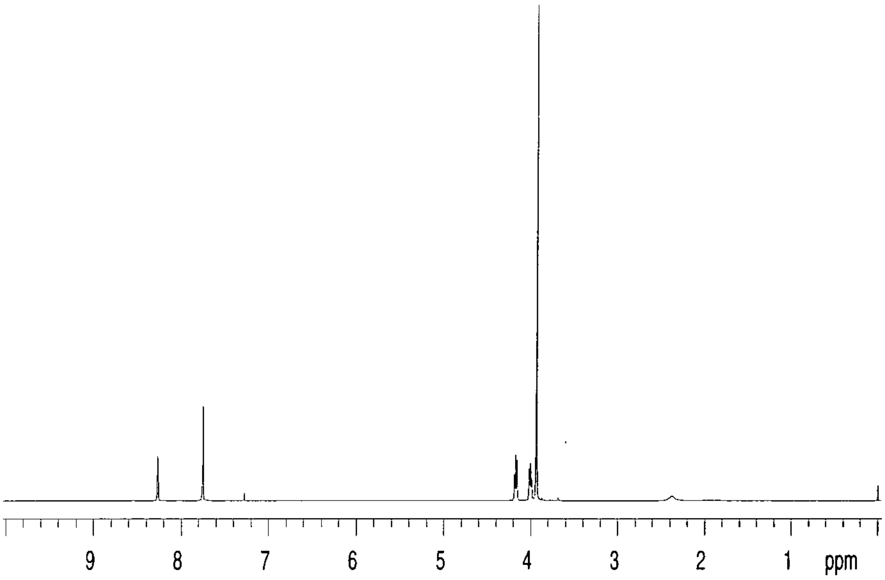
Appendix 1.3

^{1}H NMR spectrum (300 MHz, acetone-d6) of Dimethyl 5-hydroxyisophthalate



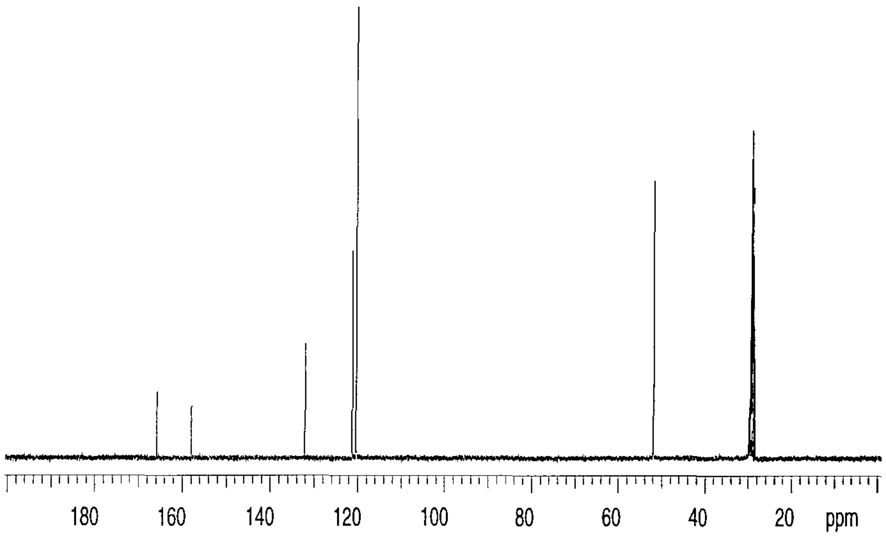
Appendix 1.4

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of Dimethyl 5-(2-hydroxyethoxy)isophthalate



