radiochemical investigation of unsaturation in polyethyl methacrylate

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THESIS

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by

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RADIOCHEMICAL INVESTIGATION OF UNSATURATION IN POLYETHYL METHACRYLATE

Investigation of unsaturation in samples of polyethyl methacrylate using radiochlorine (^{36}Cl) of known specific activity as a tracer.

Radiochemical Investigation of Unsaturation in Polyethyl Methacrylate

Ethyl methacrylate was polymerised at 60°C in a 50% solution with benzene using α, α' azo - bisisobutyronitrile as initiator. The polymers were purified by reprecipitation from benzene using methanol as precipitant. The number average molecular weights of the polymers were measured in benzene solution using a Pinner Stabin osmometer. The graph of molecular weight^{-1} against$\sqrt{\%\ \text{initiator}}$ shows that the molecular weight is independent of initiator concentration and thus indicates that transfer occurred during polymerisation.

Polymer unsaturations were determined by reaction with (^{36}Cl) chlorine of known specific activity. Using a gas pipette, calculated quantities of radiochlorine were distilled by the usual cold line vacuum technique into solutions of polymer in carbon tetrachloride. Reaction was carried out in sealed tubes at 25°C in absence of air and light. The chlorinated polymers were purified by two precipitations from carbon tetrachloride solution using methanol as precipitant. Solutions of radiochlorinated polymer were counted in a liquid counter.

Graphs of milligrams of chlorine per gram of polymer against reaction time show a linear increase of chlorine content with reaction time, which is attributed to a side reaction.

Extrapolation to zero reaction time gives a value 0.30 chlorine atoms per polymer chain, corresponding to reaction of chlorine with the double bonds present. Assuming that one chlorine atom per double bond has reacted then 30% of the chain ends contain double bonds. This is exactly the same result as has been calculated for polymethyl methacrylate.[1] The agreement is fortuitous since methyl methacrylate shows no transfer at all during polymerisation and termination in polyethyl methacrylate must therefore occur by a different mechanism.

Termination in polyethyl methacrylate could occur:-

(a) Partly by transfer to monomer giving unsaturated ends and partly by transfer to solvent giving saturated ends.

(b) Entirely by transfer to solvent, but since this occurs by two mechanisms, only one of which results in double bonds at chain ends, and since only 30% of chain ends react with chlorine, the normally accepted type of solvent transfer reaction is assumed to predominate, i.e.

$$R(CH_2 - CHY)^{\bullet}n + SH \rightarrow R(CH_2 - CHY)nH + S^{\bullet}$$

REFERENCE

1. Allen, P.W., Ayrey, G., Merrett, F.M. and Moore, G.G. J. Poly. Sci. 1956 22 549.

INTRODUCTION

The term polymer is usually applied to substances composed of at least one hundred repeating units. An addition polymer is derived from multiple combination of an unsaturated monomer and has the same percentage composition as the monomer, e.g. $nCH_2 = CHY \rightarrow (-CH_2 -CXY)_n$. The free radical mechanism of polymerization (discussed later) would predict that in nearly every case the addition vinyl polymer would have a regular structure of the "head to tail" type.

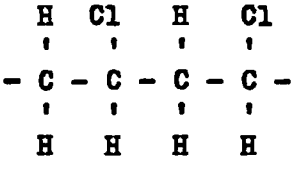
$$R^{\cdot} + CH_2 = CHY \rightarrow RCH_2 -CHY^{\cdot} \longrightarrow R(CH_2CHY)_n.CH_2CHY^{\cdot}$$

In this propagation reaction the free radical always adds to the olefin in such a way as to give the more stable free radical. Several studies of polymer structure by chemical methods have established this. Polyvinyl chloride has chlorine atoms on alternate carbon atoms. Polyvinyl acetate, polystyrene and polyacrylic esters also have this alternating structure. See P.J. Flory[1] for evidence of the head to tail structure.

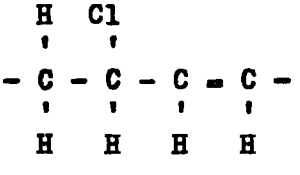
While the major structure of the vinyl polymers is undoubtedly this regular head to tail arrangement of units there is increasing evidence that there are random units which are not accounted for by this simple head to tail arrangement. There is evidence that polyvinyl chloride has some tertiary chlorine atoms $-\overset{\overset{|}{}}{\underset{\underset{Cl}{|}}{C}}-$. These must be produced by a radical rearrangement

or a chain transfer reaction during the growth of the polymer chain. There may be other abnormal structures (i.e. structures which are different from the repeat unit) in the polymer chain. These may be chain ends, branches, oxygenated structures or impurities incorporated in the chain.

Unsaturated groups are often present in polymers in small amounts either at chain ends (formed during termination by disproportionation - see later) or in the main chain. The chain of polyvinyl chloride is:-



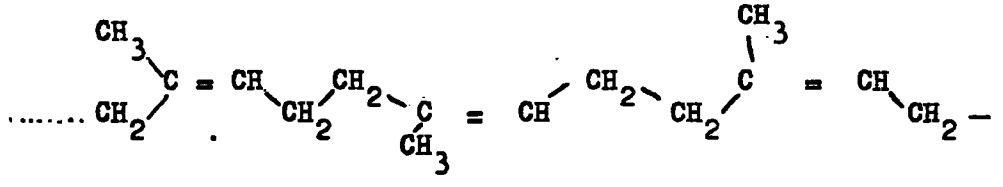
Hydrogen chloride can be removed thermally thus causing unsaturation in the chain:-



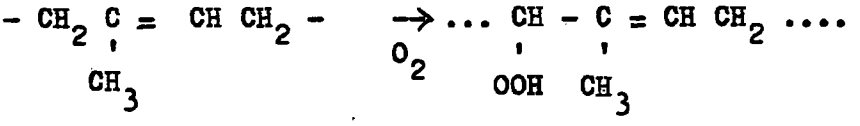
Small amounts of unsaturated centres in polymer chains are important for a number of reasons. They may form centres for cross linking reactions, as in the vulcanization of rubbers, points at which modification of the polymer can be brought about by reactions such as grafting, points of weakness towards oxidative attack or centres at which degradation may be initiated.

In polyvinyl chloride for example, unsaturation could activate the chain for hydrogen chloride loss producing further unsaturation and leading eventually to the complete degradation of the chain to a conjugated polyene.

Isoprene $CH_2 = \overset{CH_3}{\overset{|}{C}} - CH = CH_2$ polymerises to give rubber. The isoprene units are linked head to tail and rubber has the cis pattern.



Raw rubber is soft and tacky and the tensile strength and resistance to abrasion are low. These properties are changed markedly by vulcanization which consists in heating rubber with 5 - 8% of sulphur. The nature of the vulcanization process is uncertain, but it undoubtedly involves establishment of sulphur cross links between hydrocarbon chains. Initial attack is probably not at double bonds of the poly-isoprenoid chain, but at activated allylic positions. Similar allylic oxidation to a hydroperoxide is probably the first step in the ageing of rubber due to air oxidation.



As a result of the oxidation process the long chains of atoms are broken, a comparatively small amount of oxidation doing considerable damage. If there are ten thousand units in the structure of the rubber molecule then the breaking of one link is sufficient to reduce the average molecular size to five thousand units. Ten links broken would bring the average chain length down to only one thousand units and yet it would be impossible chemically to detect such a small amount of oxidation. The effects of oxidation are better revealed by the much larger change in mechanical properties which it brings about.

Grassie and Melville[2] showed the importance of unsaturated ends in the degradation of polymethyl methacrylate. Polymethyl methacrylate degrades on heating by first being rendered unstable at the ends of the polymer chains, this being followed by a chain degradation reaction which yields only monomer. The instability produced at the ends of the molecules is most likely due to the formation of a small free radical and also a large one. Rapid stripping off of monomer units is a reasonable assumption since it is known that large radicals are thermally unstable. Degradation proceeds from the ends which have been produced by disproportionation, that is double bond or single bond ends. One of these ends is much less stable than the other. The energies of activation of the degradation reaction through the two types of bonds are 31 and 42 K cals.

It is possible to vary the rate of initiation by changing the nature of the end groups in the polymer molecules. Once this initiation has occurred there is no change in the characteristics of the depolymerization.

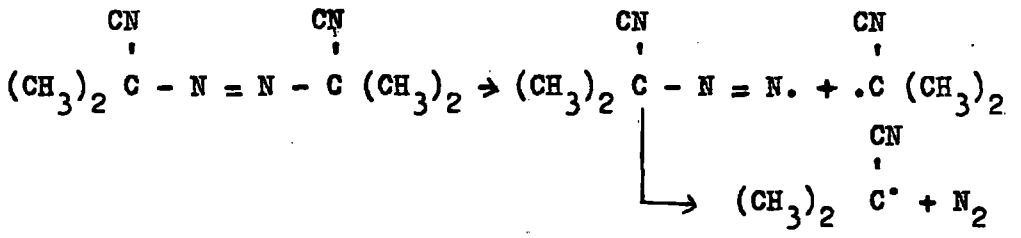
The importance of unsaturation has been illustrated and it is necessary to consider how unsaturation in the polymer chain arises. In order to discuss termination and transfer as sources of unsaturation the mechanism of free radical polymerization must be introduced.

Vinyl polymers are produced from olefins by chain polymerization reactions which usually lead to products of high molecular weight. In contrast to condensation polymers there seem to be no intermediate low molecular weight units which slowly produce the high molecular weight materials. Trimers and tetramers have never been detected and at intermediate stages monomer is still present together with polymers comparable in size to those present in the final stages. Evidently the growing polymer chain is formed by consecutive addition of monomer units. Moreover, polymerization of the monomer is strongly catalysed by free radicals. Examples are the radicals formed on decomposition of benzoyl peroxide:-

$$\underbrace{C_6H_5\,COO - OOC\,C_6H_5 \rightarrow C_6H_5\,COO^{\bullet} \rightarrow C_6H_5^{\bullet}}$$

$$C_6H_5 - C_6H_5 + C_6H_5\,COO\,C_6H_5 + C_6H_5COO\,H$$

or α,α' - azo - bis - isobutyronitrile.



Conclusive evidence for a free radical mechanism is afforded by detection in the polymer of radical fragments from the initiator. Polymethyl methacrylate when prepared with bromo benzoyl peroxide contains bromine which cannot be removed by precipitation. See C.C. Price, R.W. Kell and E. Krebs.[3]

The chain reaction proceeds by the stages of initiation, propagation and termination.

Initiation. Here a free radical ($R^{\bullet}$) attaches itself to the olefin and produces the new radical consisting of the initiator fragment and one unit of monomer.

$$R^{\bullet} + CH_2 = CHY \rightarrow RCH_2 - \dot{C}HY$$

Propagation. This step is a rapid one, the new radical grows by successive addition of monomer.

$$RCH_2 - \dot{C}HY + nCH_2 = CHY \rightarrow R\,(CH_2\,CHY)^{\bullet}\,n + 1$$

Termination may occur by several processes.

(a) Coupling is termination by combination of two growing radicals.

$$2\ R\ (CH_2\ CHY)^{\bullet}n \rightarrow R\ (CH_2\ CHY)n - (CHY\ CH_2)n\ R$$

(b) Disproportionation involves transfer of a hydrogen atom to another molecule to terminate it or to start a new chain. It has been suggested that disproportionation gives a hydrogen radical,

$$R - (CH_2\ CHY)n - CH_2CHY^{\bullet} \rightarrow R\ (CH_2\ CHY)n - CH = CHY + H^{\bullet}$$

$$\downarrow H^{\bullet} \longrightarrow R\ (CH_2\ CHY)n - CH_2\ CH_2\ Y$$

or a new chain $H - (CH_2\ CHY)^{\bullet}$ It is more likely that this is only a special case of chain transfer in which one growing chain abstracts a hydrogen atom from another growing chain or polymer molecule.

By use of radioactive initiators and a study of the number of initiator fragments per polymer molecule Bevington, Melville and Taylor[4] obtained the following results:-

At 25°C with styrene the disproportionation of radicals is of negligible importance whereas for methyl methacrylate disproportionation occurs about twice as frequently as combination. At 60°C with methyl methacrylate disproportionation occurs six times as frequently as combination, whereas for styrene disproportionation is quite negligible. The results for methyl methacrylate are shown below.

Temperature °C	0	25	60
Average No. end groups/molecule	1.25	1.19	1.08
Fraction of radicals undergoing disproportionation	0.60	0.68	0.85

However Allen, Ayrey, Merrett and Moore[5] find the average number of initiator fragments per polymer molecule to be 1.24 and the fraction of polymer radicals terminated by disproportionation can be calculated to be 0.61. This difference between results is accounted for by different treatment of osmotic pressure data.

It can be seen that termination by disproportionation gives rise to one double bond per two polymer chains, whereas termination by combination does not produce double bonds. Disproportionation is important in the termination of polymethyl methacrylate, but the mechanism for the termination of polyethyl methacrylate is not known and so there is interest in establishing this.

(c) Chain transfer. In order to explain the approximate constancy of molecular weight during polymerization Schulz[6] concluded that the process which causes cessation of polymer growth is of the same kinetic order as polymer growth. On the other hand, there is an abundance of evidence to show that the molecular weight of the polymer decreases on dilution of the monomer with an inert solvent. Staudinger and Scwalbach[7] by polymerizing a 50% solution of vinyl acetate in benzene obtained a polymer of roughly half the molecular weight of a polymer prepared from undiluted vinyl acetate at the same temperature.

