Thermal Degradation of Polyacrylates

Thesis for Degree of Doctor of Philosophy

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Thermal Degradation of Polyacrylates

Summary of Ph.D. Thesis.

John G. Speakman

As an introduction to the degradation of polyacrylates, the degradation reactions of other vinyl polymers are broadly classified and degradation mechanisms occurring in related polymer systems are discussed. Detailed degradation studies of poly(methyl acrylate), poly(t-butyl acrylate) and poly(benzyl acrylate) have already been carried out and the results of these are mentioned.

Monomer and polymer sample preparation and experimental apparatus used to degrade the polymers and to analyse the degradation products are described. Five polymers were studied: poly(ethyl acrylate), poly(n-propyl acrylate), poly(iso-propyl acrylate), poly(n-butyl acrylate) and poly(2-ethyl hexyl acrylate).

Qualitative studies of the degradation of the polymers were made using the dynamic molecular still. The major products were analysed and found to be alcohol, olefin, carbon dioxide and short chain fragments from the poly(primary acrylates) and olefin and carbon dioxide alone from poly(iso-propyl acrylate). Insolubility was found to develop in all the polymers except poly(2-ethyl hexyl acrylate). Thermal volatilisation analysis and thermogravimetric analysis of the five polymers showed that the thermal stabilities

of the poly(primary acrylates) are a little lower than that of poly(methyl acrylate). Poly(iso-propyl acrylate) is less stable than the poly(primary acrylates), but more stable than poly(t-butyl acrylate).

A thorough quantitative examination of the degradation products from the poly(primary acrylates) at 315°C was carried out. At early stages of degradation, carbon dioxide and olefin are evolved with a molar ratio close to unity. After about 35% conversion, carbon dioxide production begins to exceed that of olefin. Alcohol production appears to be slightly autocatalytic in character. Cross-linking also appears to develop slowly at early stages of degradation and more rapidly as degradation proceeds. As the size of the alkyl group of the ester increases, the ratio of short chain fragments to ester decomposition products increases, whereas the rate of cross-linking decreases.

Poly(iso-propyl acrylate) gives quantitative yields of olefin and 60% of the theoretical yield of carbon dioxide when heated for long periods at 265°C. The infrared spectrum of the residue shows that anhydride peaks develop on degradation and small amounts of water, corresponding to anhydride production, are found among the degradation products. The residue rapidly becomes insoluble, probably because of intermolecular anhydride linkages.

Infrared studies of the residues from the degradation of some poly(primary acrylates) were carried out. They provided evidence to support suggested mechanisms for degradation product evolution.

A brief investigation of two polymers at lower degradation temperatures is described. Poly(n-butyl acrylate) was studied at 241°C and poly(iso-propyl acrylate), at 195°C.

The overall characteristics of the degradation mechanisms are discussed. The poly(primary acrylates) are thought to degrade by a radical mechanism and all the major degradation reactions have a common initiator, radical I

I

Various reaction mechanisms for the observed major and minor degradation reactions are suggested. Many of these are similar to mechanisms proposed by other authors, but some are original. The evidence for these mechanisms is discussed. Suggestions are made as to further work which may help to prove and relate the various degradation mechanisms occurring in the polyacrylates.

Preface

The work described in this thesis was carried out between October 1965 and May 1969 in the Chemistry Department of Glasgow University under the direction of Professor J.M.Robertson C.B.E.,F.R.S..

I would like to thank my supervisor, Dr N.Grassie, for his advice and encouragement throughout this period of study. Thanks are due also to Mr G.McCulloch and other members of the technical staff, who carried out the routine analyses, and to all those who have helped me, especially other research workers in the Polymer Group. Dr A. Baker and Mrs F.Lawrie have given me generous help in the interpretation of infrared spectra and in other aspects of infrared investigations.

During the first sixteen months of the period of research, I received a grant from the Science Research Council.

The portion of the work concerned with poly(2-ethyl hexyl acrylate) was carried out with T.I.Davies and is also described in his Thesis for the degree of B.Sc. (Glasgow, 1969). Otherwise all the work has been performed by myself.

John G. Speakman

Glasgow 17th May 1969

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Chapter 1 Introduction

1(i) The Title

Thermal degradation studies of five acrylate homopolymers, namely, poly(ethyl-),(n-propyl-),(iso-propyl-),(n-butyl-) and (2-ethyl hexyl acrylates) are described in this thesis. The studies were carried out isothermally under high vacuum conditions. Previous work, carried out under the same conditions, on poly (methyl-)[1,2,3],(benzyl-)[1] and (t-butyl acrylates)[4] is also discussed and compared.

The processes described as 'thermal degradation' in the title and throughout the thesis are those resulting from the heating of a sample of the polymer at temperatures above ambient until chemical reaction is observed at a conveniently measurable rate. Chemical reaction may manifest itself by elimination of volatile material or change in molecular weight.

1(ii) Degradation of Polymers

Degradation of polymers can be brought about by a large number of agencies. In the natural 'weathering' of polymeric material, ultraviolet and visible radiation, combined with oxidation by atmospheric oxygen, play a large part. If the material is subjected to mechanical stress or increase in temperature, then mechanical or thermal degradation may also occur. These four agencies, radiation, oxidising agents, mechanical stress and heat most commonly cause deterioration in polymer properties, and the interest in polymer degradation stems from the need to prevent or retard the chemical processes which they induce. All of these degradation processes are very complex, but the study of thermally-induced degradation processes appears to present fewest difficulties and has been given most attention.

Polymer degradation should not be thought of entirely in a negative sense, however. It can be used as a method of recovering monomer, for example methyl methacrylate, and it is important in such cases to find the optimum conditions for efficient reaction. Another positive application of thermal degradation lies in the preparation of carbon fibres by heating polyacrylonitrile fibres to temperatures above 1500°C in an inert atmosphere.

There have been two recent monographs covering polymer degradation in general[5,6], and four dealing with the narrower fields, relevant to this thesis, of degradation of vinyl polymers[7], and thermal degradation of polymers[8,9,10].

1(iii) Thermal Degradation of Vinyl Polymers

Polymer degradation studies can be traced back to the work of Williams[11], who showed that isoprene is produced in significant yield on heating natural rubber. This and similar experiments indicated that polymers are made up in some way of units of low molecular weight material. The relationship between monomer and polymer was first demonstrated by Staudinger and coworkers in their classic work on polystyrene[12], which they used as a model for natural rubber. Among Staudinger's work is to be found one of the earliest examples of another use of polymer degradation: to provide information on the structure of the polymer chain. In this case[13], he showed that polystyrene consists of monomer units linked mainly in a head to tail fashion. About this time, also, there appeared many papers devoted to theoretical descriptions of polymer degradation, for example, those by Kuhn[14] and Simha[15].

Because of the many competing reactions in most degrading polymer systems, it was not possible to make a great deal of progress in the understanding of degradation processes until more sophisticated techniques for analysing the reaction products gradually became available in the post-war years. It is now possible to subdivide thermal degradation reactions of vinyl polymers into four types. Generally, more than one type of degradation will be found in any polymer system, but, as shown below, there are systems which exemplify each type almost exclusively.

Process	Typical Polymer
A. Random Scission	Polyethylene
B. Unzipping to Monomer	Poly(methyl methacrylate)
C. Side Group Rearrangement	Polyacrylonitrile
D. Side Group Elimination	Poly(vinyl acetate)

A. Random Scission

Montroll and Simha[16] assumed that since there is a regular, repeated pattern of bond strengths throughout the polymer chain, rupture is likely to occur at random. This would produce, as volatile material, a continuous spectrum of short chain fragments similar to, but of much lower molecular weight than, the original polymer. The upper limit of molecular weight of this material would be the molecular weight of the largest molecules which could distill over from the hot degradation zone.

The first studies of thermal degradation of polyethylene[17] showed that the degradation products are, indeed, a continuous spectrum of hydrocarbon fragments, as predicted by this theory. However, in later work[18], it became evident that there were some discrepancies from the theory. According to Simha and Montroll's theory, the rate of bond scission should remain constant throughout the degradation, but Oakes and Richards found that it decreased with time. This discrepancy was explained by the suggestion that there were some weak-links in the polymer chain. It is thought to be extremely difficult to remove the last traces of oxygen from monomers containing carbon-carbon double bonds, and the oxygen becomes copolymerised into the polymer chain. This produces some weak links in the neighbourhood of the oxygen atoms which break preferentially to the normal carbon-carbon bonds. Similar weak-links have been suggested for other polymer systems[19,20].

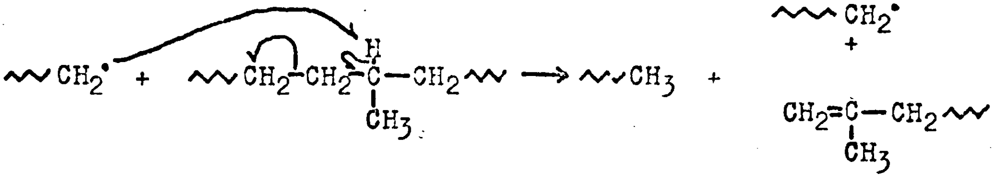
Oakes and Richards observed a second discrepancy from the theoretical picture: their polyethylene samples degraded at a much lower temperature than model compounds such as n-hexadecane. This was explained by branching in the polymer chain of these polyethylene samples, which had been prepared under high pressure conditions. Tertiary hydrogen atoms are thus produced and they are particularly liable to radical attack[21]. Thus branched polyethylene is much less thermally stable than straight-chain paraffins. More recently, it has been shown[22] that polyethylene prepared with a Ziegler-Natta type catalyst, which gives an unbranched polymer chain, is stable to much higher temperatures than branched polyethylene.

A reaction scheme for the thermal degradation of branched polyethylene is as follows:

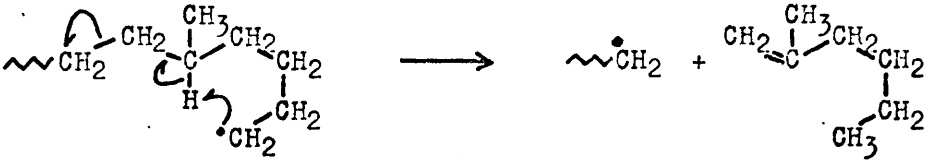
1. Initiation by scission at weak links:

$$M \longrightarrow R^{\bullet} + R^{\bullet}$$

2. Propagation by Intermolecular Transfer



or 3. Propagation by Intramolecular Transfer.



4. Termination by collision of two 'live' radicals.

Fig 1.1

Random Chain Scission in Polyethylene by Inter- and Intramolecular Transfer

B. Unzipping to Monomer

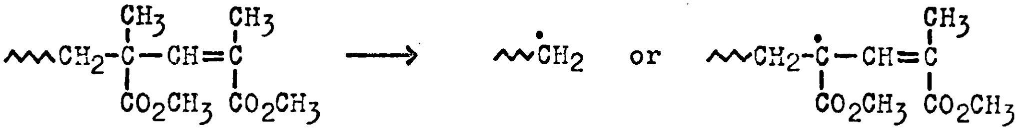
In some of the earliest studies of common homopolymers, for example, polystyrene and polyisoprene, there was found to be a large amount of monomer among the degradation products. Simha[15] explained this by suggesting that degradation occurs preferentially from chain ends. This would mean that the molecular weight would fall linearly with monomer production.

Grassie and Melville[23] supplied experimental evidence to test Simha's theory in the case of poly(methyl methacrylate), which was known to produce large yields of monomer on degradation. The agreement was unsatisfactory, especially in the case of low molecular weight polymer, which retains its original molecular weight even after 60 % of the sample has degraded to monomer. Grassie and Melville supplied a theoretical explanation by suggesting that a chain reaction occurs, the reverse of polymerisation, by bond scission to form radicals at the chain ends, followed by a rapid unzipping, the kinetic chain length of which is sufficient to destroy completely polymer molecules of molecular weight less than 100,000.

Further work by these authors substantiated this theory by showing that a radical inhibitor retards the chain reaction[24], and that a small amount of acrylonitrile copolymerised with methyl methacrylate prevents unzipping proceeding through acrylonitrile units[25], resulting in a quite different type of degradation. Grassie and Vance[26] showed that the unstable chain ends are those with a double bond. Termination in the free radical polymerisation of poly(methyl methacrylate) has been shown to be by disproportionation, so that exactly half of the polymer chains have a double bond at one end.

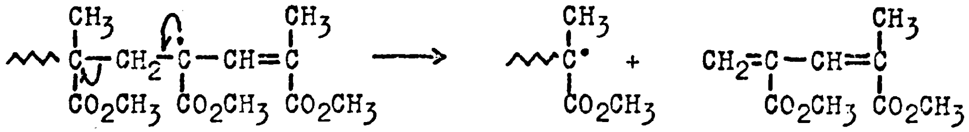
The thermal degradation of poly(methyl methacrylate) can be summarised by the following reaction scheme:

1. Initiation (slow)



$$\sim CH_2-\underset{CO_2CH_3}{\overset{CH_3}{C}}-CH=\underset{CO_2CH_3}{\overset{CH_3}{C}} \longrightarrow \sim\dot{C}H_2 \quad \text{or} \quad \sim CH_2-\underset{CO_2CH_3}{\dot{C}}-CH=\underset{CO_2CH_3}{\overset{CH_3}{C}}$$

2. Propagation (fast)



$$\sim\underset{CO_2CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CO_2CH_3}{\dot{C}}-CH=\underset{CO_2CH_3}{\overset{CH_3}{C}} \longrightarrow \sim\underset{CO_2CH_3}{\overset{CH_3}{C}}\cdot + CH_2=\underset{CO_2CH_3}{C}-CH=\underset{CO_2CH_3}{\overset{CH_3}{C}}$$

Thereafter monomer is produced by a similar process.

Fig 1.2

Depropagation of Poly(Methyl Methacrylate)

The termination step, by combination of or disproportion between two radicals, appears to come on average after production of 1000 monomer units. If the molecular weight is lower than 100,000, then most of the polymer molecules will degrade completely to monomer before termination occurs, and little change in the molecular weight of the residual polymer will be observed. Molecules terminated at one end by a catalyst residue and at the other by a saturated chain end degrade at a rather higher temperature by random chain scission followed by rapid unzipping as before.

These results were treated mathematically with some success by Simha, Wall and Blatz[27]. Madorsky[28], using a different type of apparatus, obtained results in good agreement with those of Grassie and Melville, and also showed that there may be weak links in poly(methyl methacrylate) prepared with a free-radical catalyst.

Other polymers which behave in a similar manner to poly(methyl methacrylate) are poly(α-methyl styrene)[29], and polytetrafluoroethylene[30,31]. The poly(α-methyl styrene) samples investigated were prepared ionically. Hence they had no unsaturated chain ends and the depropagation reaction was initiated by random scission.

Polystyrene also produces considerable amounts of monomer on degradation, but this is accompanied by smaller amounts of dimer, trimer and tetramer[13]. Thus a propagation step involving intramolecular transfer (fig 1.1) competes with the monomer producing depropagation step (fig 1.2).

Depolymerisation reactions can be seen to depend on the polymer structure. Generally, these reactions are initiated by the formation of polymer radicals. In the case of polymers formed from 1:1 disubstituted monomers, the polymer radicals are stabilised by the steric effects of large groups on either side of the active carbon atom and often by the inductive effect of an alkyl substituent or the resonance effect of a conjugated substituent. The stabilised radical can very easily move down the polymer chain, producing monomer molecules as it does so. Polymers formed from singly substituted monomers, however, give radicals which have much less stabilisation and they rapidly react either to return to the original polymer molecule or to produce inter- or intramolecular chain transfer.

As mentioned on page 5, a tertiary hydrogen atom is abstracted from a polymer chain by a radical more readily than a secondary hydrogen atom. Polymers from 1:1 disubstituted monomers have only secondary hydrogen atoms on the polymer chain, whereas polymers from singly substituted monomers have one tertiary hydrogen atom per monomer unit. Since abstraction of a hydrogen atom from a polymer chain is an integral part of the chain transfer reactions (fig 1.1), polymers from singly substituted monomers are much more liable to these reactions than those from 1:1 disubstituted monomers.

C. Side Group Rearrangement

Heat induces a rearrangement in the chemical structure of some polymers without simultaneous evolution of volatile material. Polymethacrylonitrile and polyacrylonitrile develope intense coloration when heated under vacuum below 200°C. The exact temperature at which coloration sets in depends on the conditions of polymerisation[32]. Burlant and Parsons[33] proposed that a rearrangement of the nitrile groups occurs to form a conjugated carbon nitrogen system. This would explain the coloration. Grassie and McNeill[34] suggested that the coloration process is ionic in nature and is initiated by small amounts of hydrolysed nitrile units in the polymer.

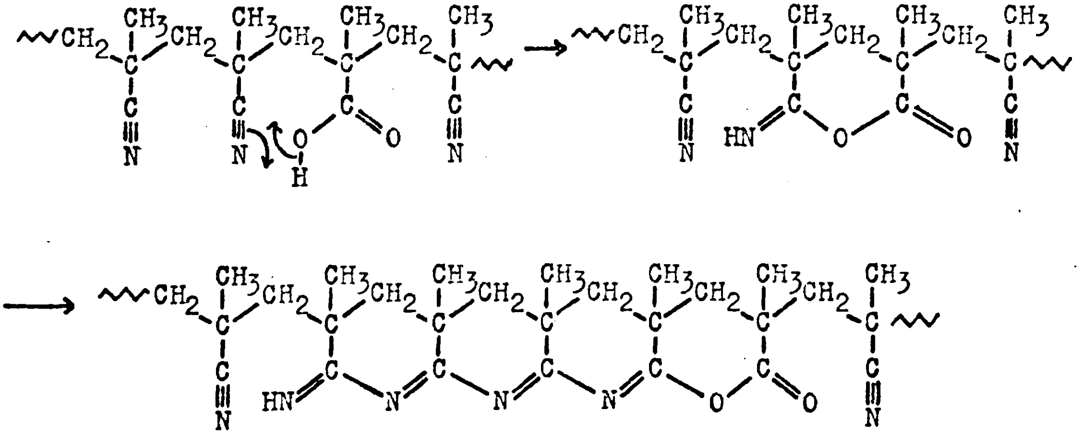


Fig 1.3

Coloration Reaction in Polymethacrylonitrile

Interchain linking may occur during this coloration process[35], causing the insolubility observed particularly in degraded polyacrylonitrile.

D. Side Group Elimination

The thermal decomposition of alkyl esters with a hydrogen atom on the β-carbon of the alkyl group occurs by a cyclic mechanism to yield an acid and an olefin[36,37,38].

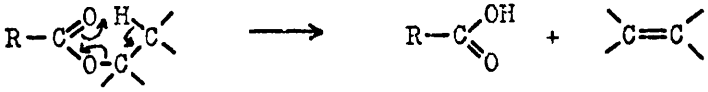


Fig 1.4

Thermal Decomposition of Alkyl Esters with a Hydrogen Atom on the β-Carbon of the Alkyl Group

The ease with which the reaction occurs depends on the number of β-hydrogen atoms and on the inductive effects of substituents on the alkyl group - that is, on the availability of the β-hydrogen atoms on the alkyl group[37,38].

Poly(vinyl acetate) was found[39] to degrade by this mechanism above 190°C, to yield acetic acid and polyacetylene. Once one double bond is formed in the polymer chain, it weakens the bond in the next ester group between the β-carbon and hydrogen atoms, so that a molecular chain reaction is produced.

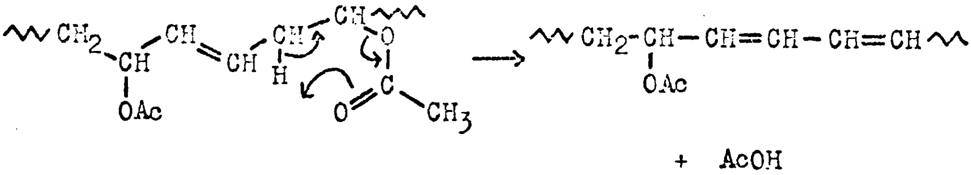


Fig 1.5

Elimination of Acetic Acid from Poly(Vinyl Acetate)

Poly(vinyl chloride) gives degradation products analogous to those of poly(vinyl acetate), that is, hydrogen chloride and polyacetylene, in a chain reaction. However, a similar mechanism is not possible and Arlman[40] proposed that elimination of hydrogen chloride takes place by a radical process, initiated near unsaturated groups at chain ends.

A partial side-group elimination reaction of considerable relevance to the present work is the elimination of water from poly(methacrylic acid). Grant and Grassie[41] studied this reaction at 200°C.

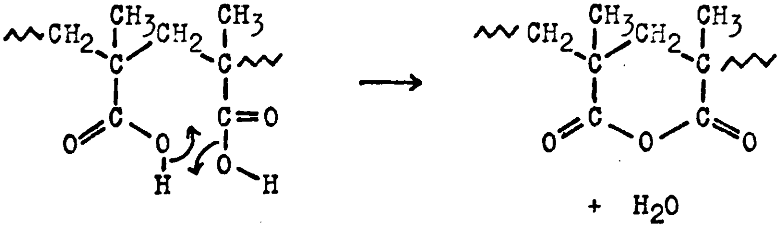


Fig 1.6

Elimination of Water from Poly(Methacrylic Acid)

The acid groups combine in pairs along the polymer chain.

Insolubility was observed and explained by cross-linking through some intermolecular anhydride formation.

1(iv) Thermal Degradation of Polyesters

It may be relevant to the subject of polyacrylate degradation to mention thermal degradation studies on polyesters. Ritchie[42] and Goodings[43] have made surveys of the thermal degradation of model compounds for both poly(ethylene terephthalate) and poly(ethylene fumarate) and have also studied the thermal degradation products of the polymers. The initial reaction in the polymers is the scission of the alkyl-oxygen bond of the ester group to produce a carboxyl and a vinyl end group. Thereafter, the reaction scheme becomes very complex, and a variety of products is obtained. Addition of free radical inhibitors does not suppress the degradation reactions, indicating that random homolytic scissions, rather than chain prooesses, propagate the reactions. The polyesters degrade at a measureable rate above 280°C.

1(v) Thermal Degradation of Methyl Methacrylate/Methyl Acrylate Copolymers

Methyl methacrylate polymer is often stabilised industrially by copolymerising a small number of methyl acrylate units into the polymer chain. This has the effect of inhibiting the unzipping reaction by blocking it at acrylate units. McNeill[44] used thermal volatilisation analysis to illustrate the increased stability of the copolymers over pure poly(methyl methacrylate). He also showed that higher members of the acrylate series have the same stabilising effect, but he suggested that they may have a different blocking mechanism from poly(methyl acrylate).

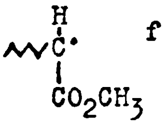
Grassie and Torrance[45,46,47] studied a range of copolymers from 100/1 to 2/1 methyl methacrylate/methyl acrylate and also 100/1 and 10/1 methyl methacrylate/ethyl acrylate. The following is a summary of their findings:

(a) The stability of the copolymers increases with increasing methyl acrylate content.

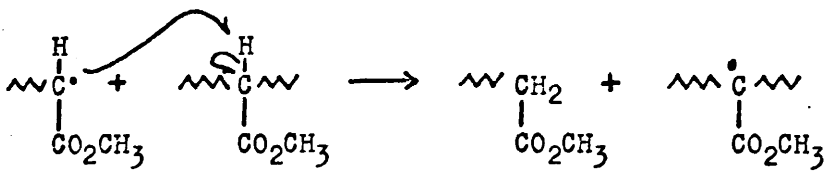
(b) A significant result~~s~~ of this work was the observation that one carbon dioxide molecule is produced per chain scission. The following reaction scheme was proposed.

1/ Random chain scission to give polymer radicals.

2/ Depropagation through sequences of methyl methacrylate units (see fig 1.2) until

3/ radical  $\sim\!\sim\overset{H}{\underset{CO_2CH_3}{C}}\cdot$ forms at a methyl acrylate unit.

4/ This radical transfers intermolecularly:



5/ A cyclic step between the polymer radical and a neighbouring methacrylate unit produces carbon dioxide, a poly(methacrylate) type radical and a chain scission.

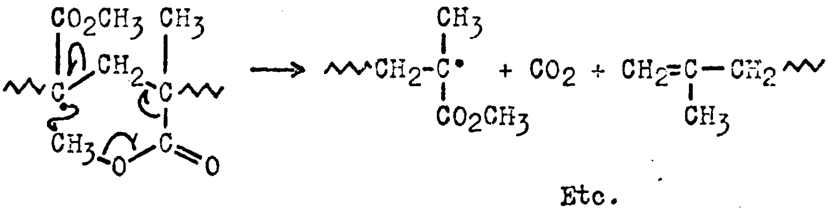


Fig 1.7

Degradation Mechanism for Methyl Methacrylate/Methyl Acrylate Copolymers

Reaction 5 in this scheme is based on a mechanism proposed by Fox and others[48] for the production of carbon dioxide in the photodegradation of poly(methyl acrylate).

(c) No methanol was found in the degradation products, even in the case of 2/1 copolymer. This is a surprising result when compared with Kane's findings[1,3] that methanol is a major component in the volatile fraction of poly(methyl acrylate) degradation products. Grassie and Torrance proposed that a requirement for methanol production is at least three methyl acrylate units adjacent to one another. On the other hand, Strassburger and others[49] have observed a small amount of methanol in the degradation products of 4/1 methyl methacrylate/methyl acrylate copolymer.

(d) The rate of chain scission is proportional to a power of the methyl acrylate content of the copolymer less than 0.5. By considering the kinetics of the reaction, Grassie and Torrance concluded that the radical which initiates the chain scission step (step 5, fig 1.7) can attack any hydrogen atom on the polymer chain and not necessarily the tertiary hydrogen of a methyl acrylate unit. This does not alter finding (b) - a similar reaction scheme involving carbon dioxide elimination is given.

(e) A short chain fragment fraction, amounting to 13 % of the original weight of polymer, is observed in the degradation products of a 2/1 copolymer at 300°C. This compares with a figure of 38 % found by Kane[1] for the short chain fragment yield from poly(methyl acrylate).

(f) Methyl methacrylate/ethyl acrylate copolymers behave very similarly to methyl methacrylate/methyl acrylate copolymers on degradation.

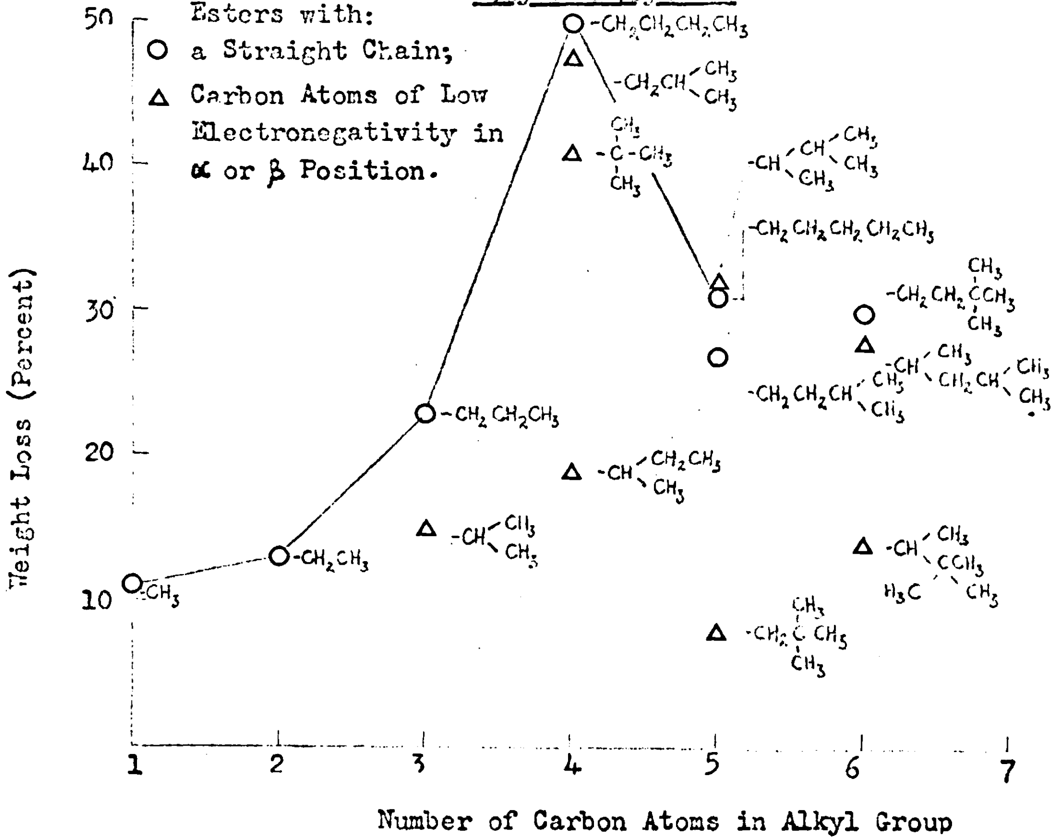
1(vi) Thermal Degradation of Higher Members of the Polymethacrylate Series

Crawford[50] carried out a survey of some physical and chemical properties of seventeen members of the polymethacrylate series. He degraded samples of the polymers under standard conditions for 100 minutes at 250°C and measured the percentage volatilisation of the polymers and the refractive index of the volatiles collected at -70°C. The refractive index of the volatiles from poly(primary methacrylates) was shown to be close to that of monomer.

The volatiles from poly(secondary methacrylates) have lower refractive indices than the monomers and poly(t-butyl methacrylate) gives a volatile fraction identified as iso-butene. Fig 1.8 shows Crawford's results for the polymer stabilities, measured as the percentage volatilisation under his standard conditions. He found that the polymethacrylates with a carbon atom of low electronegativity in the α or β position of the alkyl group are the most stable.

Grassie and MacCallum[51] carried out a thorough investigation of the thermal degradation of poly(n-butyl methacrylate). They found that, after prolonged heating at 250°C, only 40 % of the theoretical yield of the monomer is obtained. Small amounts of 1-butene are found, the infrared spectrum indicates the formation of glutaric anhydride type rings and some insolubility developes. They suggested that some acid groups are formed in the polymer by elimination of butene by a radical mechanism during both polymerisation and degradation. The acid groups then catalyse the elimination of butene from neighbouring n-butyl acrylate units. Water is also lost in the same reaction to produce anhydride groups which effectively block the depropagation reaction.

Fig 1.8 Comparison of Thermal Stability of Polymethacrylates



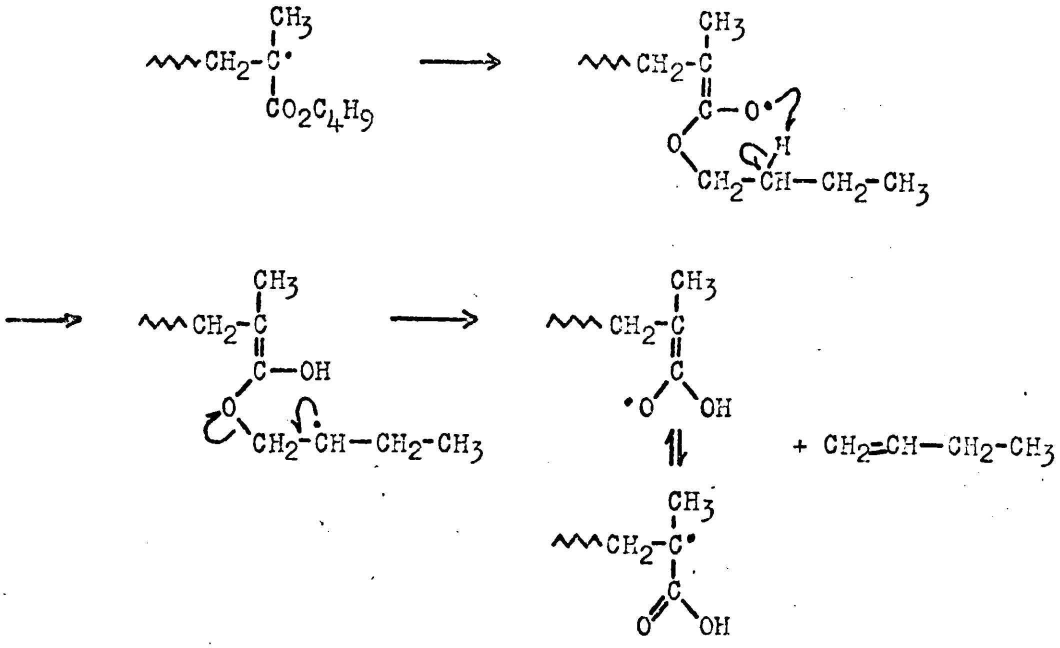


Fig 1.9

Elimination of 1-Butene from Poly(n-Butyl Methacrylate) by a Radical Mechanism

Grant and Grassie[52] earlier studied poly(t-butyl methacrylate) under similar conditions, but at 180-200°C. Very little monomer (about 4 % of the theoretical yield), but large yields of iso-butene and water are recovered. The iso-butene production is autocatalytic in character and a mechanism was proposed for this molecular chain reaction(fig 1.10). The acid groups formed soon couple together to produce anhydride groups and eliminate water as described in 1(iii)D

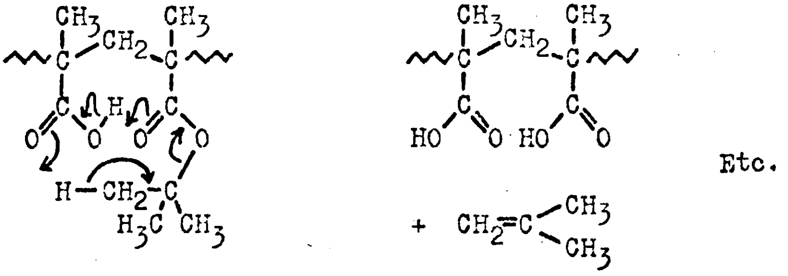


Fig 1.10

Elimination of Iso-Butene from Poly(t-Butyl Acrylate) by an Acid-Catalysed Molecular Mechanism

1(vii) Thermal Degradation of Polyacrylates

Grassie and Weir[4], in connection with Grassie and Grant's work on poly(t-butyl methacrylate), studied poly(t-butyl acrylate). They found the degradation products of the two polymers to be similar, except in that no monomer was observed in the degradation products of the polyacrylate. Poly(acrylic acid) is first produced, by a mechanism of the type shown in fig 1.10, and this is followed by elimination of water to form poly(acrylic anhydride). Carbon dioxide was observed in the degradation products but the amount was not measured. Schaefgen and Sarasohn[53] carried out a similar investigation and gave figures of 86 % iso-butene, 11 % water and 3 % carbon dioxide for the composition of the volatile degradation products. They found that the residue is insoluble in organic solvents, but slowly soluble in sodium hydroxide solution, suggesting that it contains anhydride groups, some of which are intermolecular cross-links.

Poly(methyl acrylate) thermal degradation, studied by Madorsky and Straus[28,54], is very different from poly(t-butyl acrylate) degradation. Volatilisation from the former polymer does not begin until the temperature reaches 280°C, whereas the latter volatilises at 190°C. Carbon dioxide, methanol and short chain fragments are the principal volatile products from the former; it is not possible for a product analogous to iso-butene to be eliminated.

Cameron and Kane[3] found a similar composition for the volatile degradation products of poly(methyl acrylate), and suggested that the large proportion of short chain fragments implies that random chain scission followed by intramolecular transfer (fig 1.1) is the principal route of degradation. The molecular weight of the degrading polymer is found to fall catastrophically, also indicative of a random chain scission process. Coloration and insolubility were observed in the residue[1] and attributed to the formation of carbon-carbon double bond conjugation in the polymer chain and to radical coupling between neighbouring chains (fig 1.11) respectively. The rate of development of insolubility was found to depend upon the conditions of polymerisation.

Mechanisms were proposed for carbon dioxide and methanol formation (figs 1.12 and 1.13)

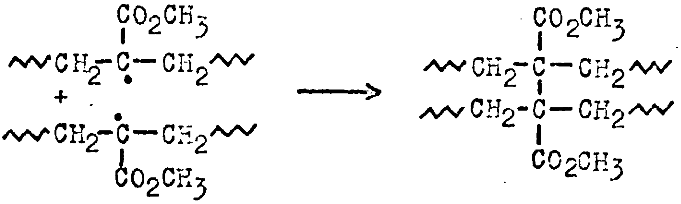


Fig 1.11 Cross-Linking Reaction in Poly(Methyl Acrylate) by Radical Coupling

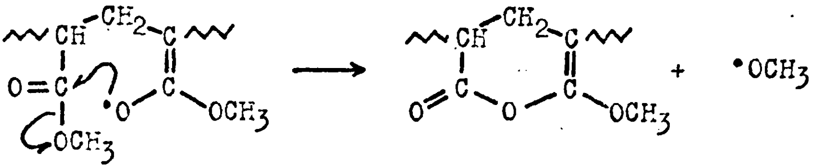


Fig 1.12 Production of Methanol in Poly(Methyl Acrylate) Degradation

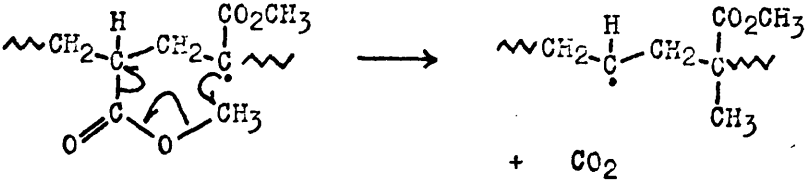


Fig 1.13 Production of Carbon Dioxide in Poly(Methyl Acrylate) Degradation

The appearance of small amounts of methyl methacrylate in the degradation products supports the reaction mechanism shown in fig 1.13. This reaction is similar to one proposed by Torrance[45] (fig 1.7) and Fox[48]. Another reaction scheme suggested by Cameron and Kane might explain both the cross-linking reaction and alcohol production (fig 1.14).