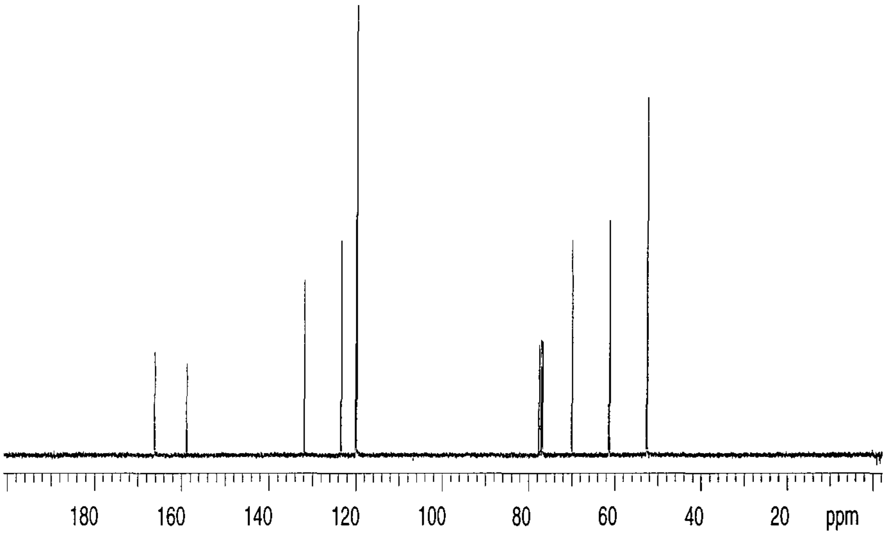
Appendix 1.5

^{13}C NMR spectrum (75 MHz, acetone-d6) of Dimethyl 5-hydroxyisophthalate



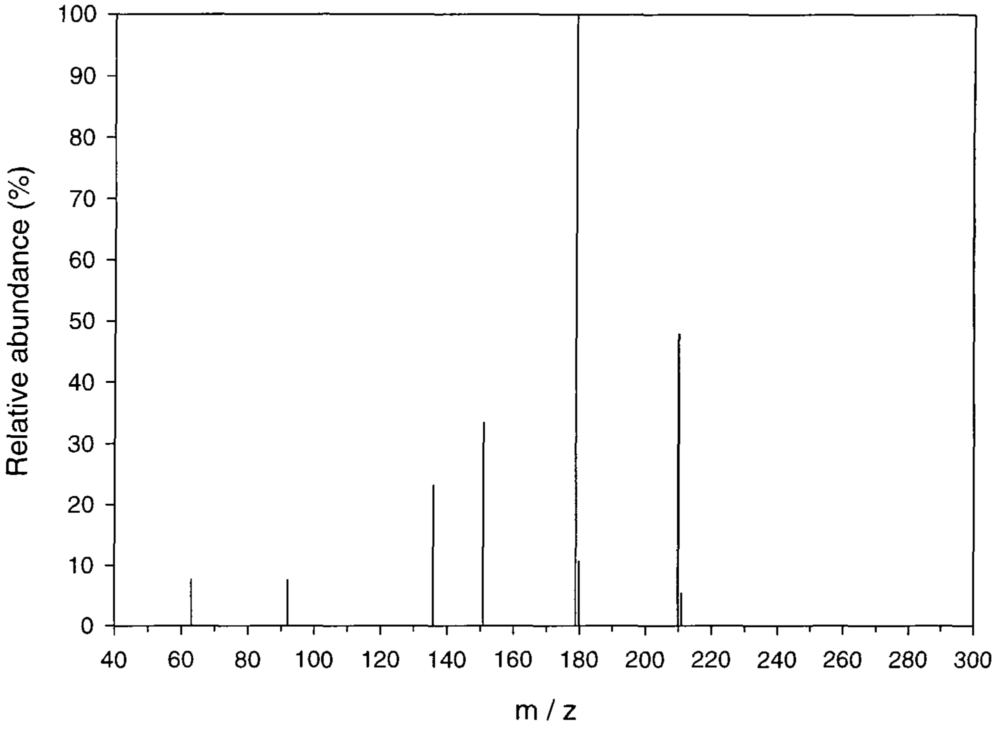
Appendix 1.6

^{13}C NMR spectrum (75 MHz, CDCl$_3$) of Dimethyl 5-(2-hydroxyethoxy)isophthalate