A reaction in which the free radical centre is somehow transferred from a growing chain to another molecule would explain these observations. The growth of the chain previously bearing the free radical would thereby be terminated, and the molecule acquiring the radical should be capable of starting a new chain which would grow at the same rate. A prominent mechanism for chain transfer reactions of this nature consists in removal by the chain radical of a hydrogen atom from the molecule which intervenes, i.e. the transfer agent. The chain molecule loses its capacity for further growth, and the transfer agent acquires radical character in consequence of the transfer process.

(i) The solvent represented by SH, may react with the growing radical as follows:-

$$R\ (CH_2 - CHY)^{\bullet}n + SH \rightarrow R\ (CH_2 - CHY)nH + S^{\bullet}$$

and the solvent radical $S^{\bullet}$, presumed to be sufficiently reactive to add a monomer molecule, (if it is not so reactive, SH is an inhibitor or retarder rather than a transfer agent) proceeds to grow a new chain.

$$S^{\bullet} - n\ (CH_2 = CHY) \rightarrow S\ (CH_2 - CHY)^{\bullet}n$$

A halogen atom if present, or possibly a labile group, may be similarly transferred instead of a hydrogen atom with equivalent results.

(ii) The initiator may also function as a transfer agent. This may take place in the case of benzoyl peroxide according to the following mechanism in which the peroxide undergoes a radical induced decomposition.

$$R\,(CH_2 - CHY)^{\bullet}n + (C_6H_5\,COO)_2 \rightarrow R\,(CH_2 - CHY)n - OOC\,C_6H_5 + C_6H_5\,COO^{\bullet}$$

(iii) The monomer must also be considered as a potential transfer agent.

(A) Possibly a proton may be transferred from the β carbon atom of the radical chain to the unsaturated monomer as follows:-

$$-CH_2 - \overset{X}{\underset{|}{C}}H^{\bullet} + CH_2 = \overset{X}{\underset{|}{C}}H \rightarrow -CH = CHX + CH_3\,\overset{X}{\underset{|}{C}}H^{\bullet}$$

This is chain transfer by disproportionation between the chain radical and monomer.

(B) The monomer may perform a similar function to the solvent, an atom (often hydrogen) being transferred from the monomer to saturate the radical. The ensuing growth from the transfer radical produces a polymer molecule bearing a terminal unit which retains the vinyl group. Thus assuming that the point of attack is the substituent X, the sequence of reactions set off by chain transfer with the monomer may be represented as follows:-

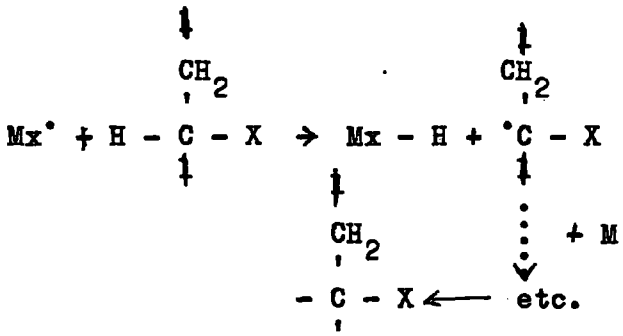
$$Mx^{\bullet} + CH_2 = \underset{\displaystyle X}{CH} \rightarrow Mx - H + CH_2 = \underset{\displaystyle X^{\bullet}}{CH} \xrightarrow{+ M \text{ etc.}} CH_2 = CH - X - Mx$$

Another chain radical may acquire the terminal unit of the molecule $CH_2 = CH - X - Mx$ in one of its propogation steps. Thus the terminal unsaturated unit may be incorporated as one of the units combined in another growing chain. When this occurs a branched polymer molecule is produced:-

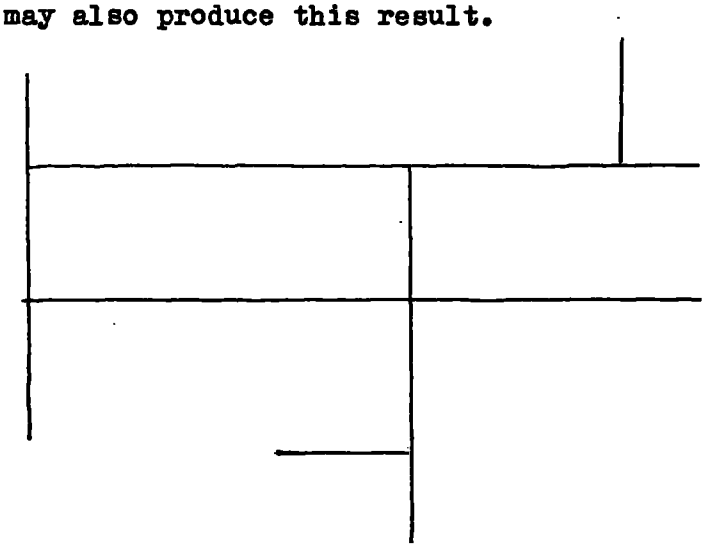
$$\begin{array}{l} \quad My \\ \quad | \\ \quad CH_2 \\ \quad | \\ CH - X - Mx \\ | \\ M_3 \end{array} \qquad (d)$$

This latter process is likely to become important only at higher conversions.

(iv) Chain transfer may also occur with a previously formed polymer molecule. This type of transfer produces no net increase in the number of molecules. The point of attack might again be located in the substituent X, or it might involve removal of the tertiary hydrogen on the substituted chain carbon. The following sequence of reactions in which the latter alternative has been assumed would then lead to a branched polymer molecule.



The immediate result of the intervention of the chain transfer process indicated in the first step is the termination of the growing chain and the reactivation of a polymer molecule. This then adds monomer to generate a branched molecule containing a tri-functional unit, the structure being formally similar to (d). It is also apparent that a given polymer molecule may undergo repeated reactivation in the above manner with growth of an additional branch at each recurrence. Manifoldly branched molecules may be produced (see below). Chain transfer with monomer may also produce this result.



It can be seen that unsaturation is produced in the chain only by process (iii), i.e. transfer of a hydrogen atom between monomer and polymer radical. Unsaturation measurements may determine the extent to which the particular process occurs.

The end groups of high polymer molecules account for only a small fraction of the total weight , but they are of great importance in several respects.

(a) One chemical method of determining molecular weight has been the use of end group analysis. This does require that the number and kind of end groups (two or one in a linear polymer) is known. It is also necessary to be as certain as possible that all the polymer molecules in the sample have the same end groups. This is not easy, if branching occurs in polymer growth the end group method fails. In such molecules as polyesters the terminal carboxyl group can be titrated. This method becomes increasingly insensitive as the molecular weight increases. It has been used principally in the molecular weight range, 15,000 to 25,000, which is fairly common in condensation polymers. If the polymer is completely linear, quantitative determination of all the end groups which may be present provides a direct measure of the number of molecules present and hence of the number average molecular weight. Carothers and Natta [8] determined the molecular weights of

polyesters from W-hydroxydecanoic acid. The molecular weights were estimated by titration with standard alcoholic potash of the polyesters dissolved in chloroform/alcohol mixture. Phenolphthalein was used as an indicator. No difficulty was encountered in titrating the highest member of the series where the acid hydrogen was only one part in 25,000. The average equivalent weight measured by titration will be identical with the average molecular weight only if each molecule bears a terminal carboxyl group in the manner required by the theoretical structure. Accidental loss of terminal carboxyl groups under the conditions of preparation seemed unlikely, but indication of the absence of such loss was provided by independent estimations of molecular weight.

(b) The end groups are usually quite different structurally from the bulk of the polymer, and they act as centres for chemical reaction. In this connection the degradation of polymers (as discussed earlier) and the formation of block copolymers are of particular importance.

(c) Another reason for the interest in the end groups is the evidence they can provide on the mechanisms of the individual steps in the growth of the polymer molecule. It was pointed out previously that termination by disproportionation gave rise to one end group containing a double bond per two chains.

Termination by transfer of a hydrogen atom from monomer to polymer radical also produces end groups which contain double bonds. Accurate determinations of the end groups could therefore lead to information about the initiation and termination steps, and about transfer and retardation processes. There is therefore some interest in being able to measure accurately the number of double bonds present in a polymer and various methods have been developed for this purpose.

The drastic iodine - mercuric acetate method is the standard procedure used for determination of unsaturation in butyl rubbers. It has been described by Gallo, Wiese and Nelson[9]. A solution of butyl rubber in carbon tetrachloride is reacted for 30 minutes with iodine in the presence of mercuric acetate and trichloro acetic acid. The excess iodine is titrated with sodium thiosulphate. The iodine number (centigrams of iodine per gram of polymer) is calculated from:-

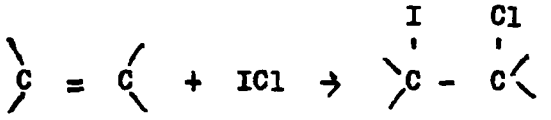
$$\text{Iodine Number} = \frac{\text{ml} \times N \text{ of } Na_2S_2O_3 \times 126.91 \times 100}{\text{gms. of sample} \times 1000}$$

The mole per cent unsaturation is related to the iodine numbers by:-

$$\text{Mole per cent unsaturation} = \frac{M \text{ (iodine number)}}{126.91\ F}$$

where, M is average molecular weight of monomer unit.

F is stoichiometric factor depending on reaction conditions. The addition of halogens to a double bond is often a reliable method for determination of unsaturation. In butyl rubbers, however, there are complicating reactions and the reliability of results from halogen procedures has been subject to question.[10] A reliable and convenient method for the determination of unsaturation in hydrocarbons, polymers and olefins can generally be based on the addition of iodine chloride to a carbon-carbon double bond.



The procedure usually consists in adding excess iodine chloride to a solution of an unsaturated compound and after a suitable reaction period determining by titration the amount of iodine chloride remaining. This iodine chloride method yields accurate results for most olefins and polymers. However, when iodine chloride is added to highly branched olefins and polymers, the reaction is abnormal in that the additional products formed possess steric strain and tend to decompose. The decomposition products react further with iodine chloride , thus leading to high unsaturation values. Kolthoff, Lee and Johnson[10] modified calculations of unsaturation from iodine chloride results to give values which were considered reliable for butyl rubbers.

The results so obtained gave good agreement with values obtained by drastic iodine - mercuris acetate methods.

McNall and Eby[11] prepared samples of butyl rubbers with known unsaturations by using C^{14} labelled isoprene. They estimated the unsaturations by using the drastic iodine - mercuric acetate method which they found to be reliable, but they had to increase the results by 15% to estimate accurately the amount of isoprene in the co-polymer. The iodine equivalent for this method is thus 2.61 instead of 3. The amount of di-olefin entering the polymer was measured directly by isotope tracer techniques. This should determine the unsaturation accurately, assuming that there is one double bond for each molecule of isoprene entering the polymer. This assumption should be sound, because there is no evidence of cross linking in the soluble butyl polymers and end group unsaturation is negligible. Dimers of isoprene in butyl rubber which could cause abnormalities in unsaturation measurements are also absent.

Kaufmann's method, which has been modified by Byrne and Johnson[12], can be used to measure polymer unsaturation. The polymer sample is allowed to react with an aqueous methanol solution of bromine and sodium bromide containing a little hydrochloric acid as a catalyst. The excess bromine is treated with potassium iodide solution and the liberated iodine treated with sodium thiosulphate. The method has been tested with a

number of pure compounds [13] and it has been established that halogenation of double bonds takes place without any substitution reactions. Sodium bromide is believed to form a complex which is a mild brominating agent with little tendency to substitute.

$$Br_2 + NaBr \rightleftharpoons Na\ Br.\ Br_2$$

$$R - CH = CH - R + NaBr.\ Br_2 \rightarrow RCHBrCHBrR + NaBr$$

The solubility of sodium bromide in methanol is insufficient to provide the excess bromine ions necessary to complete bromination. Without excess bromide use of the reagent is subject to serious error because of substitution. Modified Kaufmann bromination is suitable for some compounds, but has been found to give anomalous results with double bonds of the acrylic type.

The methods described cease to be useful at unsaturations below about 0.5 mole per cent. Below this level the accuracy of ordinary chemical methods becomes inadequate. The unsaturation of polyethyl methacrylate is probably about 0.1 mole per cent, which is outside the range of satisfactory quantitative methods of investigation. Radiochemical techniques should enable this difficulty to be resolved - the use of a reagent labelled with a suitable radioactive isotope should enable very low double bond contents to be determined; for higher unsaturations

it would permit determinations to be carried out on extremely small samples of polymer.

Although either of the conventional methods (except Kaufmann's) could in theory provide a basis for the development of a radiochemical procedure for unsaturation determination (using e.g. I^{131} or Cl^{36}) the mechanisms of the reactions are not well understood. A radiochemical method[14] using Cl^{36} has been used successfully for butyl rubbers with unsaturations around one mole per cent. It is however capable of sufficient sensitivity to measure much lower unsaturations. Little attempt has been made in the past to use chlorine for the quantitative estimation of double bonds in polymers partly because of difficulties in handling chlorine and also because of the readiness with which chlorine will react with hydrocarbons by free radical substitution processes. Chlorine is an attractive reagent however, from the radiochemical point of view, since there is a suitable isotope available and the preparation of radiochlorine is readily accomplished.[15] Quantitative manipulation of chlorine can now be carried out on a vacuum line without difficult using greaseless stopcocks. (G. Springham & Co. Ltd.) with Viton A fluorocarbon diaphragms.

Measurement of unsaturation gives information about the number of double bonds per gram of polymer. If the number

average molecular weight of the polymer is known then the number of double bonds per polymer molecule can be calculated.