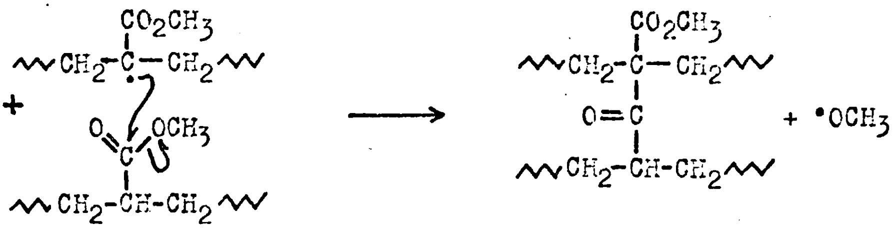


Fig 1.14 Simultaneous Cross-Linking and Alcohol Production from Poly(Methyl Acrylate)

Poly(benzyl acrylate) was also studied by Cameron and Kane[1] and was found to have similar degradation characteristics to poly(methyl acrylate), although the temperature at which volatilisation begins is some 30C° lower (250°C).

Other relevant studies of the thermal degradation of polyacrylates were carried out by Conley[55], Noel[56] and McCormick[57].

Conley[55] investigated the changes in the infrared spectrum of films of poly(ethyl acrylate) degrading in air at temperatures between 100°C and 200°C. He found no functional group changes in the residue. The volatiles are made up mainly of short chain fragments which show signs of oxidation. No monomer was detected.

Noel[56] followed the temperature-programmed degradation of poly(iso-propyl acrylate) by observing the change in thermal conductivity of the volatiles. He concluded that degradation occurs by ester decomposition unaccompanied by chain scission.

McCormick[57] pyrolysed ethyl acrylate and 2-ethyl hexyl acrylate polymers in a nitrogen atmosphere and swept the volatile degradation products on to a gas chromatography column. When the pyrolysis was carried out at 500°C, the monomer yields from the two polymers were found to be 7 % and 12 % respectively. When pyrolysis was carried out by increasing the temperature step-wise from 200°C to 400°C, the mononer yields were smaller: 6 % and 2.5 % respectively. In all his pyrolysis studies of polyacrylates the yield of alcohol predominated over the yield of monomer.

1(viii) Aim of the Present Work

It is obvious, from the different degradation patterns of poly(methyl acrylate) and poly(t-butyl acrylate), that the structure of the alkyl part of the ester group in the polyacrylates is important in determining the temperature and mechanism of breakdown. From a study of a series of polyacrylates, it is hoped to explain further and interrelate the complex degradation mechanisms which occur. In addition to the reactions which take place in the degradation of poly(methyl acrylate), the possibility exists of an olefin elimination reaction in the polymers to be studied. The extent of this reaction and its dependence on the number of β-hydrogen atoms in the alkyl group will be investigated. Poly (2-ethyl hexyl acrylate) has been chosen also to examine the effect of a bulky side group, which may, for example, prevent cross-linking between neighbouring polymer chains.

Chapter 2 Experimental Procedures

2(i) Preparation of Monomers

Neither n-propyl acrylate nor iso-propyl acrylate is available commercially. They were prepared by the method of Rehberg and Fisher[58]. This is an ester exchange reaction involving reflux of a mixture of the appropriate alcohol with an excess of methyl acrylate in the presence of a suitable strong acid as catalyst.

A. Preparation of n-Propyl Acrylate

1.5 Kg methyl acrylate (B.D.H.Ltd), 360 g 1-propanol (W.B. Nicholson Ltd), 6 g p-toluene sulphonic acid (B.D.H.Ltd) and 60 g hydroquinone (Ilford Ltd) were refluxed for 4 hours. Methanol and methyl acrylate were then distilled off and distillation was maintained until the temperature of the distilling liquid reached 99°C. Methyl acrylate boils at 80.5°C, methanol at 65.0°C, n-propanol at 97.1°C[59] and n-propyl acrylate at 123°C[60]. The hydroquinone was added as a polymerisation inhibitor.

580 g crude n-propyl acrylate was recovered by distillation of the viscous and dark coloured reaction mixture under vacuum. Gas-liquid chromatography (G.L.C.) of this product on a 6 ft x 1/4 in 25 % carbowax 1000 column at 108°C showed one main peak and two small impurity peaks identified by retention times as n-propyl acrylate, methyl acrylate and n-propanol. Fractional distillation of the mixture under vacuum was carried out. 600 ml was collected,

in five fractions. The third, fourth and fifth fraction were taken and again distilled under vacuum. 350 ml was recovered and the last 300 ml of this was taken, and found to be pure n-propyl acrylate by gas chromatography on carbowax 1000 and dinonyl phthalate columns (see fig 2.1 a & b). 270 g of pure n-propyl acrylate was obtained, representing a yield of 40 %. This material was stabilised by addition of 0.9 g of hydroquinone and stored in a refrigerator.

B. Preparation of iso-Propyl Acrylate

1.6 Kg methyl acrylate (B.D.H.Ltd), 650 g iso-propanol (W. Jarvie Ltd), 11 g p-toluene sulphonic acid (B.D.H.Ltd) and 90 g hydroquinone (Ilford Ltd) were refluxed for 60 hours. Methanol and methyl acrylate were then distilled off and distillation was maintained until the temperature of the distilling liquid reached 95°C. iso-Propanol boils at 82.4°C[59] and iso-propyl acrylate at 108-112°C[61]. 520 g of crude iso-propyl acrylate was recovered by distillation of the residual material under vacuum. Purification was performed as for n-propyl acrylate above. 230 g of pure iso-propyl acrylate was obtained, representing a yield of 14 %. Chromatograms of crude and pure material are shown in fig 2.1 c & d.

2(ii) Preparation of Dilatometers

Polymerisations were carried out in 250 ml dilatometers containing a magnetic stirrer. The dilatometers

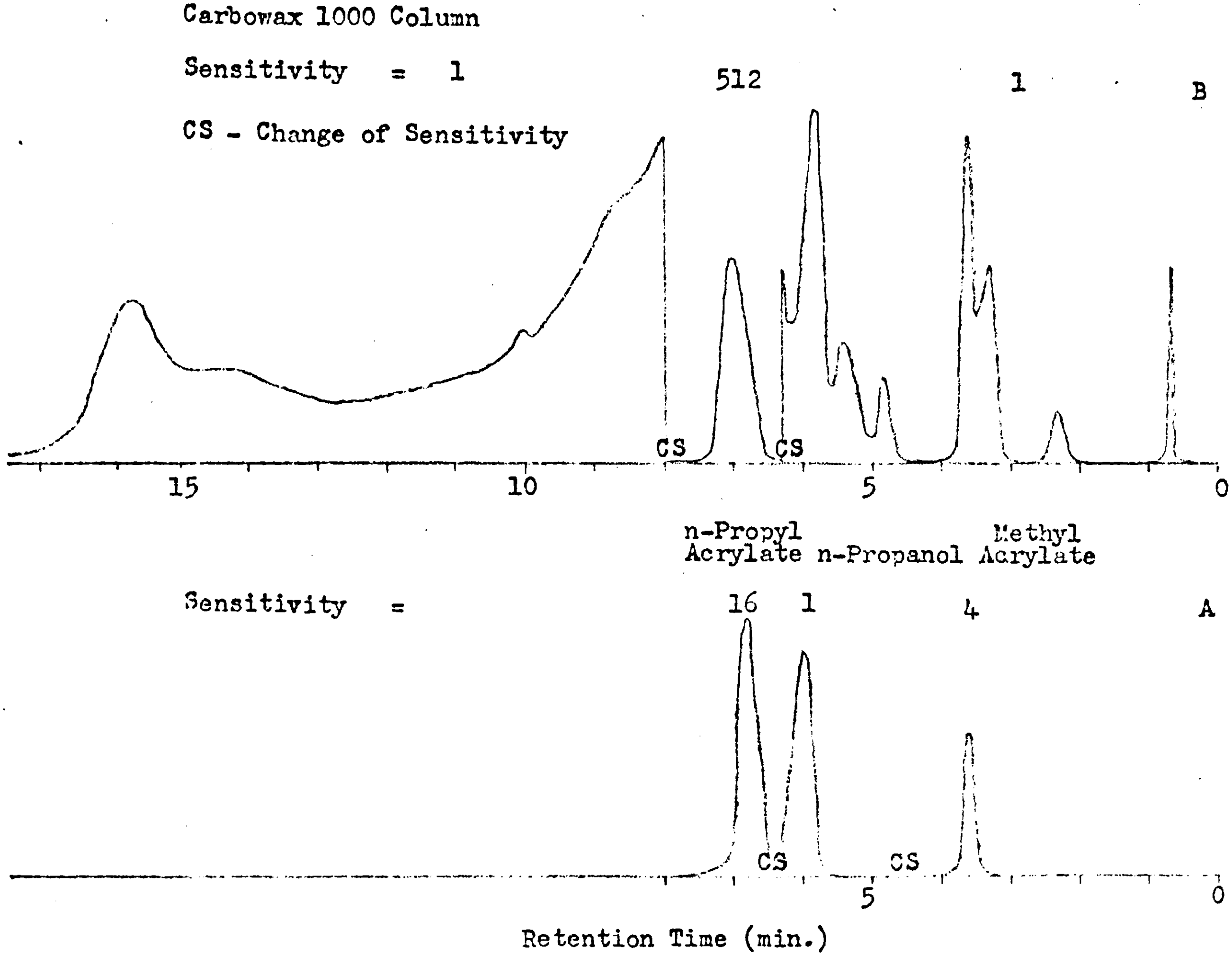


Fig 2.1 G.L.C. of n-Propyl Acrylate Monomer A. Before and B. After Purification

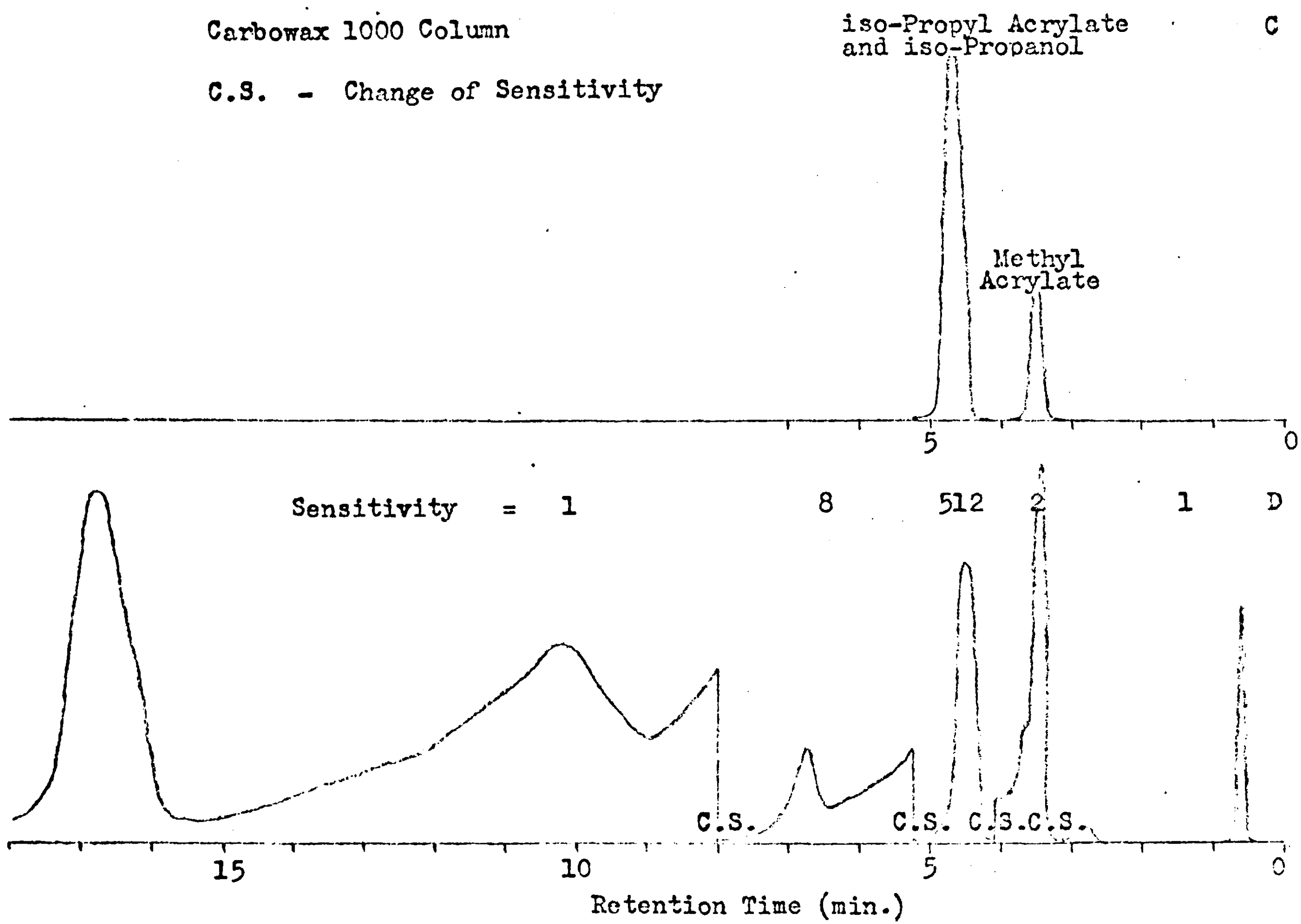


Fig 2.1 G.L.C. of iso-Propyl Acrylate Monomer C. Before and D. After Purification

were washed with cleaning fluid, distilled water and Analar acetone and dried by pumping to high vacuum. They were flamed out to remove volatiles absorbed on the glass.

2(iii) Purification and Introduction of Initiator

In all the polymerisations $\alpha\alpha'$azobisisobutyronitrile (AZBN) (Kodak Ltd) was used as initiator. It was recrystallised from methanol, and added to the dilatometer as a standard benzene solution. The benzene was removed under vacuum.

2(iv) Purification of Solvent

The solvents used in the polymerisation of each monomer are given in the following table.

Table 2.1

Solvents Used in Polymerisations

Monomer	Solvent
Ethyl acrylate	Analar ethyl acetate (Hopkin & Williams Ltd)
n-Propyl acrylate	n-Propyl acetate (B.D.H.Ltd)
n-Butyl acrylate	n-Butyl acetate (B.D.H.Ltd)
iso-Propyl acrylate	iso-Propyl acetate (Fisons Ltd)
2-Ethyl hexyl acrylate	Analar benzene (B.D.H.Ltd)

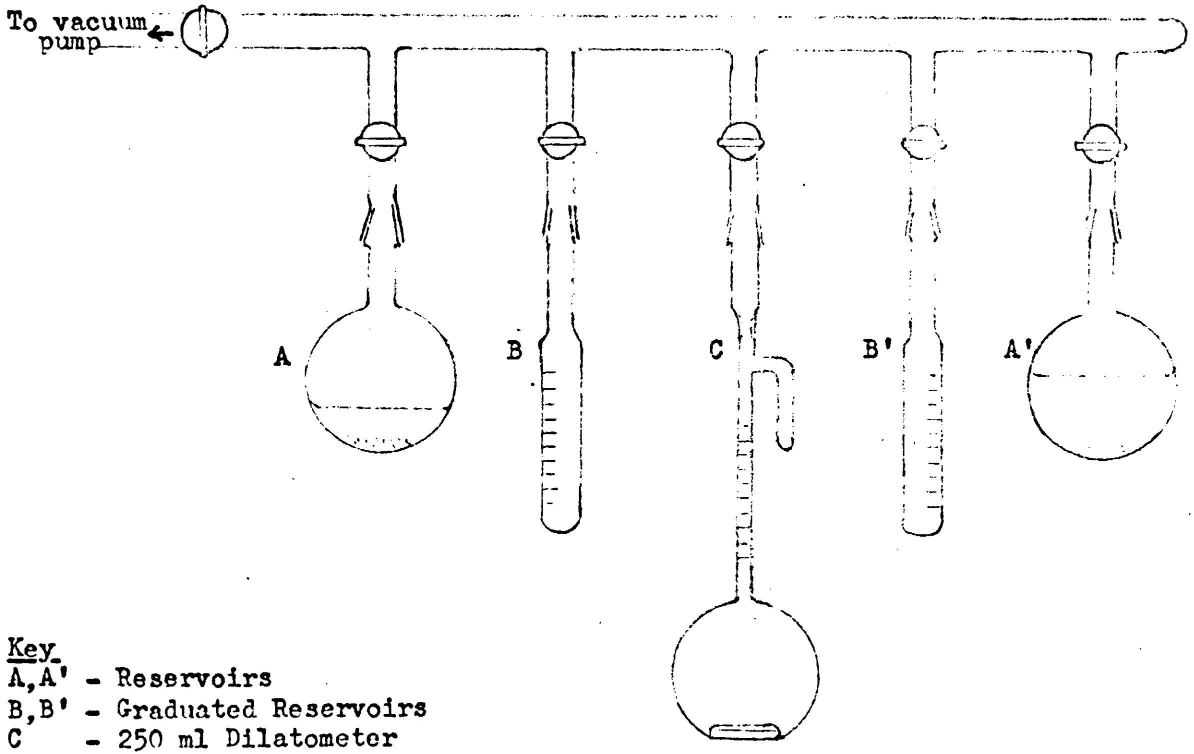
The acetates were chosen because of their similar chemical structure to the acrylates, so that if a few molecules of solvent were incorporated in the polymer chain, minimal interference with the polymer structure would result. Analar benzene was used as solvent for the 2-ethyl hexyl acrylate polymerisation, 2-ethyl hexyl acetate being unavailable commercially.

Solvents were purified by treatment for 24 hours with dried calcium chloride, then overnight with ground calcium hydride to remove all traces of water. They were degassed by the freezing and thawing technique and distilled under vacuum into a graduated reservoir(see fig 2.2).

2(v) Purification of Monomers

n-Butyl acrylate (Koch Light Laboratories Ltd), ethyl acrylate (B.D.H.Ltd) and 2-ethyl hexyl acrylate (Union Carbide Ltd) were obtained stabilised by inhibitors of the hydroquinone type. Before polymerisation, all the monomers were allowed to stand for 24 hours over dried calcium chloride followed by treatment overnight with ground calcium hydride, to remove any traces of water. For all monomers except 2-ethyl hexyl acrylate, the inhibitor was removed by distilling twice under vacuum (see fig 2.2); each time the first and last 10 % of the liquid was discarded. The second distillation was into a graduated reservoir. The monomer was then thoroughly degassed three times. It was thereafter ready

Fig 2.2 Arrangement of Vacuum Line



Key
A,A' - Reservoirs
B,B' - Graduated Reservoirs
C - 250 ml Dilatometer

for distillation into the polymerisation vessel.

2-Ethyl hexyl acrylate was purified in a different manner because its low volatility at room temperature made normal distillation under vacuum impracticable. A conventional vacuum distillation apparatus with an oxygen-free nitrogen leak was used. The collecting vessel was a graduated reservoir which was connected to the polymerisation dilatometer by a glass tube. The monomer distilled over at 85-86°C under a pressure of 0.8 mm mercury into the reservoir which was cooled to -80°C. 100 ml of monomer was used, the first 10 ml of which was allowed to pump away; the next 44 ml was collected. The distillation apparatus was then removed and the reservoir closed at the top with a ground glass stopper. The monomer was then thoroughly degassed as described above.

2(vi) Introduction of Monomer and Solvent into Dilatometers

Purified monomer was distilled under vacuum into the dilatometers except in the case of 2-ethyl hexyl acrylate. In this case, the monomer was poured into the dilatometer with the system under high vacuum. The tube between the reservoir and dilatometer was then sealed under vacuum and the reservoir removed. In all cases, once the monomer had been introduced into the dilatometer, it was kept at -196°C to prevent polymerisation.

Solvent was introduced to the dilatometer in all cases by distillation under vacuum from a graduated reservoir. Once the polymerisation mixture of initiator, monomer and solvent had been made up in the dilatometer, it was frozen with liquid nitrogen, pumped to a pressure of less than 10^{-5} torr and the dilatometer sealed at the constriction.

2(vii) Polymerisation

All polymerisations were carried out at 40.0±0.1°C in a stirred thermostat bath. The thermostat bath had a glass floor and, by placing a magnetic stirrer below the bath, the glass-covered magnet inside the dilatometer could be activated and hence used to maintain uniform temperature within the dilatometer.

Some monomer and polymer density data have been obtained for methyl acrylate[62], ethyl acrylate[63] and n-butyl acrylate[64]. Densities of ethyl and 2-ethyl hexyl acrylate monomers at 20°C are also known[65]. From this data, an approximate relationship between volume contraction and percentage conversion for each polymer at the polymerisation temperature could be derived. The polymerisations were followed dilatometrically and taken no further than 20 % conversion, then stopped by pouring the contents of the dilatometer into 3 litres of Analar methanol or methanol/water mixture.

2(viii) Purification of the Polymer

The precipitated polymer was removed by filtration, dried under vacuum, redissolved in fresh solvent and reprecipitated by slowly dripping the polymer solution into well stirred precipitant. This process was repeated twice. Finally the polymer was dissolved in benzene and freeze dried until a vapour pressure of less than 10^{-5} torr was obtained at room temperature. Thermal Volatilisation Analyses and thermogravimetric analyses of the polymers revealed no significant amount of solvent after this treatment (see 3(iii) and 3(iv)).

Table 2.2 summarises the polymerisation data. Only 5 of these polymer samples were used in this work.

The polymers vary in appearance from poly(ethyl acrylate) and poly(iso-propyl acrylate), which are tough, leathery elastomers at room temperature, to poly(n-butyl acrylate) and poly(2-ethyl hexyl acrylate), which are soft and exhibit low viscosity at room temperature and run freely on heating.

2(ix) Molecular Weight Determinations

Throughout this work, number average molecular weights were measured. Flory[66] has described methods and theory of determining molecular weights.

Methods for finding number average molecular weight are based on the colligative properties of polymer solutions and are fully described in a monograph by Bonnar, Dimbat and Stross[67]. The two types of apparatus employed in the present work are the vapour pressure osmometer (V.P.O.) and the high speed membrane osmometer (M.O.).

Table 2.2

Polymerisation Data
All polymerisations done at 40°C

Polyacrylate	Initiator Concentration W/V mon	Monomer Concentration V/V	% Conversion	Weight of Polymer (g)	Molecular Weight (millions)
Ethyl P5E	0.081 %	24.9 %	10	5.13	12.70
n-Butyl P6B	0.105 %	20.5 %	16	8.45	1.15
Ethyl P9E	0.252 %	20.0 %	14	7.05	0.87
n-Butyl P10aB	0.108 %	48.5 %	20	12.69	2.80
n-Butyl P10bB	0.108 %	48.5 %		17.83	1.40
n-Butyl P10cB	0.108 %	48.5 %		17.50	0.87
n-Propyl P12P	0.097 %	19.4 %	9	5.87	2.30
iso-Propyl P13I	0.105 %	18.4 %	9	5.85	0.65
2-Ethyl Hexyl P14H	0.110 %	17.3 %	16	5.72	0.25

A. Vapour Pressure Osmometer (Hewlett-Packard Inc)

Operation of this instrument (fig 2.3) depends on the difference in resistance (ΔR) between two thermistor beads when one is coated with solvent and the other with polymer solution in an atmosphere saturated with solvent vapour[68]. Provided that the temperature is kept constant, the resistance depends on the vapour pressure round the bead, which, in turn, depends on the number of solute molecules per unit weight of solvent (n).

$$\Delta R \propto n$$

But $n \propto c/\bar{M}n$ Where c is the concentration in g/100 g solvent and $\bar{M}n$ is the number average molecular weight.

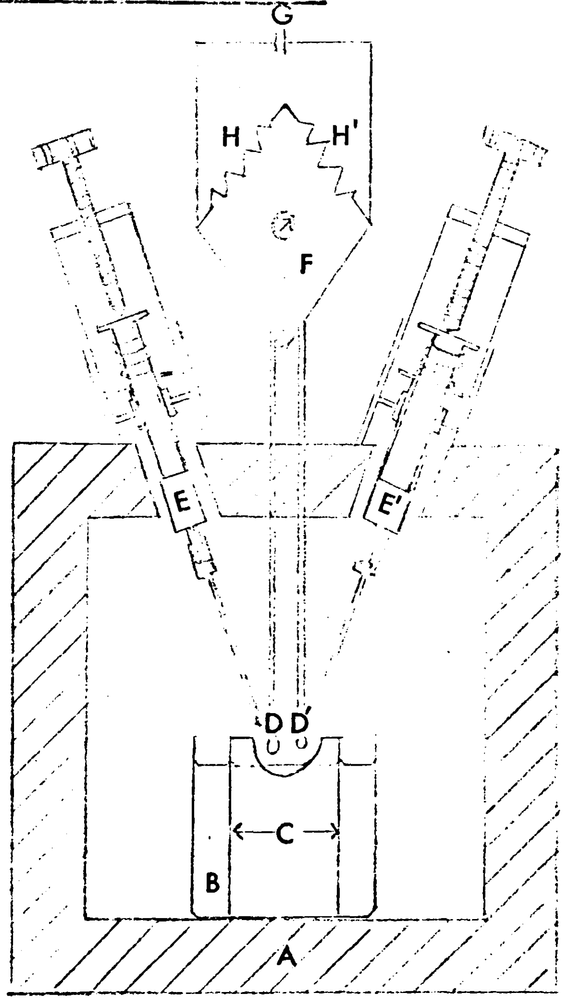
$\therefore \bar{M}n = Kc/\Delta R$ where K is a constant.

The units of ΔR are not important since the instrument is calibrated with a standard compound, in this case benzil.

The value of $\Delta R/c$ used is that at infinite dilution $(\Delta R/c)_{c\to 0}$ since interactions between polymer molecules are significant even at low concentrations. To find this, several concentrations are made up, the graph of $\Delta R/c$ vs c is found and extrapolated to infinite dilution.

The apparatus is accurate to ±1 % up to molecular weight 2000 and ±10 % up to molecular weight 20,000 and may be used provided that the vapour pressure of the solute is negligible compared with that of the solvent.

Fig 2.3 Vapour Pressure Osmometer



A - Insulated jacket with heating element
B - Solvent in cup
C - Wick
D - Thermistor bead + Drop of solvent
D'- Thermistor bead + Drop of solution
E - Solvent syringe
E'- Solution syringe
F - Wheatstone Bridge
G - 1.5 V Mercury battery
H and H'-Matched resistors

B. High Speed Membrane Osmometer (Hewlett-Packard Inc)

The osmotic pressure (π) of a solution at constant temperature (T) depends on the number of solute molecules per unit weight of solvent (n)

$$\pi = nRT \quad \text{(van't Hoff's Law)}$$

where R is the gas constant

again, using the nomenclature above,

$$\pi = Kc/\overline{M}n$$

$$\text{and } \overline{M}n = Kc/\pi \quad .$$

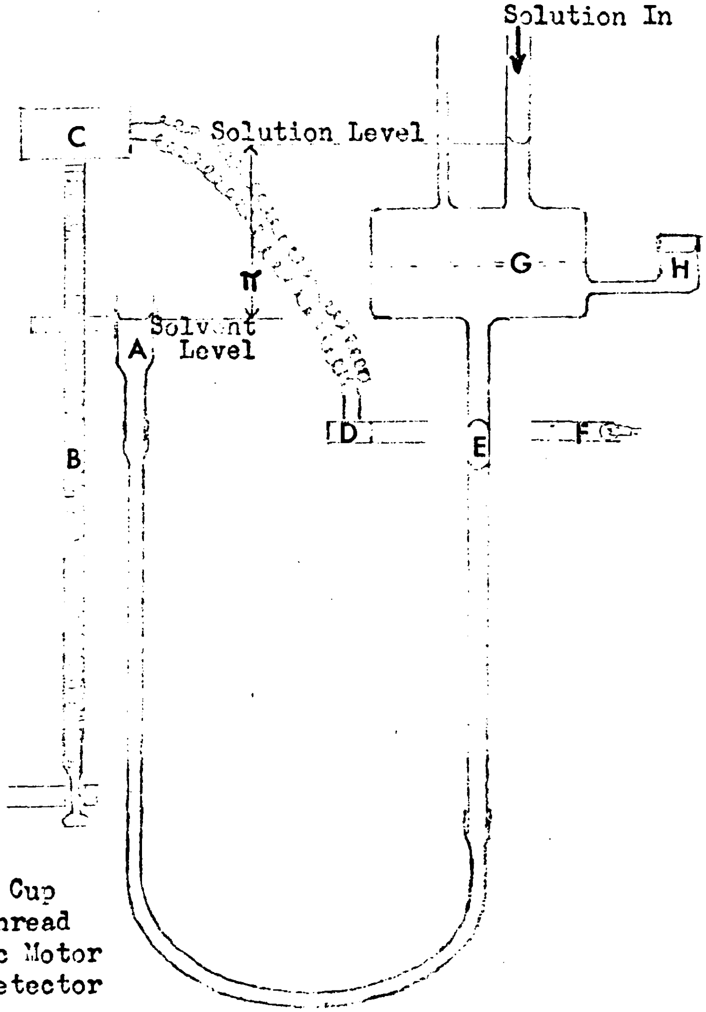
As with the V.P.O., the value of π/c used is that at infinite dilution and it is found in a similar manner to $(\Delta R/c)_{c \to 0}$

A schematic drawing of the M.O. is shown in fig 2.4. This instrument is a refined form of the osmotic balance[69]. It is accurate to ±5 % in the molecular weight range 20,000 to 1,000,000.

For both the V.P.O. and M.O. concentrations of the solutions supplied were approximately 1 g to 100 g solvent. The concentrations were obtained by evaporating the solvent (generally toluene) from a 1 ml portion of the solution in an air oven at 120°C and weighing the containing vessel empty and with the residual polymer.

These two instruments do not cover accurately the whole molecular weight range. Molecular weights between 2,000 and 20,000 are only approximate.

Fig 2.4 High Speed Membrane Osmometer



A - Solvent Cup
B - Screw Thread
C - Electric Motor
D - Light Detector
E - Bubble
F - Light Source
G - Membrane
H - Solvent Cup

2(x) Thermal Methods of Analysis

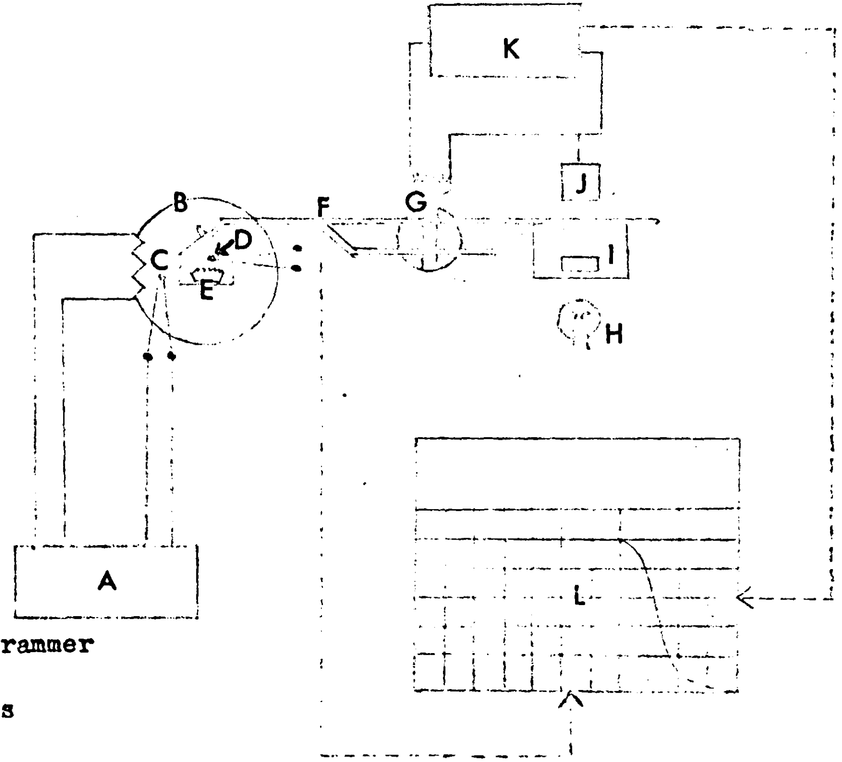
Various methods have been devised for studying continuously the changes in the nature of a substance on heating. Most of these methods have been applied to polymers and are widely described in the literature[70]. It has been usual to programme the temperature of the polymer and observe the changes produced in one or more properties. The two methods used in this work both follow this principle.

A. Thermogravimetric Analysis (T.G.A.)

Madorsky and his coworkers used an electrically heated balance to study weight changes in a large number of polymers[10]. Most of this work was done isothermally, but similar apparatus has been devised in which sample weight is plotted graphically against temperature or time in linearly temperature programmed degradations[71]. Many polymer systems have been studied in this way and there have been many theoretical methods devised for obtaining kinetic data from T.G.A.[72], but, in general, insufficient parameters are obtained except in cases where there are only a few simple processes involved in the degradation reaction.

In the present work the degradation processes are too complex to allow collection of kinetic data, but T.G.A. thermograms supplied qualitative information for the preliminary investigations of the degradations. The Dupont 950 Thermogravimetric Analyzer.

Fig 2.5 Thermogravimetric Analyser



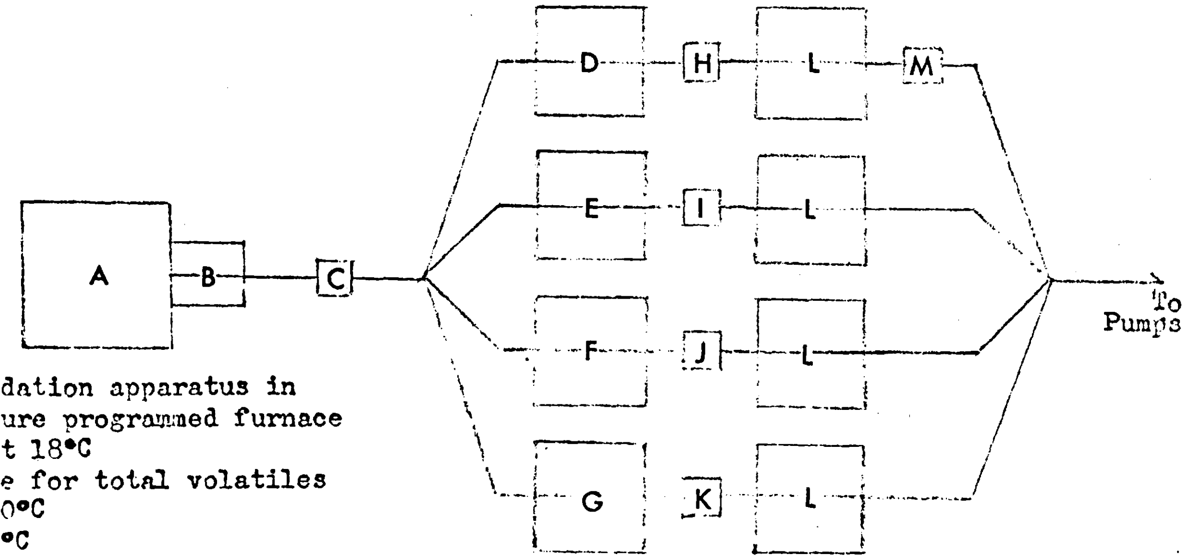
A - Temperature Programmer
B - Furnace
C and D-Thermocouples
E - Sample
F - Balance Arm
G - Drive Coil
H - Light Source
I - Shutter
J - Light Detector
K - Amplifier etc.
L - x-y Plotter

(fig 2.5) was used. The samples were heated at 50°/min from room temperature to 500°C in an atmosphere of oxygen-free nitrogen. It is not possible to obtain a high vacuum with this apparatus and, in general, T.G.A. gives better results when performed at atmospheric pressure since spattering effects are greatly reduced. Although no major inconsistencies are observed in relating T.G.A. runs under nitrogen to other degradation results found in vacuum, the studies are not strictly comparable.

B. Thermal Volatilisation Analysis (T.V.A.)

McNeill devised an apparatus[73] which enables the pressure of volatiles evolved from a sample decomposing under vacuum to be measured. The temperature is increased linearly and a plot of pressure against time is obtained. A later modification[74] is shown schematically in fig 2.6. A series of parallel traps at different temperatures is incorporated into the system and the pressure measured after each one. This apparatus is known as the Differential Condensation T.V.A. and a typical thermogram is shown in fig 2.7. Since the system is continuously pumped, the pressures are small and are measured by means of Pirani Gauges (Edwards High Vacuum Ltd). As with T.G.A., kinetic data for simple degradation reactions can be obtained, but polyacrylates present too complicated a degradation pattern for this, and the thermograms obtained can be only qualitatively interpreted.