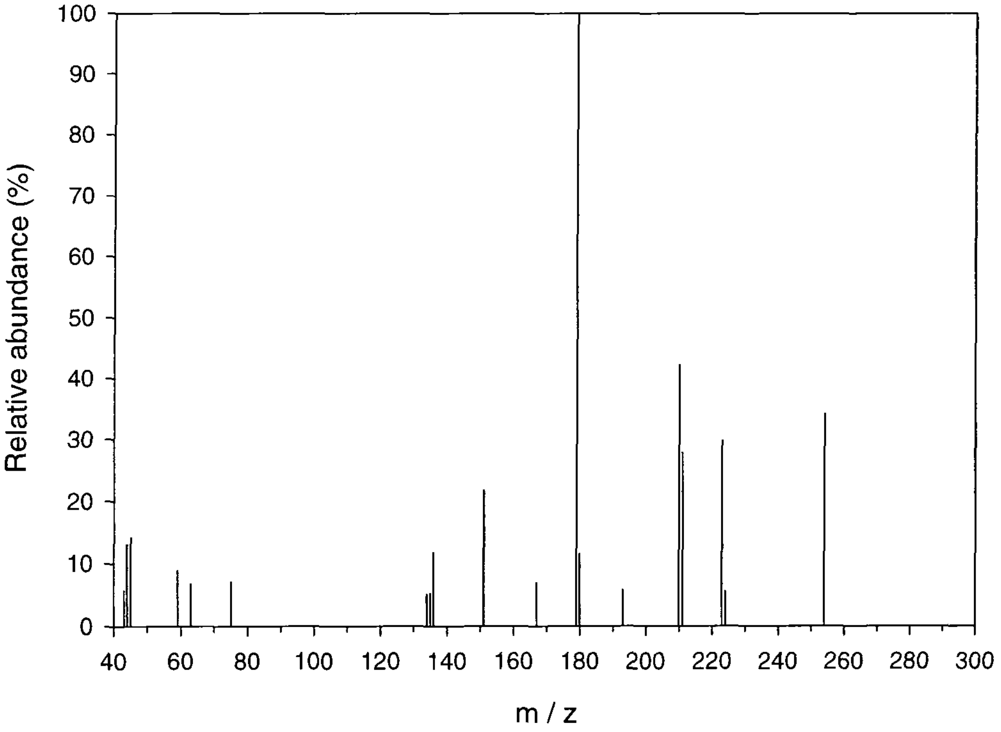
Appendix 1.7

Mass spectrum (EI) of Dimethyl 5-hydroxyisophthalate



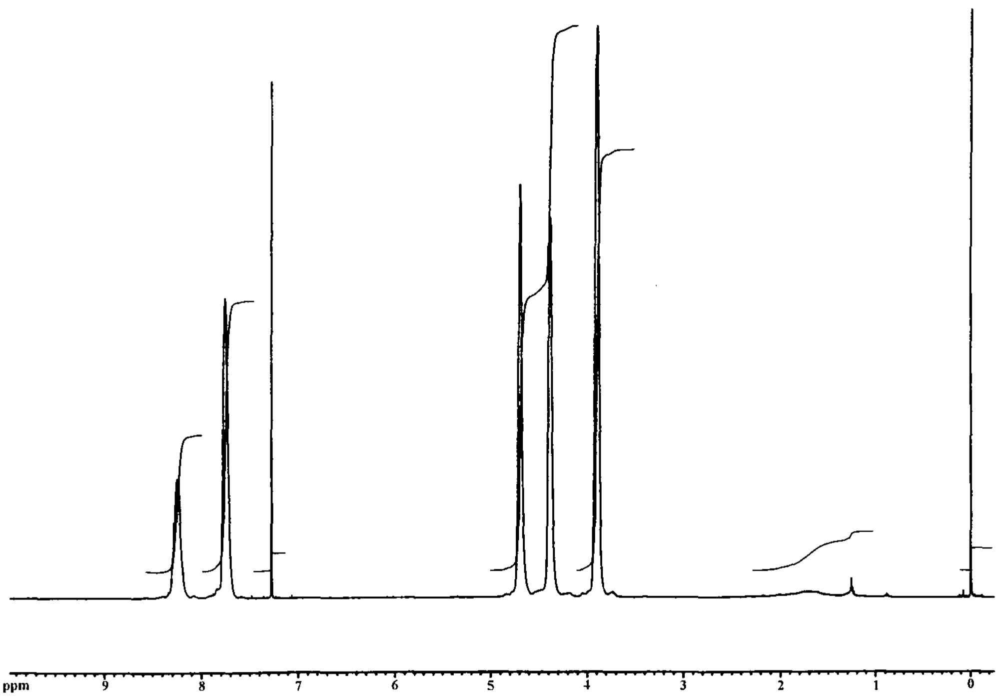
Appendix 1.8

Mass spectrum (EI) of Dimethyl 5-(2-hydroxyethoxy)isophthalate



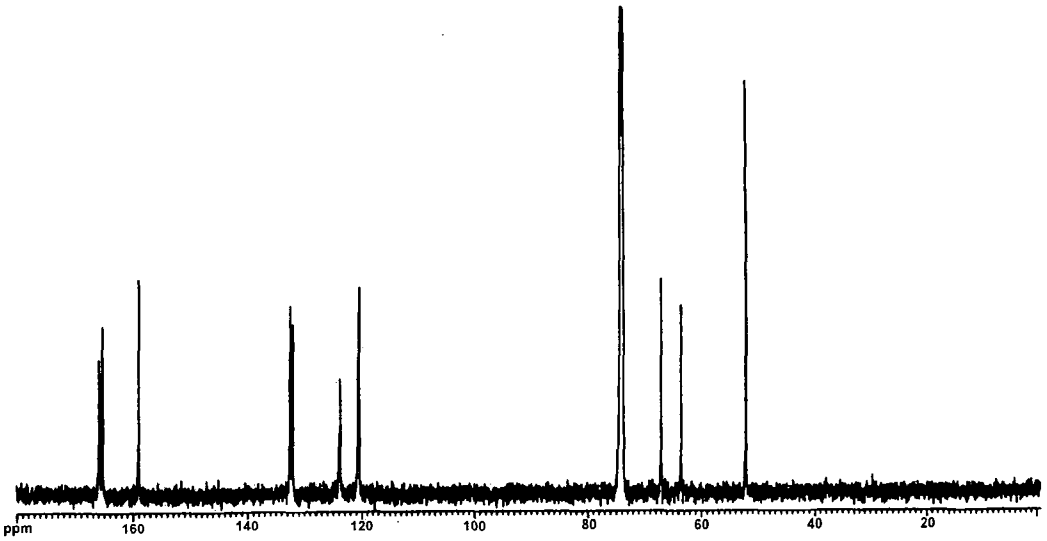
Appendix 1.9

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of polymer from the polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate)