The molecular weight range of the samples of polyethyl methacrylate to be studied was to be between 150,000 and 400,000. Classical methods of molecular weight determination such as depression of freezing point and elevation of boiling point are applicable only to very low molecular weights, below about 10,000. There are two methods of measuring molecular weights applicable in the range 150,000 to 400,000; they are viscometry and osmometry. However, only osmotic pressure measurements lead to the number average molecular weight which is required to calculate the number of double bonds per polymer chain from unsaturation determinations. Viscosity measurements lead to a molecular weight which depends not only on the number of polymer molecules, but also on their size.

The work subsequently described had as its object the investigation of unsaturation in polyethyl methacrylate and comparison of the results with available data on the better known methyl ester.

The experimental procedure involved:-

(1) Preparation of a series of polymer samples.

(2) Determination of the molecular weights by osmometry.

(3) Estimation of unsaturation in the polymers by reaction

with radiochlorine under closely controlled conditions.

From these results, the number of double bonds per polymer molecule for each sample could be derived, and hence deductions could be made about transfer and termination mechanisms in the polymerization of ethyl methacrylate.

EXPERIMENTAL

(a) Purification of Materials

Monomer

Ethyl methacrylate was supplied containing about 0.1% of hydroquinone to act as polymerization inhibitor. The inhibitor was removed by washing with aqueous caustic soda. The monomer was then washed with distilled water and distilled under reduced pressure, the middle fraction being collected. It was dried over pure calcium chloride and stored at $0^{\circ}C$.

An infra red spectrum of the monomer was obtained and checked for signs of inhibitor. The aromatic peak at about 800 $cm.^{-1}$ was not present, therefore the monomer was free of inhibitor.

Initiator

The initiator $\alpha\,\alpha'$ - azo - bis-isobutyronitrile was used in all polymerizations. It was purified by two re-crystallisations from alcohol. The solutions were heated only to $50^{\circ}C$ for the minimum possible time to avoid decomposition.

Solvents

(a) Benzene was used as a solvent during the polymerization of ethyl methacrylate and also as a solvent for osmometry.

Analar benzene was thoroughly dried by refluxing over sodium wire and then fractionated twice retaining the middle fraction.

(b) Carbon tetrachloride was used during the reaction of polymers with radiochlorine. "Analar" carbon tetrachloride without any further purification was used.

Precipitant

Methyl alcohol used to precipitate the polymers formed after polymerization was "Analar." The methanol used to precipitate polymers after reaction with radiochlorine was as supplied in bulk by I.C.I.

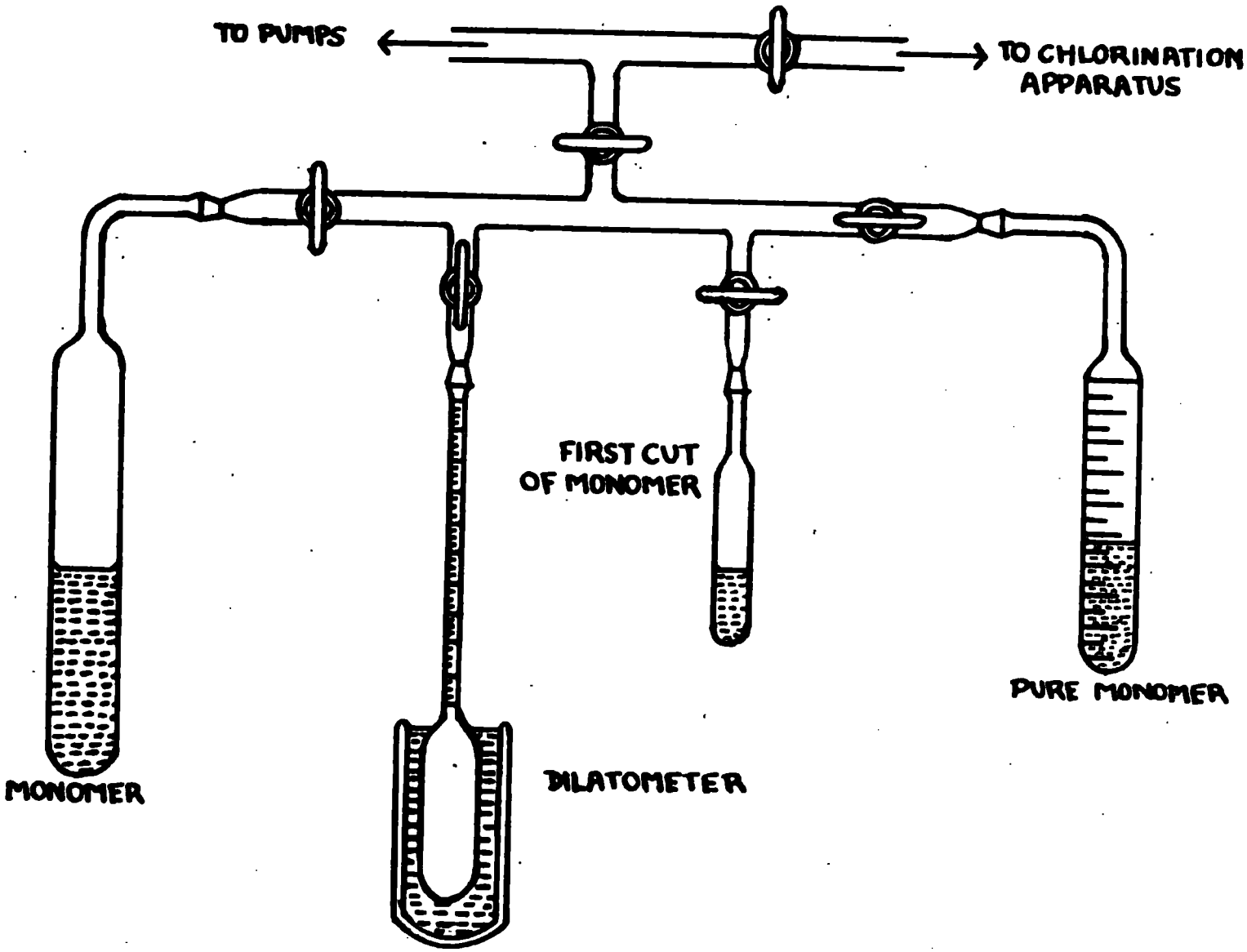
(b) Preparation of Polymers

Polymerizations were conducted in 50% (vol./vol.) benzene solution in vacuo at $60.0^{\circ}C \pm 0.1^{\circ}C$.

Two dilatometers of 82.8 and 66.2 mls. capacity and having graduated stems were used throughout. The necks of the dilatometers were collapsed and thickened to facilitate sealing off under vacuum after filling. The dilatometers were cleaned out with benzene (to remove polymer and monomer left from previous polymerization), rinsed with acetone, then water and finally filled with chromic acid and allowed to stand. They were rinsed with distilled water and dried in an oven.

A known weight of initiator was washed with the requisite

VACUUM SYSTEM FOR FILLING DILATOMETERS.



amount of pure benzene into a dilatometer which was then attached to the vacuum system, cooled in liquid air and evacuated to $< 10^{-4}$ m.m. The solution was then degassed three times. The monomer was filtered into a large vessel in order to remove calcium chloride. The vessel, attached to the vacuum system was cooled in liquid air, evacuated to $< 10^{-4}$ m.m. and degassed three times. The monomer was then distilled under high vacuum into a calibrated reservoir, after the first fraction had been collected in a small vessel and discarded. The distillation was carried out by the usual cold line technique and it was fairly slow. The monomer polymerized slightly during this process and if distilled too quickly a skin formed on the surface preventing further evaporation. During the operation the monomer was protected from strong light since this also causes polymerization. The vessels containing monomer were so attached to the vacuum line that they could be shaken and the polymer skin broken. When the required amount of monomer (as measured by the calibrated reservoir) had been distilled over, the dilatometer was sealed off under vacuum and kept in liquid air until required for polymerization.

Polymerizations were followed dilatometrically using the data of Mackay and Melville[16] for methyl methacrylate. The formula used to calculate the contraction in volume for 10%

polymerization was:-

$$Vc = V(1 + 0.0013\,\Delta T)\,\frac{\%\,P}{F \times 100}$$

Vc = contraction in volume.

V = total volume (i.e. volume of dilatometer).

0.0013 = co-efficient of expansion of polymerization material.

ΔT = temperature of thermostat - room temperature

= $(60 - 20)^{\circ}C = 40^{\circ}C$.

%P = percentage polymerization, i.e. 10%.

It was calculated for 10% polymerization that a contraction of 1.12 mls. on the scale was necessary for the 66.2 ml. dilatometer and 1.405 mls. for the 82.8 ml. dilatometer.

The dilatometer was placed in the thermostat at $60^{\circ}C$ and readings taken on the dilatometer scale initially and then every 30 seconds. The scale readings were plotted against the time of reaction in minutes. There was an intial expansion in volume followed by a contraction after a few minutes, the rate of which depended on the amount of initiator present. The theoretical maximum volume of monomer/benzene solution is never reached since contraction due to polymerization occurs before it reaches $60^{\circ}C$. This volume was found by extrapolating the lines on the graph due to expansion and contraction until they met. The maximum volume was then read directly off the graph and the required contraction (1.12 or 1.40 mls.) was allowed to take

place. Readings of volume were taken every two minutes and plotted to check that polymerization was proceeding smoothly. When the required contraction had taken place the dilatometer was removed from the bath and quickly placed in cold water. The drop in temperature to $0^{\circ}C$ was sufficient to stop polymerization.

Purification of Polymers

The dilatometer was opened by cutting off the top and the contents were poured into one litre of methanol which was vigorously stirred.

Originally the stirring was done by hand using a glass rod. The method was found to give a polymer sample which often had a hard glassy appearance (probably due to trapped solvent). The polymers were difficult to grind and it was found necessary to develop a more efficient method before the polymers could be used in chlorination experiments.

A small magnet enclosed in a glass capsule and firmly secured by black wax was used as a stirrer. The methanol could be very vigorously stirred and the polymer mixture slowly added. The precipitated polymer was filtered using a No. 3 glass filter pad and then dried in a vacuum desiccator by means of an oil pump. The dried polymer was dissolved in pure benzene and reprecipitated with methanol. The polymers were precipitated

four times before they were finally obtained in an acceptable state. All polymers were precipitated by this method and were found to be easy to dry and very easy to grind up.

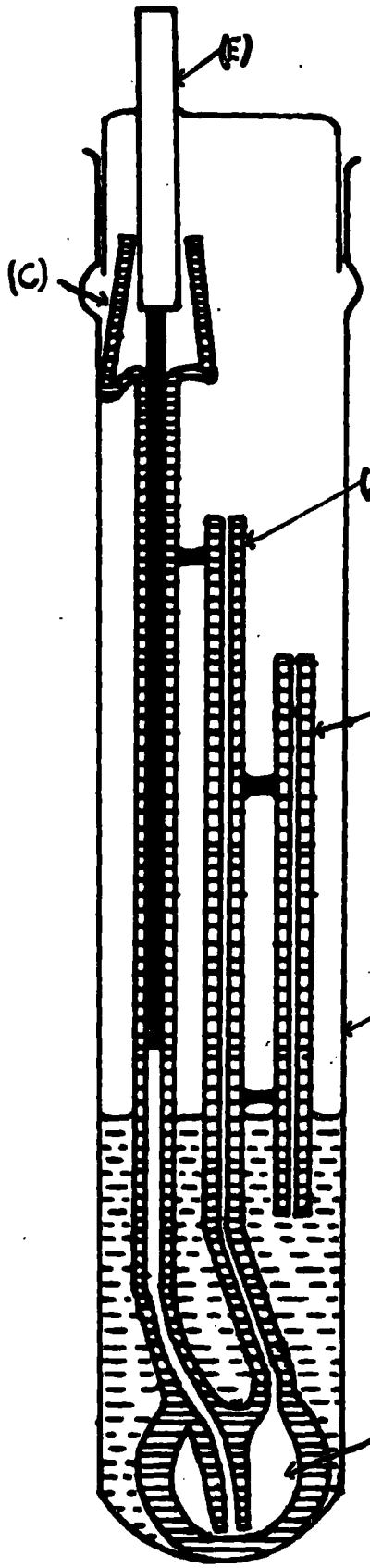
The polymers were ground up to fine powders and infra-red spectra were obtained using the potassium chloride disc technique. The spectra were examined for the monomer peak at ca. 880 $cm.^{-1}$. None was found indicating the polymers to be free from monomer.

400 mg. of No. 1 polymer were chlorinated using inactive chlorine. The infra-red spectrum of the resulting polymer was examined for disappearance of peaks or traces of new peaks, as compared with the spectrum of the original polymer. It was expected that there would be no difference, since it was thought that the amount of chlorine combining with the polymer would be too small to be detected by infra-red analysis. Comparison of infra-red spectra for original and chlorinated polymer showed this expectation to be realised.

(c) Measurement of Molecular Weights

Molecular weights were determined on polymers obtained after the final precipitation. An osmometer of the type described by Pinner and Stabin[17] was used.

The glass parts of the osmometer and outer jacket were cleaned prior to use by standing them in a strong solution



THE PINNER-STABIN OSMOMETER.

Cross Sectional View.