Fig 2.6 Schematic Drawing of the Differential Condensation T.V.A.



A - Glass degradation apparatus in
  in temperature programmed furnace
B - Cold ring at 18°C
C - Pirani gauge for total volatiles
D - Trap at -100°C
E - Trap at -75°C
F - Trap at -45°C
G - Trap at 0°C
H - K - Pirani gauges
L - Traps with liquid nitrogen (-196°C)
M - Pirani gauge for non-condensibles

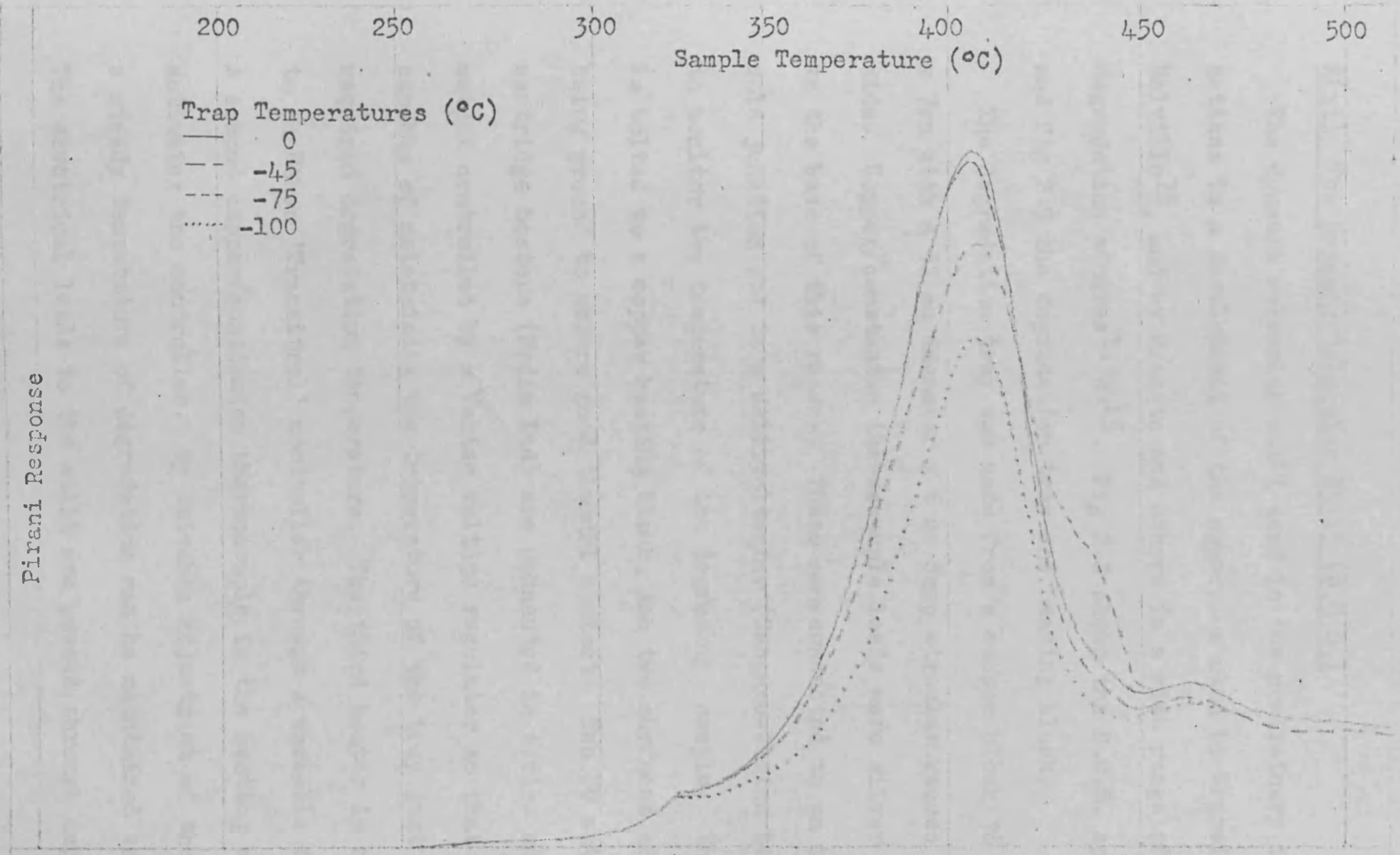


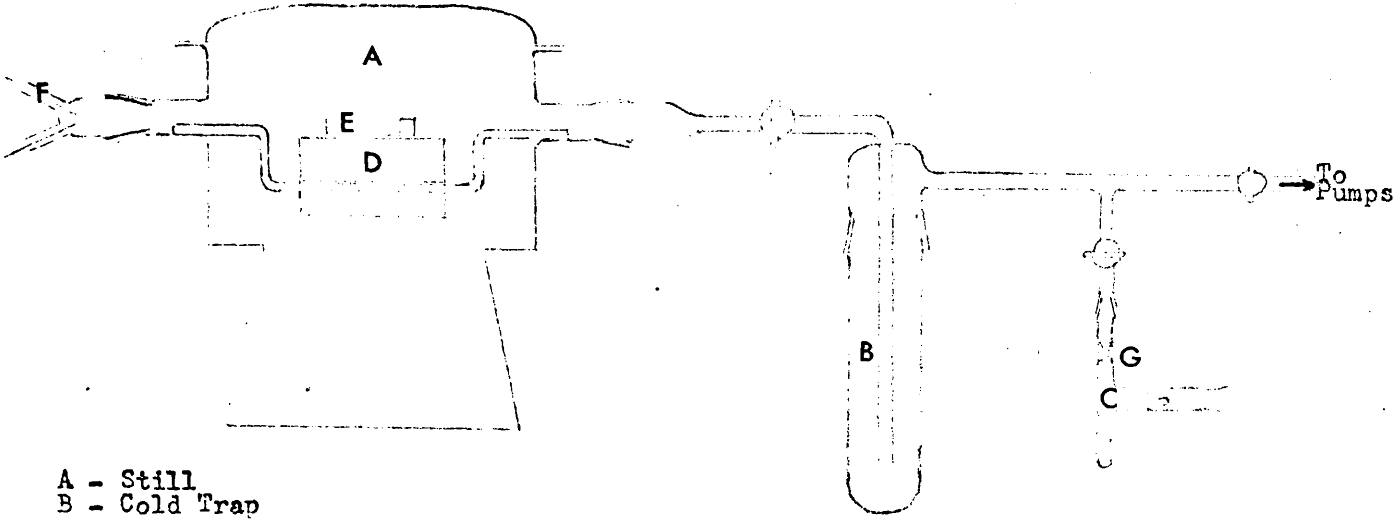
Fig 2.7 T.V.A. Thermogram of Poly(Ethyl Acrylate) (P5E)

2(xi) The Dynamic Molecular Still (D.M.S.)

The dynamic molecular still used in the preliminary investigations is a development of the apparatus used by Grassie and Melville[75], and by Grassie and others in a wide range of polymer degradation studies[1,39,45]. Fig 2.8 shows the D.M.S. apparatus and fig 2.9 the degradation tray and heating block.

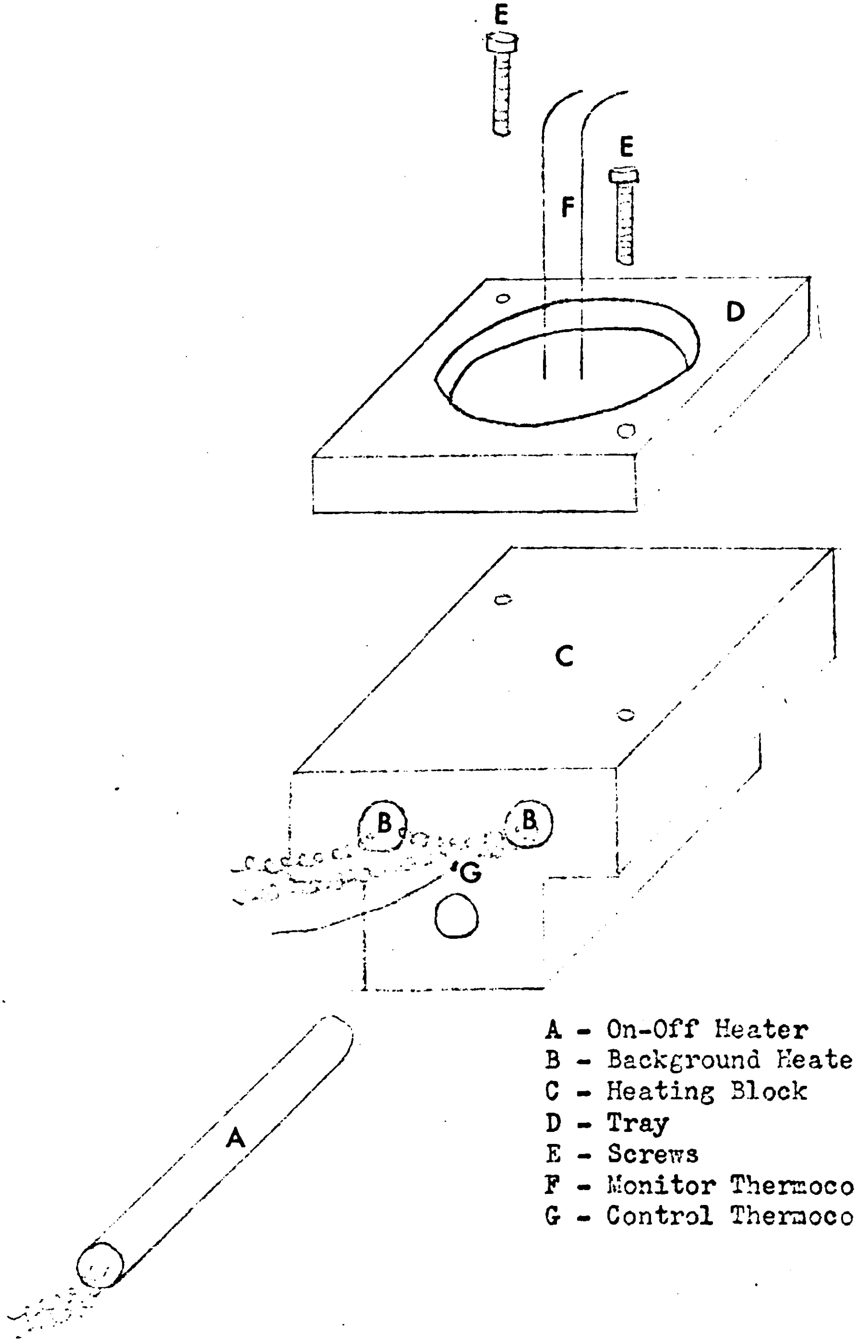
The degradation tray was made from a copper block 36 mm x 36 mm x 7mm with a 32 mm diameter x 6 mm deep circular recess in one side. Copper/constantan thermocouple leads were silver soldered to the base of this recess. These were connected to an ice/water cold junction and to a millivoltmeter (Sangamo-Weston Ltd) used to monitor the temperature of the degrading sample. The tray is bolted to a copper heating block, the two surfaces of contact being ground to ensure good thermal contact. Two 50 watt/240 volt cartridge heaters (Hedin Ltd) are connected in series and their output controlled by a Variac voltage regulator so that they were capable of maintaining the temperature of the tray just below the required degradation temperature. The third heater is connected to an Ether 'Transitrol' controller through a variable transformer. A second copper/constantan thermocouple in the heating block activates the controller. By suitable adjustment of the controls a steady temperature of degradation can be maintained to ±1.0°C. The electrical leads to the still are passed through capillary

Fig 2.8 The Dynamic Molecular Still



A - Still
B - Cold Trap
C - Volatile Collecting Vessel
D - Heating Block (see fig 2.9)
E - Tray (see fig 2.9)
F - Channel for Electrical Leads (these are not shown)
G - Constriction

Fig 2.9 Heating Block and Tray for D.M.S.



A - On-Off Heater
B - Background Heaters
C - Heating Block
D - Tray
E - Screws
F - Monitor Thermocouple
G - Control Thermocouple

tubing which is sealed with picein wax.

The sample for degradation was prepared by dissolving a known weight of polymer in toluene, pouring the solution into the tray and adding enough copper powder (60-80 mesh Hopkin and Williams Ltd) to cover the polymer and ensure good thermal contact. The solvent was then evaporated off, and the system pumped out to less than 10^{-5} torr and degradation begun.

The apparatus was continuously pumped during degradation and the condensible volatiles were collected in a trap (B) at -196°C. From there they could be distilled into a graduated tube (C). This tube was weighed empty. Once the volatiles had been condensed into it, it was sealed at G and weighed again. The difference in the weights gave the weight of volatiles minus a small correction for the air in the tube initially (about 4 mg). The gases were analysed using an MS10 mass spectrometer (A.E.I.Ltd). Weight loss in the degrading sample was found by weighing the degradation tray plus polymer and copper powder before and after degradation.

2(xii) Objections to the Use of the D.M.S. for the Study of Polyacrylates

The dynamic molecular still has many advantages over other methods for the study of polymer degradation reactions. Some of these are:

1/ Very good thermal contact between polymer and heater. This means that with a suitable temperature controlling system, very accurate and steady temperature settings can be obtained[76].

2/ A high vacuum can be maintained during degradation by continuous pumping. This enables the volatile products to escape from the hot zone as quickly as possible and minimises the chance of secondary reactions occuring between products. Also, very good thermal insulation of the heating block and tray can be achieved.

3/ Use of the degradation tray enables weight losses to be calculated readily.

However, the degradation of polyacrylates shows characteristics which are not easily studied by the D.M.S. in its usual form. Thus, some objections to its use are as follows:

A. Catalysis of Secondary Reactions by Copper

In some of his earlier work on the thermal degradation of poly(methyl acrylate), Kane[1] used the form of molecular still described above. He found that the copper powder catalyses thermal breakdown of methanol to carbon monoxide and hydrogen, in a similar manner to that found by Hasegawa[77]. He therefore adopted a new type of degradation tray which had a lining of platinum on the inside surface. This has the disadvantage that spattering occurs with loss of unreacted polymer since there is no hindering, copper-powder layer. Also, it is by no means certain that platinum will not catalyse reaction.

Another reaction known to be catalysed by the presence of copper powder is the elimination of hydrogen chloride from poly(vinylchloride)[78]. Use of iron and silver degradation trays was also found to be unsatisfactory in this case. Recently it has been suggested[79] that copper may catalyse the evolution of acetic acid from poly(vinyl acetate).

B. Collection of Short Chain Fragments

Cameron and Kane[1,3] found that up to 90 % of the weight loss from degradation of poly(methyl acrylate) consists of short chain fragments with an average molecular weight of 704. Madorsky[54] gives a value of 73 % and an average molecular weight of 633 for this fraction. It is not easy to measure accurately the amount of this material with the D.M.S. since it is too involatile to reach the cold trap (B) and, instead, condenses on the walls of the still. Cameron and Kane used a glass surface fitted directly over the heating block of the still to collect it. It is desirable that the whole of this fraction should be recovered and measured, however, and the D.M.S. is not entitely satisfactory for this purpose.

C. Recovery of Residue

In the present work it was found that the residue becomes partly insoluble. This results in a hard, caked mass of residue and copper powder which is difficult to remove from the degradation tray for analysis.

For these reasons it was decided to use the D.M.S. only for qualitative investigations and a new type of degradation apparatus, the sealed tube, was devised for quantitative measurements.

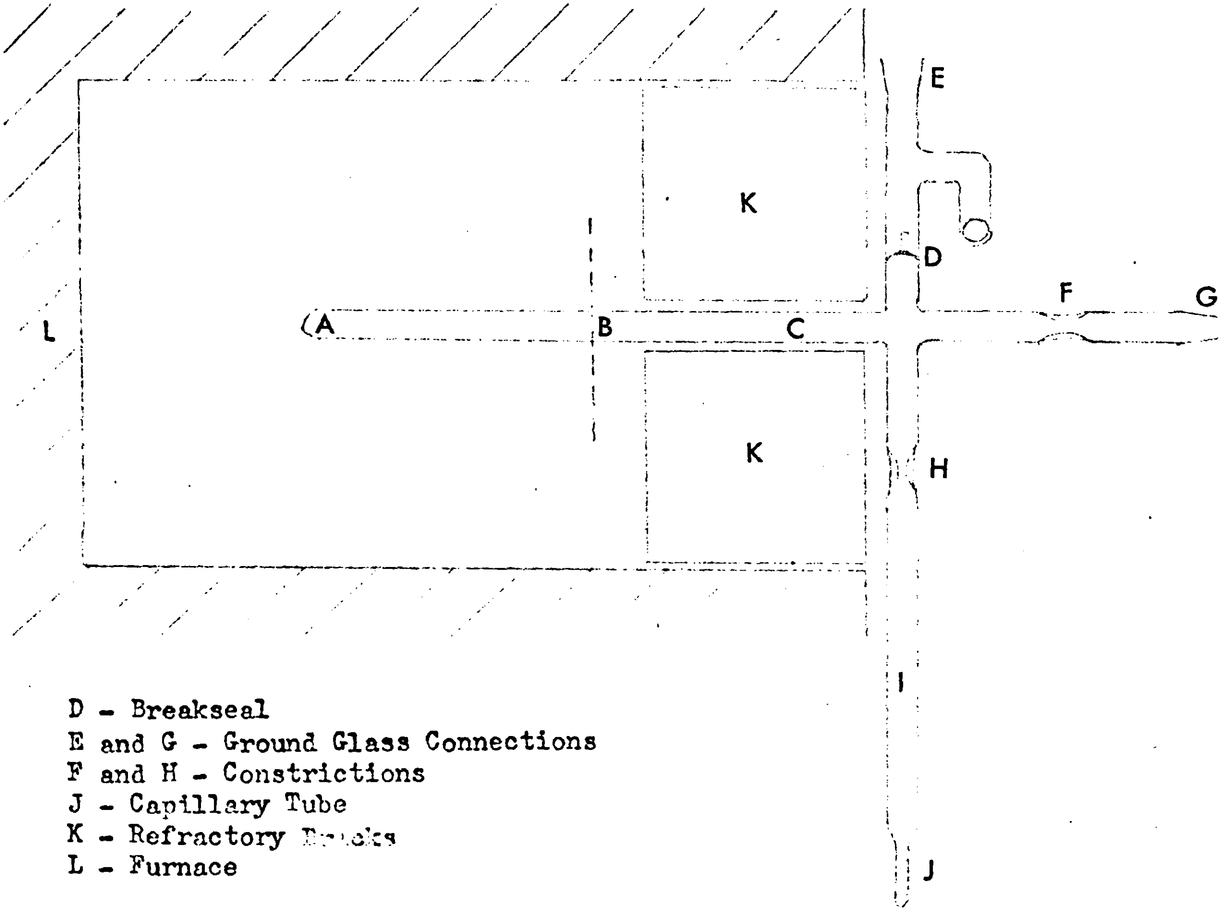
2(xiii) Sealed Tube Degradations

The sealed tube is shown in fig 2.10. It was made of 12 mm outside diameter, medium wall, pyrex glass. Before use it was washed overnight with cleaning fluid, then with distilled water and finally Analar acetone. It was dried by pumping out to high vacuum, then limbs A and I were flamed out to remove absorbed volatiles.

Polymer was introduced into the tube in two ways. In earlier work the polymer was dissolved in Analar toluene and the required volume pipetted down a long thistle funnel into section A as shown in fig 2.11(a). The solvent was removed by distillation under vacuum and the tube sealed off at the constriction, F (fig 2.10) under a pressure of less than 10^{-5} torr.

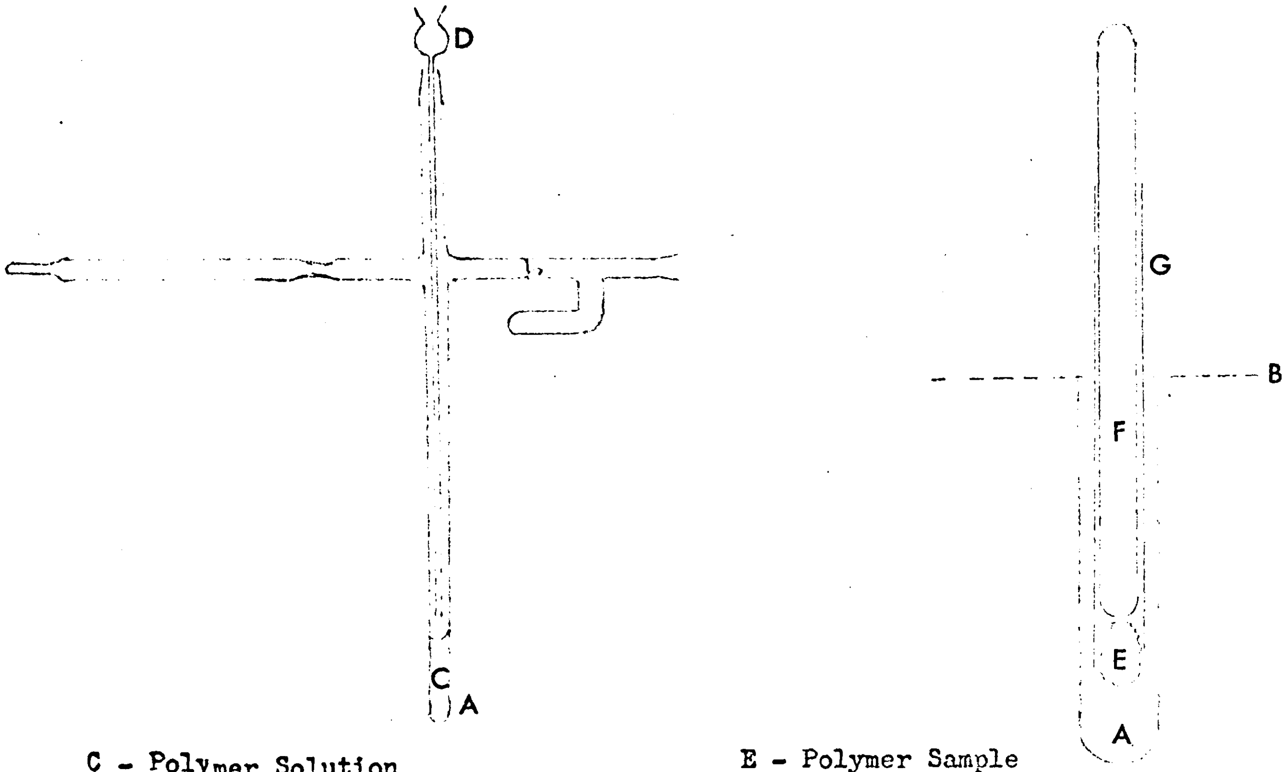
Later it was found more convenient to introduce the polymer into the tube by cutting the glass at B and using the device shown in fig 2.11(b). This prevented the polymer sticking to the sides of the glass except at end A. End A was glass-blown back into

Fig 2.10 Sealed Tube Degradation Apparatus



D - Breakseal
E and G - Ground Glass Connections
F and H - Constrictions
J - Capillary Tube
K - Refractory Bricks
L - Furnace

Fig 2.11 Introduction of Polymer into Sealed Tube



2.11a

2.11b

C - Polymer Solution
D - Thistle Funnel

E - Polymer Sample
F - Glass Rod
G - Glass Tube

position on the tube and the tube evacuated and sealed as before.

Degradations were performed in a Catterson-Smith G31LX type electric furnace. This is fitted with an Ether 'Transitrol' controller and temperature control of ±1°C is obtained provided that the furnace is allowed to come to equilibrium for 24 hours. There is found to be a small vertical temperature gradient inside the furnace, but none horizontally. The entrance is closed by two refractory bricks, 10 cm thick. Three holes 15 mm in diameter were bored through the bricks at the same horizontal level. Through these three sealed tubes can be inserted, one containing a chromel/alumel thermocouple to monitor the temperature, and the other two for simultaneous degradations. The end I of the sealed tube is immersed in liquid nitrogen to ensure that the pressure inside the tube remains low and to collect volatile material.

The thermocouple is led to an ice/water cold junction and to a 'Doran' thermocouple potentiometer (Derritron Instruments Ltd). The thermocouple leads can also be switched to a Honeywell-Brown recorder which is used to check that the temperature remains constant between potentiometer readings.

After the reaction the sealed tube can be used to fractionate the products as follows. Gases can be analysed by breaking the break seal D and distilling the gases into a suitable measuring device (see 2(xiv)). Liquids collect in the capillary at J, and limb I can be sealed off at the constriction, H, to isolate them. Short chain fragments collect in the 'cold ring' at C and may be separated from the residue by cutting the tube at B.

2(xiv) Analysis of the Gaseous Volatiles

The apparatus shown in fig 2.12a was used to analyse the gases. It consists basically of a constant volume manometer (C.V.M.) similar to that used by Kane[1] and an infrared gas cell 12 cm long by 4.5 cm in diameter (Techmation Ltd). The method of operation of the C.V.M. has been described by Kane. The whole system is evacuated to a pressure of less than 10^{-5} torr, then taps B and F are closed. With capillary J in ice to keep the vapour pressure of liquids low, the break seal on the sealed tube is broken and the gases distilled into limb Z of the C.V.M.. The level of mercury in limb L is adjusted to the zero mark and the pressure of the non-condensible gases measured from the height of mercury in limb R. Limb Z is then allowed to warm up to room temperature with tap C closed and the pressure of condensible gases is measured similarly. Tap G is closed and U-tube U is surrounded by liquid nitrogen. The condensible gases are then allowed to condense into this tube. Tap F is closed and the gases are allowed to warm up to room temperature. Part of the gases occupy the infrared gas cell, which is then separated from the line and the spectrum

Fig 2.12a Gas Analysis Apparatus

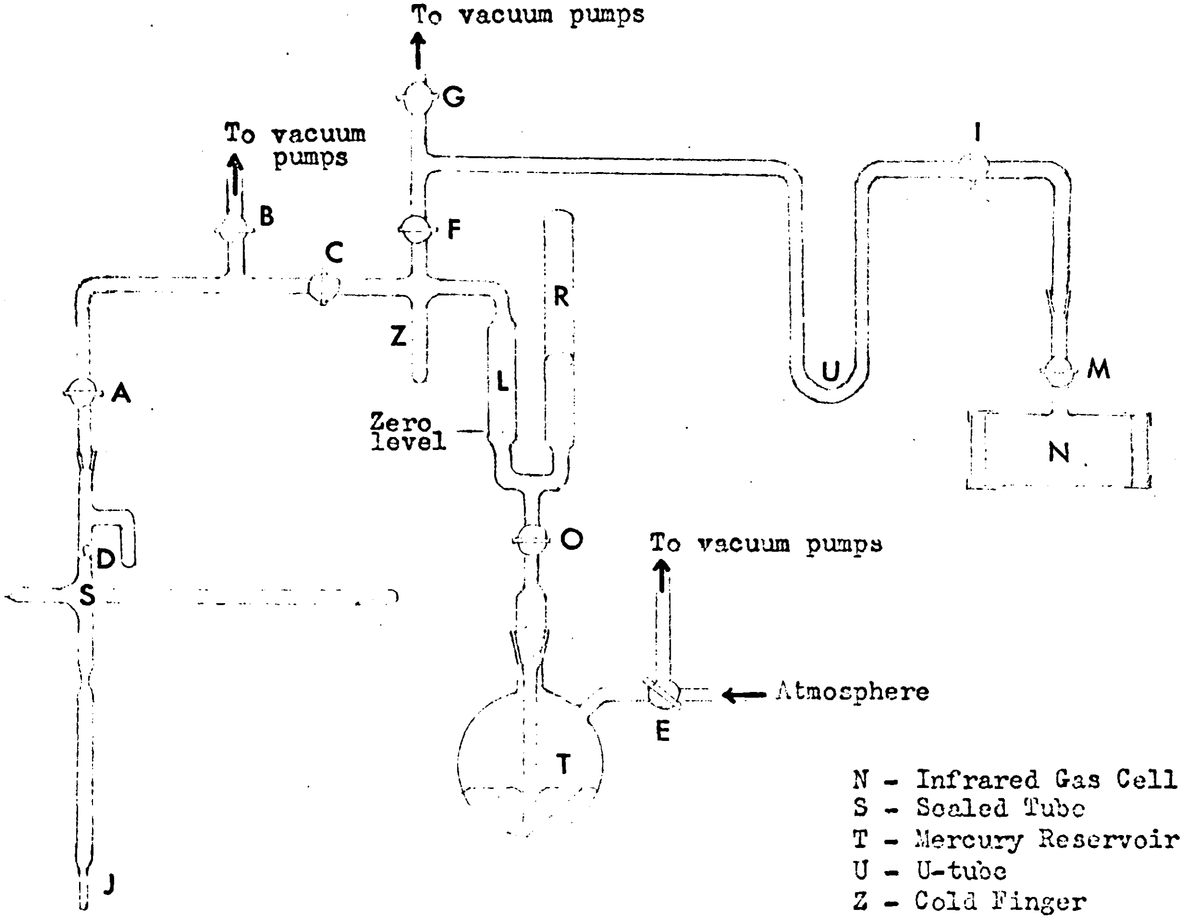
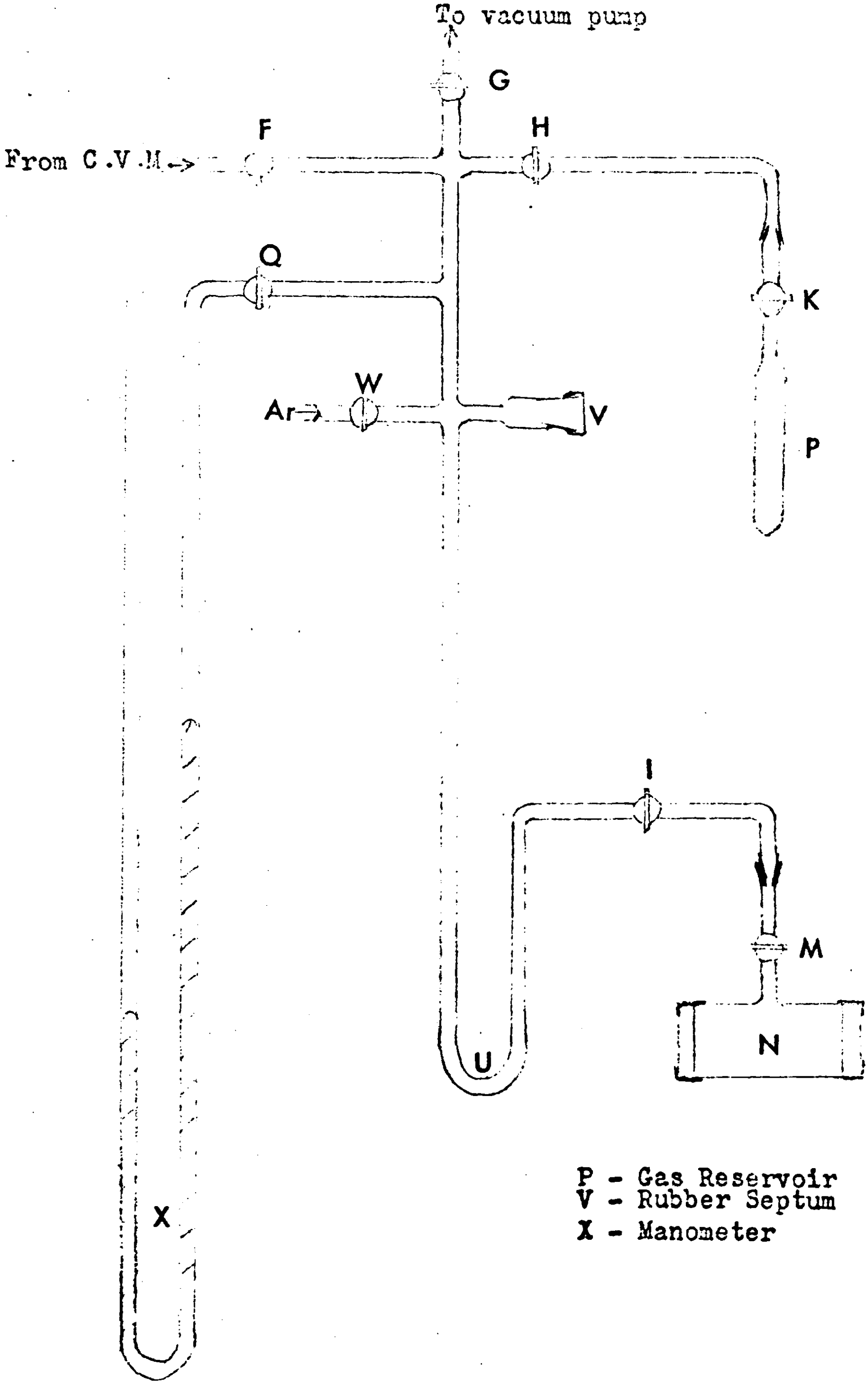


Fig 2.12b Gas Analysis Apparatus



P - Gas Reservoir
V - Rubber Septum
X - Manometer

of the gases is obtained on a Perkin Elmer 257 Grating Infrared Spectrophotometer. An identical infrared gas cell is evacuated completely and placed in the reference beam of the spectrometer. The infrared detectors are flushed with oxygen-free nitrogen. These precautions enable quantitative analysis of carbon dioxide to be made with minimal interference from carbon dioxide in the atmosphere. The same instrument was used in all the other infrared studies described in this thesis. The volume of the C.V.M. was found as shown in Appendix A, to be 30.5 ml for the part enclosed by taps C and F and 423 ml for the part enclosed by the sealed tube (with tap A open) and taps B and F. The total number of moles (n) of gas recovered from the degradation can be found as follows:

By the General Gas Law

$PV = nRT$ where P is the pressure

V is the volume

R is the Gas Constant

and T is the absolute temperature

In all experiments room temperature was taken as 295°A and the gas constant $R = 6.24 \times 10^3$ ml$\times$cm.Hg/mole$\times$C°.

For the smaller system

$$n = \frac{30.5}{6.24 \times 10^3 \times 295} \times P$$

or $n = 1.657 \times 10^{-5}\ P$

For the larger system

$$n = \frac{423}{6.24 \times 10^{3} \times 295}\ P$$
$$= 2.30 \times 10^{-4}\ P$$

In both cases, P is in units of cm.Hg.

By the use of standard samples of carbon dioxide (British Oxygen Ltd), ethylene, propylene and 1-butene (all Matheson Inc., C.P. Grade), peaks for infrared absorption by the gases were measured and graphs obtained of optical density of the peak against pressure of the gas on the C.V.M..

In this way the gaseous fraction could be analysed and, in the cases of the polymers of ethyl, n-propyl, iso-propyl and n-butyl acrylate, was measured as weight of total gas, weight of carbon dioxide and weight of olefin. In the case of poly(2-ethyl hexyl acrylate) the infrared spectrum was used only to confirm that the gaseous fraction was mainly carbon dioxide.

Gas chromatographic data presented in this thesis was obtained using a Microtek 2000R Research Gas Chromatograph with a flame ionisation detector, except where otherwise stated. A 10 ft by 1/4 in 30-60 mesh silica gel column and a 24 ft by 1/8 in 40 % silver nitrate/benzyl cyanide column were used to look for traces of gases other than those mentioned above. The detector will not detect carbon dioxide, carbon monoxide, hydrogen or oxygen. The apparatus shown in fig 2.12b was used. After infrared analysis of the gases they are condensed back into the U-tube, U. Tap I is closed and the gases allowed to warm to room temperature and fill the system enclosed by taps F, G, H, I and W and by the manometer. A 'solvent' gas, argon, which will not be detected on the chromatograph is allowed to flow in until the system is at atmospheric pressure. Samples of gas are then withdrawn through septum V by means of a gastight syringe (Hamilton Co Inc) and injected into the chromatograph.