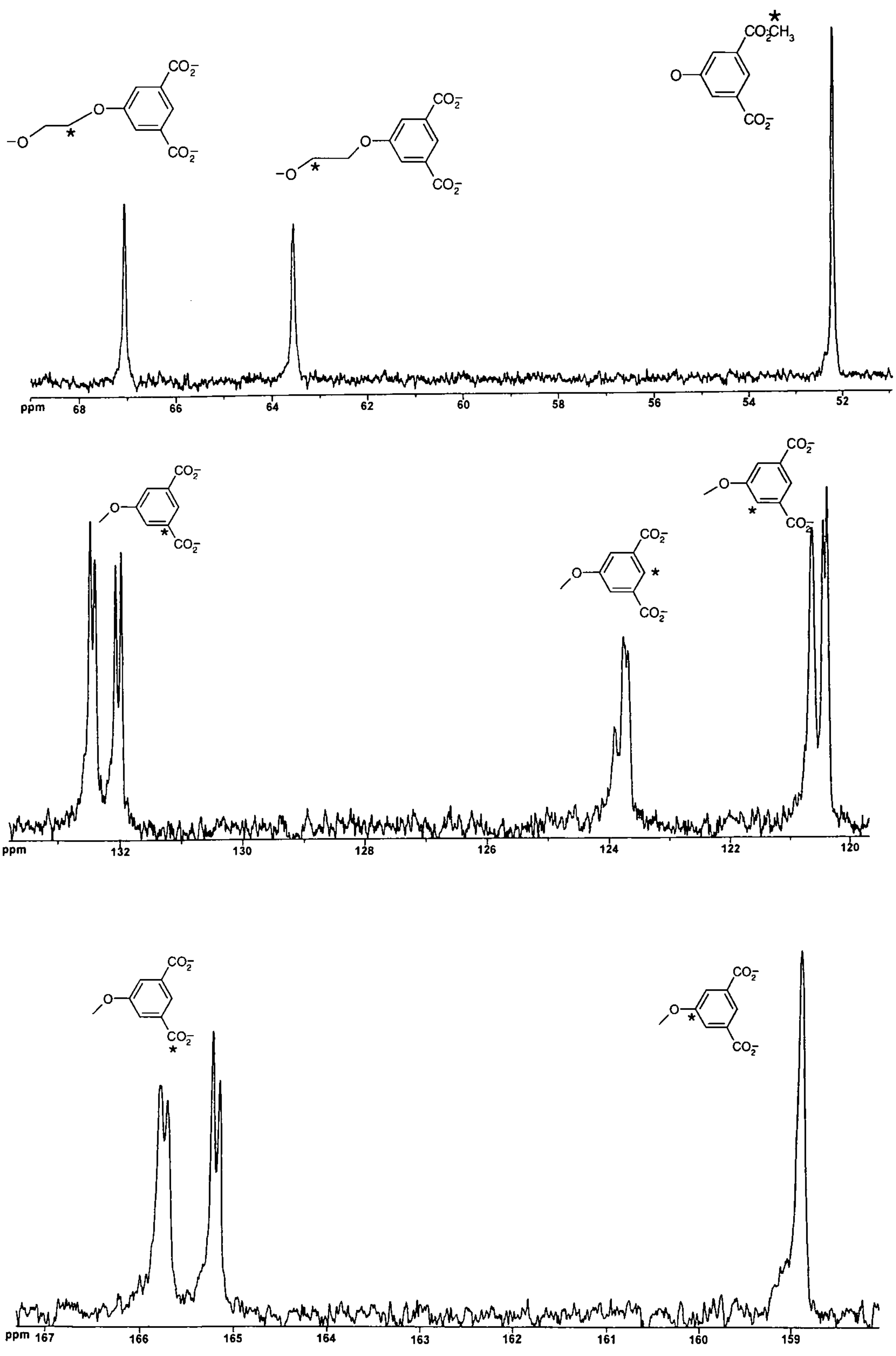
Appendix 1.10

^{13}C NMR spectrum (125 MHz, tetrachloroethane-d2) of polymer from the polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate



Appendix 1.11

Expansion of ^{13}C NMR spectrum (125 MHz, tetrachloroethane-d2) of polymer from polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate

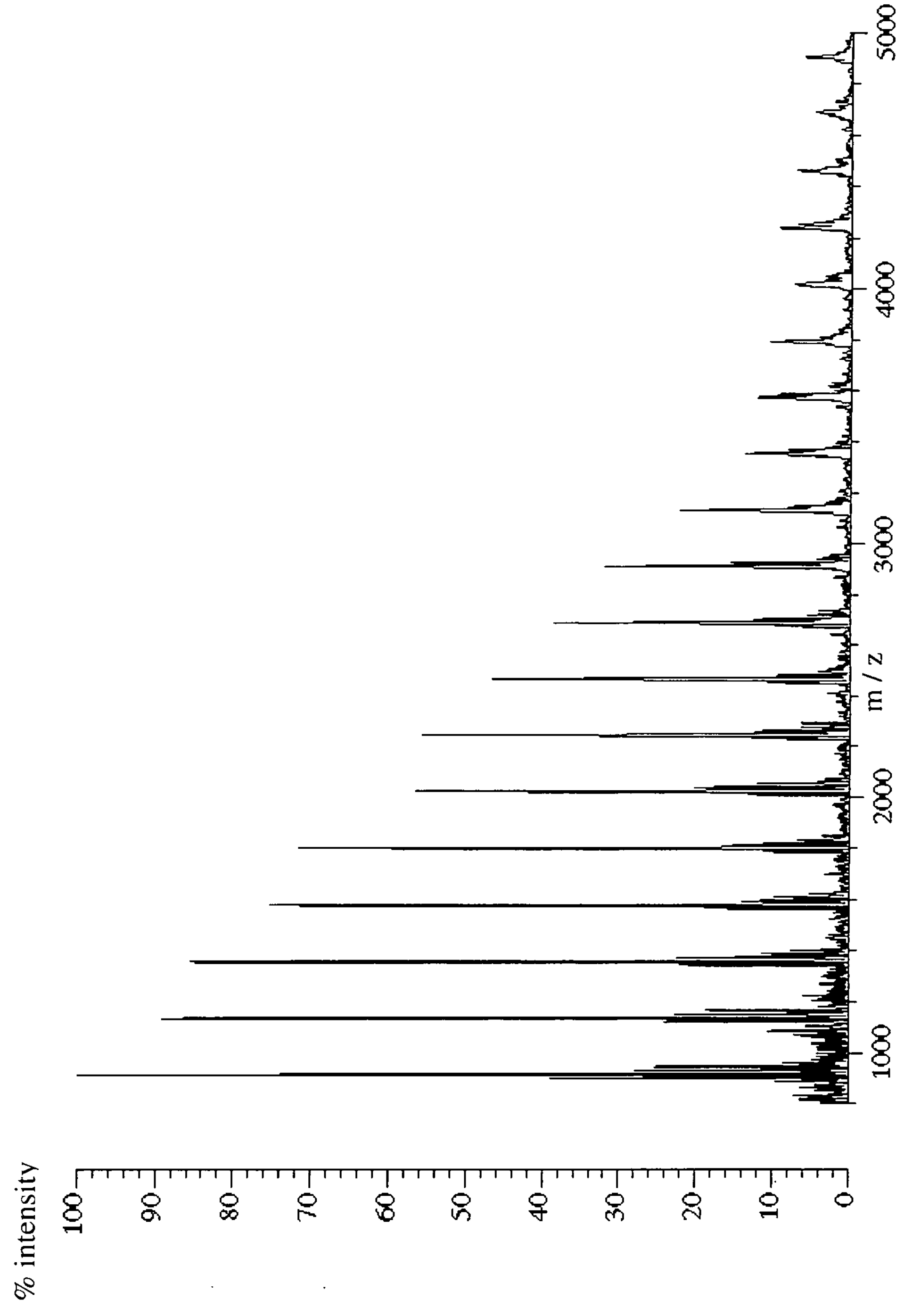


APPENDICES 2.1 to 2.4

MALDI-TOF mass spectra

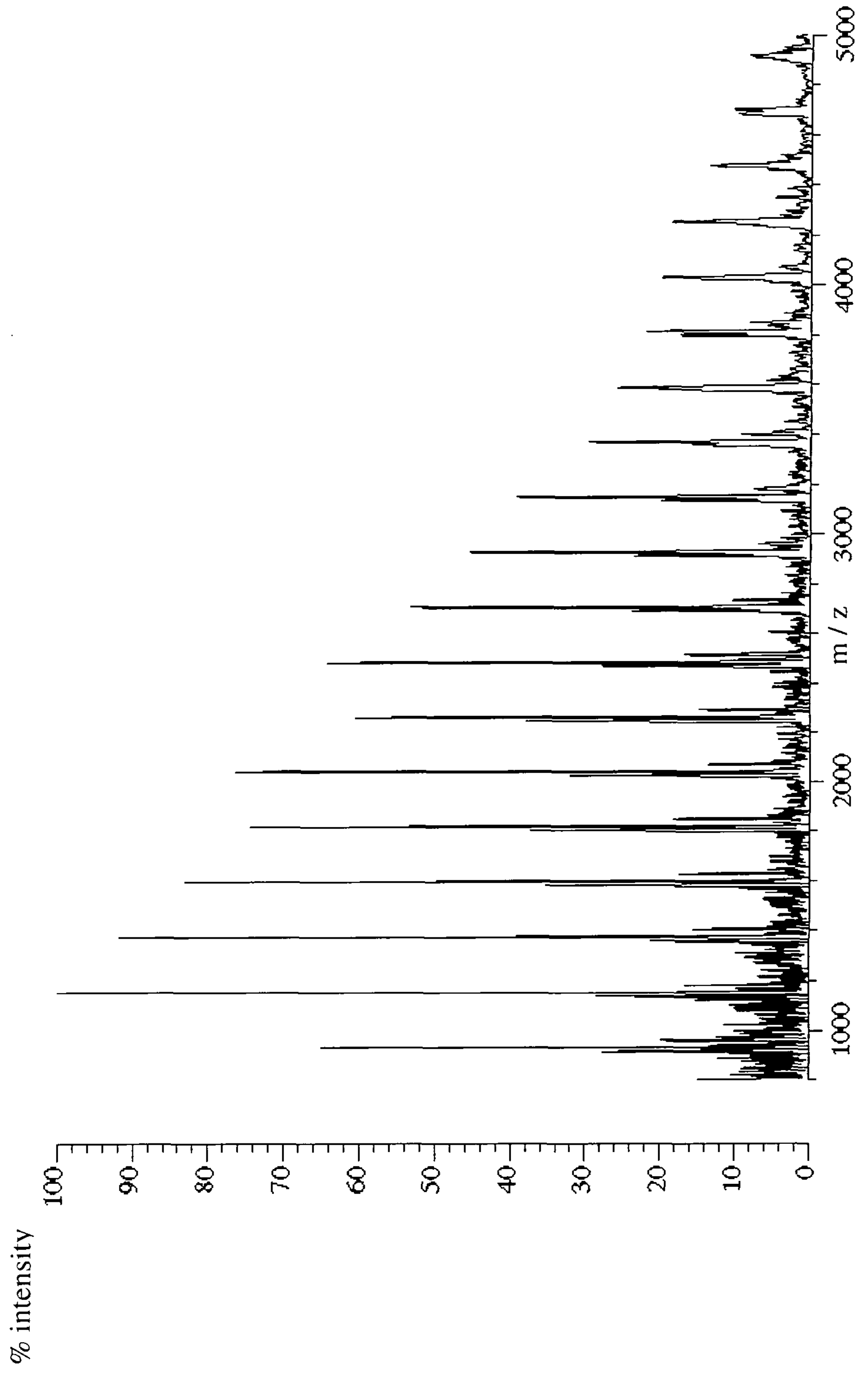
Appendix 2.1

Representative MALDI-TOF spectrum of a hyperbranched polyester from the polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate, after 10 hours polymerisation.