(Metal plates which support the membranes are not shown).

of chromic acid for about two weeks. Owing to the small volume of the capillary compared with the volume of the cell (A) the osmometer acts as a very sensitive thermometer. The thermostatic bath was therefore controlled to 0.01°C. A travelling microscope with a scale reading to 0.001 cm. was used. The telescope had a pivoted mount which enabled the centre of the cross hair to be found on each meniscus in turn. Flat circular gel cellophane membranes were used which were supplied immersed in aqueous acetone and were conditioned before use. The water was displaced by replacing one third of the liquid daily with acetone. On the fourth day the whole of the liquid was poured off and replaced with pure acetone. This was repeated on the fifth day also. The acetone was then gradually replaced by benzene in the same manner. At no time were the membranes allowed to dry out. Benzene was used as the solvent and purified as described previously. ~~Working under~~ Covered by benzene in a shallow dish the membranes were fitted in the osmometer. The outer jacket (B) was supported vertically in the thermostatic bath and about 100 ml. of benzene were added. The osmometer was placed inside the jacket and about 10 ml. of benzene were placed in the filling (C) bulb of the osmometer. The air was displaced from the cell and the benzene rose in the measuring capillary (D) and oozed from the top. A plug of absorbent tissue was used to

absorb this liquid while the cell was examined for bubbles. If any were present they were removed by inserting the needle of the hypodermic syringe into the filling tube and alternately delivering and withdrawing solvent. When the cell was bubble free, and with the filling bulb still partly filled the levelling rod (E) was carefully inserted into the filling tube as far as it would go, all the liquid issuing from the measuring capillary being absorbed on tissue. The bore of the reference capillary (F) was thoroughly wetted with benzene by attaching a rubber tube and alternately raising and lowering the liquid level. The levelling rod was slowly withdrawn with rotation to depress the level of solvent in the measuring capillary. About 2 ml. of clean mercury were placed in the filling bulb and excess solvent was absorbed with tissue. The outer jacket cover was then placed in position. After about 15 minutes (until thermal equilibrium was attained) the position of the levelling rod was altered so that the level of solvent in the measuring capillary was close to that in the reference capillary.

The osmometer assembly was now left at rest until no further movement of the level in the measuring capillary occurred, when the difference in levels between the two capillary tubes was measured. This difference should be zero with solvent on both sides of the membrane, but in practice a slight difference in

levels is usually observed. If the difference is constant and small (less than 0.05 cm.) it may be used as a correction for subsequent measurements on the polymer solution. If it was large, or non-reproducible, new membranes were used. A further test was carried out at this stage by setting the solvent level to the top of the measuring capillary and timing its fall to reference capillary level. This fall should be slow - if rapid flow was observed, due to leakage, increased pressure was applied to the plates. If a leak was still present the osmometer was reassembled.

The instrument was now used to measure the osmotic pressure of polymer solutions. A master solution was made up by weighing 0.4 g. of polymer into a 50 ml. graduated flask. The flask was made up to the mark with benzene and reweighed. The concentration of polymer in grams per hundred grams of solution was then calculated. Different amounts of the master solution were then weighed into 25 ml. flasks, benzene was added until the flasks were filled to the graduation marks and the flasks were reweighed. The concentration of these solutions in grams of polymer per hundred grams of solution were also calculated.

The most dilute of the range of solutions was tested first. The cover of the outer jacket was detached and the

mercury was removed from the filling bulb with a hypodermic syringe. The levelling rod was completely withdrawn, a rubber tube attached to the measuring capillary and the benzene was gently blown into the filling tube where it was removed with the hypodermic syringe. The polymer solution was now introduced into the cell taking care to remove liquid exuding from the top of the measuring capillary. Rinsing was repeated two or three times before finally filling the cell with the solution and restoring the levelling rod, mercury seal and outer jacket cover. After allowing 30 minutes for the attainment of thermal equilibrium the measuring capillary meniscus was set (with the levelling rod) close to the level of the reference capillary meniscus. The menisci were observed (after a lapse of 12 hours to allow them almost to reach equilibrium) until the solution level was constant over a period of several hours. This constant height difference was recorded and the whole operation repeated with the next concentrated solution and so on.

The number average molecular weight of a polymer (M_2) is related to the equilibrium osmotic pressure by the following equation:-

$$\frac{\Pi}{C} = \frac{RT}{M_2} + \frac{RTd_1}{M_1 d_2^2}\left(\tfrac{1}{2} - \mu\right)c + \frac{RTd_1}{3M_1 d_2^3}c^2$$

C = concentration in grams of solute per millilitre of solution.

d_1 = density of solvent.

d_2 = density of solute.

M_1 = molecular weight of solvent.

T = absolute temperature.

R = gas constant = 82.06 c.c. atmospheres per degree per mole.

Since measurements were confined to solutions less than 0.01 gms./ml. in concentration the third term could be neglected.

Since one atmosphere = 1033.3 gm. per $cm.^2$

π in atmospheres = hd/1033.3

where h is in centimetres and d is the density of the solution

Since C in gm./ml = $C^1 d / 100$

where C^1 is measured in g/100g.

$$\left(\frac{\pi}{C}\right)_{C=0} = L \times \frac{d}{1033.3} \times \frac{100}{d} = \frac{L}{10.333}$$

Where L is the intercept or limiting osmotic head.

$$\therefore M_2 = \frac{10.333\ RT}{L}$$

$$M_2 = \frac{252,800}{L} \text{ at } 25^{\circ}C$$

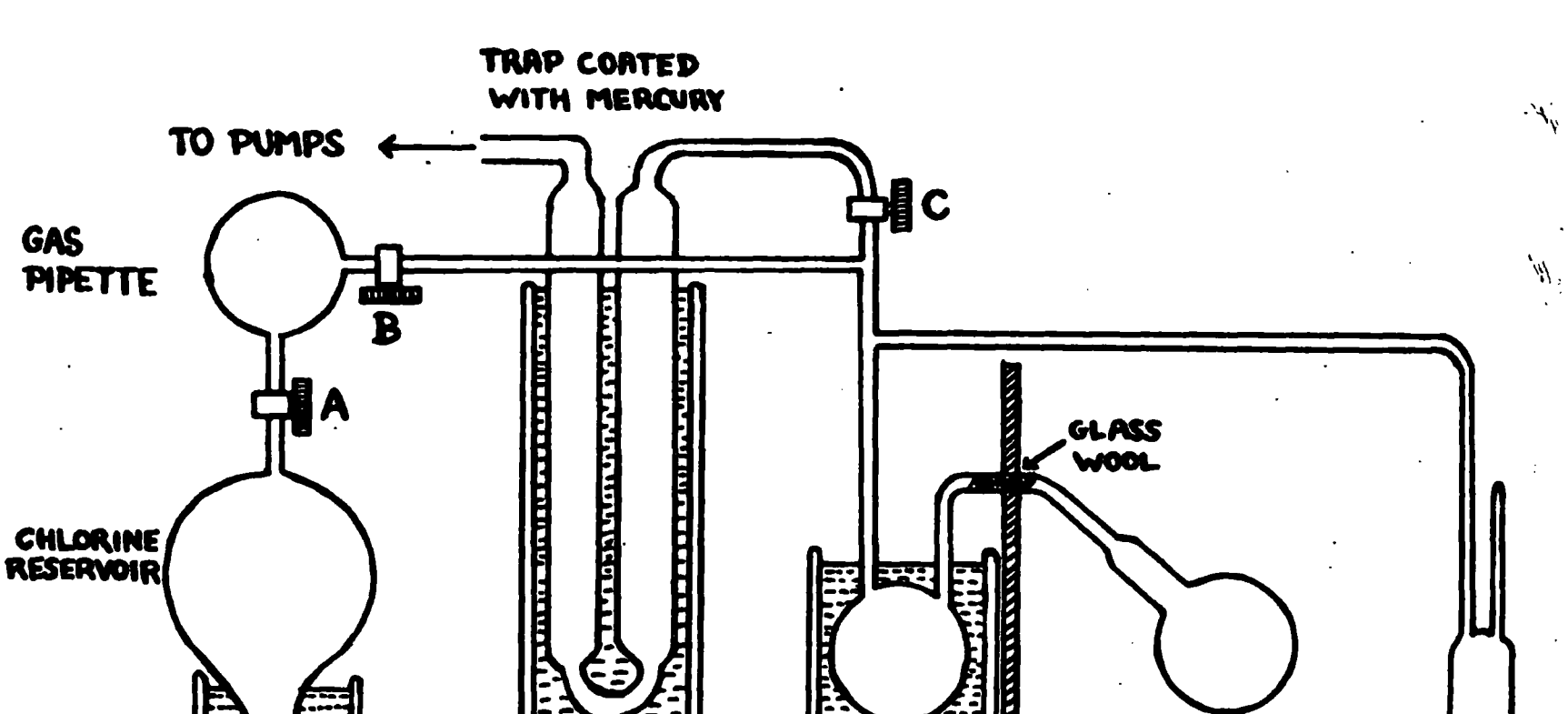
(d) Preparation of Radiochlorine

100 mg. of palladous chloride were weighed into a distilling flask which had an extended side arm at right angles

to the neck. 5 mls. of radioactive hydrochloric acid were then pipetted into the flask. The sides and neck of the flask were washed down with distilled water. The neck of the flask was then sealed by drawing it off. The flask was warmed gently in the flame of a micro bunsen to dissolve palladous chloride and then to drive off excess hydrochloric acid. This pure hydrochloric acid of reduced specific activity was collected and put aside. The drying of the palladous chloride was completed by immersion of the flask in an oil bath at 120°C for four hours. Drops of distillate which appeared on the side arm were removed with tissue paper.

When the palladous chloride was dry a plug of glass wool was inserted in the arm of the flask which was then connected to the receiving vessel on the vacuum system. The glass wool prevented spurting over of particles of elemental palladium or palladous chloride. The system was evacuated and the receiving vessel cooled in liquid air. After isolation of the system the bulb was heated with a luminous gas flame until a "palladium mirror" formed and all traces of the red palladous chloride disappeared. After completion of the reaction the bulb was removed and the chlorine was distilled into the chlorine reservoir which was then closed by means of tap A.

APPARATUS FOR HANDLING RADIOACTIVE CHLORINE.



(e) Determination of the Specific Activity of Radiochlorine

A reaction vessel was attached to the chlorinating apparatus and 10 mls. of decinormal potassium iodide solution were pipetted into it via the side arm, which was then sealed off. The reaction tube was frozen in liquid air and evacuated. Taps B and C were then closed and tap A was opened for about two minutes to fill the small bulb of the gas pipette with chlorine. Tap A was then closed, B opened and chlorine distilled into the reaction vessel. After two minutes the reaction vessel was sealed off, removed from the apparatus and placed in hot water to thaw out. Both arms of the reaction vessel were opened and the solution washed into a 50 ml. conical flask. A few drops of glacial acetic acid were added and the solution was titrated with $^{N}/_{20}$ sodium thiosulphate. Starch was used as an indicator and was added when the solution was straw coloured. From this titration the amount of chlorine delivered by the gas pipette was calculated.

The above procedure was repeated several times. Each aliquot of chlorine was absorbed in potassium iodide solution and titrated with sodium thiosulphate. The amounts of chlorine delivered by the gas pipette were calculated and by working out the ratio of each amount of chlorine to the amount which it precedes the apparatus was calibrated. This ratio was found to be 1.073 : 1.

A reaction vessel was attached to the apparatus and 1 ml. of styrene and 10 mls. of carbon tetrachloride were added by means of a hypodermic syringe. The solution was cooled in liquid air, evacuated to $< 10^{-4}$ m.m. and degassed three times. An aliquot of radiochlorine was distilled into the reaction vessel which was sealed off after two minutes and thawed out. After allowing 30 minutes for reaction to take place the reaction vessel was opened and the contents poured into a 25 ml. graduated flask. The reaction vessel was rinsed with carbon tetrachloride and the rinsings were added to the graduated flask which was then made up to the mark with carbon tetrachloride. 10 mls. of the solution were pipetted into a liquid counter and counted over 30 minutes.

This procedure was repeated several times and the ratio of the amounts of chlorine delivered by the gas pipette were calculated by comparison of the counts obtained for each aliquot of chlorine. The final result obtained was in very close agreement with that obtained using the previous method.

The specific activity of the chlorine in the reservoir was found by absorbing the first aliquot of chlorine in potassium iodide solution and finding the amount of chlorine delivered by titration with sodium thiosulphate. Knowing the ratio between successive amounts of chlorine all the amounts could be worked out. The second aliquot was absorbed in styrene in carbon

tetrachloride and thus the activity due to a known weight of chlorine was calculated. The specific activity of the chlorine was then calculated and was usually about 3,000 c.p.m. per mg. of chlorine. The first aliquot of chlorine delivered was usually 3 mg. and the fortieth about 0.2 mg.

(f) Reaction of Radiochlorine with Polymer

Benzene is a good solvent for these polymers, but it was ruled out, since it reacts easily with chlorine; so also does acetone. It was thought that chloroform might be a suitable solvent and so it was tested by absorbing 0.6 mg. of radiochlorine in 10 mls. of chloroform in a reaction vessel. The tube was left in a cupboard for two days and then excess chlorine was removed by washing the chloroform with sodium thiosulphate solution. When the chloroform was counted using a liquid counter it had a count rate of 270 c.p.m. so that chloroform is chlorinated under the conditions of reaction. Carbon tetrachloride would appear to be the most suitable solvent since it is already fully chlorinated. It was tested in a similar manner to chloroform and gave a counting rate of only 5 c.p.m. "Analar" carbon tetrachloride was therefore used as the solvent in all chlorinations of polymer carried out.