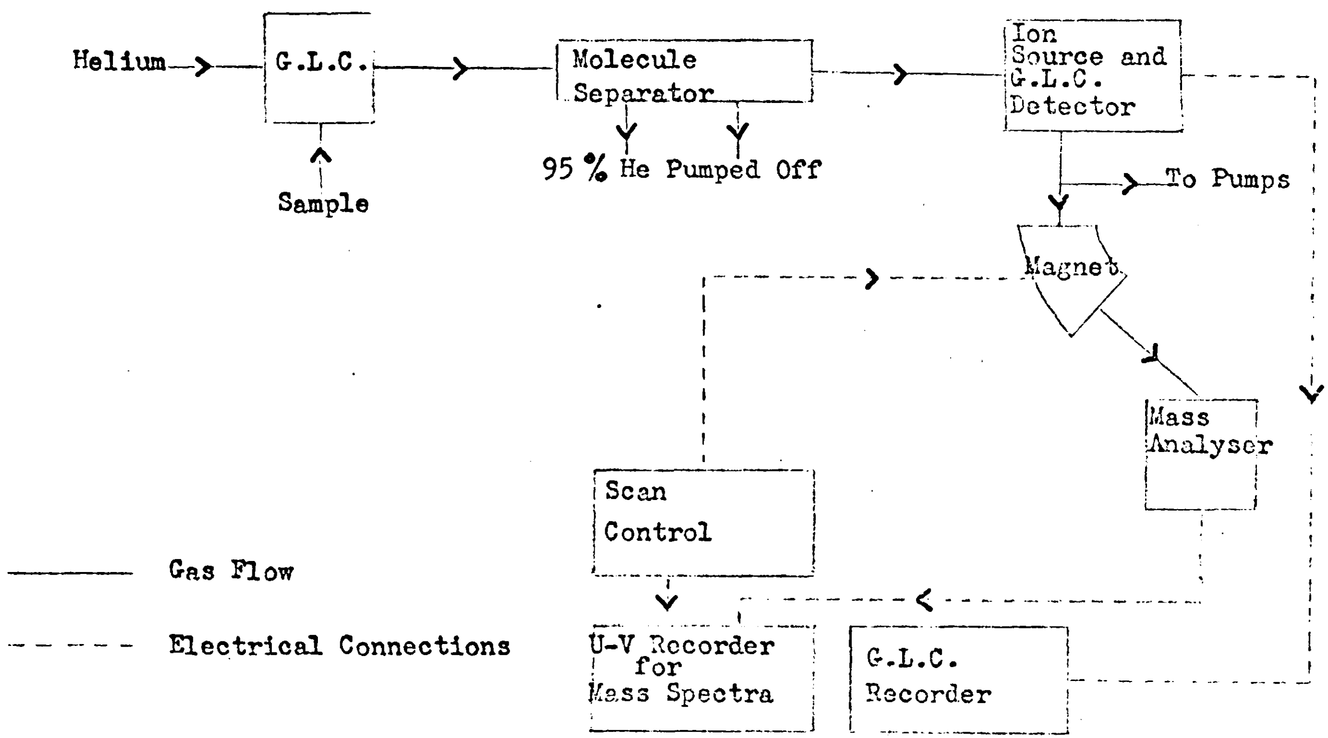
After analysis gases can be distilled into reservoir P for storage if necessary.

2(xv) Analysis of Liquid Volatiles

A. Gas Chromatograph-Mass Spectrometer (G.C.M.S.)

The volatiles from some D.M.S. degradations were analysed by means of a L.K.B.9000 combined gas chromatograph-mass spectrometer (L.K.B.-Produkter). A schematic diagram of this machine is shown in fig 2.13. The novel feature is the molecule separator (Becker-Ryhage)[80] which pumps away most of the helium atoms, so that molecules from the separated component of the mixture under analysis pass into the mass spectrometer in high concentration. The mass spectrometer scans at 20 eV which is below the ionising energy of helium except when a mass spectrum is being recorded.

Fig 2.13 G.C.M.S. - Schematic Diagram



This enables an electrometer in the ion source to be used as a detector for the gas chromatograph. The mass spectra are obtained at 70 eV. As each peak appears on the chromatograph, a mass spectrum may be obtained for the component. The column used in this work was 10 ft by 1/4 in 1 % SE30.

B. Gas-Liquid Chromatography (G.L.C.)

Limb I from the sealed tube (fig 2.10) was broken open and the contents distilled into another graduated tube. This tube was weighed before and after distillation and thus the weight of low molecular weight (distillable) liquids was found. The remaining (undistillable) liquids were combined with the short chain fragments and were analysed as such. This procedure was followed in all cases except poly(2-ethyl hexyl acrylate), where the liquids to be measured are of too low volatility to distil. In this case the whole of the fraction in limb I was analysed.

To the distilled liquids was added a known weight of solvent according to the table below.

Table 2.3

Data on Quantitative G.L.C. of Liquid Degradation Products

Polymer	Liquids Analysed	Solvent	Isothermal at
poly(ethyl acrylate)	ethanol	ethyl acetate	60°C
poly(n-propyl acrylate)	n-propanol	n-propyl acetate	85°C
poly(iso-propyl acrylate)	iso-propanol		
poly(n-butyl acrylate)	n-butanol	n-propyl acetate n-butyl acetate	70°C 100°C
poly(2-ethyl hexyl acrylate)	2-ethyl hexan-1-ol 2-ethyl hex-1-ene	ethyl benzoate	programmed

The weights of sample (W_a) and solvent (W_s) are proportional to the areas (A_a and A_s) of the peaks on the chromatograph. A sensitivity factor (f) relates these terms as follows:

$$f_a = A_a/W_a \qquad \text{and} \qquad f_s = A_s/W_s$$

A combined sensitivity factor (f) is defined such that

$$f = \frac{A_s.W_a}{W_s.A_a}$$

This factor is determined for the pairs of sample and solvent shown in table 2.3 by running blank samples. The results are given in Appendix B. Once this is determined, the weight of a sample is found from a chromatogram using the relation:

$$W_a = f . \frac{W_s . A_a}{A_s}$$

Typical chromatograms of a distilled liquid sample and of that sample plus solvent are shown in fig 2.14.

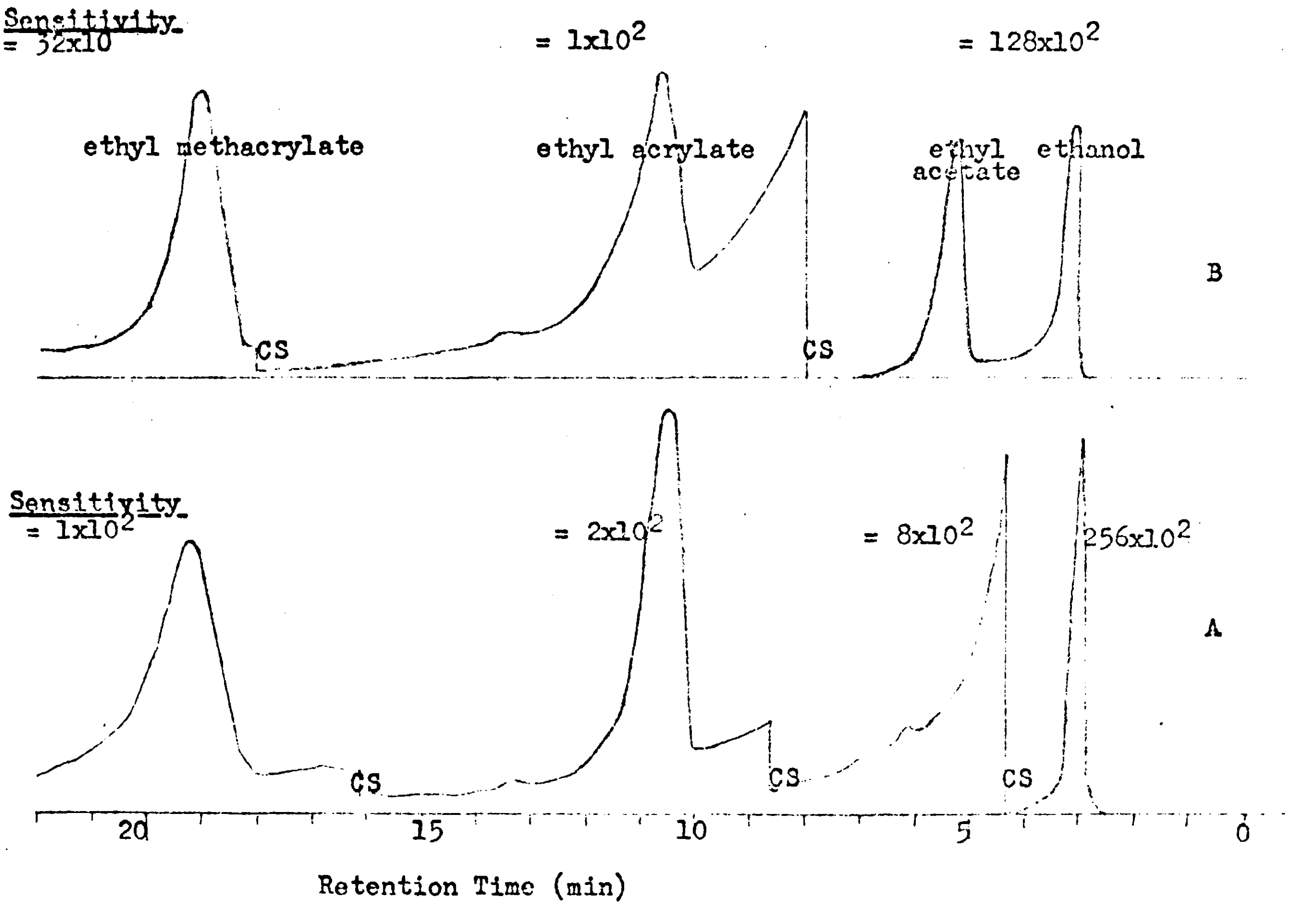
The runs were done isothermally on a 10 ft by 1/4 in 10 % dinonyl phthalate column in all cases except poly(2-ethyl hexyl acrylate); the column temperature is shown in table 2.3. A 6 ft by 1/4 in 1 % carbowax 20M column was used to study the liquids from poly(2-ethyl hexyl acrylate). These were temperature programmed from 30°C to 100°C at 5C°/min.

2(xvi) Short Chain Fragment Analysis

The undistillable liquids and the fraction of degradation products in section C of the sealed tube (fig 2.10) were combined for each sample. This fraction was weighed and then combined with the same fraction from other degraded samples of the same polymer. The molecular weight of the total was found using the Vapour Pressure Osmometer.

G.L.C. Chromatograms were run of this fraction, but it is thought that only the more volatile species passed through the 6 ft by 1/4 in carbowax 20M column used. A typical chromatogram is shown in fig 2.15. The chromatogram of some straight chain alkanes on the same column is shown for comparison.

Fig 2.14 Distilled Liquids from ST405E on G.L.C. A. Undiluted
B. With Solvent

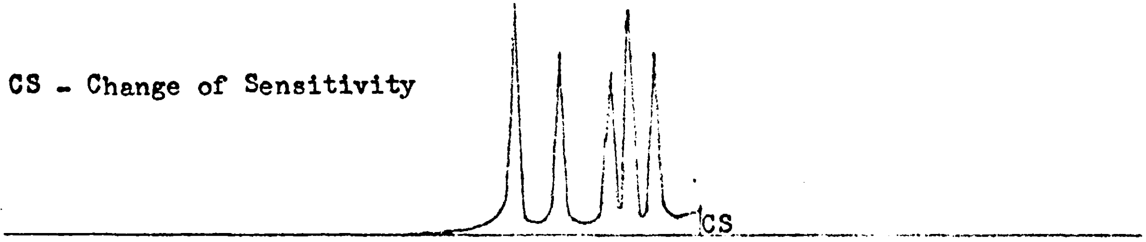


CS - Change of Sensitivity

Fig 2.15B G.L.Chromatogram of C18, 19, 20, 22 and 24 n-Alkanes

Solvent Peaks Omitted in Both Cases, For Conditions, See 2(xvi)

CS - Change of Sensitivity



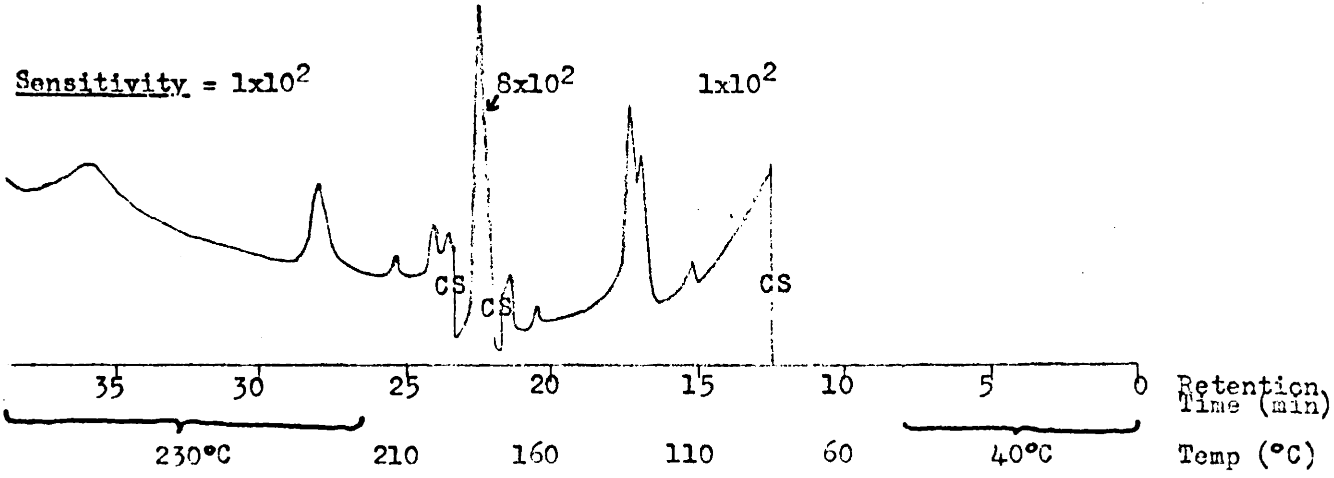


Fig 2.15A G.L.Chromatogram of Short Chain Fragments from Poly(n-Butyl Acrylate)

2(xvii) Residue Analysis

The residue in part A of the sealed tube was allowed to stand overnight in 10 ml Analar toluene. The solution was then poured through a filter paper to separate sol and gel fractions. The filter paper was washed with further Analar toluene until constant weight was attained for the dried paper and gel.

The gel was analysed by microanalysis. The molecular weight of the soluble portion was determined by osmometry. Infrared and nuclear magnetic resonance (N.M.R.) spectra (Perkin Elmer R10 N.M.R. spectrometer) were obtained of the samples dried by evaporation of toluene solvent and redissolved in Analar carbon tetrachloride.

2(xviii) Infrared Analysis of Total Residue

A series of degradations were performed on films of poly {(ethyl-),(iso-propyl-) and (n-butyl acrylate)} cast between two sodiumchloride discs. The discs were placed in the end A of a sealed tube which for these runs was made of 18 mm outside diameter tubing. The discs were marked so that they were always positioned in the same orientation in the infrared beam. The peak intensities of the changing spectra were measured and plots of optical density against time of degradation drawn for the more important peaks.

2(xix) Low Temperature Degradation Studies

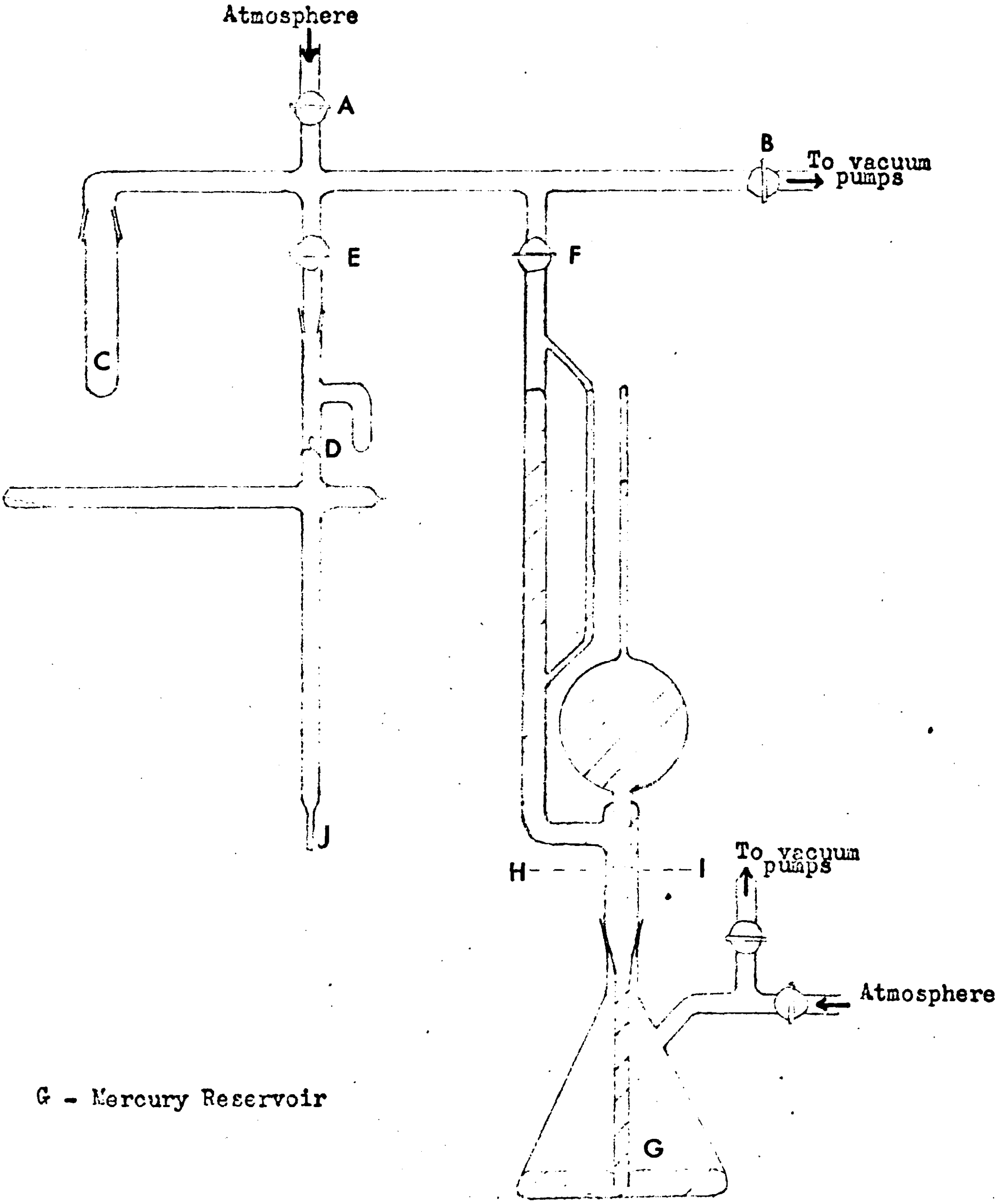
A series of degradations of poly(n-butyl acrylate) were performed at 241°C and of poly(iso-propyl acrylate) at 195°C in an attempt to study the changes in molecular weight of the polymers when little volatilisation is occurring. The residue and short chain fragment fractions were analysed as described above.

The volatiles were measured by means of a McLeod Gauge, and analysed by a M.S.10 mass spectrometer (A.E.I.Ltd)

A. The McLeod Gauge

The McLeod Gauge was constructed as shown in fig 2.16. It was calibrated by the procedure described in Appendix C. The apparatus was pumped out to a pressure of less than 10^{-5} torr. Capillary J was kept at liquid nitrogen temperature and breakseal D broken with tap B closed. The pressure of non-condensibles was found on the McLeod Gauge. The condensible gases were then distilled into trap C and tap E was closed. Trap C was allowed to warm up to room temperature and the pressure of the gases measured.

The volume enclosed by the sealed tube, trap C, the McLeod Gauge (including the bulb) and taps A and B was found approximately (since the internal volume of the sealed tubes varies slightly) as shown in Appendix C. The smaller volume enclosed by trap C, the McLeod Gauge, and taps A,B and E was found accurately. Thus



G - Mercury Reservoir

Fig 2.16 McLeod Gauge

the number of moles of non-condensible and total gases could be found for each sample using the General Gas Law relationship

$$n = P.V/R.T$$ Symbols as on page 44

The method of calculating n is given in Appendix C

Chapter 3 Preliminary Investigations

3(i) Introduction

Before embarking on a quantitative study of the degradation of the polyacrylates, it was necessary to decide upon a suitable standard temperature, at which volatilisation occurs at a conveniently measurable rate. Although this is a much higher temperature than the polymer will meet in normal use, it is hoped that the degradation reactions observed can be related to the deterioration reactions to which the polymer is liable under normal conditions of processing and wear. It is also important to obtain a qualitative knowledge of the degradation products at this temperature, so that apparatus can be designed to analyse quantitatively all the significant reaction products.

The dynamic molecular still was used to obtain most of this information. Thermal volatilisation and thermogravimetric analyses were used to study the overall nature of the degradation.

3(ii) Dynamic Molecular Still Studies

Approximately 200 mg samples of poly(n-butyl acrylate) {P6B} were degraded for two hours at various temperatures between 290 and 360°C on the dynamic molecular still apparatus. Initial weights, weights of residue and weights of volatiles were found as described in chapter 2. The weight of large chain fragments was found as the difference between the weight of starting material and the weight of measurable reaction products, that is, residue and volatiles. Table 3.1 was drawn up from this information. The molecular weight of the soluble part of the residue was found by the High Speed Membrane Osmometer. In the runs done at 324°C and above the residue and copper powder were caked on to the tray, and no part of the residue dissolved in toluene. Fig 3.1 summarises these results graphically.

The volatiles from these degradations were analysed by mass-spectrometry. The spectra did not vary significantly. Fig 3.2 shows the spectrum of the volatiles from run MS5B at 70 eV. It can be accounted for by a mixture of carbon dioxide, 1-butene and n-butanol, the spectra of which are also shown[81].

A 2 hour degradation of 200 mg of poly(n-butyl acrylate) (MS2B) at 366°C was run outside this series. The volatiles were collected and analysed in an infrared gas cell and by G.C.M.S.. The infrared spectrum and the assignment of the peaks are shown in fig 3.3 to correspond to a mixture of carbon dioxide and butene. The G.C.M.S. chromatogram is shown in fig 3.3a. The peaks are assigned from the mass-spectra as follows:

Table 3.1

Molecular Still Degradation Data on a Poly(n-butyl acrylate) Sample of Initial Molecular Weight 1,150,000.

(2 Hour Runs at Various Temperatures)

A	B	C	D	E	F	G	H	I
MS4B	290	194.6	161.9	32.7	23.5	9.2	32,800	118
MS3B	300	192.7	118.3	74.4	39.2	35.2	19,500	100
MS10B	313	193.6	76.7	116.9	55.5	61.4	11,200	57
MS9B	324	195.0	27.5	167.5	81.7	85.8	Insol.	0
MS6B	347	190.0	17.1	172.9	77.5	95.4	Insol.	0
MS7B	355	191.8	20.1	171.7	83.5	88.2	Insol.	0
MS5B	363	191.4	—	—	—	71.8	Insol.	0

A Sample

B Temperature (°C)

C Initial Weight (mg)

D Weight of Residue (mg)

E Weight Loss (mg)

F Weight of Short Chain Fragments (mg)

G Weight of Volatiles (mg)

H Molecular Weight of Soluble Residue

I Weight of Soluble Residue (mg)

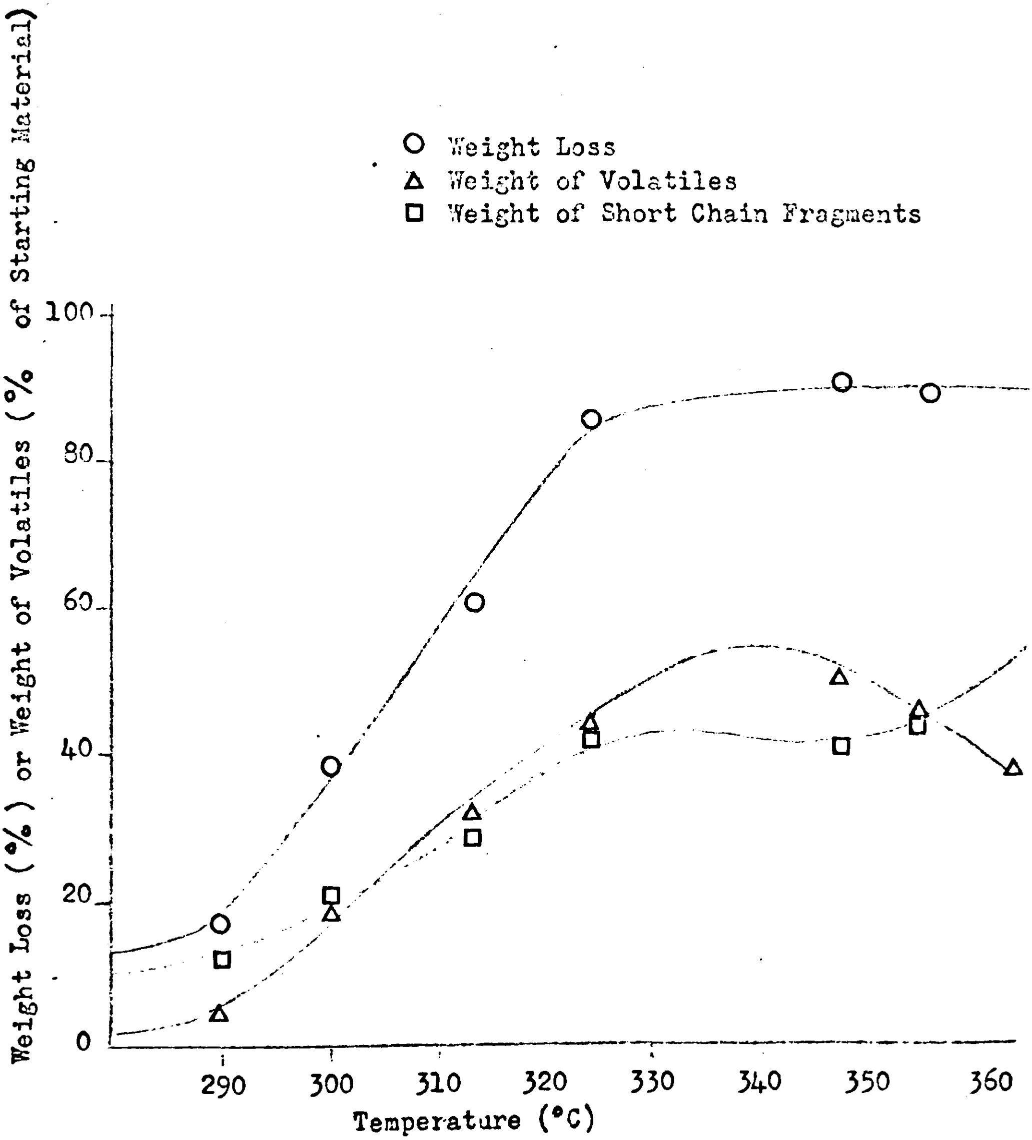


Fig 3.1 Molecular Still Degradation Data, Poly(n-Butyl Acrylate)

(all 2 hour runs)

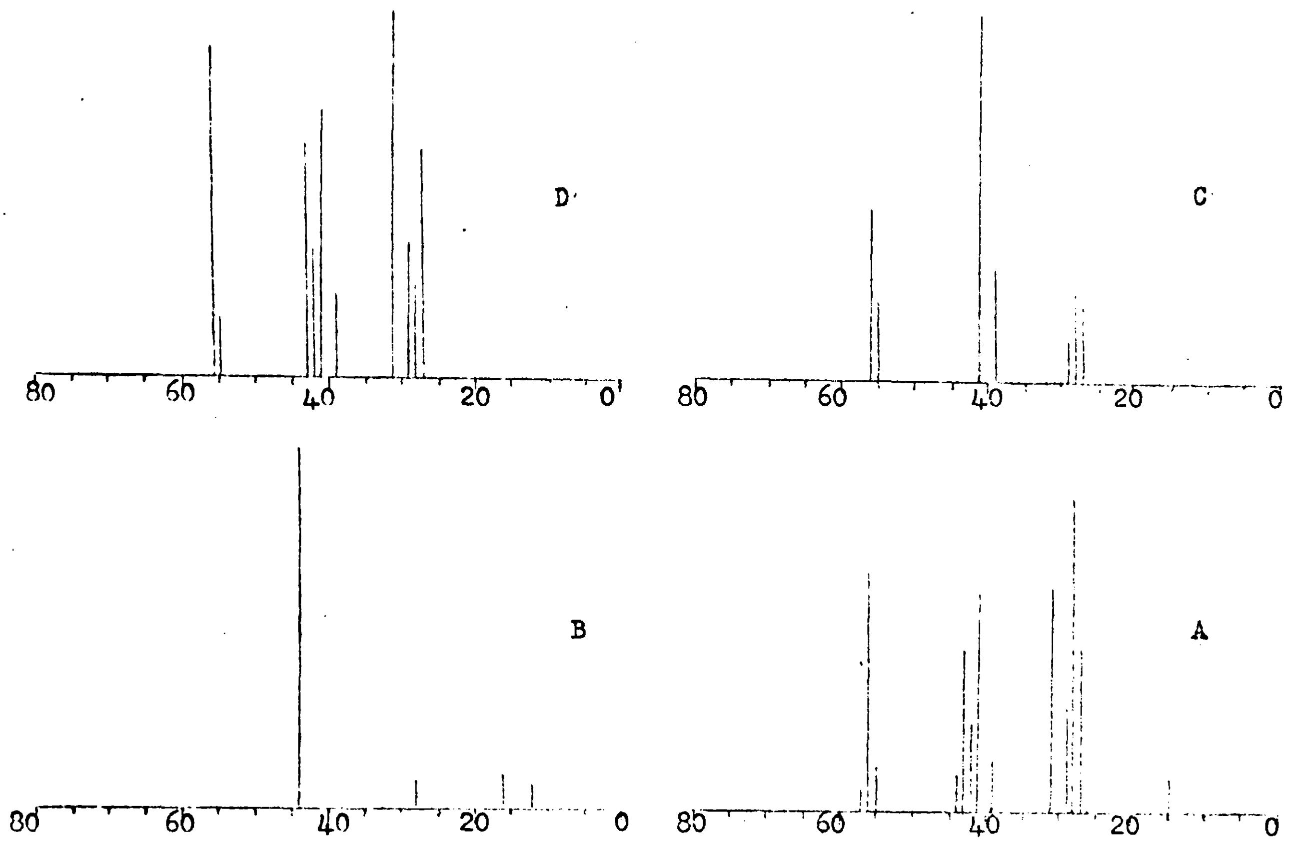


Fig 3.2 Mass Spectra of A — Volatiles from JMS5B, B — CO_2, C — 1-Butene, D — n-Butanol

Fig 3.3 Infrared Spectrum of Gases from JMS2B

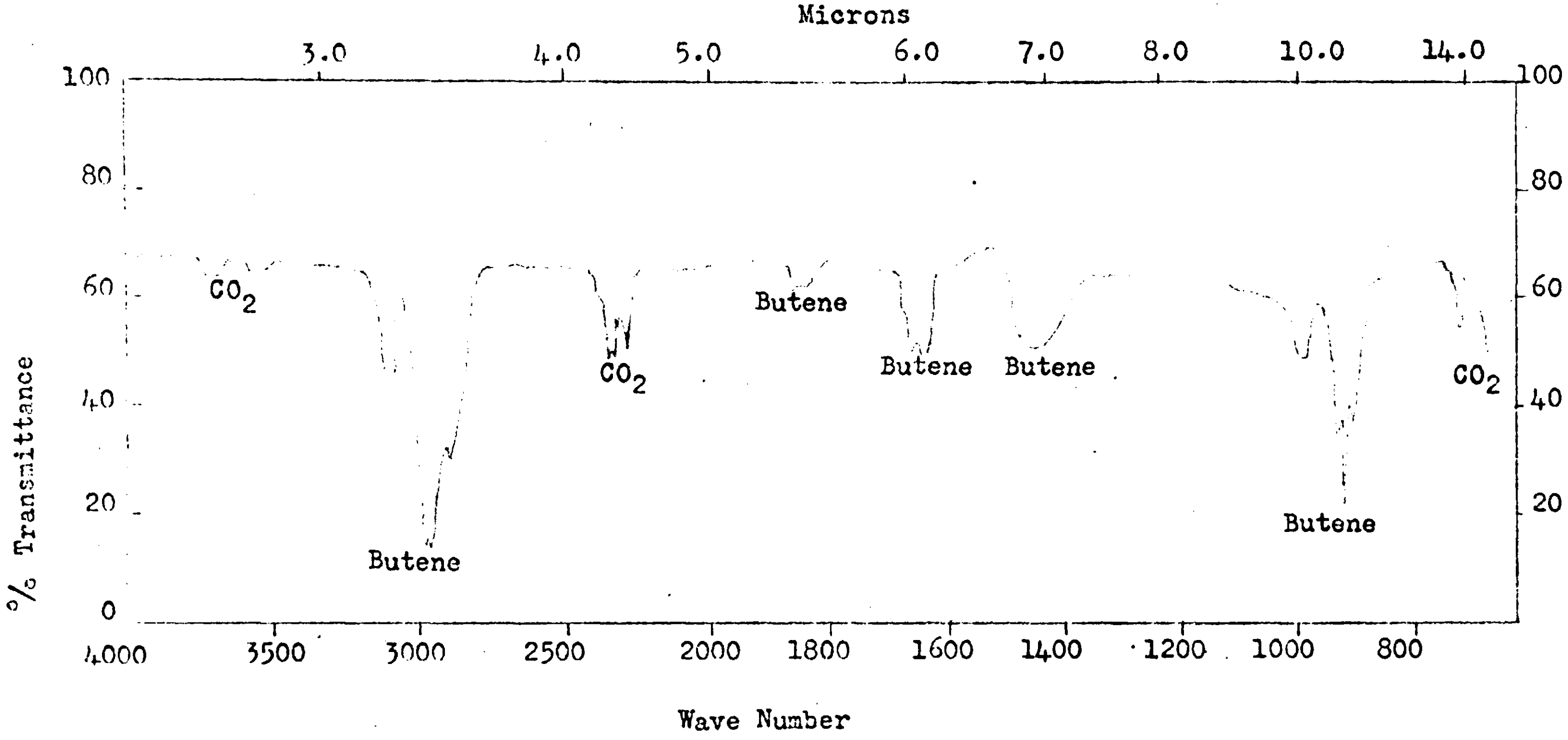


Fig 3.3a G.C.M.S. Chromatogram of Volatiles from MS2B

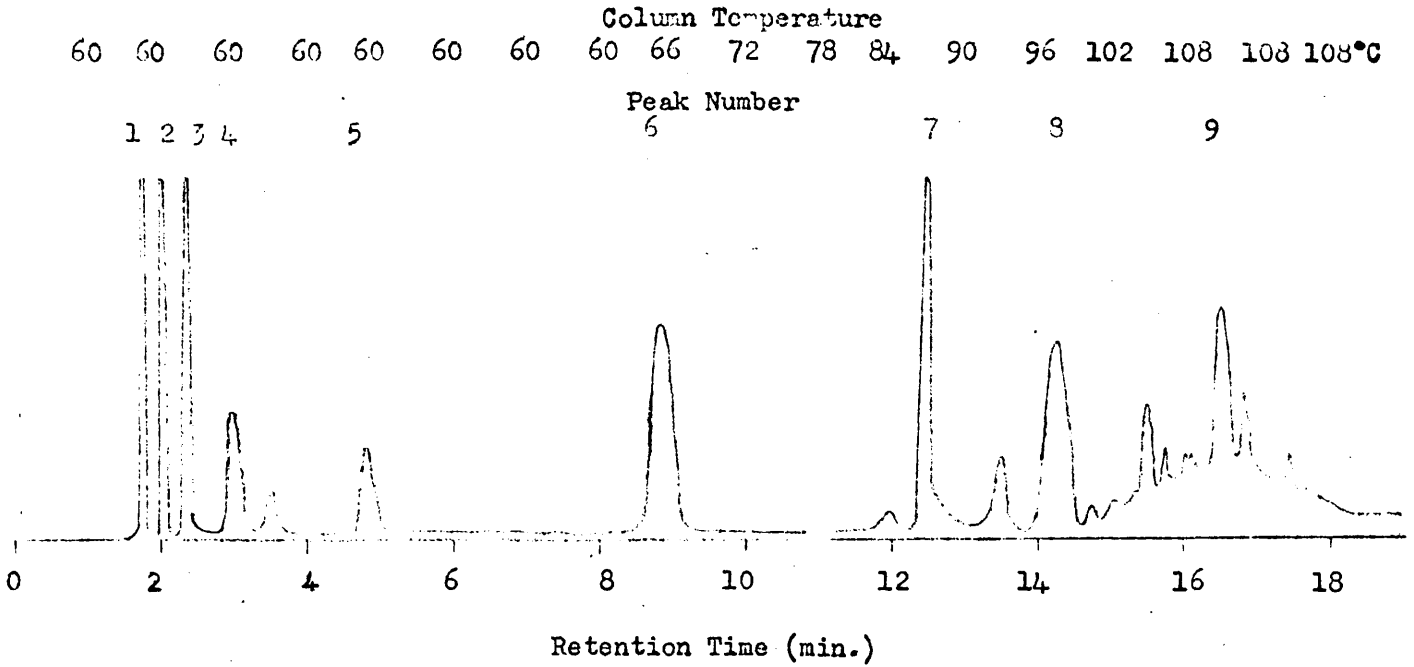


Table 3.2

Chromatograph Peak	Component
1	chloroform (solvent)
2	n-butanol
3	n-butyl acrylate
4	n-butyl methacrylate

The mass-spectra of the higher molecular weight components were not easy to analyse because they rarely gave a significant parent peak and because peaks above mass 200 in the mass-spectrum were difficult to assign with certainty. However the following table gives a list of the main mass-spectrum peaks of the later components in the chromatograph.