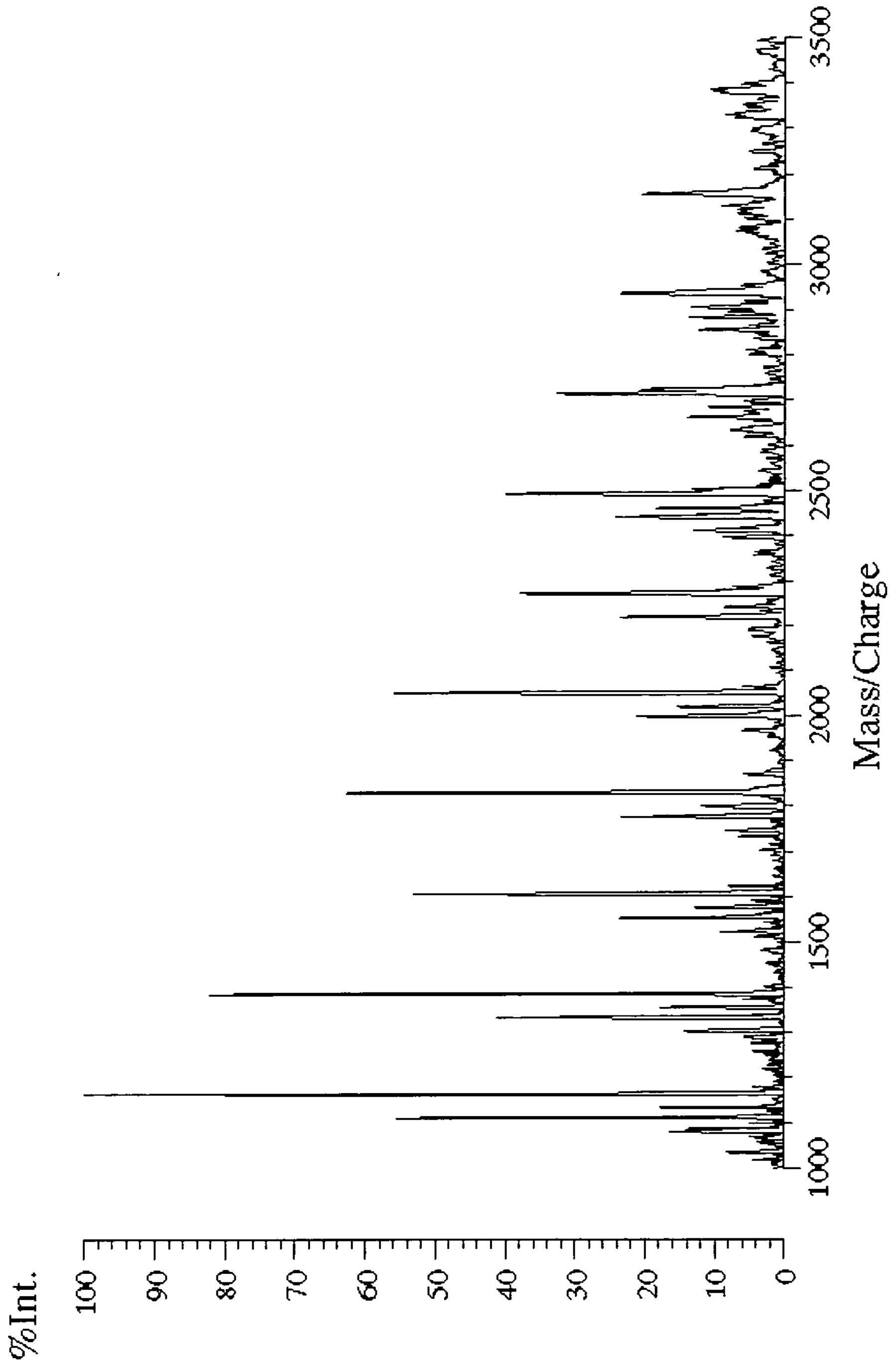
Appendix 2.2

Representative MALDI-TOF spectrum of a hyperbranched polyester from the polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate, after 10 hours polymerisation, with KCl added to matrix.