From trial results it was decided to use a ratio of

radiochlorine : polymer of 0.785 : 100 mg. This ratio of chlorine to polymer would give a large excess in all cases and at the same time give a constant concentration of chlorine. The weights of the aliquots of chlorine were calculated and then the weight of polymer required for each aliquot could also becalculated. The weight of polymer used varied between 300 and 100 milligrams. In the cases where the weight of polymer would have fallen below 100 milligrams two or more aliquots of chlorine were used. By means of the gas pipette it was possible to deliver several aliquots of radiochlorine into the reaction vessel and still know exactly how much had been added. The appropriate weight of polymer was weighed into a 25 ml. conical flask and about 5 mls. of carbon tetrachloride added. The flask was corked and the polymer left for about two hours until it had dissolved. The polymer solution was added by means of a hypodermic syringe to the reaction vessel which was then sealed off. The reaction vessel was cooled in liquid air, evacuated to $< 10^{-4}$ m.m. and the solution degassed three times. A hair dryer was used to speed up the thawing out of the solution. The required amount of chlorine was distilled into the solution from the gas pipette. After allowing two minutes for the distillation the reaction vessel was removed from the apparatus and placed in a thermostatic bath maintained at $25 \pm 0.1^{\circ}C$ which was kept in a dark

cupboard. The reaction time was taken as having started one minute after the vessel had been placed in the thermostatic bath. When the desired reaction time had elapsed both necks of the reaction vessel were opened.

(g) Purification of Reacted Polymer

The first method tried was to shake the polymer solution with 5 mls. of decinormal sodium thiosulphate solution in a separating funnel. After ~~standing overnight~~ fifteen hours the carbon tetrachloride layer was separated off and the thiosulphate layer was washed with two lots of carbon tetrachloride which were added to the main solution. This solution was placed in the separating funnel and shaken up with 10 mls. of decinormal sodium thiosulphate. The carbon tetrachloride layer was removed and made up to 25 mls., 10 mls. of which were pipetted into a liquid counter and counted over one hour. The count was corrected for dead time and background and knowing the specific activity of the radiochlorine the amount of chlorine combining with one gram of the polymer sample was calculated. This calculated quantity of chlorine was much higher than expected.

The solution of polymer in carbon tetrachloride left after extraction with sodium thiosulphate was precipitated with methanol. The polymer was weighed after drying, dissolved in

12 mls. of carbon tetrachloride and 10 mls. were counted. The amount of chlorine combined with one gram of polymer was less than that indicated by counting of the solution after extraction with sodium thiosulphate.

The second method was to pour the polymer solution into 600 mls. of methanol which was vigorously stirred using a magnetic stirrer. The polymer precipitated in a very finely divided state initially, however, when the rate of stirring was reduced the particle size gradually increased. It was allowed to stand for one hour and then stirred up again fairly gently. If the precipitated polymer was allowed to stand in methanol overnight it was obtained in a state which was difficult to dry and remove from the filter pad. The polymer was therefore filtered immediately using a filter pad of No. 3 porosity. The polymer usually formed a dry skin which peeled easily off the filter pad. It was broken up into smaller pieces and placed in a vacuum desiccator which was evacuated with a oil pump. When dry it was weighed into a 12 ml. graduated flask which was made up to the mark with Analar carbon tetrachloride. When the polymer had dissolved, 10 mls. of the solution were pipetted into a liquid counter and counted over an hour. The count per gram of polymer and hence the amount of chlorine in milligrams per gram of polymer were calculated. The solution after counting along with

the solution left in the graduated flask was reprecipitated in methanol. The polymer was again dried, weighed, made up to 12 mls. in carbon tetrachloride and 10 mls. of solution counted. The polymer obtained had a lower specific activity than previously, but the specific activity stayed constant after several further precipitations so the results obtained from the second precipitation were used.

Counts were carried out on polymer solutions of various concentrations and in calculating the amount of chlorine combining with a gram of polymer it was assumed that concentration did not change the counting efficiency. A radioactive polymer was taken, dissolved in 12 mls. of carbon tetrachloride and 10 mls. of solution were counted. The solution was progressively diluted and counted and the activity per gram of polymer calculated in each case. There was a small random scattering of activities indicating that there were no absorption effects.

In the results given the polymers were precipitated with methanol since this method would appear to give the more reliable and reproducible results.

(h) Reaction of Monomer with Radiochlorine

The following test was carried out to see whether

chlorine gave an addition or substitution reaction with ethyl methacrylate.

A hypodermic syringe with a long needle was used to introduce 2 mls. of the monomer and about 8 mls. of carbon tetrachloride into the reaction vessel. The reaction vessel was then sealed and the solution cooled in liquid air and degassed three times. An aliquot of chlorine from the gas pipette was distilled into the reaction vessel which was sealed off after two minutes. It was allowed to stand in a cupboard for one hour and then it was opened and the contents were poured into 25 mls. of distilled water in a separating funnel. The funnel was shaken vigorously and allowed to stand until a clear cut separation was made. The solution was run off into a 12 ml. graduated flask and made up to the mark with carbon tetrachloride. 10 mls. of the solution were pipetted into a liquid counter and then counted for 30 minutes. The count from 12 mls. of the solution corrected for dead time and background was 1,717 c.p.m. The amount of chlorine added to the monomer was 0.883 mg. and this would have given a count of 3,227 c.p.m. if absorbed in styrene and carbon tetrachloride.

The activity obtained with monomer is thus half the count obtained with styrene which is known to add chlorine. In the case of the monomer half of the chlorine must have been lost in the form of hydrochloric acid. The count on 10 mls. of

water gave a count rate of 2,000 c.p.m. for the 25 mls. of water. The count would be expected to be higher than that on the monomer solution since water is less dense than carbon tetrachloride and so there is a higher counting efficiency.

Chlorine must therefore have a substitution reaction with ethyl methacrylate. It is likely, therefore, that any reaction between chlorine and unsaturated groups in polyethyl methacrylate will be by substitution, giving one chlorine atom per double bond.

(i) Counting Technique

10 ml. portions of solutions were counted in a halogen quenched liquid counter (20th Century Electronics, type M 6 H), using a Dynatron Type 200 scaling unit, along with a type 1014 Probe unit. The paralysis time on the external quenching unit was set at 500 μseconds. The counter was supported in a lead castle. The counter efficiency was checked periodically with a standard source and was found to remain constant.

The plateau of the liquid counter was obtained by plotting applied voltage against counting rate while using a standard source. It had a plateau which extended over 100 volts and all counts were taken using an applied potential of 410 volts

which lay one-third of the way along the plateau.

In each determination of polymer activity 10 mls. of polymer/carbon tetrachloride solution were counted and results corrected to 12 mls. since this was the volume in which the polymer had been dissolved. When the counter was emptied of polymer solution it was rinsed twice with carbon tetrachloride and then twice with acetone. The counter was dried by blowing a jet of compressed air into it. At the end of each day the counter was filled with chromic acid solution and left overnight. The background counting rate was taken twice each day and was always between 12 and 14 c.p.m. When radiochlorine was absorbed in styrene and the solution counted the counter was cleaned very carefully after use and the background taken after each count. When styrene was used the activity seemed to be more easily absorbed by the glass of the counter.

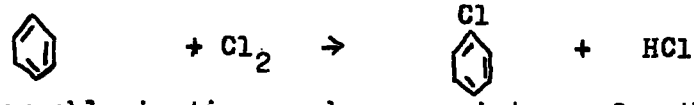
Since the liquids counted were volatile the counter had a fairly loosely fitting polythene stopper which had a small hole in it. Polythene expands when exposed to carbon tetrachloride and so the stopper quickly expanded to give a tight fit in the neck of the liquid counter.

RESULTS AND DISCUSSION

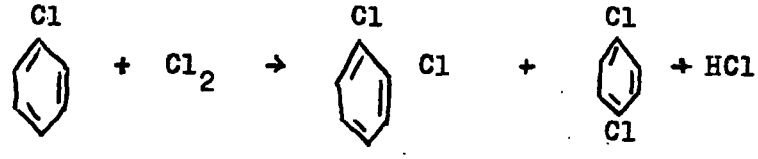
Reactions of Halogens with Compounds which contain Double Bonds

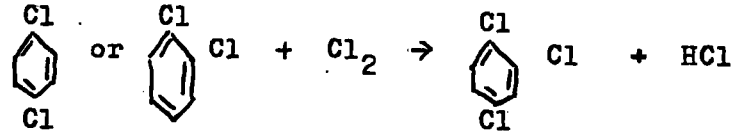
Halogens react with compounds which contain double bonds in a variety of ways and under a variety of reaction conditions.

Benzene reacts with chlorine in two different ways depending upon reaction conditions. Addition occurs if dry chlorine is passed through benzene boiling under reflux in the presence of strong light. Benzene hexachloride forms. $C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$. However, if dry chlorine is passed through benzene boiling under reflux and containing a catalyst such as iodine or iron wire, then substitution occurs.



Further chlorination produces a mixture of ortho and para dichlorobenzenes initially and finally 1, 2, 4, trichlorobenzene.





If bromine is added to ethylene (dissolved in carbon tetrachloride) in the absence of light there is little reaction. Reaction occurs when the solution is irradiated with ultra-violet light. The reaction is then thought to occur by the following mechanism:-

$$Br_2 \xrightarrow[h\upsilon]{} 2\,Br^{\bullet}$$

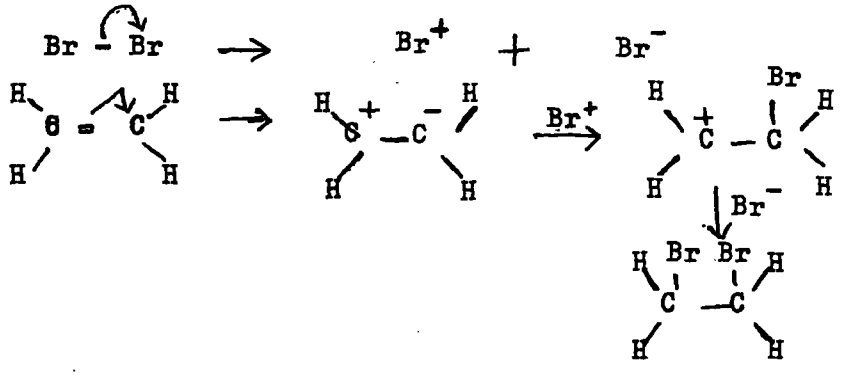
$$Br^{\bullet} + CH_2 = CH_2 \rightarrow Br - CH_2 - CH_2^{\bullet}$$

$$Br - CH_2 - CH_2^{\bullet} + Br_2 \rightarrow Br - CH_2 - Br + Br^{\bullet}$$

Chlorine gas reacts quickly with ethylene gas and ethylene dichloride is formed.

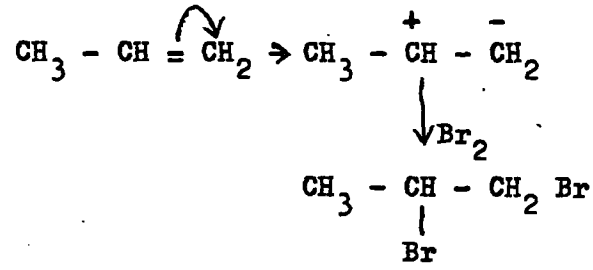
$$CH_2 = CH_2 + Cl_2 \rightarrow Cl\,CH_2 - CH_2\,Cl$$

Bromine gas would give a similar reaction. Dipoles influence the electronic arrangement in reacting molecules so that they are polarized at the time of reaction.

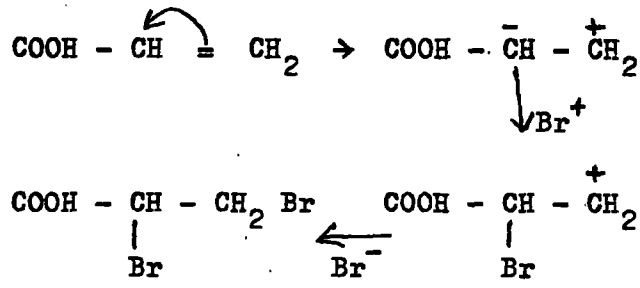


The methyl group is electron repelling and so in propylene it

exerts an inductive effect since it increases the electron density between the double bond. Bromination proceeds more quickly with propylene than it does with ethylene.



The carboxyl group is electron attracting and so in acrylic acid the electron density between the double bond is decreased. Bromination proceeds more slowly with acrylic acid than it does with ethylene.



Butadiene 1,3 has a pair of doubly bonded carbon atoms adjacent to each other. Butadiene is known as a conjugated diene, because in characteristic addition reactions the two centres of unsaturation function as a unit rather than as isolated double bonds. When butadiene is treated with bromine the first molecular equivalent of reagent is taken up so much

more rapidly than the second that a dibromide fraction is easily isolated. The 1,2 dibromide is a minor component of this fraction; the principal fraction carried bromine atoms not on adjacent carbon atoms, but at the terminal positions 1 and 4.

$$CH_2 = CH - CH = CH_2 \xrightarrow{Br_2} Br\,CH_2\,CH = CH\,CH_2\,Br$$

1.4. addition (major product)

+

$CH_2 = CH\,CH\,Br\,CH_2\,Br$

1.2. addition (minor product)

The main reaction is thus a 1,4 addition to the conjugated system and involves disappearance of both original double bonds with establishment of a new double bond at the 2,3 position.

If propylene is chlorinated at 400°C then allyl chloride is formed. The double bond adjacent to the methyl group activates a hydrogen atom in the methyl group. The high termperature chlorination of propylene with production of allyl chloride in preference to addition to the double bond, is ascribable to the activated character of the hydrogen atom that suffers replacement.

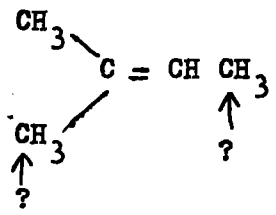
$$H_2C = C - C - \boxed{H} \rightarrow H_2C = C - C - Cl$$

Allyl Chloride

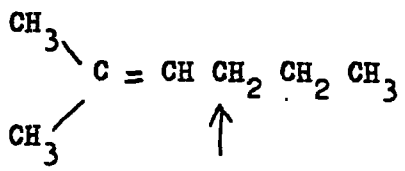
The high temperature favours dissociation of the normal addition compound.