Table 3.3

Chromatograph Peak	Main Mass Spectrum Peaks
5	134, 117
6	356, 268, 73
7	428, 341, 73
8	502, 415, 281, 147, 73
9	407, 327, 156, 18

These peaks are not given in order of height since most of them were off the scale of the mass-spectrometer. The appearance of a large peak at mass 73 in three of these spectra would indicate that these components contain butyl ester groups, which lose $CH_3CH_2CH_2CH_2O^+$ ions. Component 5 has a large parent peak and so is probably aromatic in character; possibly an impurity in the toluene solvent used to cast the polymer film.

3(iii) Thermal Volatilisation Analysis

Fig 3.4 a-f shows the TVA thermograms of 50 mg samples of the polymers under study and also of a 100 mg sample of poly(methyl acrylate) (kindly supplied by Dr I.C.McNeill), for comparison. The trap temperatures (see fig 3.2) were -100°C, -75°C, -45°C and 0°C and they are shown on the curves. The sample temperature was programmed at 10C°/min from room temperature to 500°C.

It can be seen immediately that poly(iso-propyl acrylate) behaves differently from the other polymers. It has a main peak beginning at 260°C, with a maximum at 355°C. A secondary peak occurs at 442°C and volatiles are still being evolved at 500°C.

The other five polymers show similar peak shapes - one main peak followed by a low plateau region. Poly(methyl acrylate) appears to be more stable than the remaining four polymers. It begins to volatilise at 325°C compared with 300°C and has a peak

Fig 3.4 T.V.A. Thermograms of

(a) Poly(Methyl Acrylate) (b) Poly(Ethyl Acrylate)

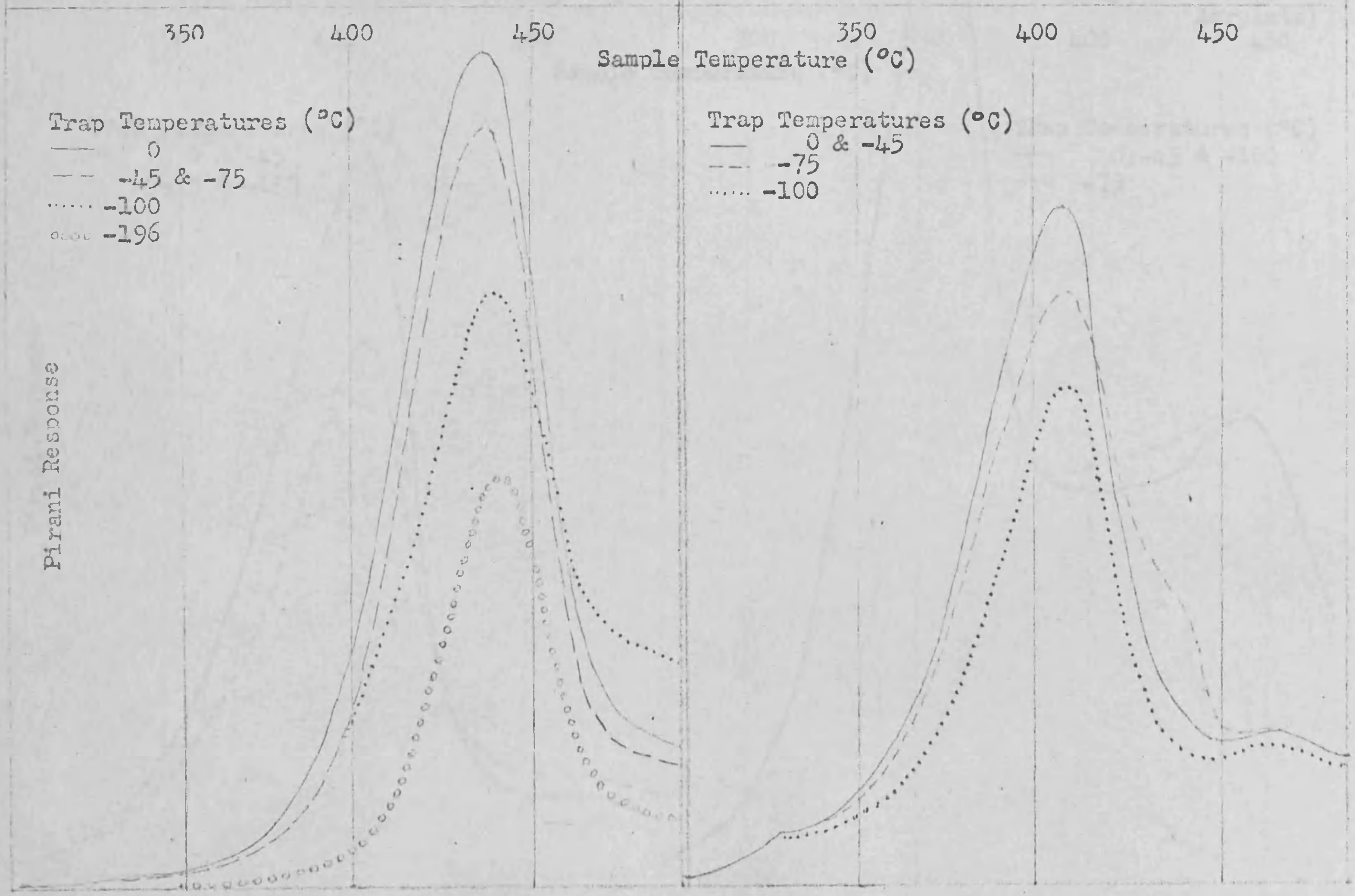
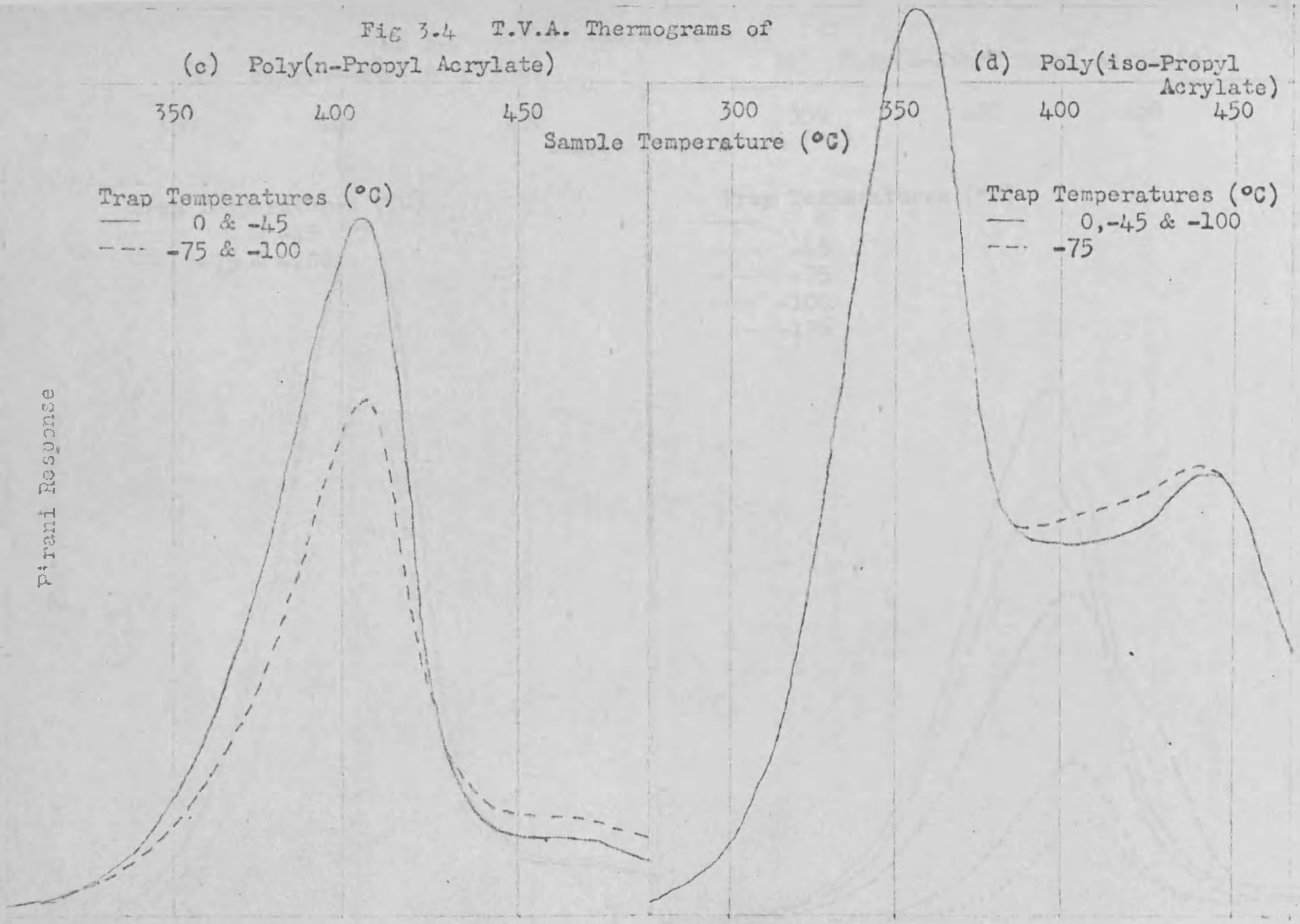


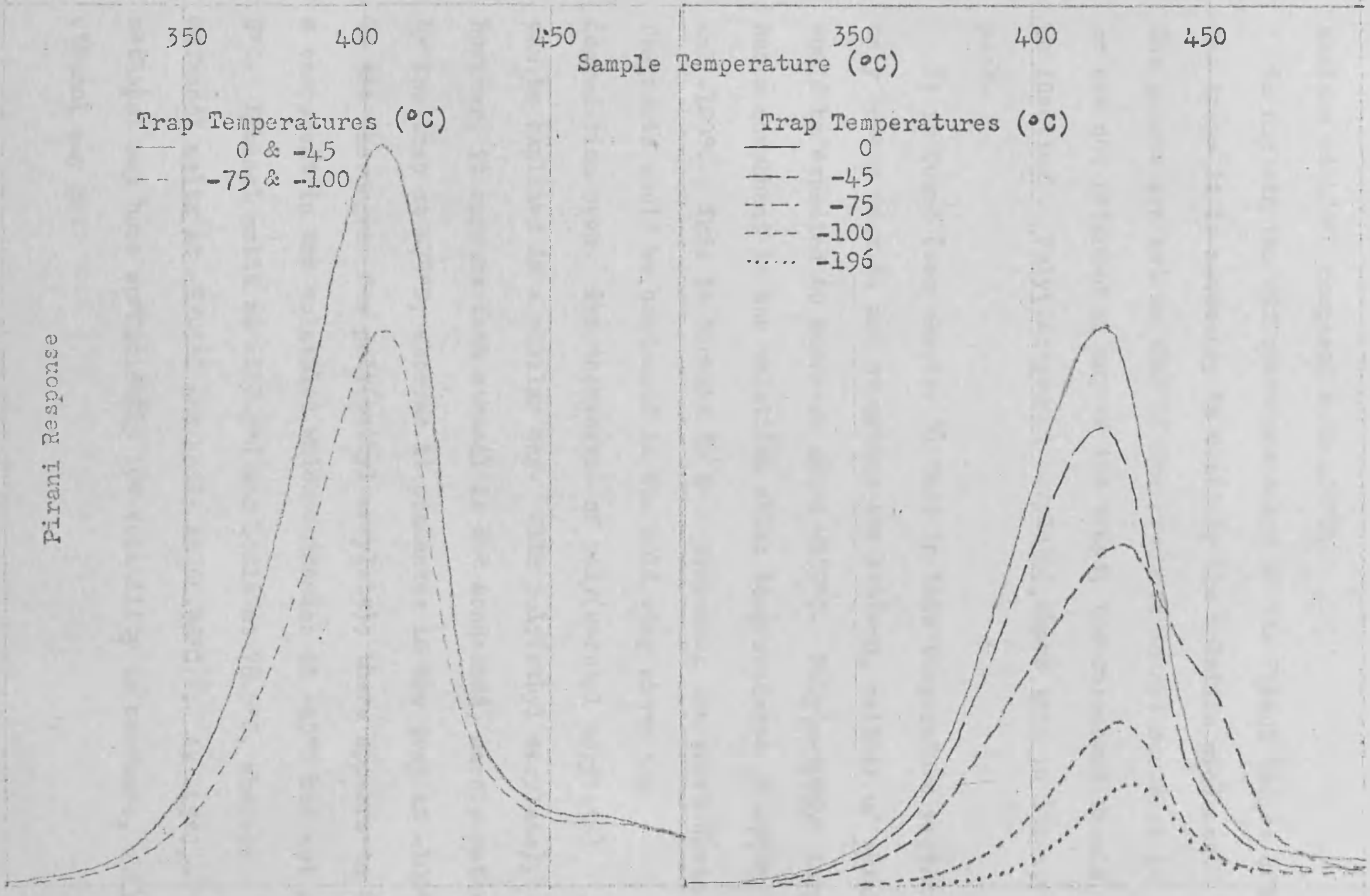
Fig 3.4 T.V.A. Thermograms of



(c) Poly(n-Propyl Acrylate)

(d) Poly(iso-Propyl Acrylate)

Fig 3.4 T.V.A. Thermograms of



(e) Poly(n-Butyl Acrylate) (f) Poly(2-Ethyl Hexyl Acrylate) maximum at 438°C compared with 405°C.

To explain the different responses of the Pirani Gauges after the traps it is necessary to consider the volatile products. The gauges are set so that if the products do not condense in or are not retarded by any of the traps, the responses should be identical. Poly(iso-propyl acrylate) shows this in its main peak.

It is found (see chapter 5) that in this temperature region, only carbon dioxide and propylene are evolved, neither of which would be expected to condense above -100°C. Poly(n-propyl acrylate) has a component in the volatiles which does condense at -75°C and -100°C. This is thought to be n-propanol; the short chain fragments would be condensed in the cold ring above the degradation oven. The thermogram of poly(n-butyl acrylate) can be explaned in a similar way. With poly(ethyl acrylate), however, it appears that ethanol is not condensed, merely retarded, by the trap at -75°C, whereas it condenses in the trap at -100°C. In the thermogram for poly(methyl acrylate), there appears to be a component in the volatiles which condenses at -45°C but not at 0°C. Ethanol melts at -117.3°C and boils at 78.5°C, whereas methanol melts at -97.8°C and boils at 64.96°C[59]. At -45°C, methanol may have sufficiently low volatility to condense, whilst ethanol may not.

Kane[1] observed very little non-condensibles in his degradation studies at 290-310°C. The peak after the trap at -196°C, corresponding to non-condensibles, does not begin until about 360°C. This peak is surprising, however, when compared with Madorsky's claim that non-condensibles composed less than 1 % of the volatile products in his degradations of poly(methyl acrylate) between 250 and 400°C.

The secondary peak from poly(iso-propyl acrylate) is associated with the break-down of the insoluble residue obtained in the present work. This is thought to consist of acid and anhydride groups and above 400°C would be expected to give a variety of small molecules, although, as fig 3.4d shows, it appears that these are mostly non-condensible at -100°C.

3(iv) Thermogravimetric Analysis

The T.G.A. thermograms of the polymers, except for poly(2-ethyl hexyl acrylate), are shown in fig 3.5(a-d). These were run at 5C°/min from room temperature to 500°C with approximately 10 mg samples.

They confirm the information from the T.V.A. thermograms. Poly(iso-propyl acrylate) volatilisation is a two-stage process beginning at 265°C and leaving 8 % residue at 500°C. The other threepolymers degrade by a one-stage process beginning at 300°C and leaving less than 5 % residue at 500°C.

Fig 3.5 T.G.A. Thermograms of (a) and (b) Poly(Ethyl-) and (n-Propyl Acrylate)

(almost identical)

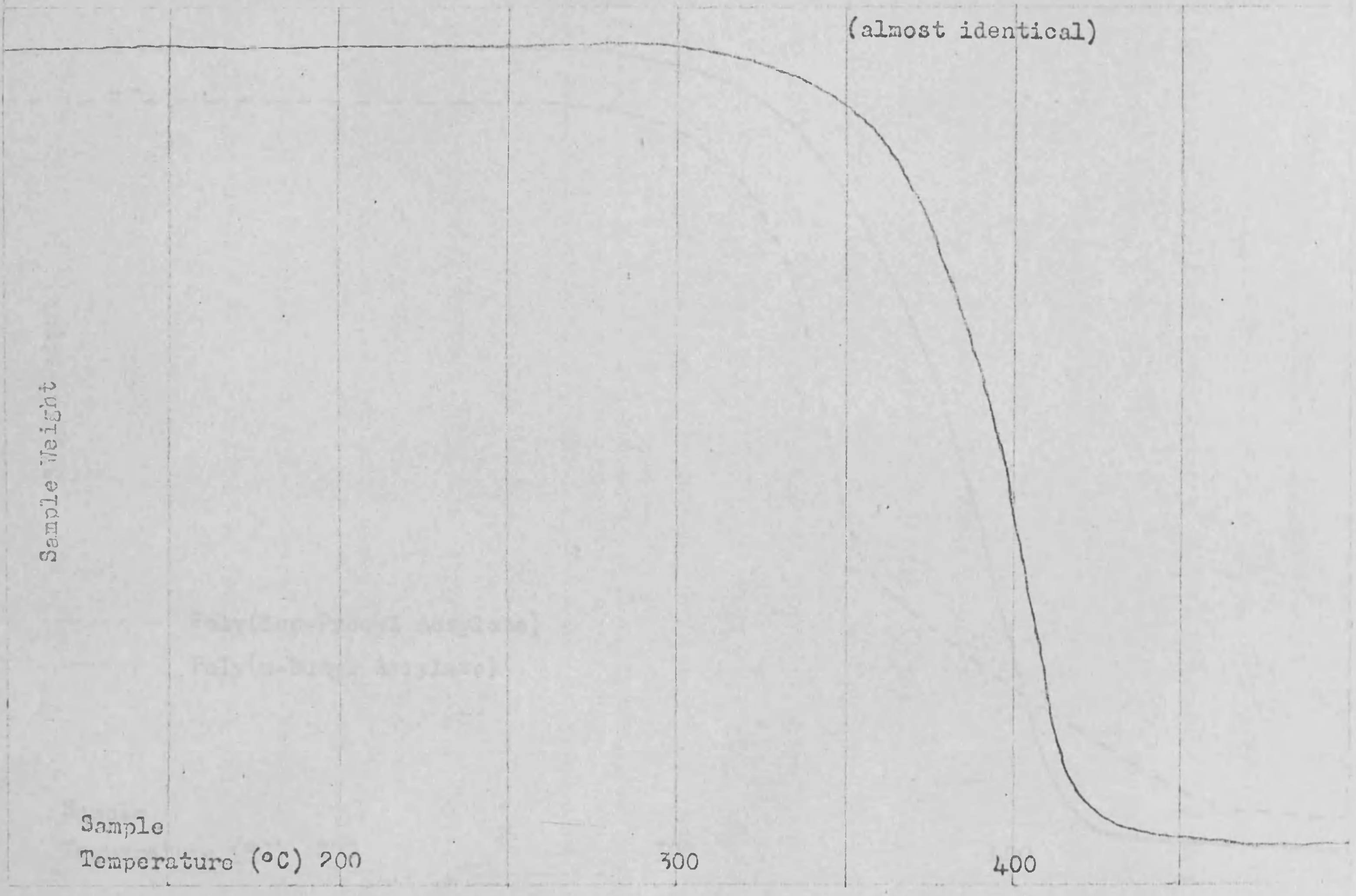
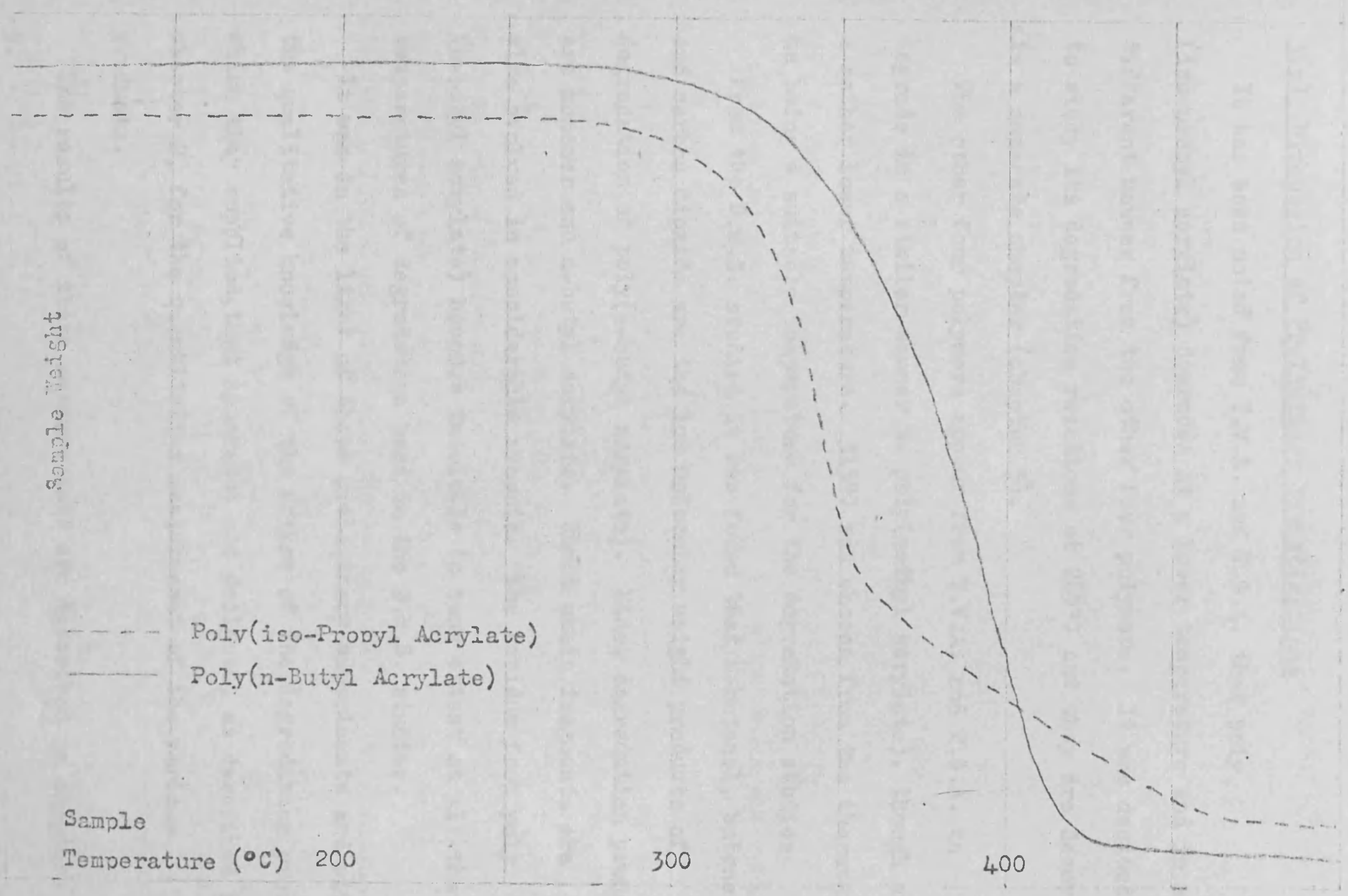


Fig 3.5 T.G.A. Thermograms of (c) Poly(iso-Propyl Acrylate) and (d) Poly(n-Butyl Acrylate)



3(v) Discussion of Preliminary Investigations

It has been noted from T.V.A. and T.G.A. that poly (iso-propyl acrylate) degrades at a lower temperature and in a different manner from the other four polymers. It was decided to study its degradation reactions at 265°C and they are described in a separate chapter (chapter 5).

The other four polymers appear from T.V.A. and T.G.A. to degrade in a similar manner to poly(methyl acrylate), though at a rather lower temperature. 315°C was chosen from the thermograms as being a suitable temperature for the degradation studies.

From the D.M.S. studies it was found that n-butanol, butene and carbon dioxide are the low molecular weight products of degradation of poly(n-butyl acrylate). Minor degradation products are monomer and n-butyl acrylate. Short chain fragments are also evolved in considerable amounts. The residue from poly (n-butyl acrylate) becomes insoluble to some extent at all the temperatures of degradation used in the D.M.S. studies.

It was in the light of these preliminary experiments and with the qualitative knowledge of the nature of the degradation products which they supplied, that apparatus was designed, as described in chapter 2, for the quantitative measurement of the various products.

The results of these measurements are described in chapters 4 and 5.

Chapter 4 Degradation Reactions of Poly(Primary Acrylates) at 315°C

4(i) Introduction

As the preliminary investigations have shown (Chapter 3), the poly(primary acrylates) all degrade at approximately the same temperatures and by a one-stage process. Poly(iso-propyl acrylate), on the other hand, decomposes at a lower temperature and by a two-stage route; it will therefore be dealt with separately (Chapter 5). In this and the following chapter a thorough quantitative analysis of the degradation products of the polymers at one temperature is described, using the degradation and analytical techniques mentioned in Chapter 2.

Although, in theory, one set of degradation experiments should be sufficient for all the significant products of degradation to be analysed, it was found difficult to separate the lighter alcohols from the gases, olefin and carbon dioxide. Two series of degradations were therefore performed at the same temperature for all the poly(primary acrylates) except poly(2-ethyl hexyl acrylate), in which case the difference in volatility between the gas, carbon dioxide, and the liquids, alcohol and olefin, is sufficient to allow good separation. The first series was used to obtain yields of carbon dioxide and olefin, and the second series gave the amounts of the other degradation products. Where only qualitative results were required, data was obtained from either set of degradations.

The degradation experiments on the poly(primary acrylates) described in this chapter were all carried out at 315°C.

Where tables of results are necessary for the understanding of the text, they appear in the vicinity of the reference to them in the text. In other cases, they appear at the end of the chapter.

4(ii) Analysis of Major Gaseous Products

The method of analysing the gases gave three pressure readings on the constant volume manometer: the total pressure of the gases was read directly on the C.V.M.; and the infrared analysis of the gases gave peak intensities which could be used in conjunction with the calibration curves to find the pressure on the C.V.M. of the carbon dioxide and olefin individually. The sum of the pressures for carbon dioxide (P_{CO_2}) and olefin (P_{olefin}) did not always agree exactly with the total pressure (P_{total}), possibly because of pressure effects on the infrared spectrum of the gases. The infrared spectrum was therefore used to find the ratio of pressure of carbon dioxide to pressure of olefin and a 'corrected pressure' (C.P.) value was obtained, such that

$$\frac{C.P._{CO_2}}{C.P._{olefin}} = \frac{P_{CO_2}}{P_{olefin}}$$

and $C.P._{CO_2} + C.P._{olefin} = P_{total}$

Table 4.3 shows how the pressures of total gas, carbon dioxide and 1-butene were calculated for poly(n-butyl acrylate). The total pressure value shown in this table is the pressure of gases at room temperature, P_{rt}, minus the pressure of gases non-condensible at -196°C, $P_{N.C.}$:

$$P_{total} = P_{rt} - P_{N.C.}$$

Use of the conversion factors given in 2(xiv) enables the number of moles of gas (n) to be calculated. The weight of gas (W) is found by multiplying n by M, the molecular weight. In the case of the non-condensibles, the weight calculated is based on the assumption that these gases are wholly carbon monoxide (see 4(iii)).

A similar method was used to find the weights of gases evolved from the other polymers. These are given in Tables 4.1, 4.2 and 4.4. Figs 4.1 to 4.4 show this data graphically with the gases plotted as percentage of the initial polymer. Tables 4.5 to 4.8 show the amount of gas (and other products as described below) as percentages of the initial polymer. Figs 4.5 to 4.8 plot the gas evolution as moles per gram monomer unit; this data is also noted in tables 4.9 to 4.12.

The amount of carbon dioxide evolved per monomer unit from poly(ethyl-),(n-propyl-) and (n-butyl acrylates) does not change greatly, although in the early stages of degradation of poly(n-butyl acrylate) the evolution is rather slower. Poly(2-ethyl hexyl acrylate), however, produces very much less carbon dioxide, about a third as much as the other three polymers.

Fig 4.1 Gas Evolution from Poly(ethyl acrylate) at 315°C

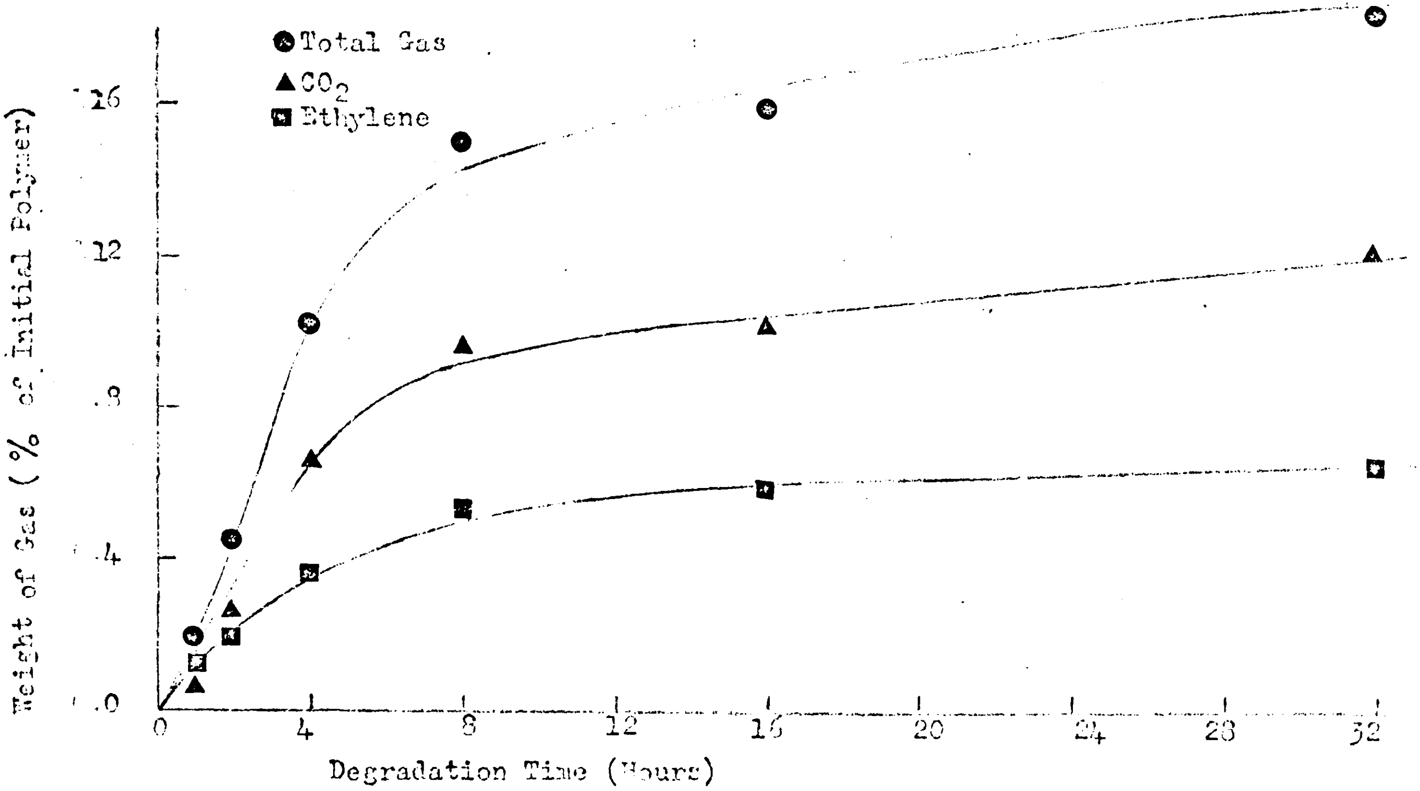


Fig 4.2 Gas Evolution from Poly(n-propyl acrylate) at 325°C

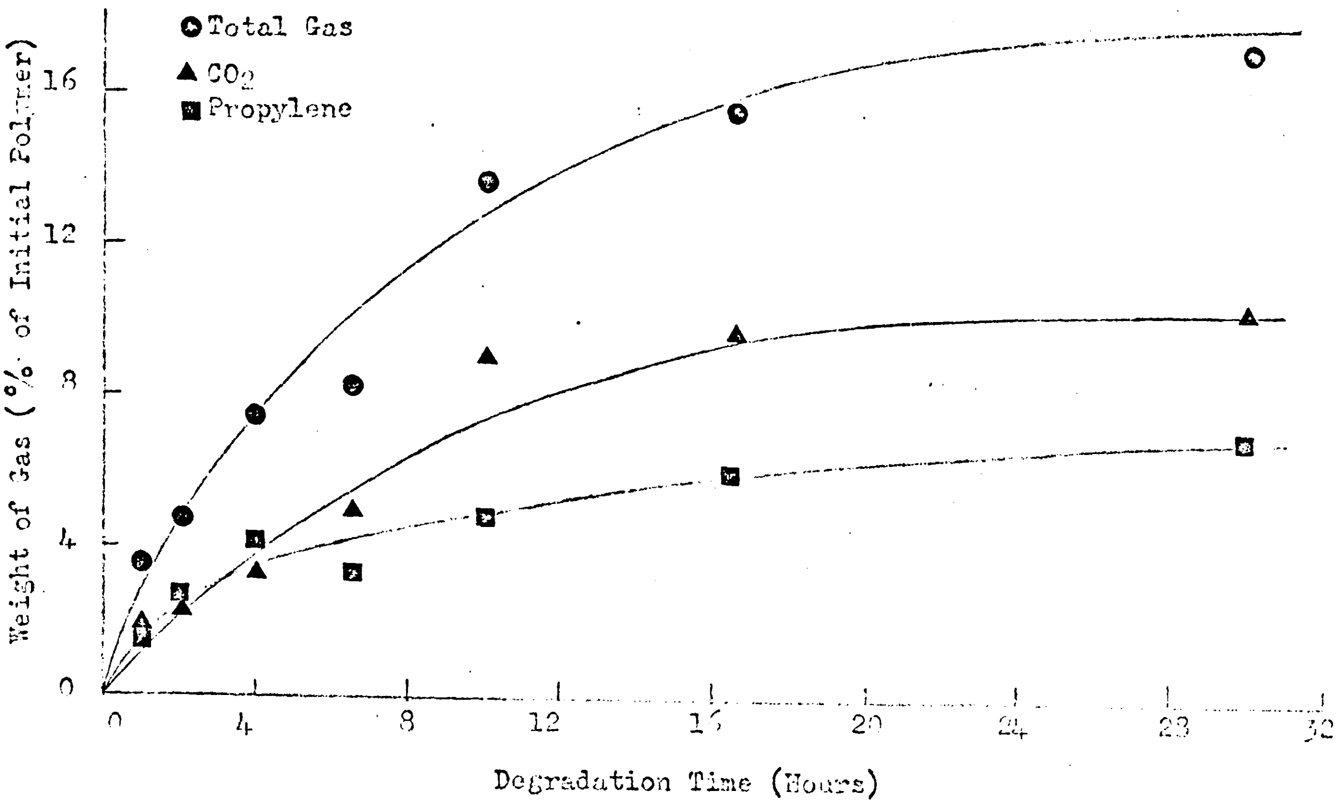


Fig 4.3 Gas Evolution from Poly(n-butyl acrylate) at 315°C

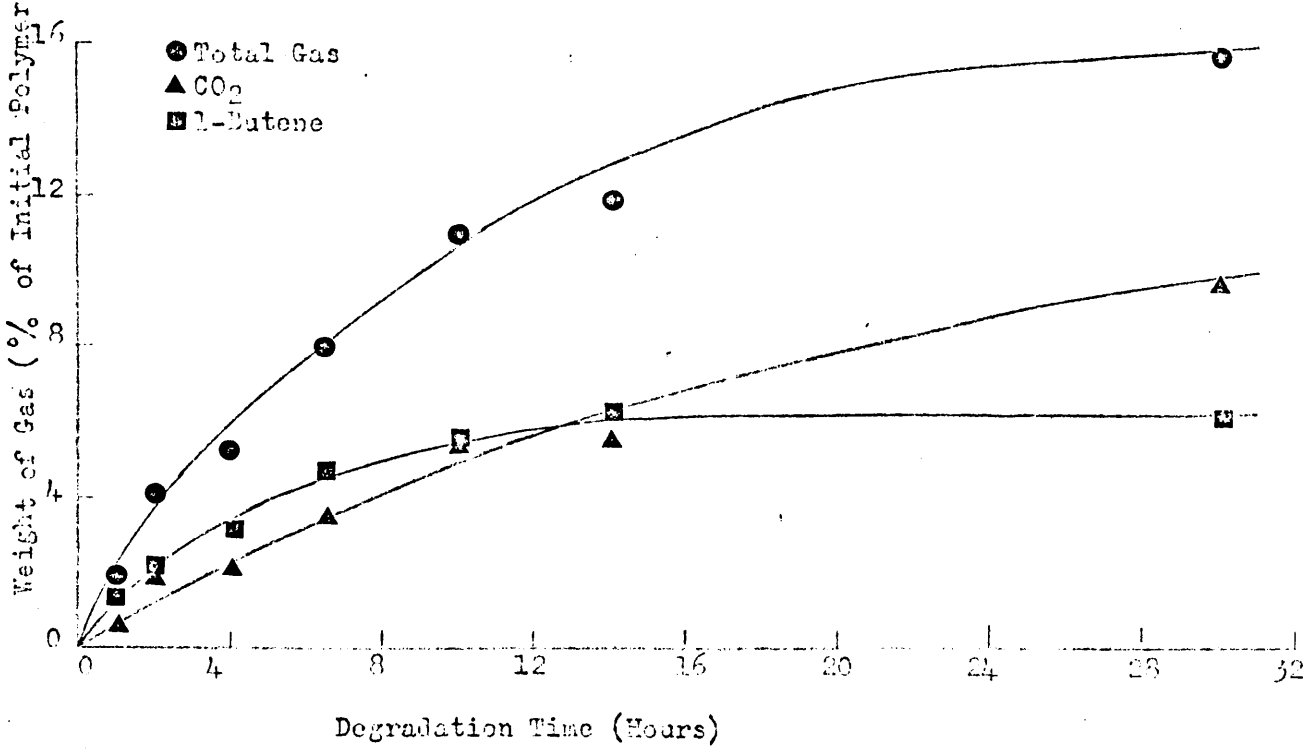


Fig 4.4 Gas Evolution from Poly(2-ethyl hexyl acrylate) at 315°C

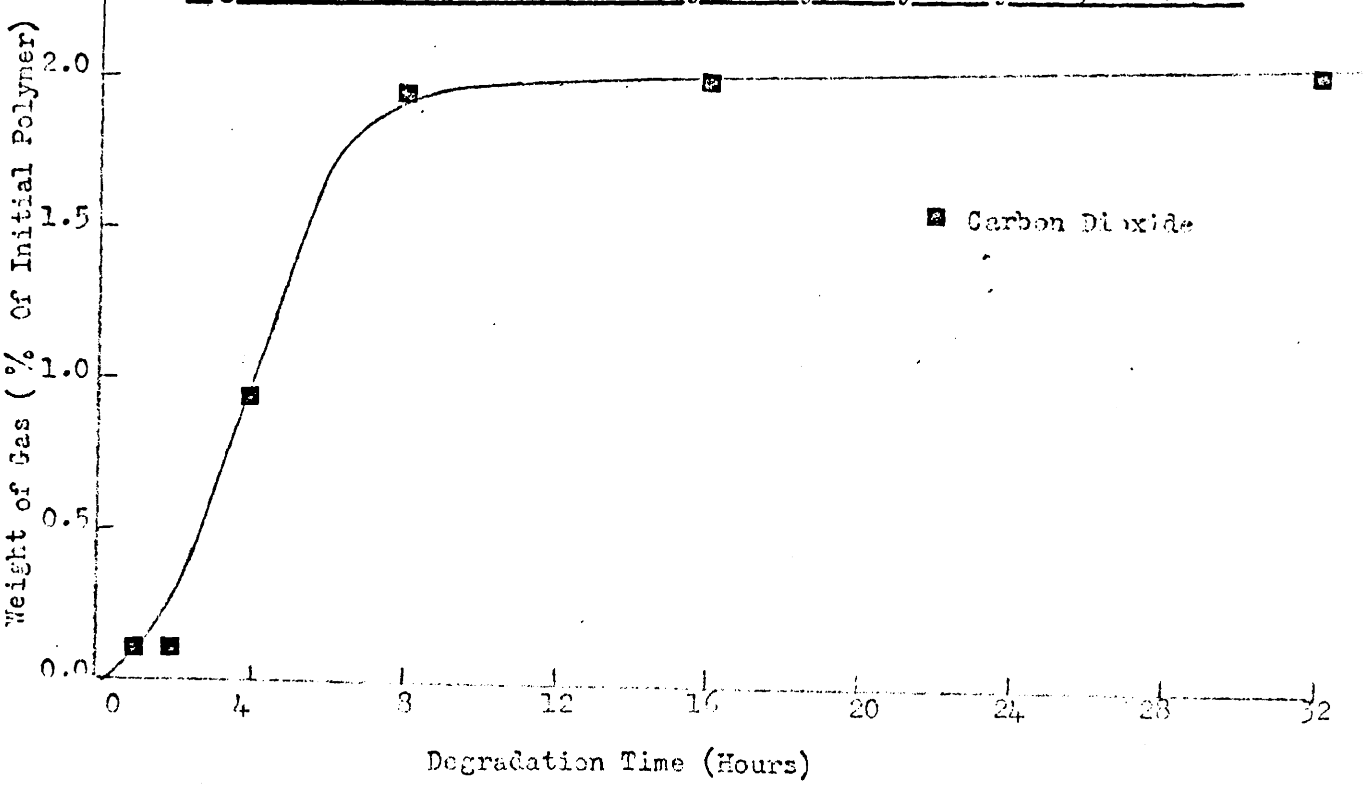


Fig 4.5 No. of Moles of Gas Evolved per Gram Monomer Unit against Time of Degradation for Poly(Ethyl Acrylate)