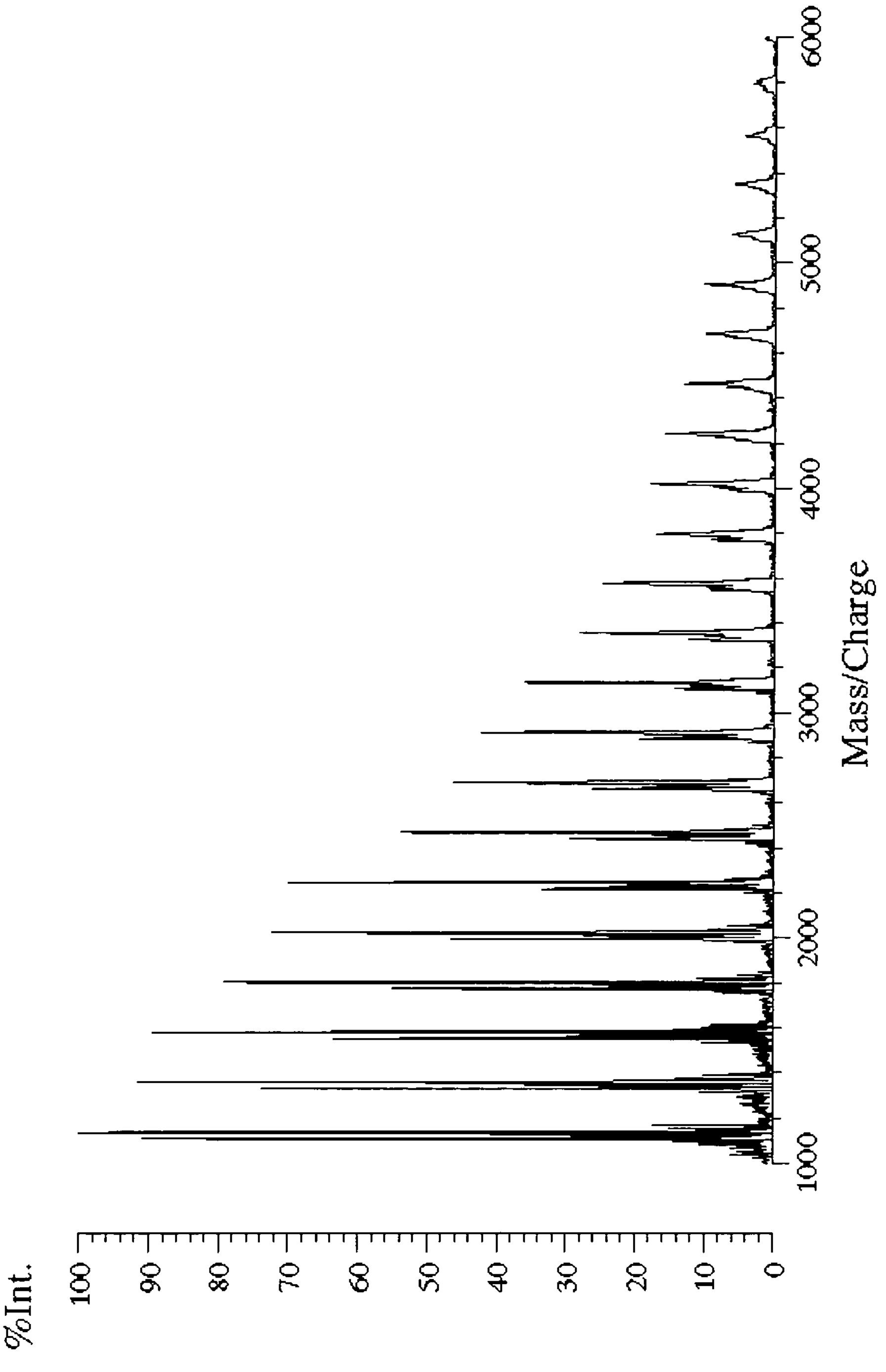
Appendix 2.3

A representative MALDI TOF spectrum of a core terminated hyperbranched polyester from the copolymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl isophthalate (24 hours polymerisation, core : monomer ratio 0.0467).



Appendix 2.4

MALDI TOF spectrum of a fully cyclised hyperbranched polyester after 6 hours reaction with dimethyl isophthalate



Algorithm used by Viscotek software for molecular weight determination[1]

The Viscotek TRISEC system, used in this study, utilises a combination of refractive index, viscometry and light scattering detectors. The excess light scattering intensity of a dilute polymer solution is related to the molecular weight of the polymer by the following equation:

The light scattering equation

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)}$$

Where, R_θ is the Rayleigh ratio at angle θ, c is concentration, M is molecular weight, P(θ) is the particle scattering function at angle θ and K is the optical constant.

The optical constant, K, is given by:

$$K = \left(\frac{2\pi^2 n_0^2}{\lambda_0^4}\right)\left(\frac{dn}{dc}\right)^2$$

Where n_0 is the refractive index of the solvent, λ_0 is the wavelength of the laser light and dn/dc is the refractive index increment.

The outputs from the three detectors are used in the following algorithm to determine molecular weight:

1). An estimated molecular weight M_{est} is calculated directed from the RALLS intensity, R_{90}, by assuming the particle scattering function $P(90^0)$ to be unity.

For $P(90^0) = 1$

$$M_{est} = \frac{R(90^0)}{Kc}$$

2). The estimated molecular weight M_{est} is used with the measured intrinsic viscosity to obtain an estimate of the radius of gyration from the Flory-Fox equation:

Flory-Fox equation

$$R_{F-F_{est}} = \frac{1}{\sqrt{6}}\left[[\eta]\frac{M_{est}}{\Phi}\right]^{\frac{1}{3}}$$

Where Φ is the Flory viscosity constant and $[\eta]$ is intrinsic viscosity.

3). The estimated radius of gyration is used in the Debye equation to estimate the angular scattering probability function P(90):

Debye equation for random coils.

$$P(\theta) = \left(\frac{2}{x^2}\right)\left[e^{-x} - (1-x)\right] \quad \text{Where}, \sqrt{x} = \frac{4\pi R_g}{\lambda_0}\sin\left(\frac{\theta}{2}\right)$$

4). The estimated P(90) is used in the Rayleigh equation to calculate an improved estimate of molecular weight:

$$\mathrm{M} = \frac{\mathrm{M}_{est}}{\mathrm{P}(90^0)}$$

5). Steps 2 to 4 are iterated until the values of M, $R_{F\text{-}F}$ and P(90) converge.

Both the Debye and Flory-Fox equations assume that the polymer molecules are in the form of Gaussian coils. It is unknown if these equations are applicable to hyperbranched polymers. Nevertheless, the TRISEC method may yield reasonable molecular weight information for hyperbranched polymers prepared by step growth polycondensation routes. A molecular weight distribution of a polymer prepared by condensation polymerisation will contain a large number of small molecules (dimers, trimers etc.). Molecules that are small, relative to the wavelength of light, have no angular dependence of light scattering intensity, for example, commercial random coil polymers obtained by a polycondensation reaction and having molecular weights < 100,000 do not exhibit any angular dissymetry.[1]

References

---

(1). Viscotek model 600 RALLS detector manual