A methylene group adjacent to a double bond is attacked more rapidly than a methyl group. The hydrocarbon (a) consumes an equivalent amount of reagent only after 16 hours whereas (b) reacts in 10 minutes.

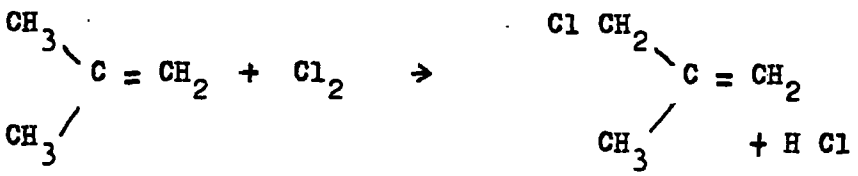
(a)



(b)



Mayer, Kuriacose and Eschard[18] showed that isobutene monomer reacts with chlorine by the reaction:-

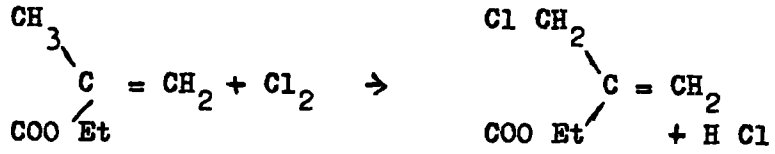


It is possible that the replaced hydrogen atom is activated by the proximity of the methyl group to the double bond.

Reaction of Chlorine with Ethyl Methacrylate

Ethyl methacrylate monomer also reacts with chlorine by a substitution reaction (See Experimental Section). The mechanism of the reaction is not known, but could be similar to

that shown for isoprene since there is a methyl group adjacent to a double bond. Assuming that a hydrogen atom in the methyl group is activated then the reaction would be:-

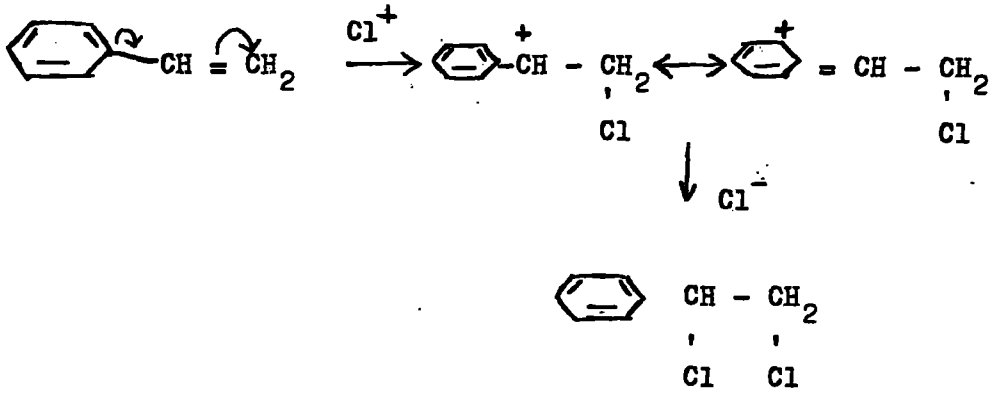


It was found experimentally that reaction between monomer and chlorine was fast. Usually an hour was allowed for reaction, but it appeared to be complete after a few minutes.

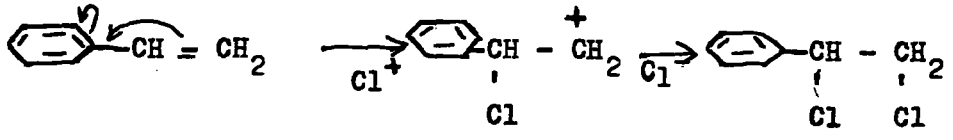
Reaction of Chlorine with Styrene

Styrene was used to absorb radiochlorine of a known weight so that the specific activity of the chlorine could be found. For this purpose it is essential that the reaction is an addition reaction and that there are no side reactions by which chlorine could be lost. If the reaction was a substitution reaction hydrogen chloride would form and could possibly be lost. It is well established that styrene has an addition reaction with chlorine and is without side reactions which could cause loss of chlorine. There are two reaction mechanisms with (a) occurring to the greater extent.

(a)



(b)



Since there are no side reactions (and therefore no loss of chlorine) and since the reaction is a fast one, the styrene is ideal for the absorption of radiochlorine during the determination of its specific activity.

Choice of Solvent

Chlorine reacts with many common solvents, particularly in the presence of air. For quantitative work on reaction of chlorine with a polymer dissolved in a solvent, the side reaction with the solvent must either be negligible, or sufficiently limited to permit a correction to be made. When radiochlorine is used, the possibility of exchange of activity between the chlorine and

a chlorinated solvent must also be examined. When samples of the pure solvents, chloroform and carbon tetrachloride were treated with known amounts of radiochlorine under similar conditions to those used in the experiments on polyethyl methacrylate solutions, and the unreacted chlorine (and hydrochloric acid produced, if any) were removed only the carbon tetrachloride showed negligible activity. Carbon tetrachloride which is a good solvent for polyethyl methacrylate was chosen for this work.

Choice of Reaction Conditions

In view of the well known tendency of chlorine to react by free radical processes in the presence of air, the exclusion of air in the reaction with polyethyl methacrylate was considered essential. Reaction mixtures were therefore thoroughly degassed to remove air, chlorine was distilled and tubes were sealed off under high vacuum. Reaction was carried out at 25°C with the exclusion of light.

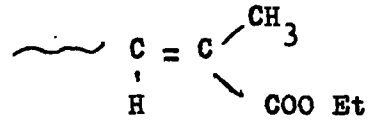
Choice of Molecular Weight Range

It would be desirable to use polymers with molecular weights which were low, in the development of the chlorination process, since greater sensitivity would be achieved. However, polymerization would be explosive at the required initiator

concentrations, and so polymers of low molecular weight cannot be produced. With polymers of high molecular weight the polymer chains are very long and the number of end groups becomes insignificant. The terminal unsaturation would become very small and it would be impossible to determine by the use of radiochlorine.

It was decided that molecular weights ranging from 150,000 to 400,000 would be suitable. The required data of initiator concentration for the production of polyethyl methacrylate samples in this molecular weight range could not be found. Data for the polymerization of methyl methacrylate was used since it was assumed that ethyl methacrylate would behave similarly during polymerization. However, transfer was found to occur during the polymerization of ethyl methacrylate and so polymers of similar molecular weight were produced despite the fact that different concentrations of initiator were used. This behaviour was not discovered immediately, and so the polymers which were studied have roughly the same molecular weight.

Reaction of Chlorine with Polymer

During the polymerization of ethyl methacrylate chain ends such as  may be formed by

disproportionation as previously explained. This structure is analagous to the structure of ethyl methacrylate which undergoes a substitution reaction with chlorine. If the termination of polyethyl methacrylate was exclusively by disproportionation then one atom of chlorine per two polymer chains would be added, (or 0.5 chlorine atoms per chain on average), assuming that reaction is similar to that of monomer.

Allen, Ayrey, Merrett and Moore[5] found that the fraction of polymer radicals terminated by disproportionation during the polymerization at 60°C of methyl methacrylate was 0.61. Thus 30% of the chain ends in methyl methacrylate might be expected to contain a double bond which could add one atom of chlorine. On average, therefore, 0.3 atoms of chlorine per chain would be expected to react with polymethyl methacrylate.

The Significance of Molecular Weight^{-1} v.s.$\sqrt{\%\ \text{initiator}}$ Plots

The plot of molecular weight^{-1} against$\sqrt{\%\ \text{initiator}}$ for polymethyl methacrylate is linear and the line passes through the origin. This indicates that mutual termination of reaction chains occurred during polymerization, that direct thermal polymerization was negligible and that transfer to initiator, solvent and monomer could be neglected. Benzene which was used as solvent during polymerization enters into chain transfer

to a comparatively small extent only. The specific reaction rate at 100°C for transfer is less than two ten-thousandths of the rate for the addition of the chain radical to methyl methacrylate monomer. A fifteen fold dilution would be required to halve the molecular weight.

The plot of molecular weight^{-1} against$\sqrt{\%\ \text{initiator}}$ for polyethyl methacrylate is linear, but it is parallel to the x axis. This shows that molecular weight is almost independent of$\sqrt{\%\ \text{initiator}}$ and is a clear indication that transfer has occurred during polymerization. This behaviour of ethyl methacrylate is very different from that of methyl methacrylate, which shows no transfer at all during polymerization.

This transfer could occur between polymer radicals and either benzene or monomer.

(a) If transfer occurred between polymer radical and monomer then end groups containing double bonds would be produced. These double bonds would be reactive to chlorine and so would be capable of being detected.

(b) Mayo[19] has suggested that an attacking radical may add to the benzene nucleus as:-

$M^{\bullet} + C_6H_6 \rightarrow$  (including resonance structures)

when more reactive benzylic hydrogensare not available. This

intermediate may then complete the chain transfer process by donating the hydrogen atom to a monomer molecule. This step is similar to direct transfer from a chain radical to a monomer,

i.e.

$$-CH_2 - \underset{\displaystyle X}{CH^{\bullet}} + CH_2 = \underset{\displaystyle X}{CH} \rightarrow -CH = CHX + CH_3 \underset{\displaystyle X}{CH^{\bullet}}$$

If this process did occur end groups containing double bonds which were reactive to chlorine would be produced.

However, benzene may act as:-

$$R(CH_2 - CHY)^{\bullet}n + SH \rightarrow R(CH_2\ CHY)n\ H + S^{\bullet}$$

in which case end groups containing double bonds would not be produced.

Calculation of Number of Chlorine Atoms per Polymer Chain

Polymer 7 - Molecular weight = 266,000

Number of monomer units in polymer chain = $\frac{266,000}{114}$

= 2,343

At zero time there is 0.04 mg. chlorine/gm. polymer.

There are $\frac{0.04}{35.5}$ mg. atoms of chlorine per $\frac{1000}{114}$ millimoles of monomer unit.

Number of chlorine atoms per unit = $\frac{0.04 \times 114}{35.5 \times 1000}$

= ~~0.00006422~~ 1.284×10^{-4}

Number of chlorine atoms per 1,000 units = ~~0.064~~ 0·128

Number of chlorine atoms per chain - 2,343 x ~~0.00006422~~ 1.284×10^{-4}.

There are 0.30 chlorine atoms per chain.

Polymer	Molecular Weight	Number of Chlorine atoms per polymer chain	
		At zero time	After 8 hours
3	219,800	0.22	0.90
7	266,100	0.30	1.26
8	258,000	0.30	1.26

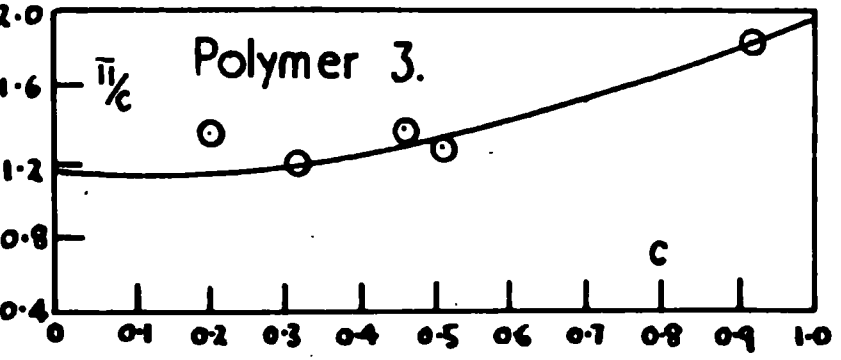
The extrapolated value of 0.30 chlorine atoms per polymer chain is significant only if the reaction of chlorine with the chain ends containing double bonds is fast; if the reaction is slow then the value is without significance. Since the reaction of monomer with chlorine is very fast, and the unsaturated structure in the polymer is closely similar, the extrapolation is regarded as valid and reasonable. The increase in chlorine content with time is attributed to a side reaction between polymer and excess chlorine. It is not practicable to use very low concentrations of chlorine in reaction with polymer. During the reaction of radiochlorine with butyl rubber[14] it was possible to work with concentrations of chlorine of the order of 0.5 to 5.0 moles per mole of double bond. However, in butyl rubbers unsaturation is about one mole per cent compared to about 0.01 mole per cent in polyethyl methacrylate. During the chlorination of polyethyl methacrylate the concentration of chlorine was of the order of

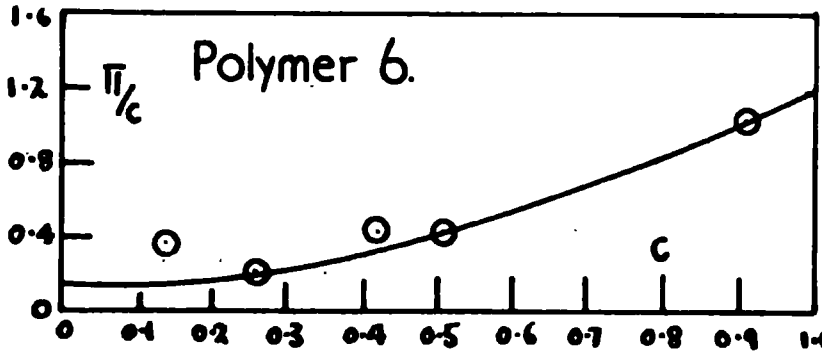
90 moles per mole of double bond. It would be difficult to handle accurately very small weights of radiochlorine and so a large amount of chlorine was available for side reactions with the polymer.