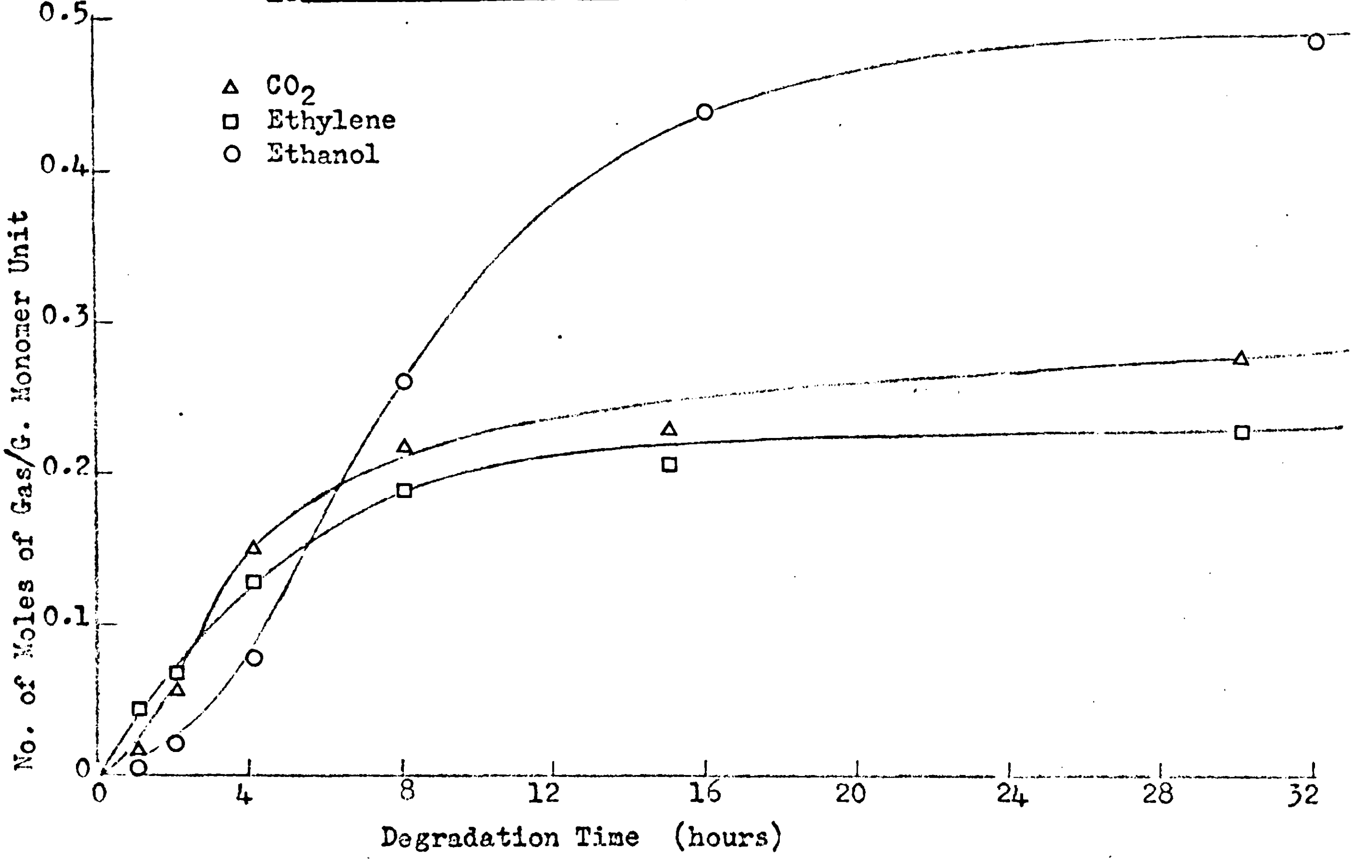


Fig 4.6 No. of Moles of Gas Evolved per Gram Monomer Unit against Time of Degradation for Poly(n-Propyl Acrylate)

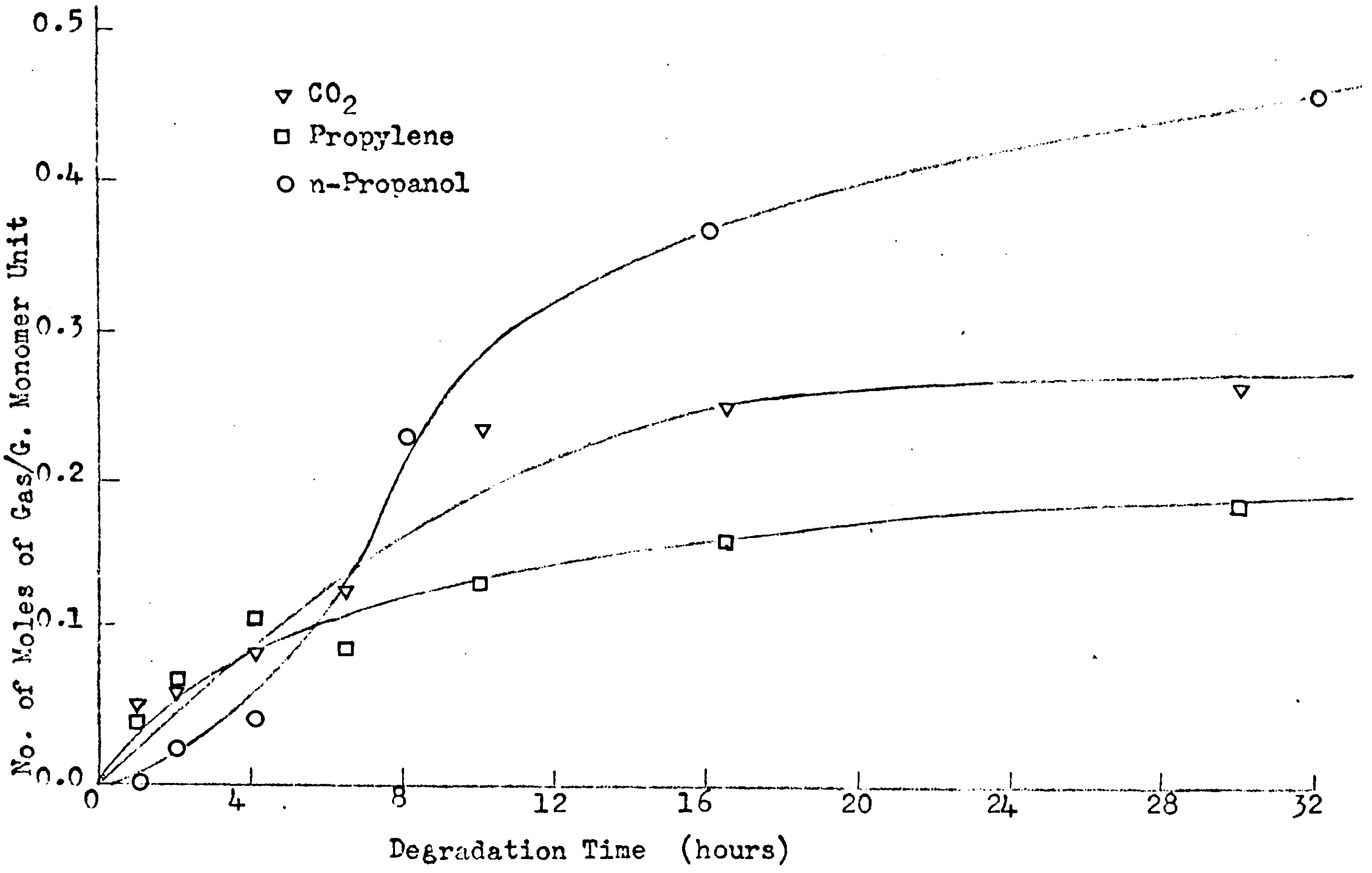


Fig 4 7 No. of Moles of Gas Evolved per Gram Monomer Unit against Time of Degradation for Poly(n-Butyl Acrylate)

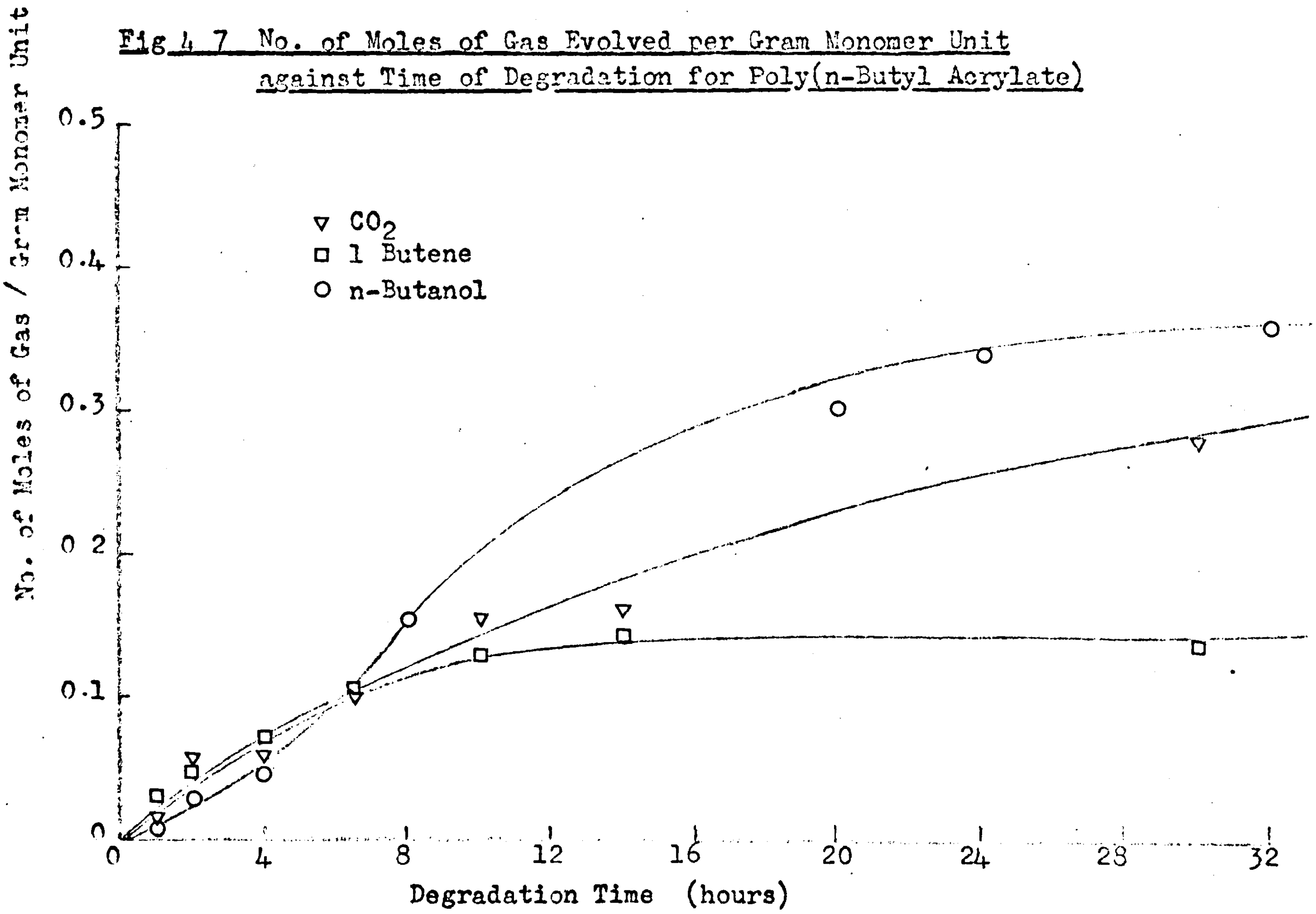
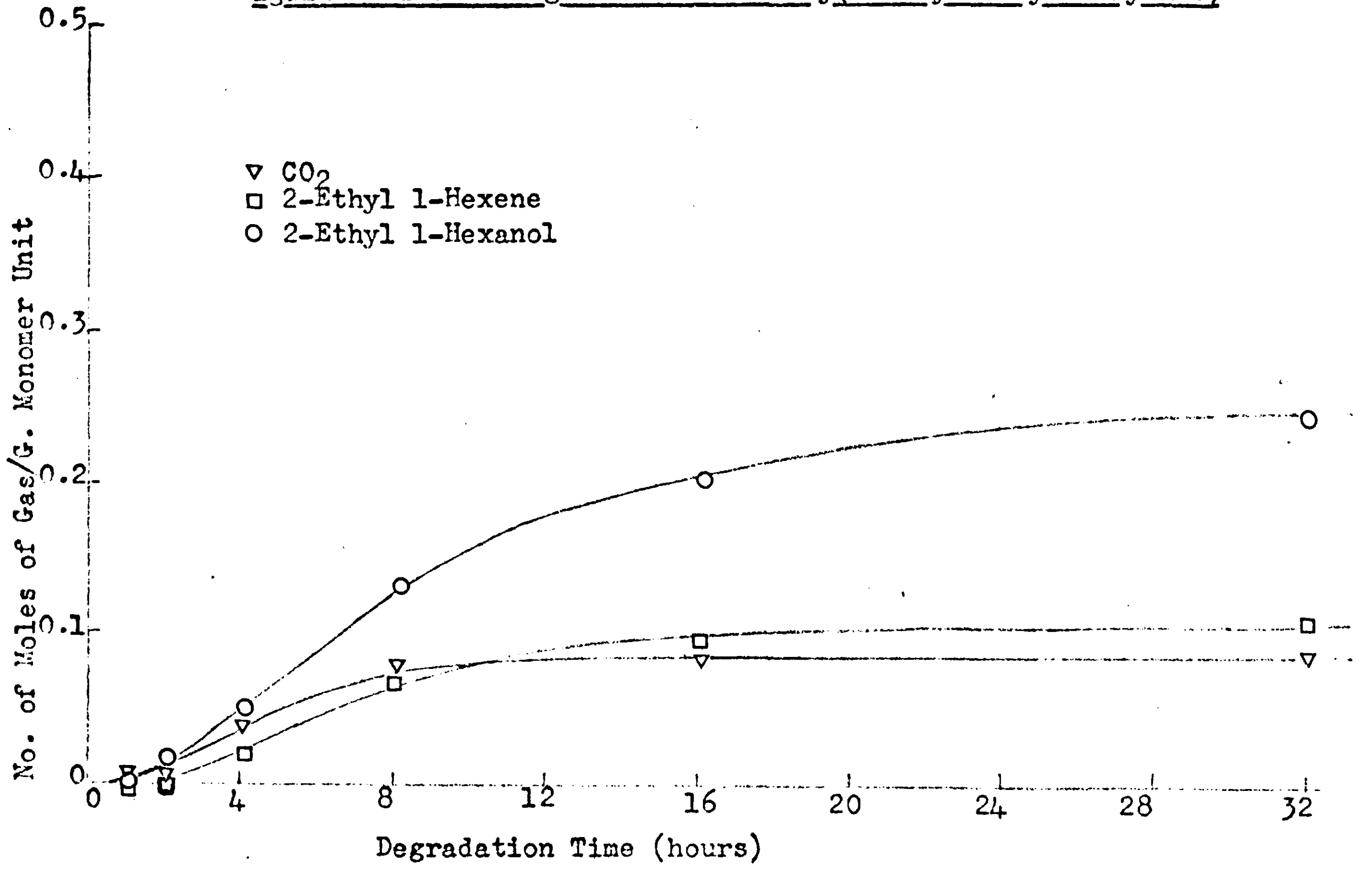


Fig 4.8 No. of Moles of Gas Evolved per Gram Monomer Unit against Time of Degradation for Poly(2-Ethyl Hexyl Acrylate)



The amount of olefin produced per monomer unit seems to depend on the number of β-hydrogen atoms on the alkyl group. Poly(ethyl acrylate) evolves more than poly(n-propyl acrylate), which evolves more than poly(2-ethyl hexyl acrylate). Poly(n-propyl-) and (n-butyl acrylate) produce similar amounts except at high conversion.

Initially, the rate production of olefin from poly(ethyl-), (n-propyl-) and (n-butyl acrylates) is rather faster than that of carbon dioxide. The molar ratio of the two gases is close to unity until about 35 % conversion after which production of carbon dioxide exceeds that of olefin. Poly(2-ethyl hexyl acrylate) also evolves carbon dioxide and olefin at similar rates until 35 % conversion, but thereafter olefin production slightly exceeds that of carbon dioxide. (see 4(viii)).

It is difficult to apply normal kinetic equations to the evolution of volatile material from these polymers. There are at least three mutually exclusive, competing reactions; namely, the intramolecular transfer reaction to produce short chain fragments, the elimination of alcohol and the reaction or reactions which produce carbon dioxide and olefin. Thus, in the reaction

acrylate unit ⟶ olefin + modified acrylate unit I

for example, the concentration of reagent (acrylate units) is continually changing not only because of this reaction, but also because of removal of acrylate units in the competing reactions-acrylate unit ——> alcohol + modified acrylate unit II

and n(acrylate unit) ——> short chain fragment

The calculation of kinetic data is normally done by use of the equation

Rate of reaction = $dA/dt = k[A]^a$ where A is a reagent or a product,

k is the rate constant

and a is a number, the order of the reaction.

It is, therefore, essential to know the concentration of reagents or products throughout the reaction.

The initial rates of production of volatile degradation products can be found, however, by plotting the rates of the reactions at various times during the degradation process and extrapolating the curve to zero time. This is done for the gaseous degradation products in figs 4.9-4.12. Estimated values for initial rates of appearance of degradation products are given in table 4.13.

In cases where a rate maximum appears, the curve after the maximum is extrapolated back to the ordinate axis to find the rate of evolution of volatiles.

Fig 4.9 Rate of Evolution of Carbon Dioxide and Olefin from Poly(ethyl acrylate) against Time of Degradation

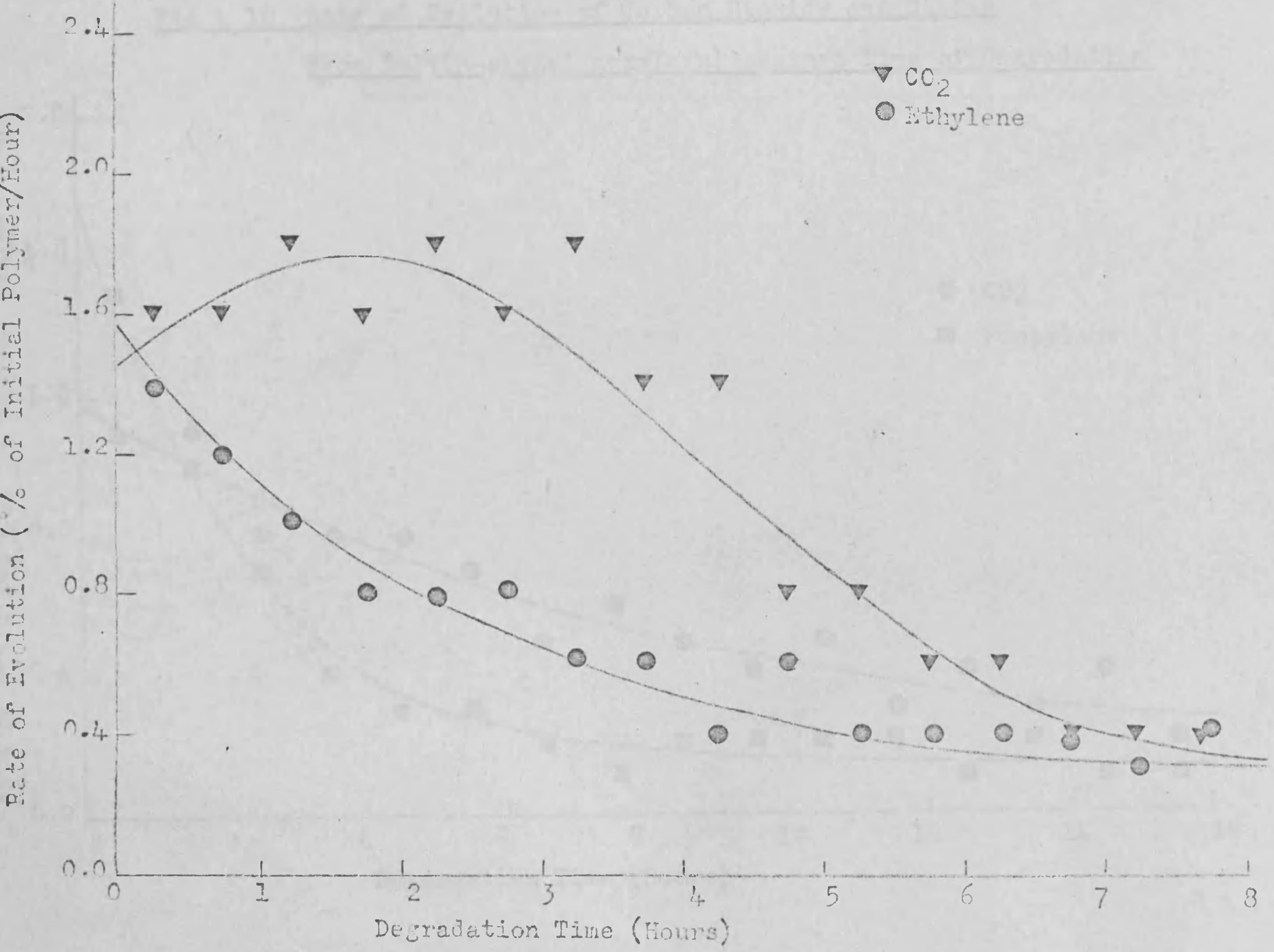


Fig 4.10 Rate of Evolution of Carbon Dioxide and Olefin from Poly(n-propyl acrylate) against Time of Degradation

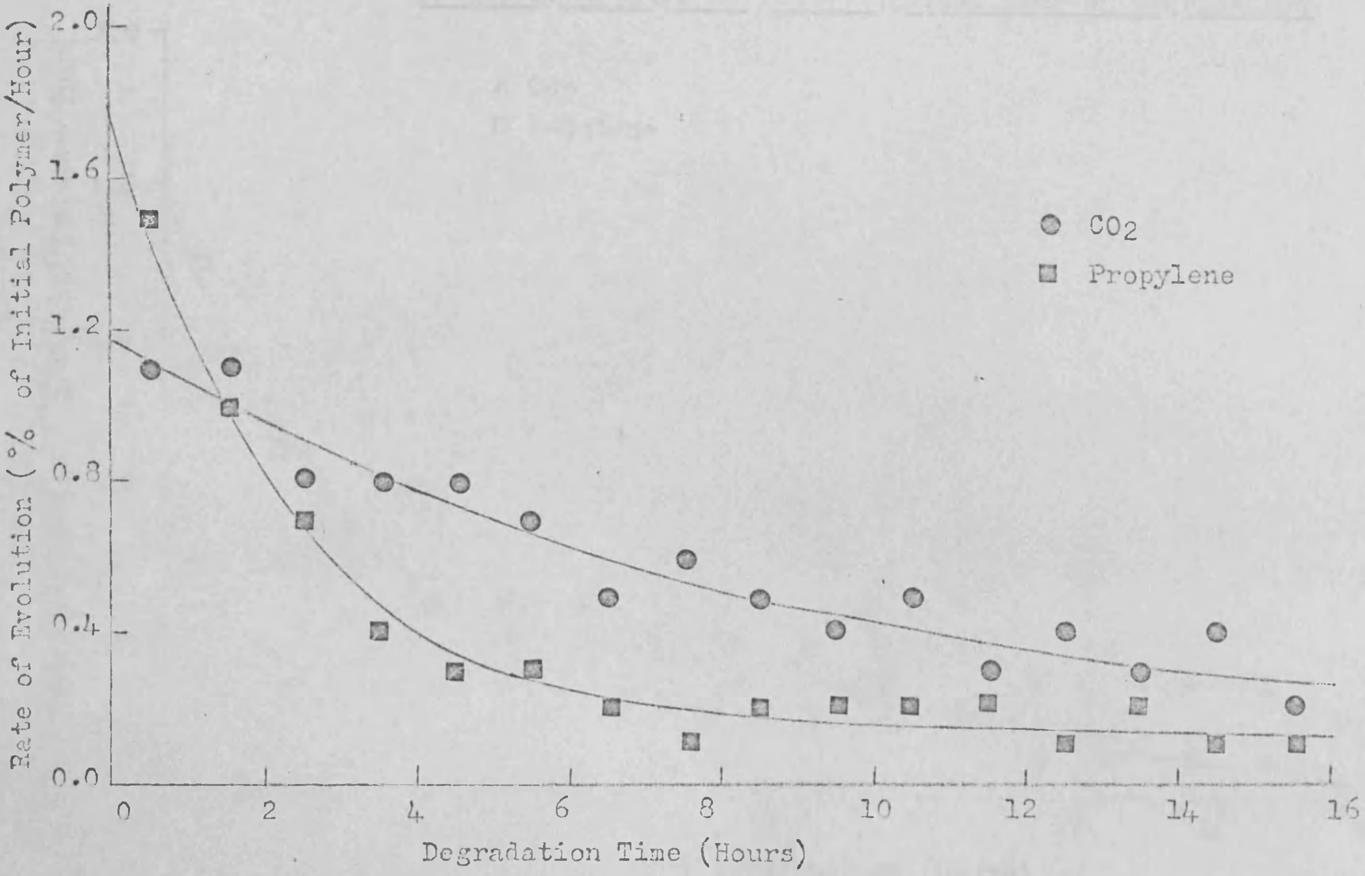


Fig 4.11 Rate of Evolution of Carbon Dioxide and Olefin from Poly(n-Butyl Acrylate) against Time of Degradation

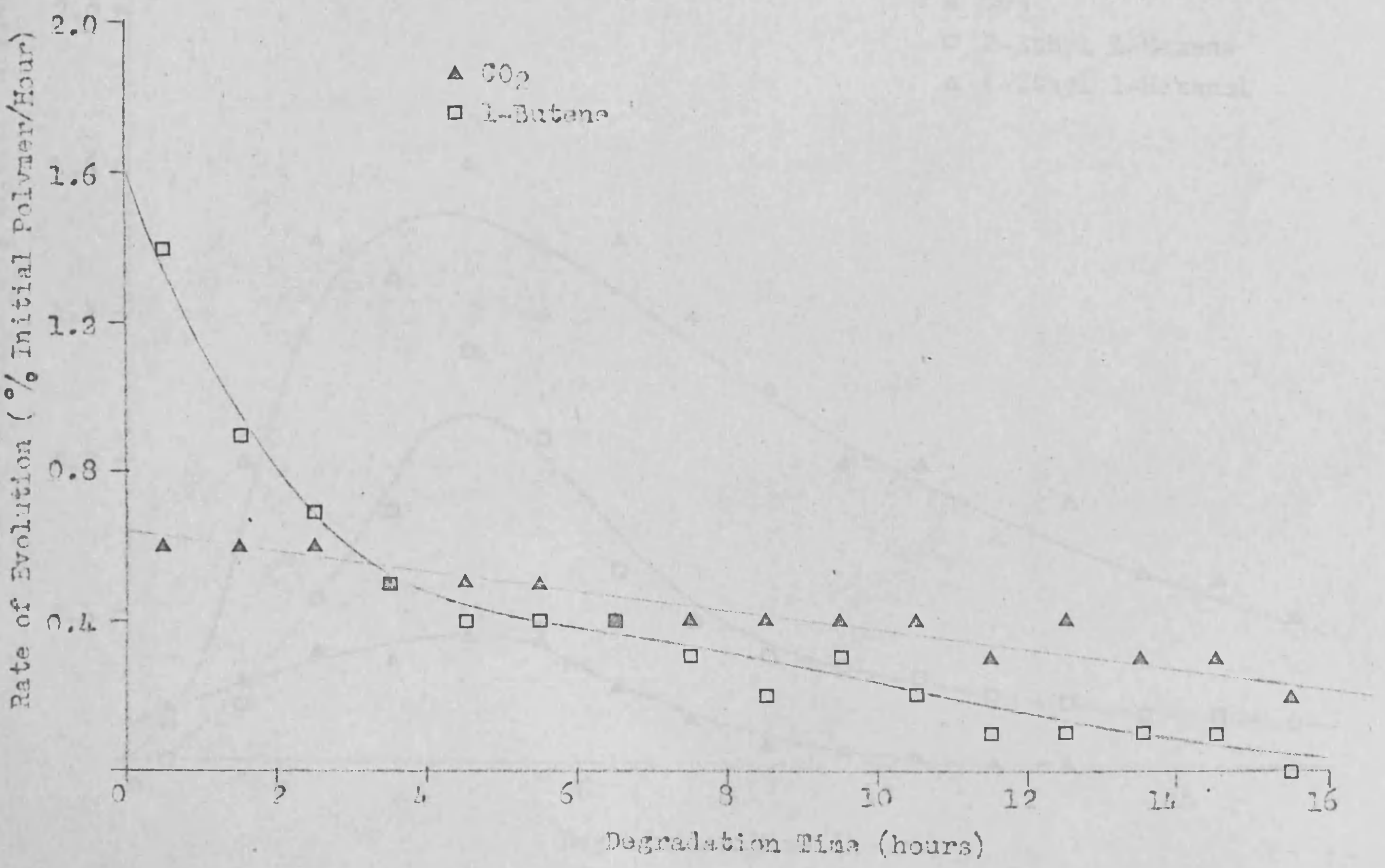


Fig 4.12 Rate of Evolution of Carbon Dioxide, Olefin and Alcohol from Poly(2-Ethyl Hexyl Acrylate) against Time of Degradation

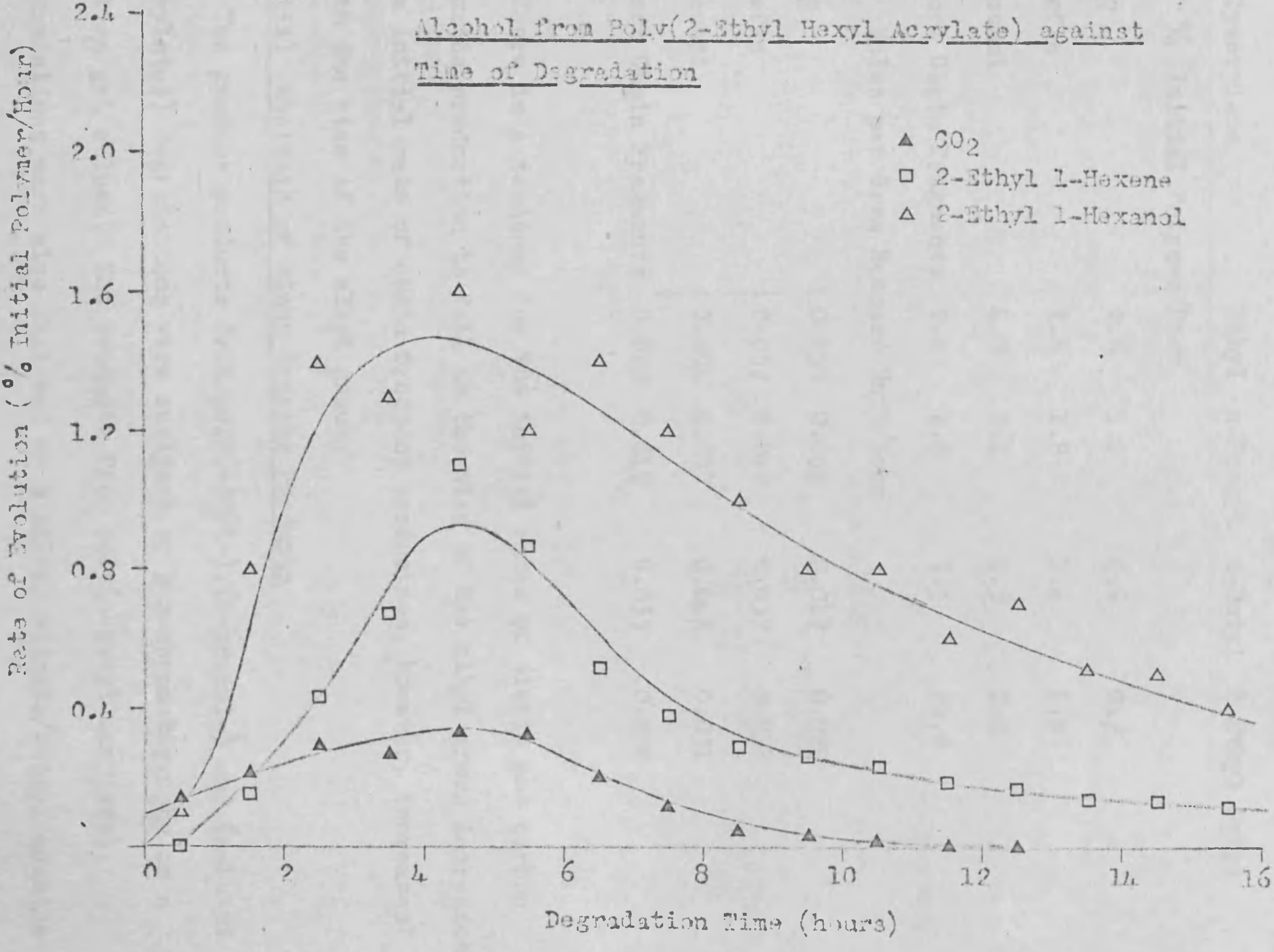


Table 4.13

Initial Rates of Production of Volatiles

Polyacrylate	Ethyl	n-Propyl	n-Butyl	2-Ethyl Hexyl
A. % Initial Polymer/Hour				
CO_2	2.6	1.2	0.6	0.7
Olefin	1.6	1.8	1.6	1.9
Alcohol	4.3	5.1	2.5	2.2
Short Chain Fragments	2.0	1.8	3.3	20.0
B. Moles per Gram Monomer Unit/Hour				
CO_2	0.059	0.033	0.017	0.029
Olefin	0.057	0.049	0.037	0.031
Alcohol	0.094	0.097	0.043	0.031
Short Chain Fragments	0.020	0.018	0.033	0.200

There is a tendancy for the initial rates of olefin and carbon dioxide production to fall as the size of the alkyl group increases. The initial rate of chain fragment production, however, increases with the size of the alkyl group.