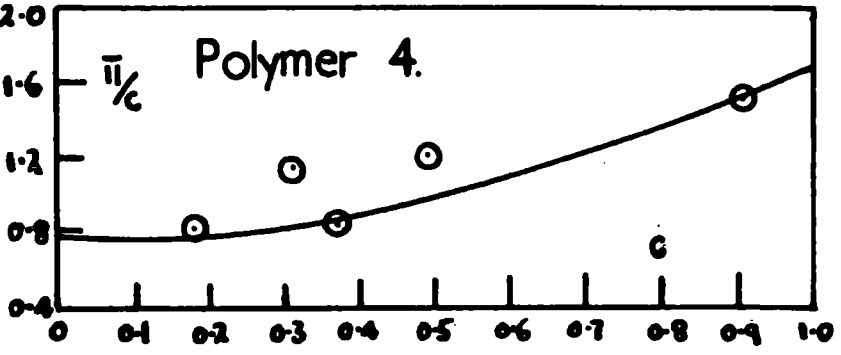
TABLE 1

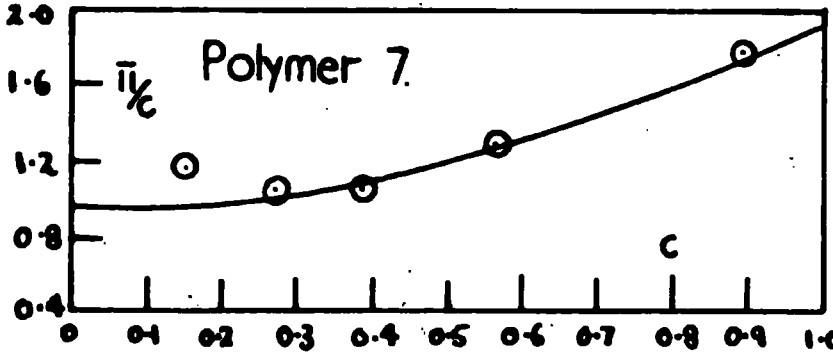
Polymer	Concentration gms. polymer/ 100 g. soln.	Osmotic pressure	Osmotic pressure/ concentration
3.	0.9075	1.6580	1.827
	0.5143	0.6555	1.275
	0.4566	0.6325	1.385
	0.3173	0.3765	1.187
	0.1988	0.2660	1.338
4.	0.9088	1.3710	1.509
	0.4951	0.6000	1.212
	0.3658	0.3125	0.854
	0.3063	0.3605	1.177
	0.1808	0.1485	0.821
5.	0.9369	1.1070	1.181
	0.5531	0.5920	1.070
	0.3987	0.4735	1.188
	0.2800	0.3030	1.082
	0.1363	0.1570	1.152
6.	0.9123	0.9370	1.027
	0.5134	0.2253	0.435
	0.4194	0.1895	0.452
	0.2627	0.0590	0.225
	0.1381	0.0540	0.391
7.	0.8953	1.5955	1.782
	0.5639	0.7325	1.299
	0.3930	0.4270	1.086
	0.2698	0.2850	1.057
	0.1500	0.1750	1.167
8.	0.9325	1.5450	1.657
	0.5266	0.6415	1.218
	0.4169	0.4590	1.101
	0.2815	0.3200	1.137

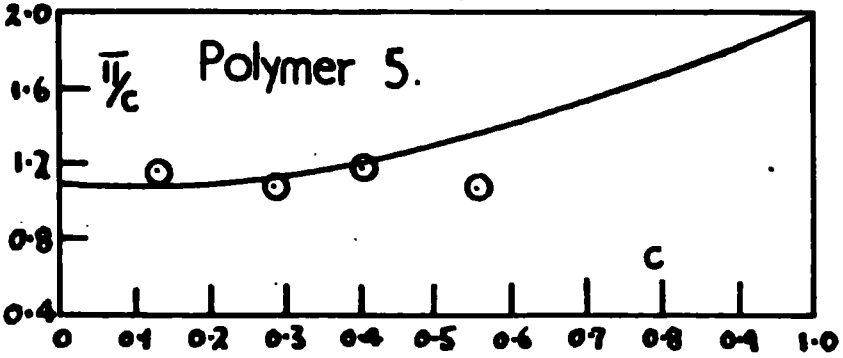
π/c vs. C PLOTS FOR POLYETHYL METHACRYLATE SAMPLES.











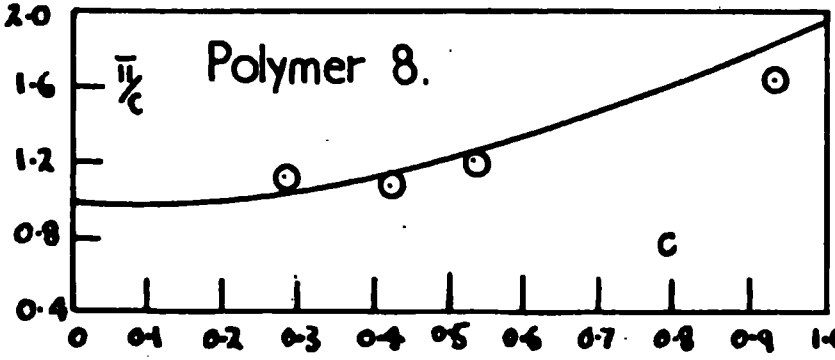
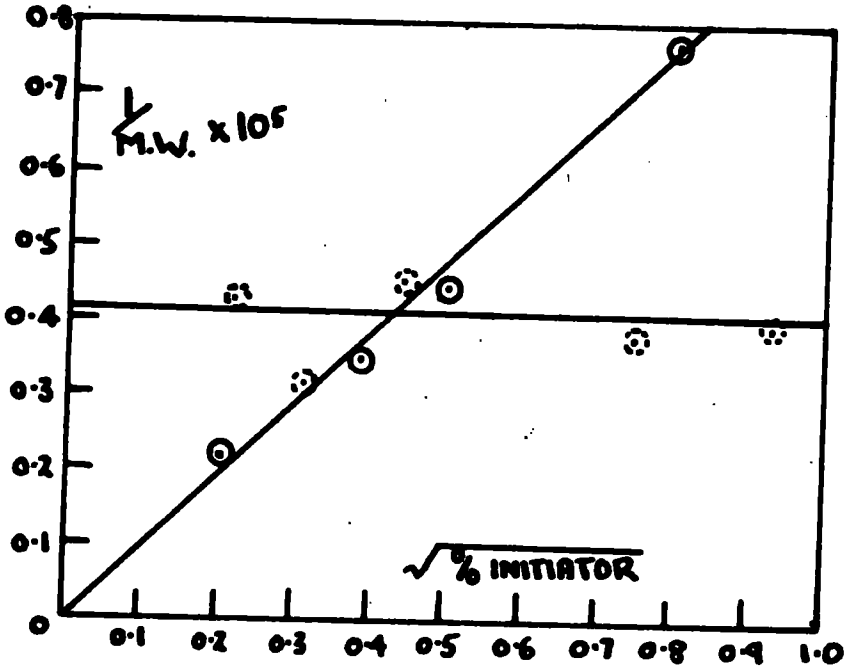


TABLE 2

Polmer	(Limiting) L(Osmotic Head)	Molecular Weight
3	1.15	219,800
4	0.79	320,100
5	1.08	235,000
6	0.14	1,806,000
7	0.95	266,000
8	0.98	258,000



Plot of $\sqrt{\%\text{Initiator}}$ vs. $\frac{1}{\text{MW}} \times 10^5$ for

Polymethyl methacrylate ⊙

and

Polyethyl methacrylate ⊙

Plot of $\sqrt{\%\text{Initiator}}$ vs $\frac{1}{\text{Time of Polymerization}} \times 10^3$ of Ethyl methacrylate

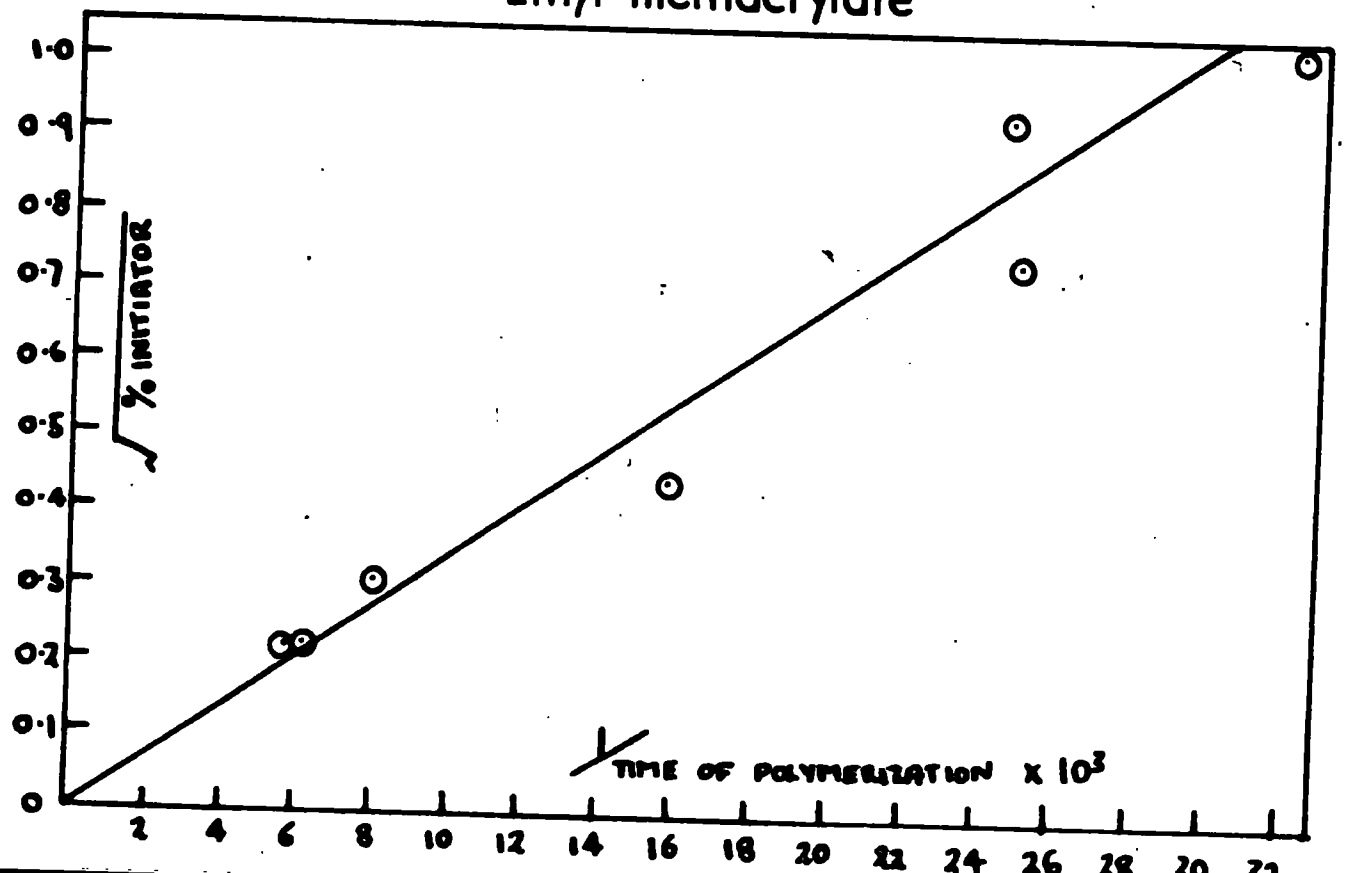


TABLE 3

POLYETHYL METHACRYLATE

Polymer	% Initiator (W/V)	$\sqrt{\%\ \text{Initiator}}$	Time (mins.) for 10% Polymerisation	Molecular weight	$1/M.W. \times 10^5$
1	1.044	1.025	29	--	--
2	0.537	0.733	40	--	--
3	0.199	0.466	63	219,800	0.455
4	0.098	0.314	124	320,100	0.313
5	0.050	0.224	173	235,000	0.425
6	0.051	0.227	163	1,806,000	0.560
7	0.549	0.741	50	266,100	0.376
8	0.871	0.933	41	258,000	0.388