4(iii) Analysis of Minor Gaseous Products

The gaseous products from poly(ethyl-),(n-propyl-) and (n-butyl acrylates) degradations were analysed by gas-chromatography on a silica gel column. The products from poly(n-butyl acrylate) degradations were also analysed on a silver nitrate/benzyl cyanide column. These columns are described in 2(xiv). Typical chromatograms are shown in figs 4.13 and 4.14. Carbon dioxide and carbon monoxide are not detected by the flame ionisation detector used. It was found in each case that the olefin peak was much larger than any other: the next largest peak was attributed to the corresponding alkane. The areas of the olefin and alkane peaks were measured and assumed to be approximately proportional to the concentrations of the substances. The ratio of alkane/olefin was found to lie in the range 8×10^{-4} to 8×10^{-3} and did not change significantly from one polymer to another, or with time of heating. A shoulder on the 1-butene peak in fig 4.14 is caused by cis-2-butene, but this is small in amount compared with 1-butene.

The gases not condensible at -196°C were studied with an MS-10 mass spectrometer. A sealed tube, containing a sample of 200mg poly(n-propyl acrylate) degraded for 14 hours at 315°C was attached to the inlet system, the enclosed air pumped out, and the break seal broken open while the volatiles in the sealed tube were cooled at -196°C. The mass spectrum obtained at 70 eV is shown in fig 4.15. By far the largest peak is that at mass number 28. Very much smaller peaks were found at mass numbers 2 and 12. The large peak at 28 was attributed to carbon monoxide which has small subsidiary peaks at 16 and 12. The small peak at mass number 2 was attributed to hydrogen. The normal sensitivity ratio of hydrogen (mass number 2)

Fig 4.13 G.L.C. of Gaseous Degradation Products from Poly(n-Butyl Acrylate) Silica Gel Column

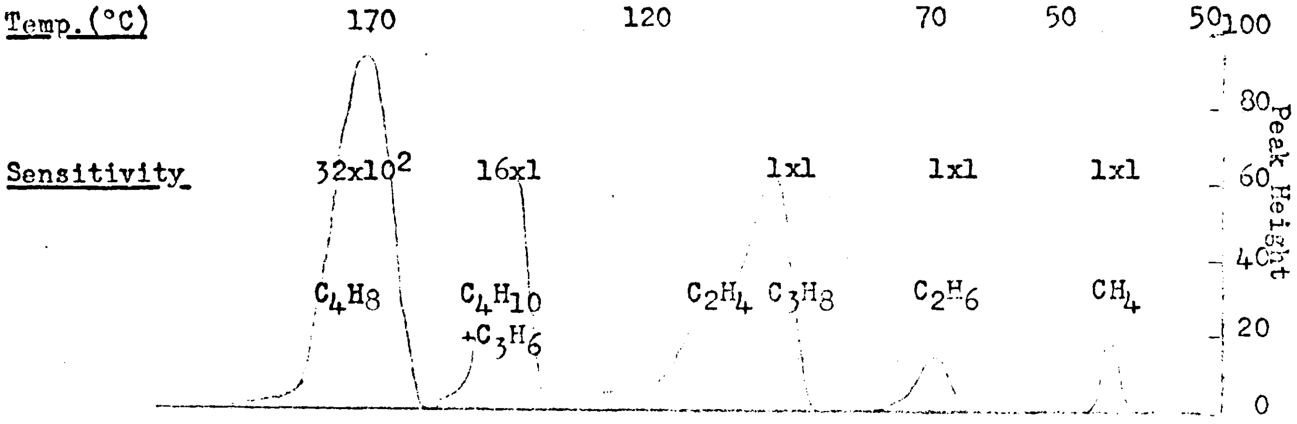


Fig 4.14 G.L.C. of Same Gas Sample on Silver Nitrate/Benzyl Cyanide Column at 25°C

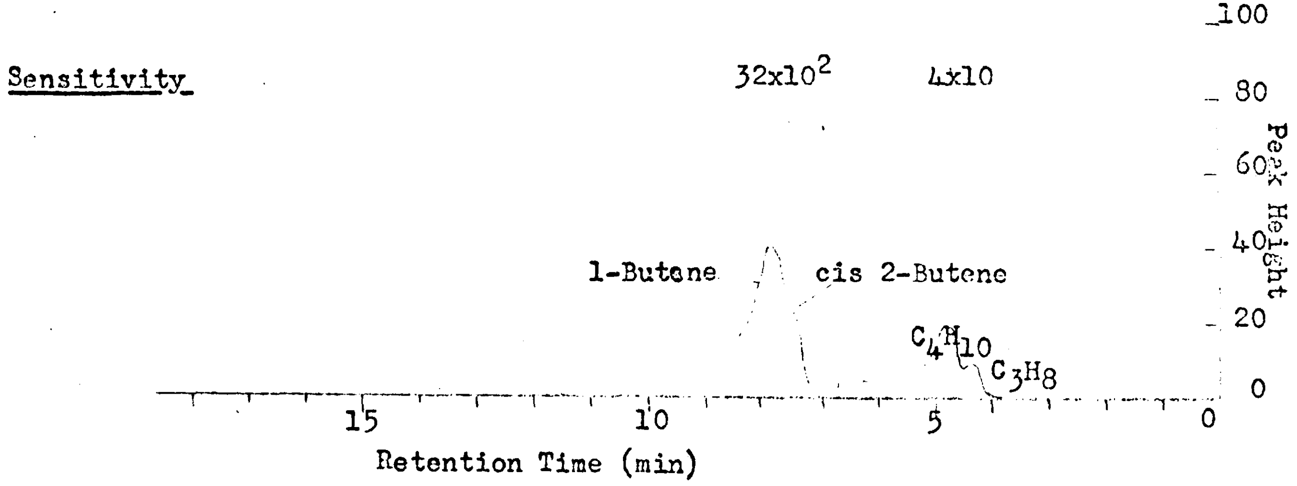
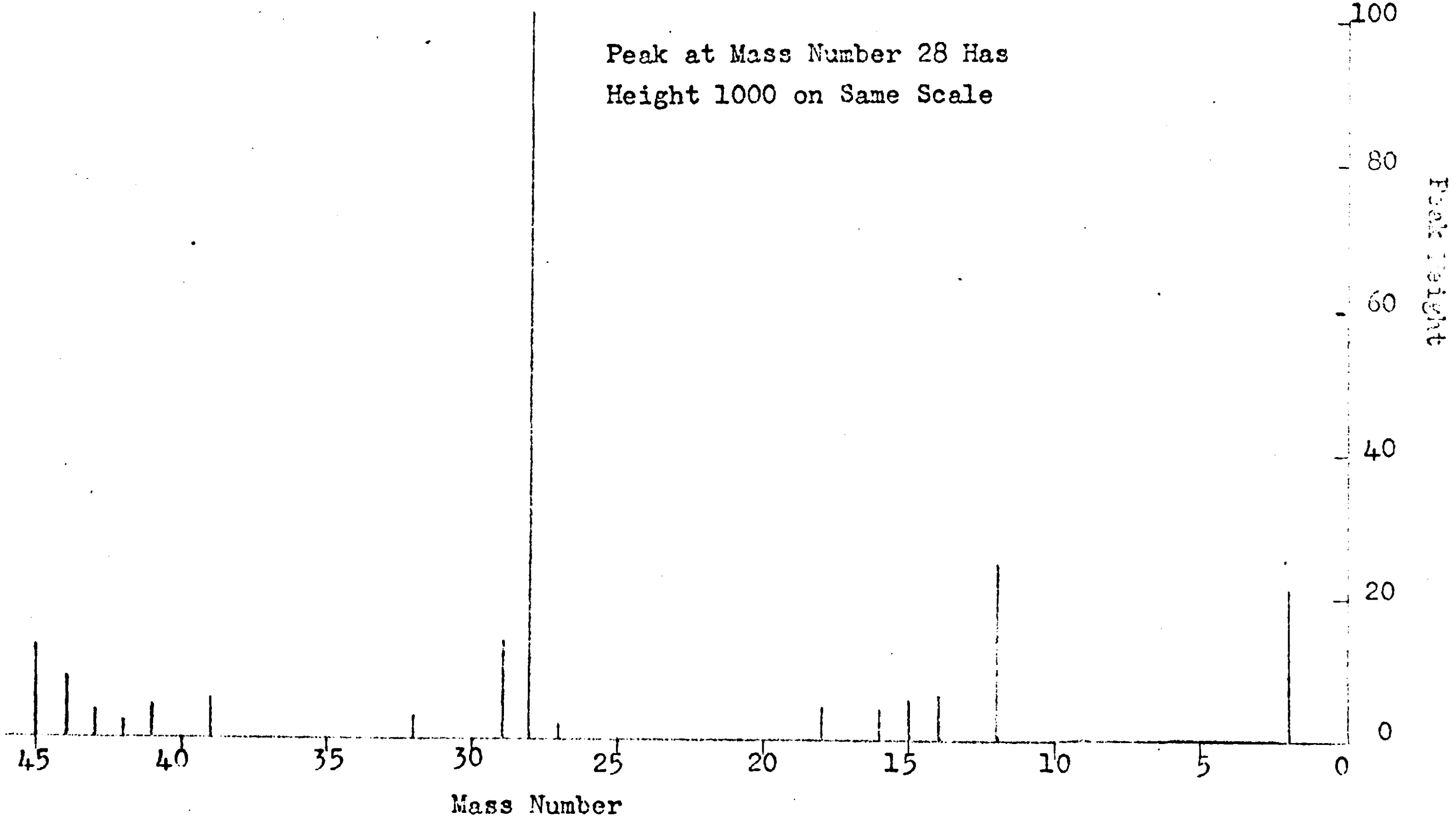


Fig 4.15 Mass Spectrum of Non Condensible Gases from Poly(n-Propyl Acrylate) Degradation



Peak at Mass Number 28 Has Height 1000 on Same Scale to carbon monoxide (mass number 28) obtained with this machine is 1.4:1. The ratio of carbon monoxide to hydrogen in the non-condensibles was therefore taken to be approximately 71:1. The non-condensible gases consist mainly of carbon monoxide.

4(iv) Analysis of the Liquid Fraction

A. Poly(Ethyl-).(n-Propyl-) and (n-Butyl Acrylates) Liquid Degradation Products

The liquid degradation products from these three polymers were sealed in limb I of the sealed tube (fig 2.10) after removal of the gases. When required for analysis this tube was broken open and the liquids were distilled into the capillary and weighed as described in 2(xv)B. A known weight of a solvent was added to the capillary and quantitative Gas-Liquid Chromatographic analysis carried out on the mixture. The results of this investigation are given in tables 4.14-4.16. The amounts of alcohol, monomer and methacrylate produced are shown as percent of initial polymer in tables 4.5-4.7 and the amount of alcohol as moles per gram monomer unit in tables 4.9-4.11.

Fig 2.14 is typical of the chromatograms obtained from the three polymers. The major peak is due to alcohol and minor peaks are observed for monomer and the corresponding methacrylate. No other component is observed in significant amount.

Figs 4.16-4.18 show the evolution of alcohol with time of

Fig 4.16 Volatile Evolution from Poly(ethyl acrylate) at 315°C

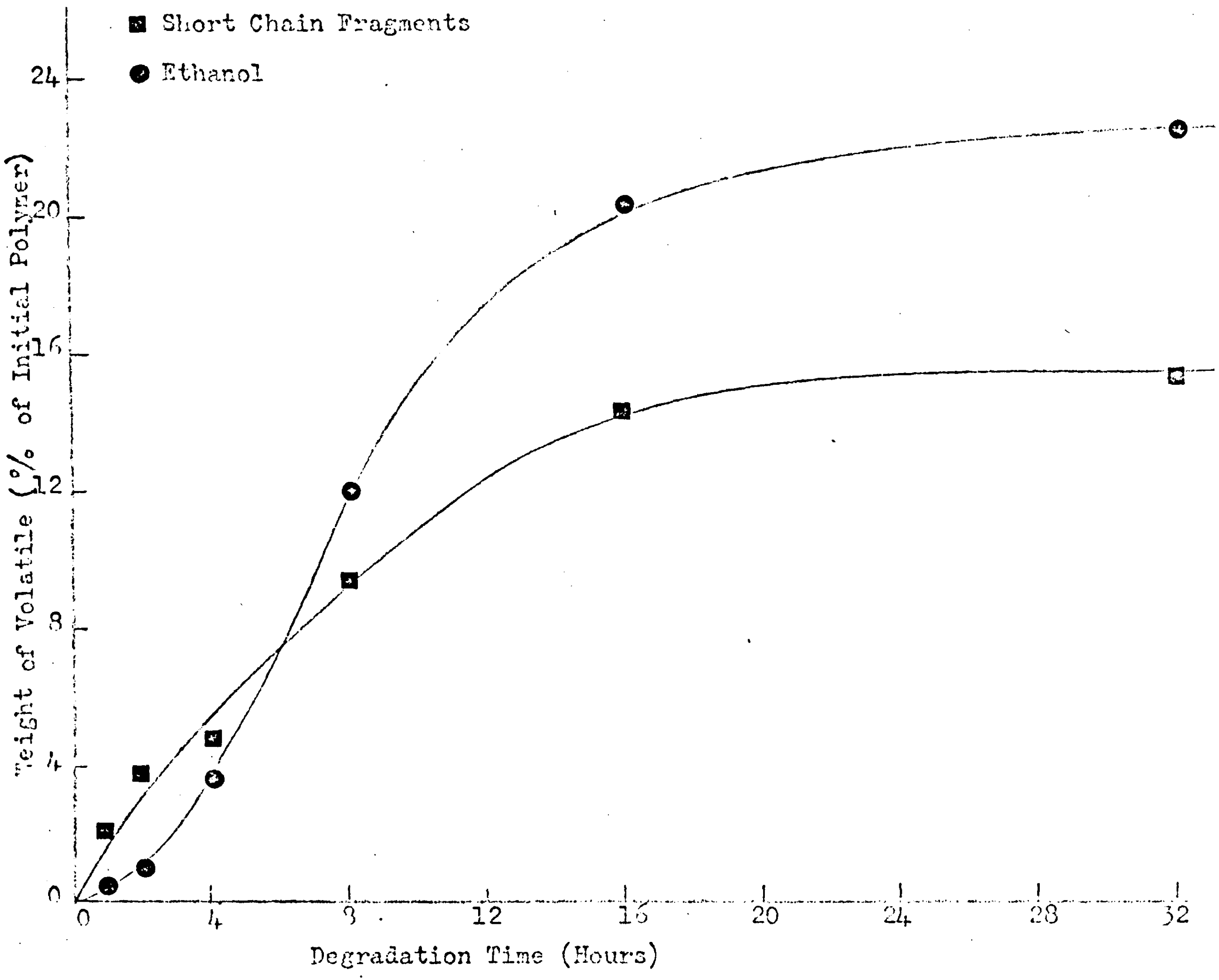


Fig 4.17 Volatile Evolution from Poly(n-propyl acrylate) at 315°C

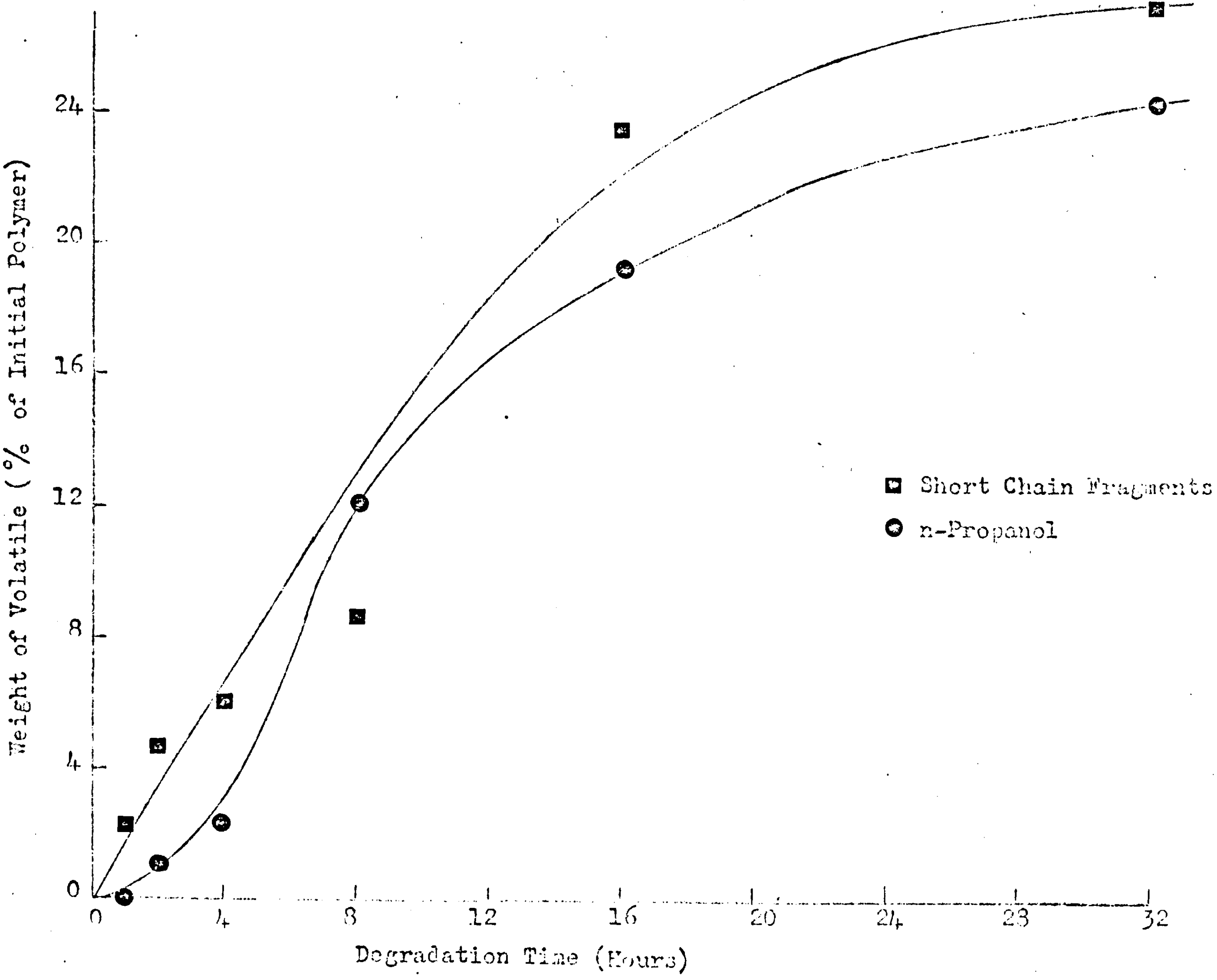
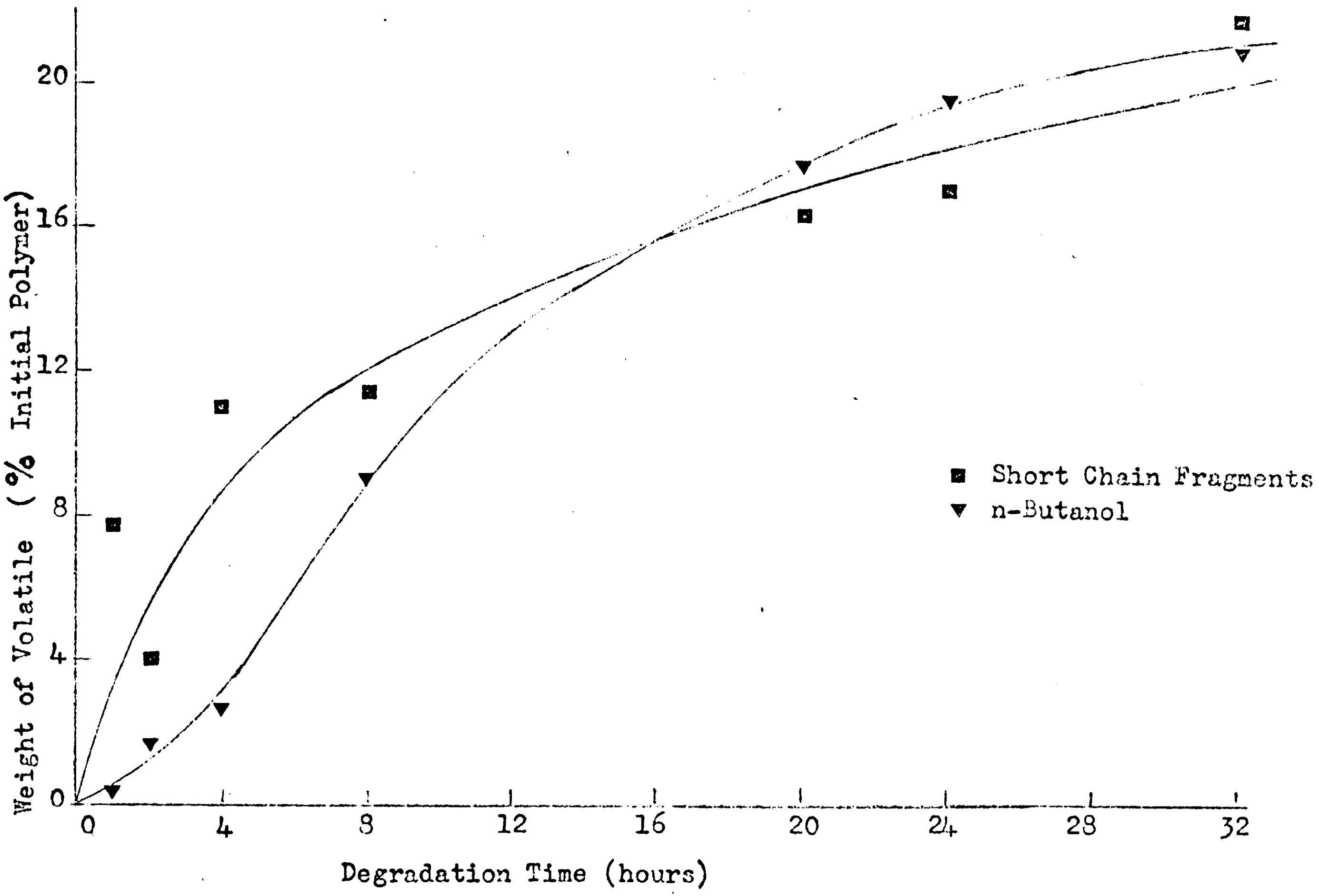


Fig 4.18 Volatile Evolution from Poly(n-Butyl Acrylate) at 315°C



degradation in terms of percent of initial polymer and figs 4.5 -4.7, in terms of moles per gram monomer unit. The production of alcohol exhibits a rate maximum and alcohol is eventually produced in greater amounts than olefin or carbon dioxide in all three cases.

The rate of evolution of alcohol is plotted against time in figs 4.21-4.23. It is difficult to find the initial rates of alcohol evolution with certainty because of the rate maxima in these curves. The curves after the rate maxima are extrapolated back to time zero to give the approximate values shown in table 4.13. As with olefin and carbon dioxide, there is a tendancy for the initial rate to fall off as the size of the alkyl group increases.

B. Poly(2-Ethyl Hexyl Acrylate) Liquid Degradation Products

There are two large peaks on the chromatogram of poly(2-ethyl hexyl acrylate) liquid degradation products, identified by their retention times as 2-ethyl 1-hexene and 2-ethyl 1-hexanol. Quantitative G.L.C. analyses of the liquids after various times of degradation were carried out as described in 2(xv)B. Tables 4.8 and 4.17 summarise these results and they are plotted in figs 4.8, 4.19 and 4.20. Rates of evolution of the liquid volatiles are shown in fig 4.12 and estimated initial rates of volatilisation in table 4.13

No attempt was made to analyse the monomer or methacrylate content of the liquid fraction. These were included for analysis in the

Fig 4.19 Volatile Evolution from Poly(2-Ethyl Hexyl Acrylate) at 315°C

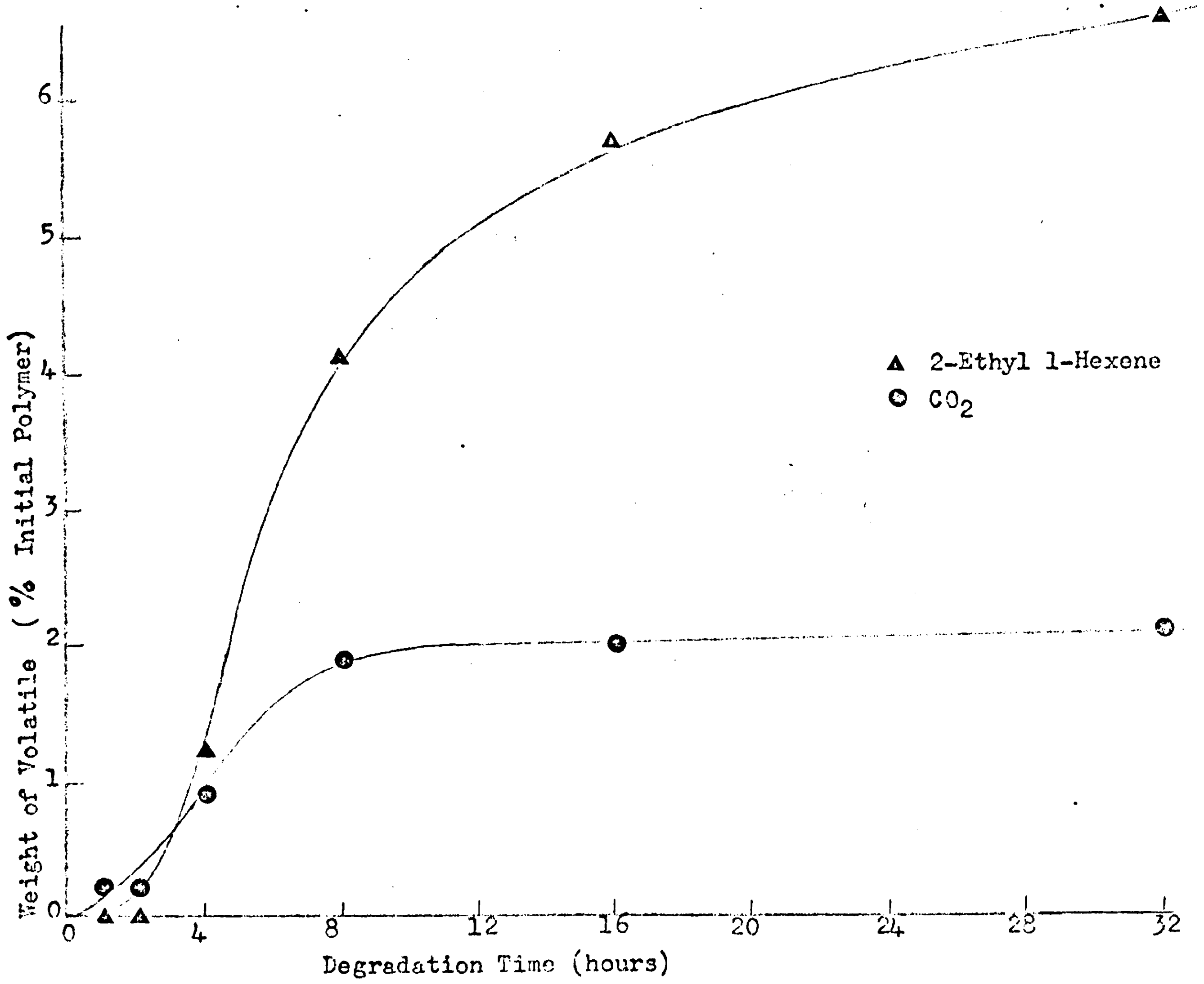


Fig 4.20 Volatile Evolution from Poly(2-Ethyl Hexyl Acrylate) at 315°C

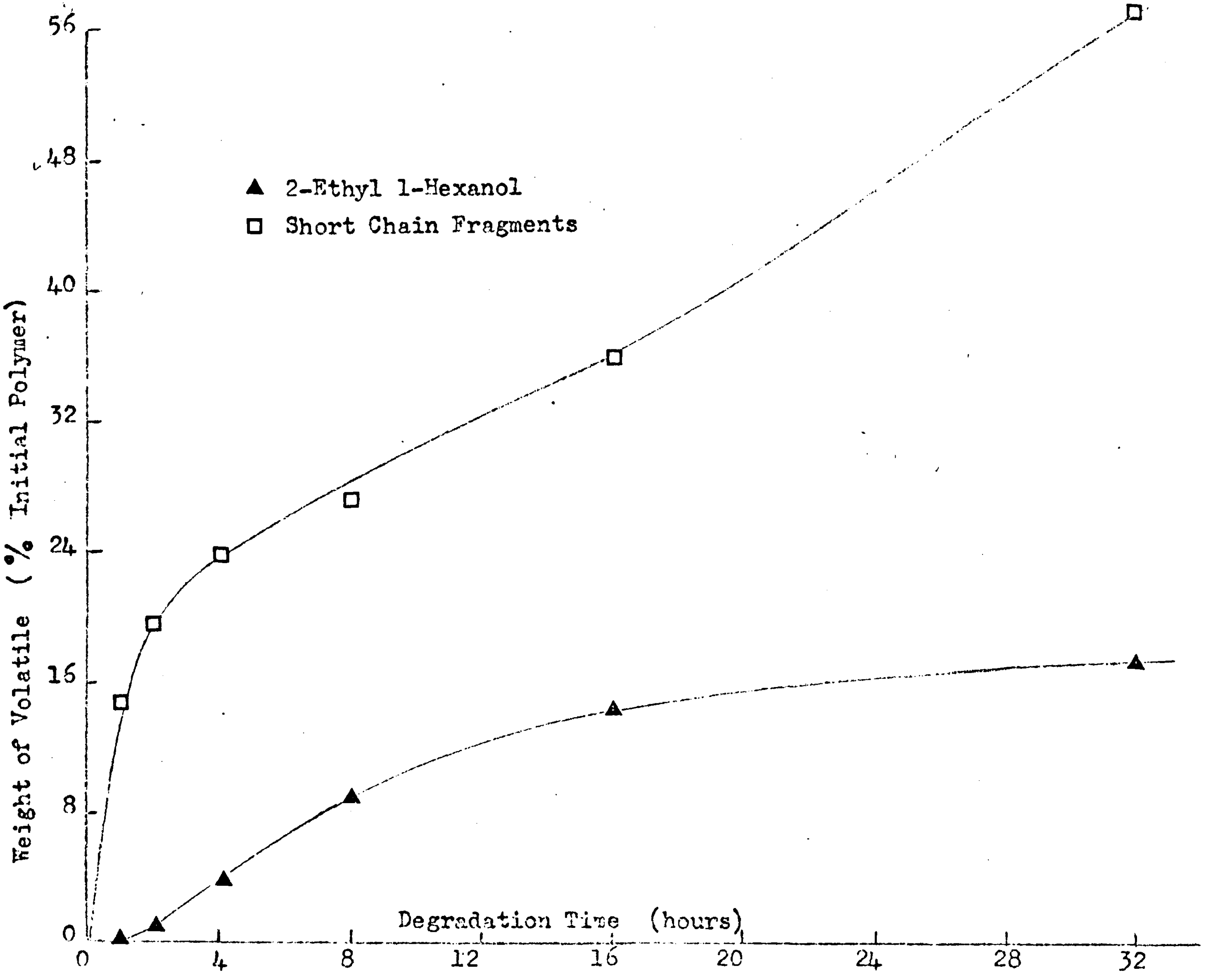


Fig 4.21 Rate of Volatile Evolution from Poly(ethyl acrylate) against Time of Degradation

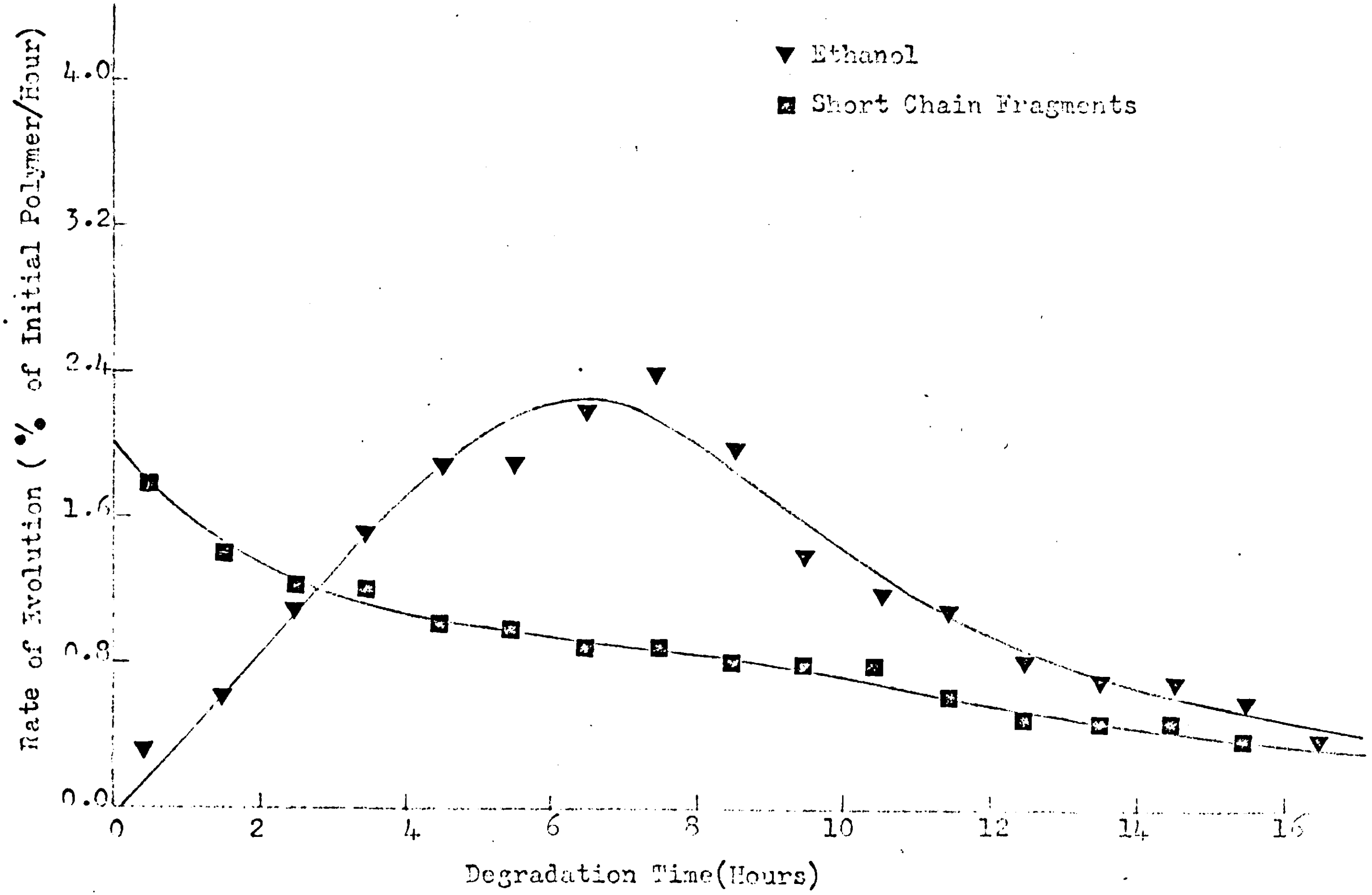


Fig 4.22 Rate of Volatile Evolution from Poly(n-propyl acrylate) against Time of Degradation.