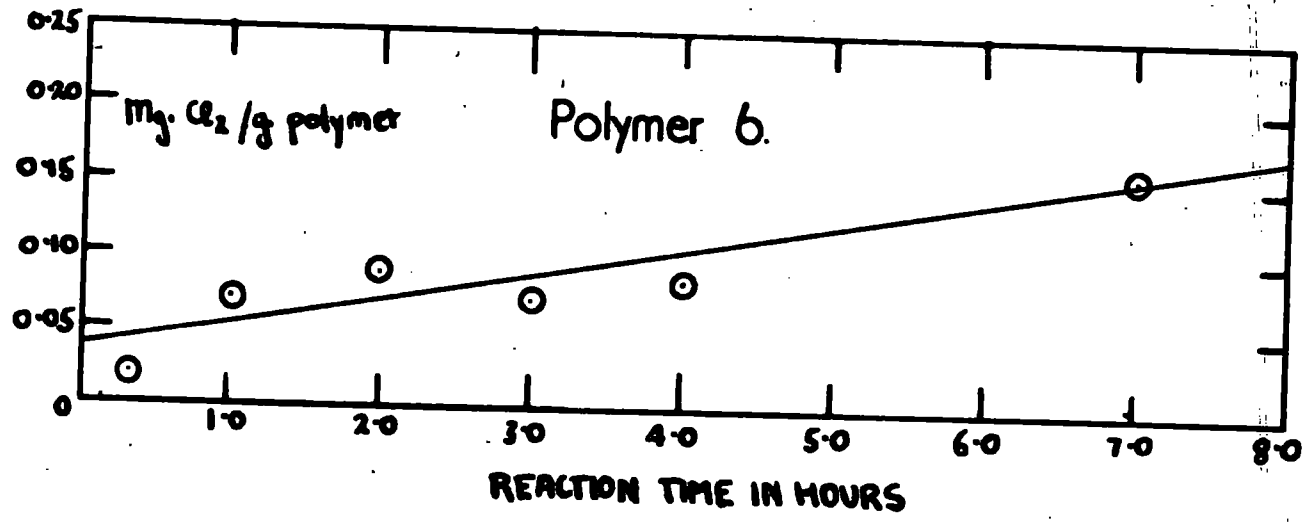
POLYMETHYL METHACRYLATE

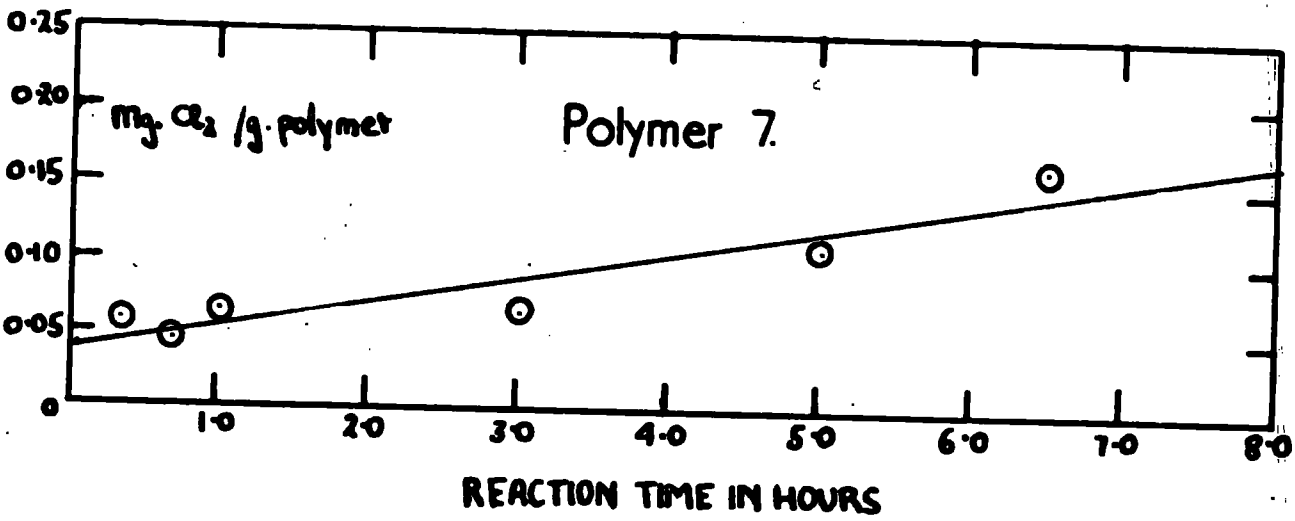
Molecular weight	$\sqrt{\%\ \text{Initiator}}$	$1/M.W. \times 10^5$
476,200	0.20	0.210
281,700	0.39	0.355
225,700	0.50	0.443
130,900	0.81	0.764

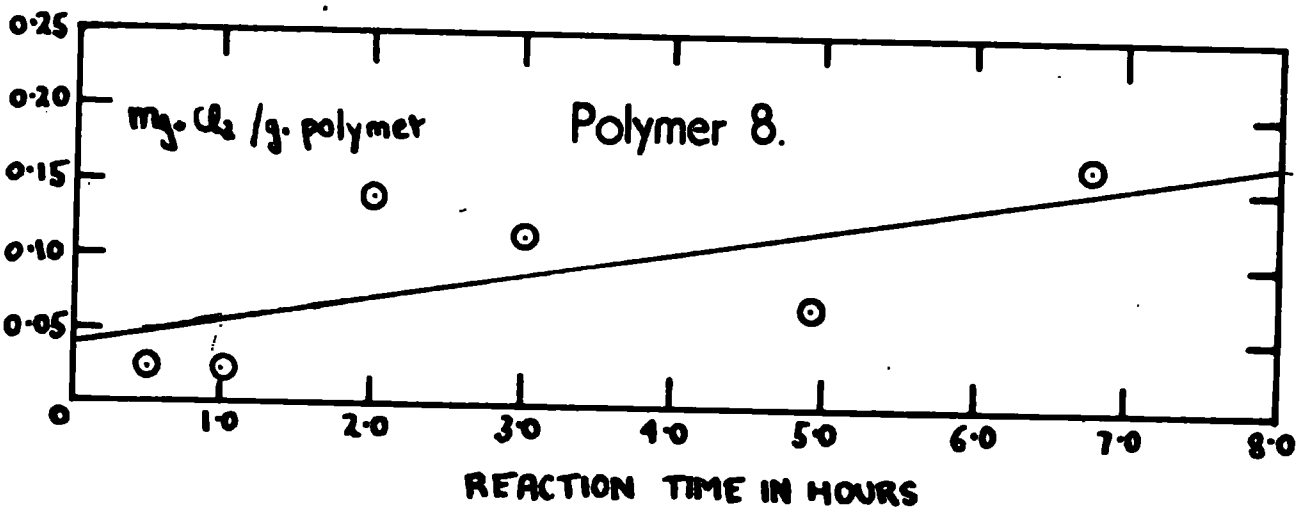
TABLE 4

Polymer	Reaction time	Weight (m.g.) of Polymer counted	Count per Minute	C.p.m. of gram of Polymer	Amount of Chlorine m.g. per gram of Polymer
3	1 hour	67.8	12.3	180.6	0.060
	2 hrs. 40 mins.	82.6	13.8	200.5	0.072
	6 hours	75.4	17.8	264.3	0.095
	7 hours	50.9	16.7	393.7	0.141
	16hrs. 35 mins.	37.0	23.7	768.6	0.276
6	20 mins.	167.8	15.4	71.5	0.019
	1 hour	217.4	48.2	266	0.073
	2 hrs. 2 mins.	250.6	69.5	332.8	0.091
	3 hours	133.8	30.3	271.7	0.074
	4 hours	145.2	53.5	328.9	0.090
	7 hours	268.9	123.5	551.1	0.151
7	20 mins.	145.1	25.4	210.0	0.057
	41 mins.	92.7	13.5	174.8	0.048
	1 hour	117.2	23.4	239.5	0.066
	3 hours	109.3	22.4	246.0	0.067
	5 hours	125.6	41.4	395.5	0.108
	6 hrs. 30 mins.	148.3	74.1	599.3	0.164
8	30 mins.	114.1	9.5	99.9	0.027
	1 hour	50.4	4	95.2	0.026
	2 hours	78.2	34.2	524.6	0.144
	3 hrs. 1 min.	96.7	34.2	424.4	0.116
	4 hrs. 52 mins.	126.1	27.3	259.8	0.071
	6 hrs. 44 mins.	61.0	30.6	601.9	0.165

Plots of Reaction Time vs. mg. Chlorine per gm. Polymer







Plot of Reaction Time vs. mg. Chlorine per gm. Polymer

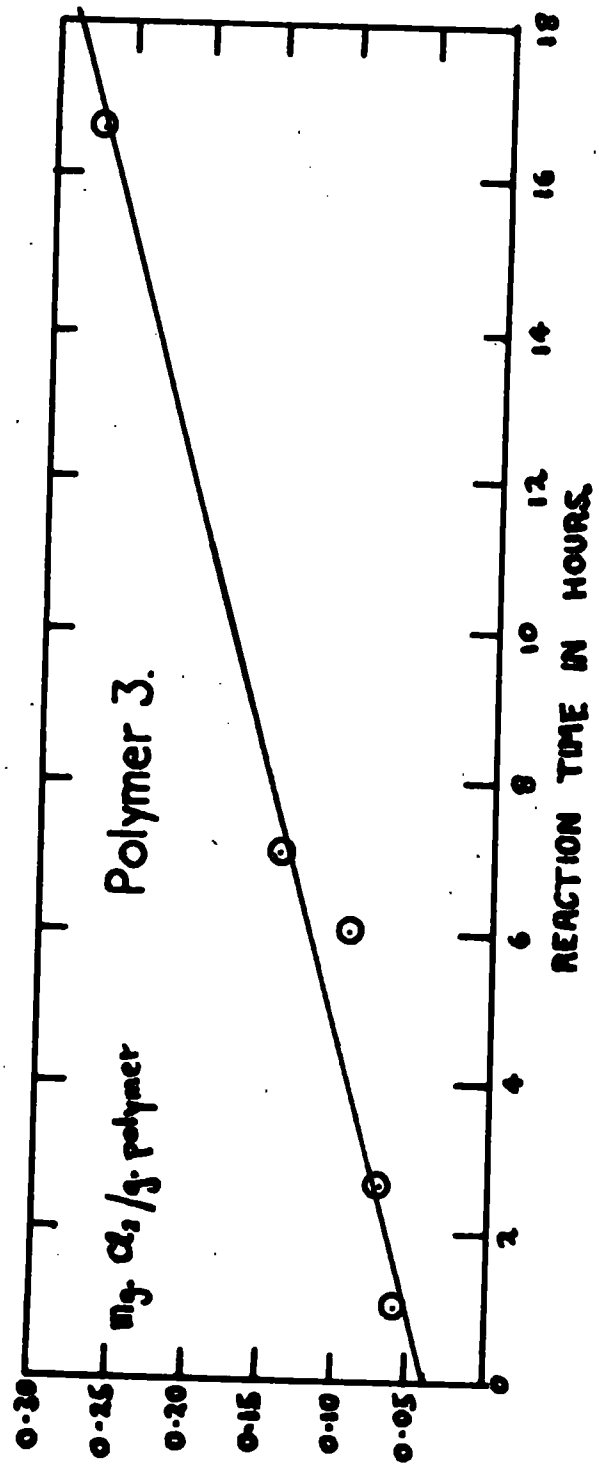


TABLE 5

Polymer	Molecular Weight	a (Intercept)	b (Slope)
3	219,800	0.034	0.014
6	1,806,000	0.037	0.016
7	266,100	0.040	0.016
8	258,000	0.041	0.016

These results were calculated using the formulae:-

$$a = \frac{\sum xi^2 \sum y - \sum xi \sum xi\, yi}{n\, xi^2 - (xi)^2}$$

$$b = \frac{n \sum xi\ yi - \sum xi \sum yi}{n \sum xi^2 - (\sum xi)^2}$$

The values of x and y are taken from Table No. 4.

TABLE 6

CALIBRATION OF THE RADIOCHLORINE GAS PIPETTE

Operation No.	Thiosulphate Titre (mls.)	Counts per Minute	Ratio of Amounts of Chlorine
1	1.05	—	1.071
2	0.98	—	1.089
3	0.90	—	1.059
4	0.85	—	—
A		1,274	1.084
B		1,149	1.074
C		1,070	1.062
D		1,008	—

Average ratio from titration = 1.073

Average ratio found radiochemically = 1.0734

Ratio used = 1.073

CONCLUSIONS

The experimental results show that polyethyl methacrylate contains 0.30 double bonds per polymer chain when polymerised in 50% solution of benzene at 60°C. Under the same conditions the methyl ester gives a polymer of similar unsaturation. The mechanism of chain termination is quite different, however, in the two cases. Some explanation of the result is therefore required. There are several possibilities.

(1) The polymer contains a small amount of impurity, capable of reacting with chlorine, copolymerised in the chain. If this were the true situation, then it must also be assumed that termination of all chains is by solvent transfer in such a way as to give no unsaturated ends.

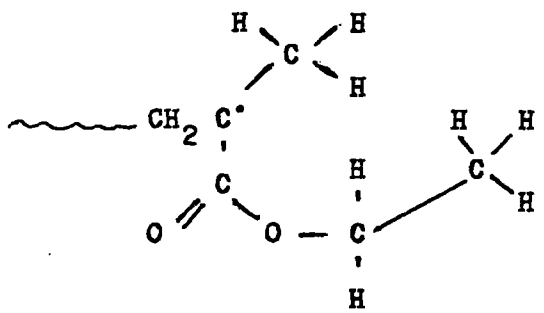
(2) Termination is partly by transfer to monomer giving unsaturated ends, and partly by transfer to solvent, giving saturated ends.

(3) Termination is entirely by transfer to solvent, but this occurs by two mechanisms, as previously considered, only one of which results in double bonds at chain ends. Since only 30% of chain ends react with chlorine, the normally accepted type of solvent transfer reaction:-

$$R(CH_2- CHY)n^{\bullet} + SH \rightarrow R(CH_2 - CHY)n\ H + S^{\bullet}$$

must be assumed to predominate.

It has been clearly established by the experiments described that termination occurs by transfer, but there is insufficient evidence to account for the observed unsaturation in an unambiguous manner. Although the unsaturation agrees exactly with that of the methyl ester, this result is regarded as fortuitous in view of the different termination process involved. The fact that these two polymerisations show quite different termination processes, although the monomers are structurally very similar, can be explained. The reactive radical centre is the ethyl ester



is shielded from attack by a similar radical by the bulky ethyl groups. Termination by combination or disproportionation requires both radical centres to approach closely, which would be difficult. The smaller solvent or monomer molecules can, however, approach the radical centre more readily.

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David B. Mounter.

7th. December 1962.