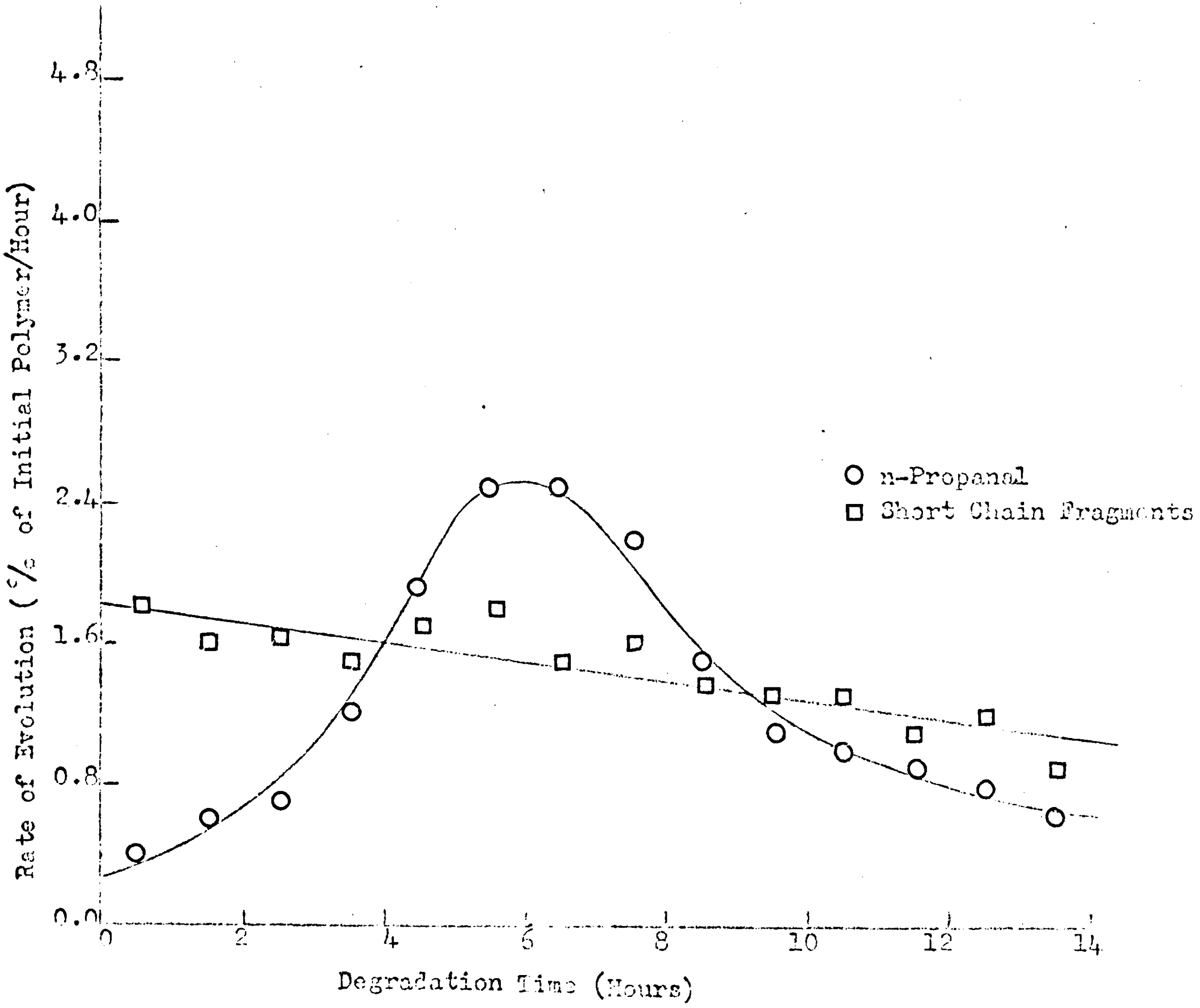
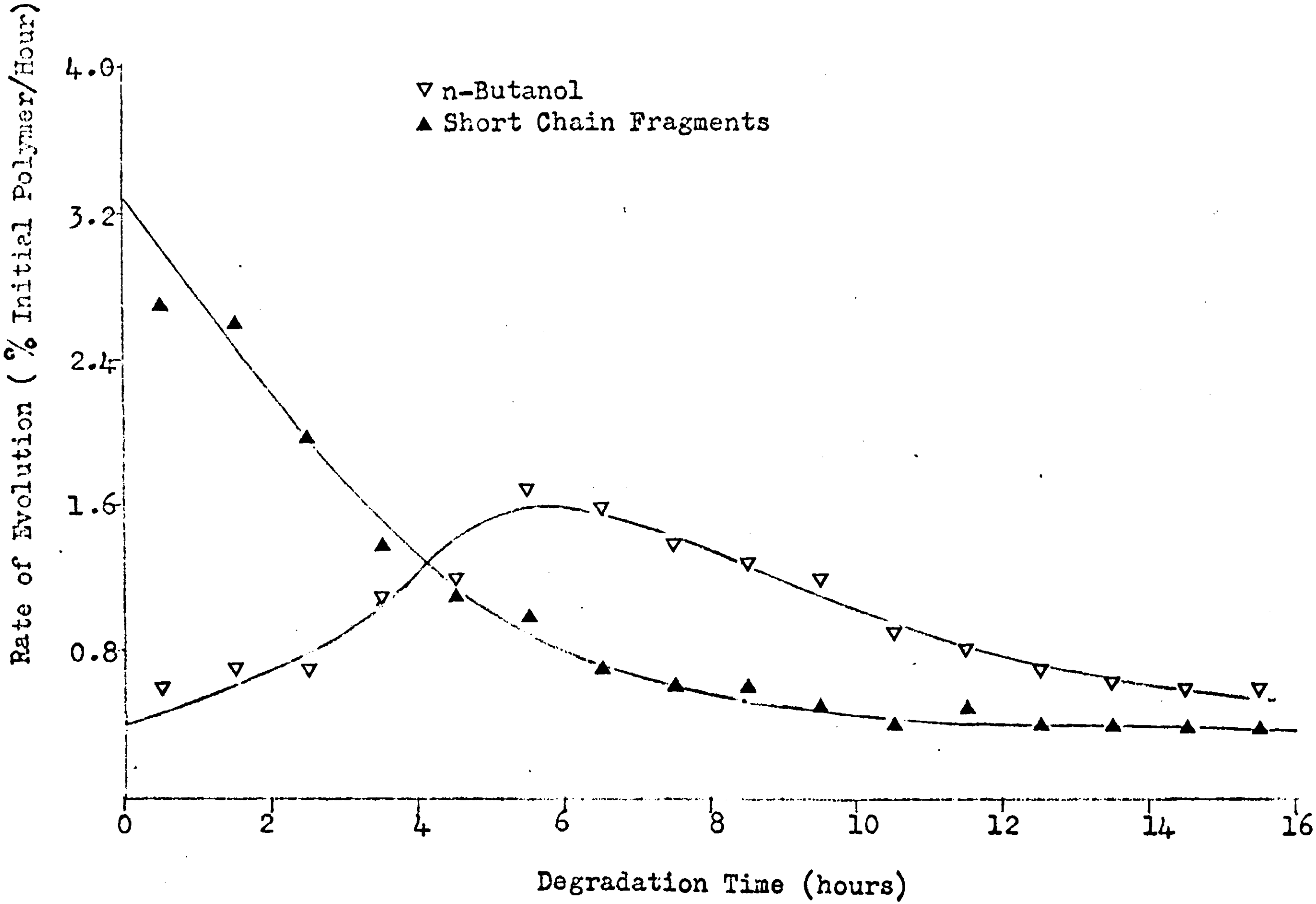


Fig 4.23 Rate of Volatile Evolution from Poly(n-Butyl Acrylate) against Time of Degradation



short chain fragment fraction.

4(v) Short Chain Fragment Analysis

In the cases of poly(ethyl-),(n-propyl-) and (n-butyl acrylates) this fraction was made up of all the material collected from the sealed tube except the residue in the hot zone (limb A, fig 2.10), the gases and those liquids which distilled over under vacuum at room temperature. In the case of poly(2-ethyl hexyl acrylate), the fraction was composed of material collected from the sealed tube at C and that portion of the liquids which could not be accounted for as 2-ethyl 1-hexene or 2-ethyl 1-hexanol.

The infrared spectra of the fraction in carbon tetrachloride solution were run when sufficient yield was obtained. The spectra are very similar to those of the original polymer samples. The carbonyl peak and the peaks in the region 1500-1000cm^{-1} show a general broadening which increases with time of degradation. Two shoulders at about 1760 cm^{-1} and 1715 cm^{-1} appear on the carbonyl peak at 1730 cm^{-1} and the C-O single bond peak at 1160 cm^{-1} become more diffuse.

There was insufficient material for molecular weight measurement except after long degradation times. Therefore, the short chain fragments from all the degradations of each polymer were combined and the molecular weight determined by the vapour pressure osmometer.

Table 4.18

Molecular Weight of Short Chain Fragment Fraction

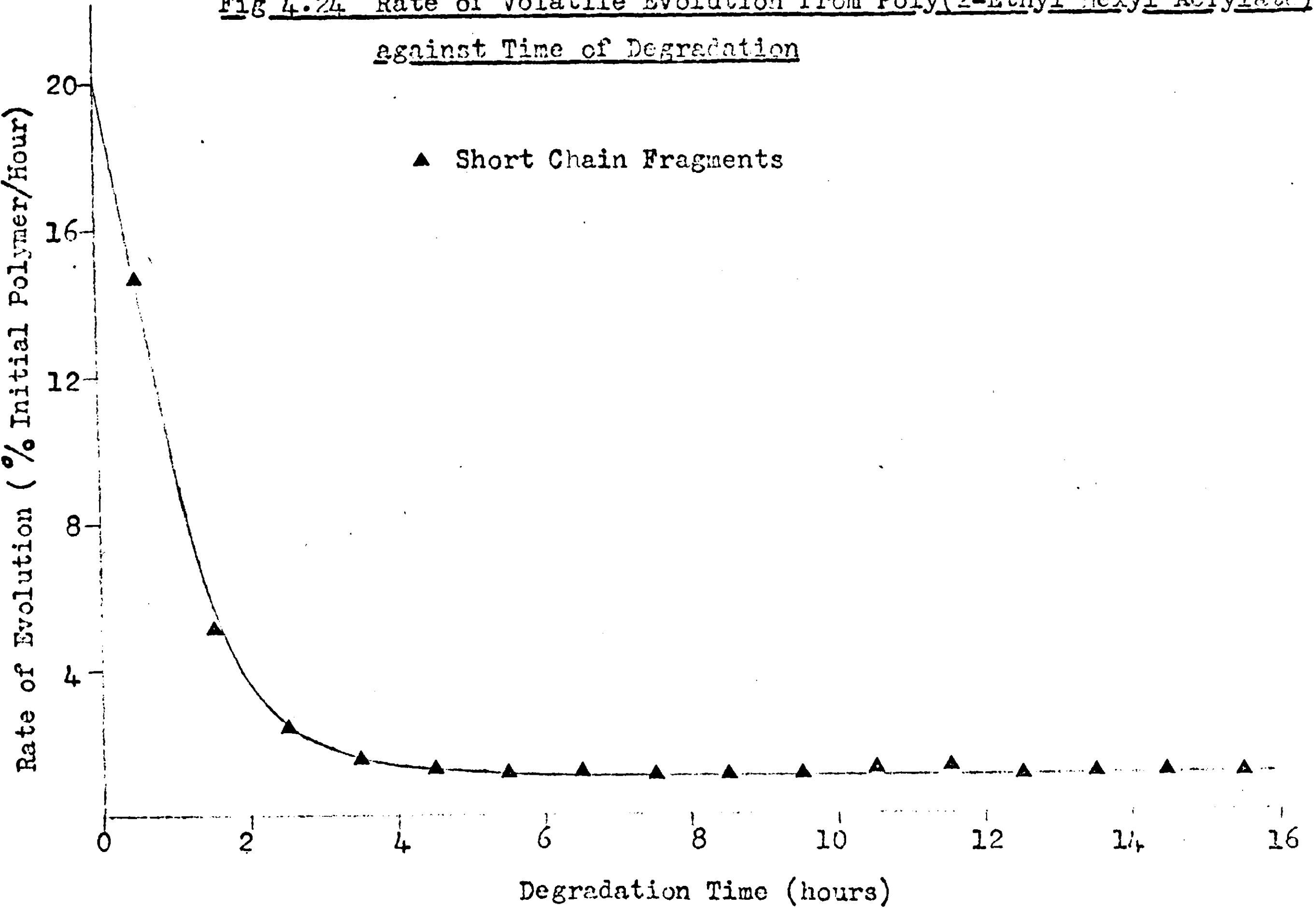
Polyacrylate	ethyl	n-propyl	n-butyl	2-ethyl hexyl
Molecular Weight	317	379	470	1,020

Figs 2.15a and 3.3a give typical chromatograms of the lower molecular weight species in a short chain fragment fraction and fig 2.15b shows retention times of some n-alkanes for comparison. It would appear that this fraction consists of a range of molecules, generally similar to the original polymer molecules but of a much lower molecular weight. There appear, from the chromatograms, to be some preferred species, but these are difficult to identify. The nature of the end groups of the oligomers has not been determined.

The fraction is yellow in colour, the intensity of the colour depending on the length of time of degradation, but all attempts to obtain significant ultraviolet or visible spectra were unsuccessful.

The weight of this fraction was determined as described in 2(xvi) and is given in tables 4.5-4.8. Table 4.13 and figs 4.16-4.18 and 4.20-4.24 show these results treated in a similar manner to that applied to the other volatile degradation products.

Fig 4.24 Rate of Volatile Evolution from Poly(2-Ethyl Hexyl Acrylate) against Time of Degradation



4(vi) Analysis of the Residue

A. Sol/Gel Analysis

The residue was dissolved or swelled in toluene and poured through Whatman No.1 filter paper. The soluble and insoluble material was separated as described in 2(xvii). Tables 4.5-4.8 give the weights of soluble and insoluble material obtained. In the case of poly(2-ethyl hexyl acrylate), no insolubility was found even after 32 hours degradation at 315°C.

This method for separating soluble and insoluble material is not considered to be entirely satisfactory because some of the very high molecular weight polymers did not filter through completely even in the undegraded state, and also it is thought that the filter papers used do not give entirely satisfactory reproducibility. To test the porosity of the filter paper to the initial polymer, polymer solution in toluene was poured through a filter paper and the paper washed with solvent repeatedly until the dried filter paper gave a constant weight. Table 4.19 gives the weights of polymer which passes through and which is retained by the paper. The molecular weight of the initial polymer and of the 'soluble' portion is also recorded.

Table 4.19

Porosity of Filter Paper to Polymers Used

Polyacrylate	ethyl	n-propyl	n-butyl	2-ethyl hexyl
Code number	P5E	P12P	P6B	P14H
Weight retained (%)	24.5	11.7	3.2	0.0
Weight passed through (%)	75.5	38.3	96.8	100.0
10^{-6}x Molecular weight original polymer	12.7	2.3	1.15	0.253
10^{-6}x Molecular weight 'soluble' polymer	0.382	0.685	1.10	0.253

The sol/gel figures in tables 4.5 and 4.6 for poly(ethyl-) and (n-propyl acrylates) should therefore be treated with caution particularly the figures at short times of degradation. After degradation for 8 hours or more at 315°C, the residue from all three polymers is more easily separated into soluble and insoluble parts, since the insoluble residue becomes brittle and is not swollen by the toluene solvent.

The non-reproducibility of the filter paper is suggested by the discontinuities in the sol/gel ratio, particularly those shown in tables 4.5 and 4.6.

Fig 4.25 shows the sol and gel fractions plotted against time of degradation for poly(n-butyl acrylate). These figures are used in fig 4.26 to compare poly(n-butyl acrylate) behaviour with other degradation studies. Kane[1] found that the percentage insolubility

Fig 4.25 Percentage Sol and Gel in Residues from Poly(n-Butyl Acrylate) against Time of Degradation

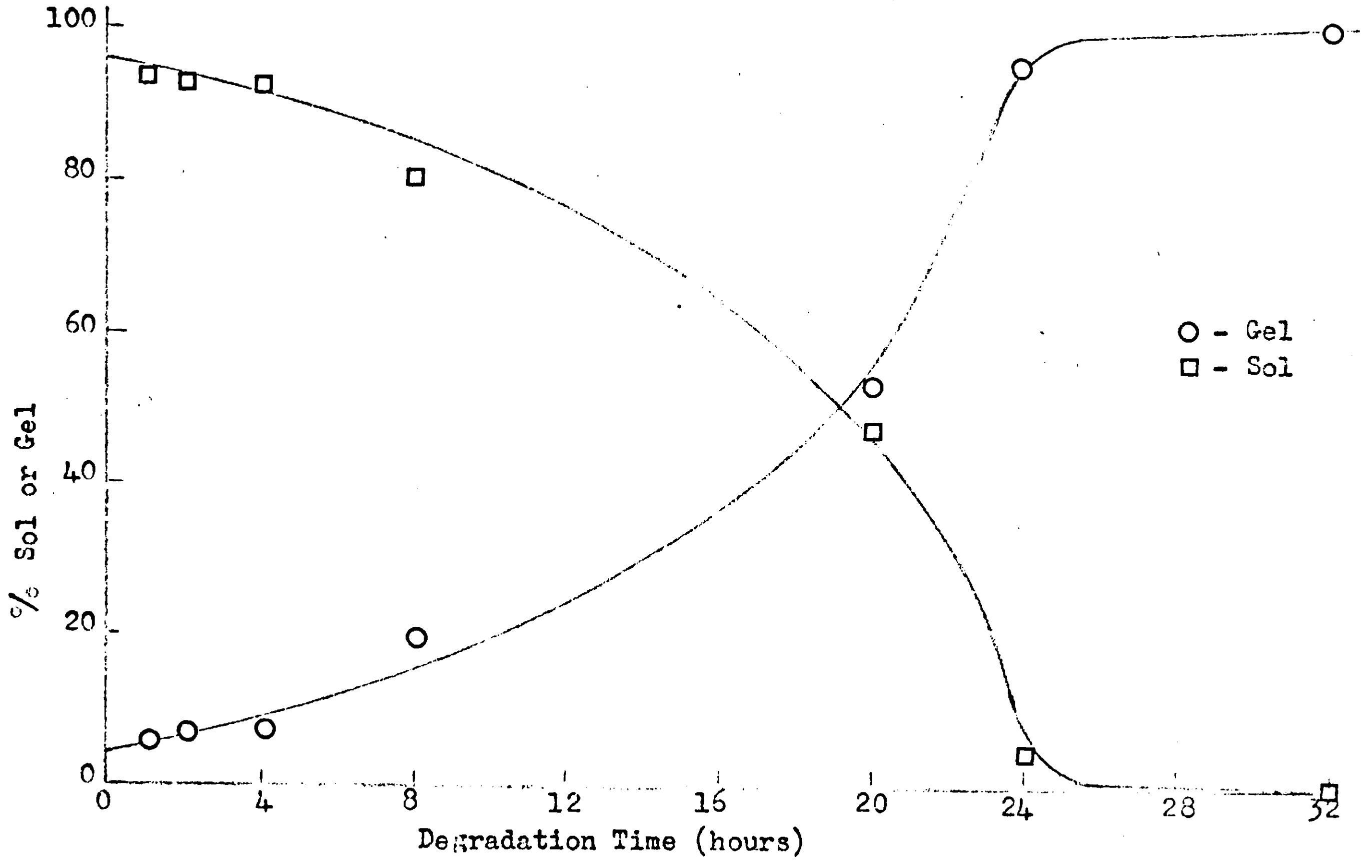
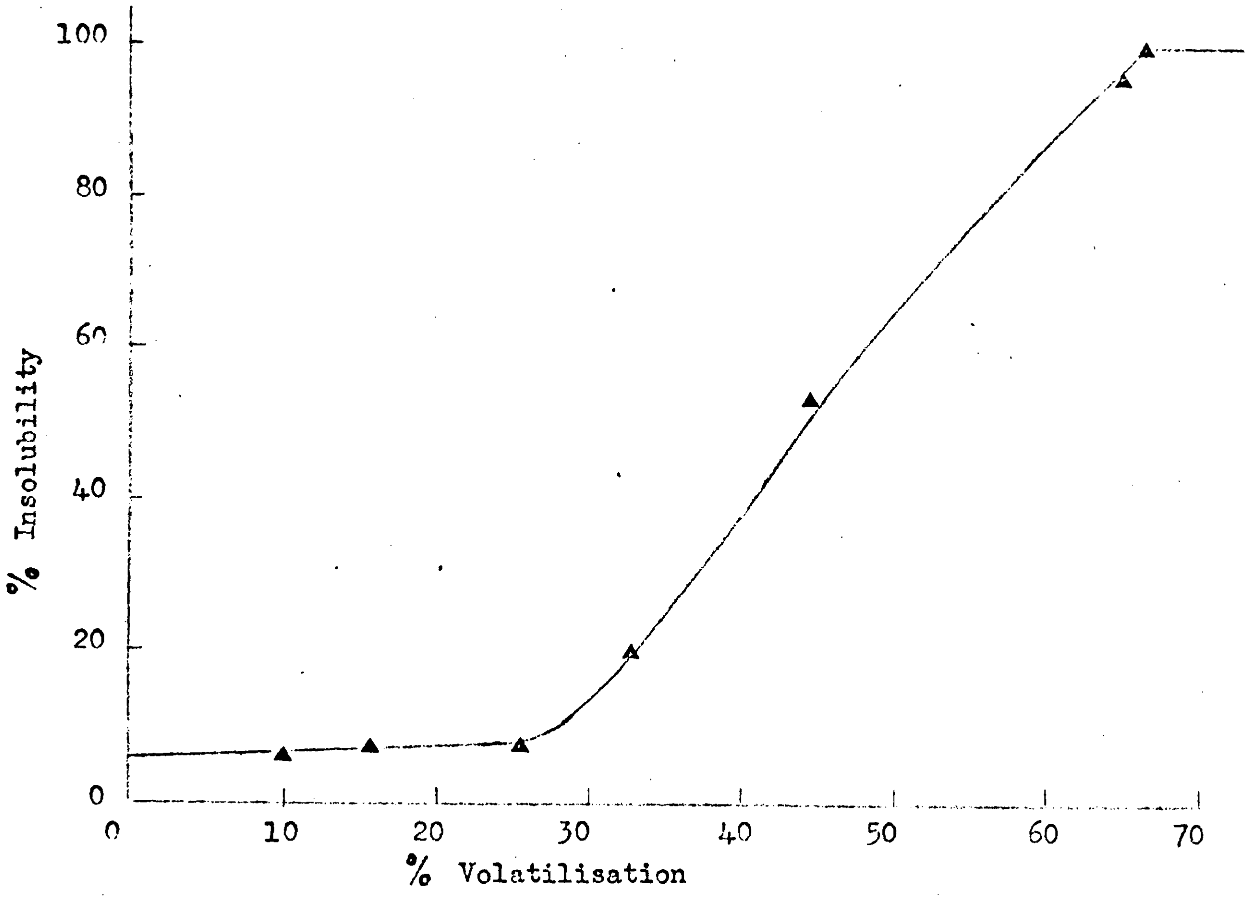


Fig 4.26 Percent Insolubility against Percent Volatilisation for Poly(n-Butyl Acrylate) Degradation



in poly(methyl acrylate) plotted against percentage conversion gave a straight line through the origin. The same plot for poly(n-butyl acrylate) (fig 4.26) also gives a reasonable straight line but it does not pass through the origin. The cross-linking reaction, which causes insolubility, like the reaction to form alcohol, appears to have an induction period in this case.

B. Weight Loss Data

Because of difficulties of separating sol and gel mentioned above, the residues from poly(ethyl-) and (n-propyl acrylates) are dealt with in their entirety. Fig 4.27a-d gives plots of percentage volatilisation against time of degradation for the four polymers.

For polymers which depropagate, either by unzipping or by intramolecular transfer, in a first-order reaction, a graph of rate of volatilisation against percentage volatilisation gives a straight line passing through the point at 100 % volatilisation, zero rate of volatilisation. In the case of poly(methyl acrylate), studied by Kane[1], good straight lines are obtained, although they meet the volatilisation axis at about 80 % rather than 100 %, reflecting the more complicated nature of polyacrylate degradation. Similar curves are drawn for the four polymers studied in the present work in fig 4.28. None of the polymers gives a single straight line. As the length of the alkyl group increases, so

Fig 4.27 % Volatilisation against Time of Degradation for Polymers of -

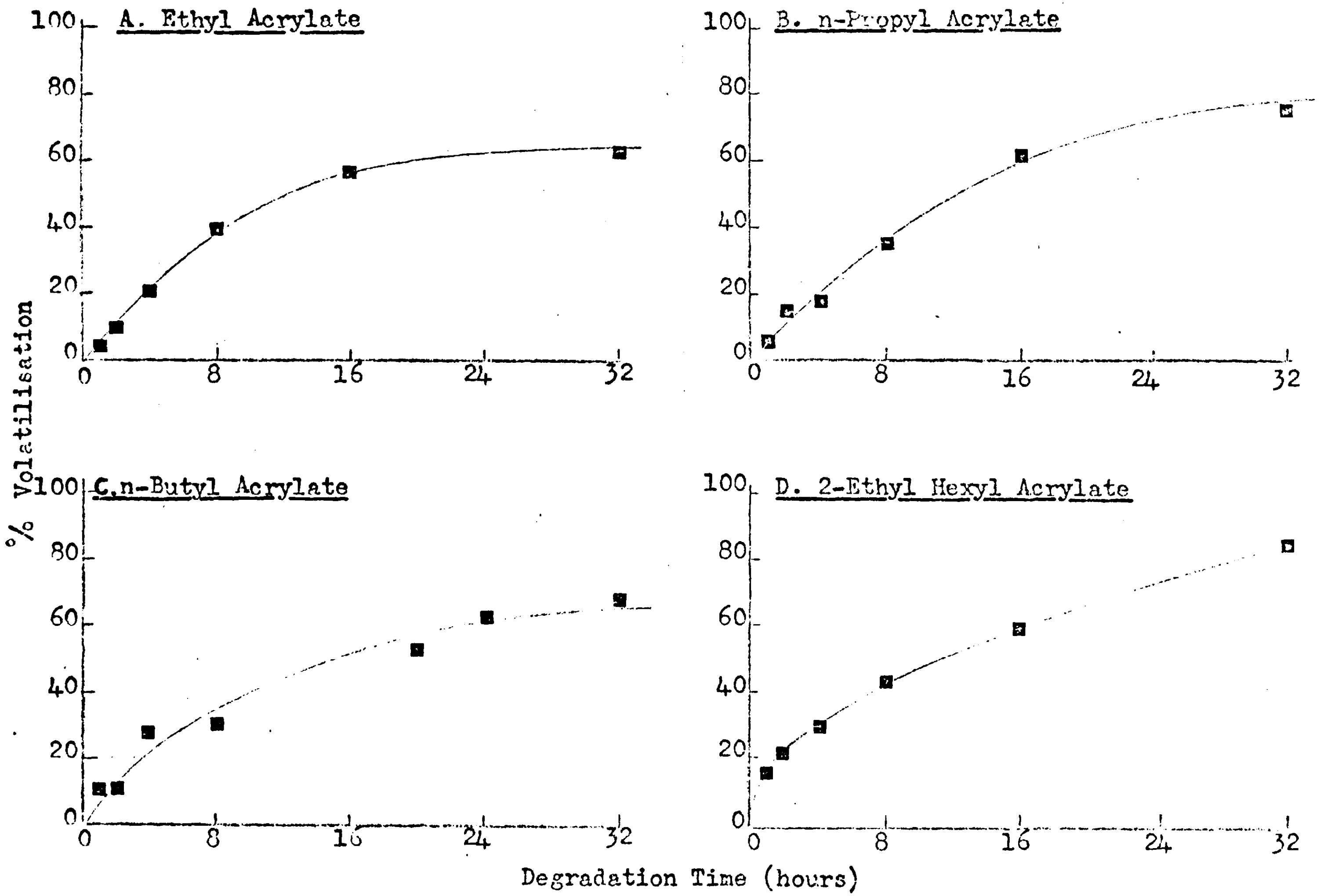
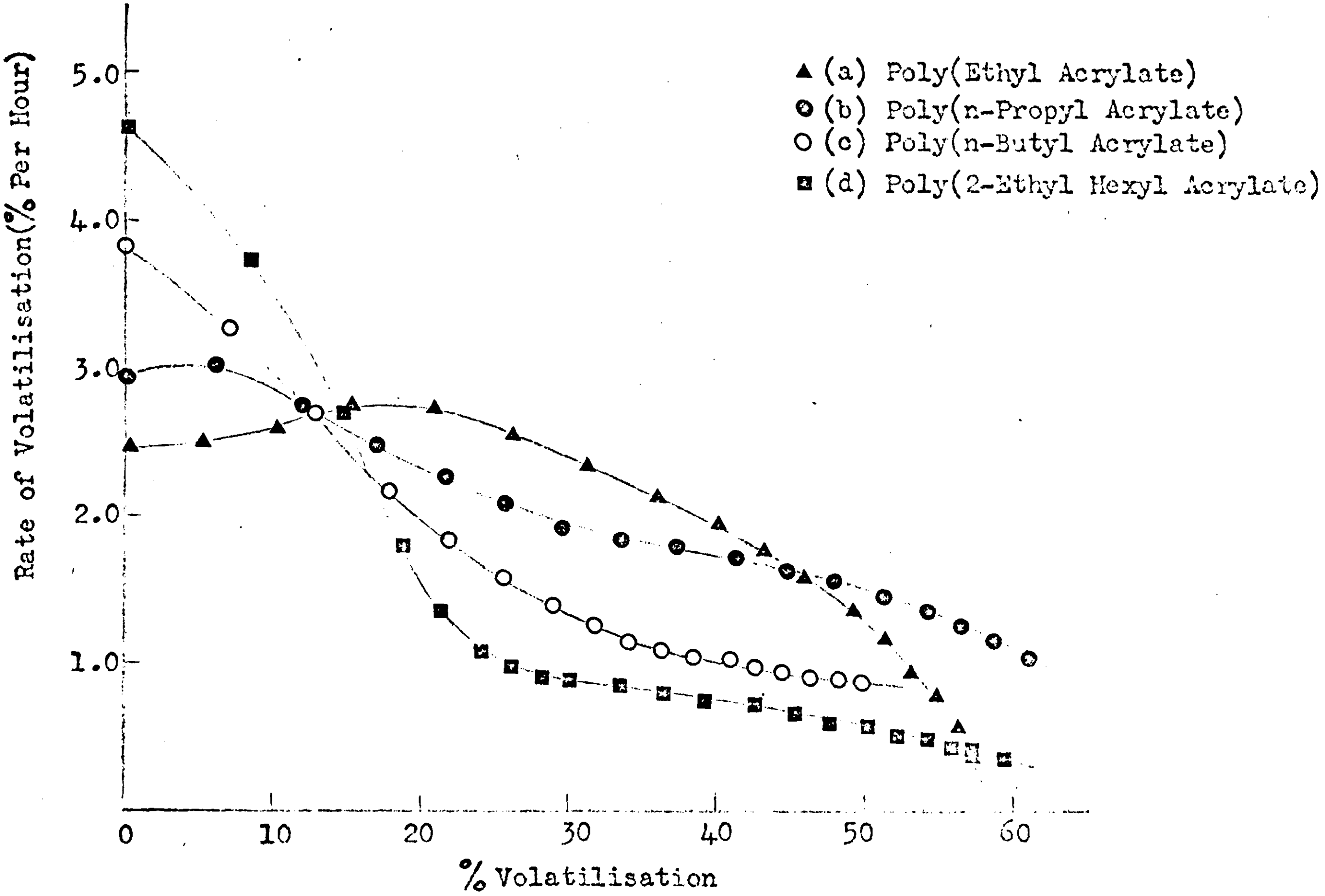


Fig 4.28 Rates of Volatilisation against % Volatilisation for



does the initial rate of weight loss, and two straight lines can be seen instead of one. Poly(ethyl acrylate) provides a smooth curve which meets the volatilisation axis at about 58 %. The curve for poly(n-propyl acrylate) also appears to meet this axis before 100 %.

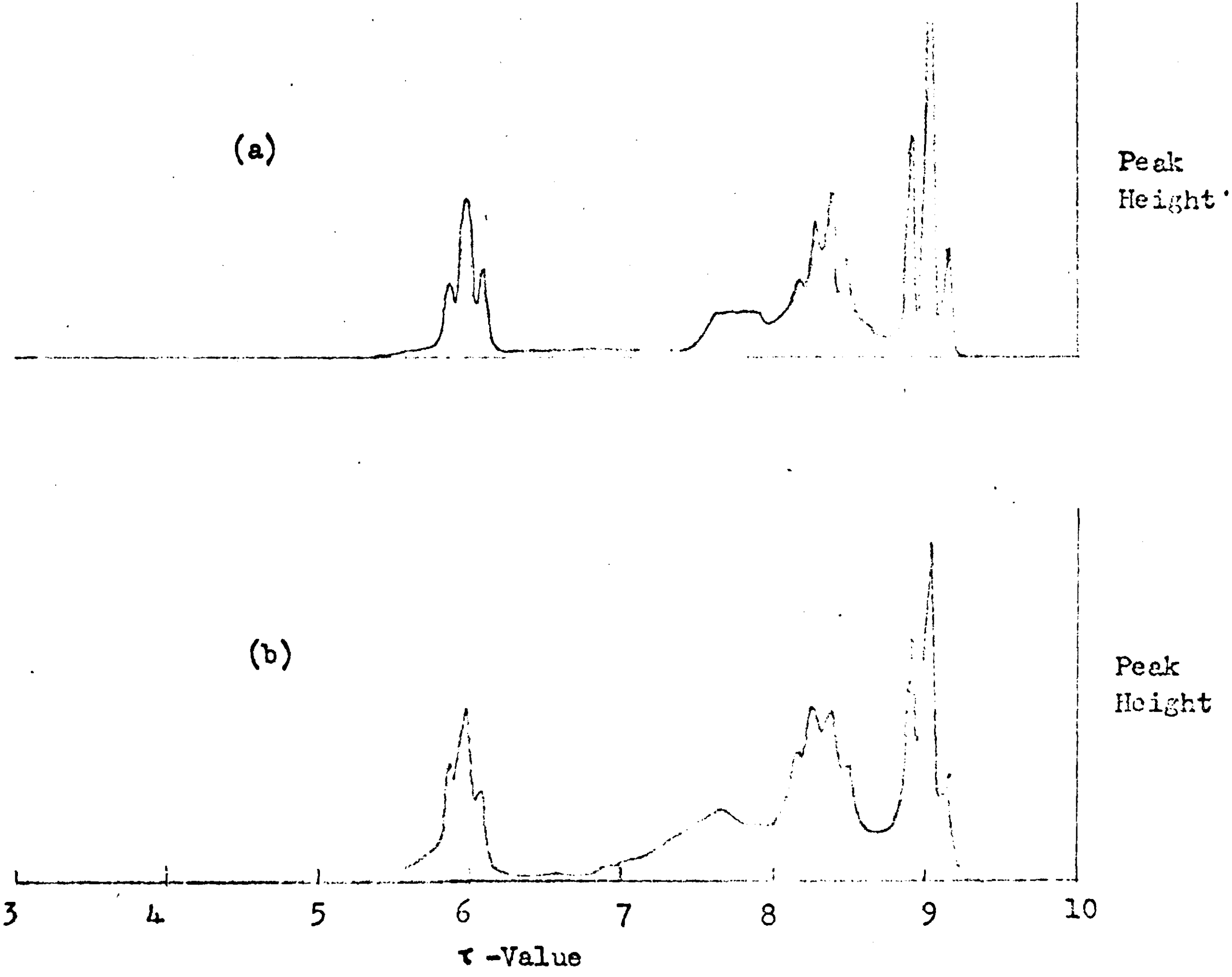
C. Soluble Residue Analysis

The soluble part of the residue was analysed by infrared and N.M.R. spectroscopy. Fig 4.29 compares the N.M.R. spectra of undegraded poly(n-propyl acrylate) and a sample degraded for 10 hours at 315°C. There is no change in shift of the peaks, the integral shows no detectable change in peak ratios, and there are no new peaks apparent.

The main change in the infrared spectrum of the soluble part of the polymer on degradation is a general broadening of the carbonyl and C-O single bond absorptions. Fig 4.30 compares the infrared spectra of solutions of the residue from poly(2-ethyl hexyl acrylate) in carbon tetrachloride. There is no change apparent in the C-H stretching absorptions between 2850 and 3000 cm^{-1}, although their intensity increases relative to the carbon-oxygen absorptions. The carbonyl peak becomes much broader and developes a clear shoulder at 1760 cm^{-1}. At earlier degradation times a small peak can be distinguished at 1810 cm^{-1}. There is a general increase in absorption in the region 1550 to 1650 cm^{-1} and a small peak

Fig 4.29 N.M.R. Spectra of (a) Undegraded Poly(n-Propyl Acrylate)

(b) Poly(n-Propyl Acrylate) Degraded for 10 Hours at 315°C (Soluble Residue)



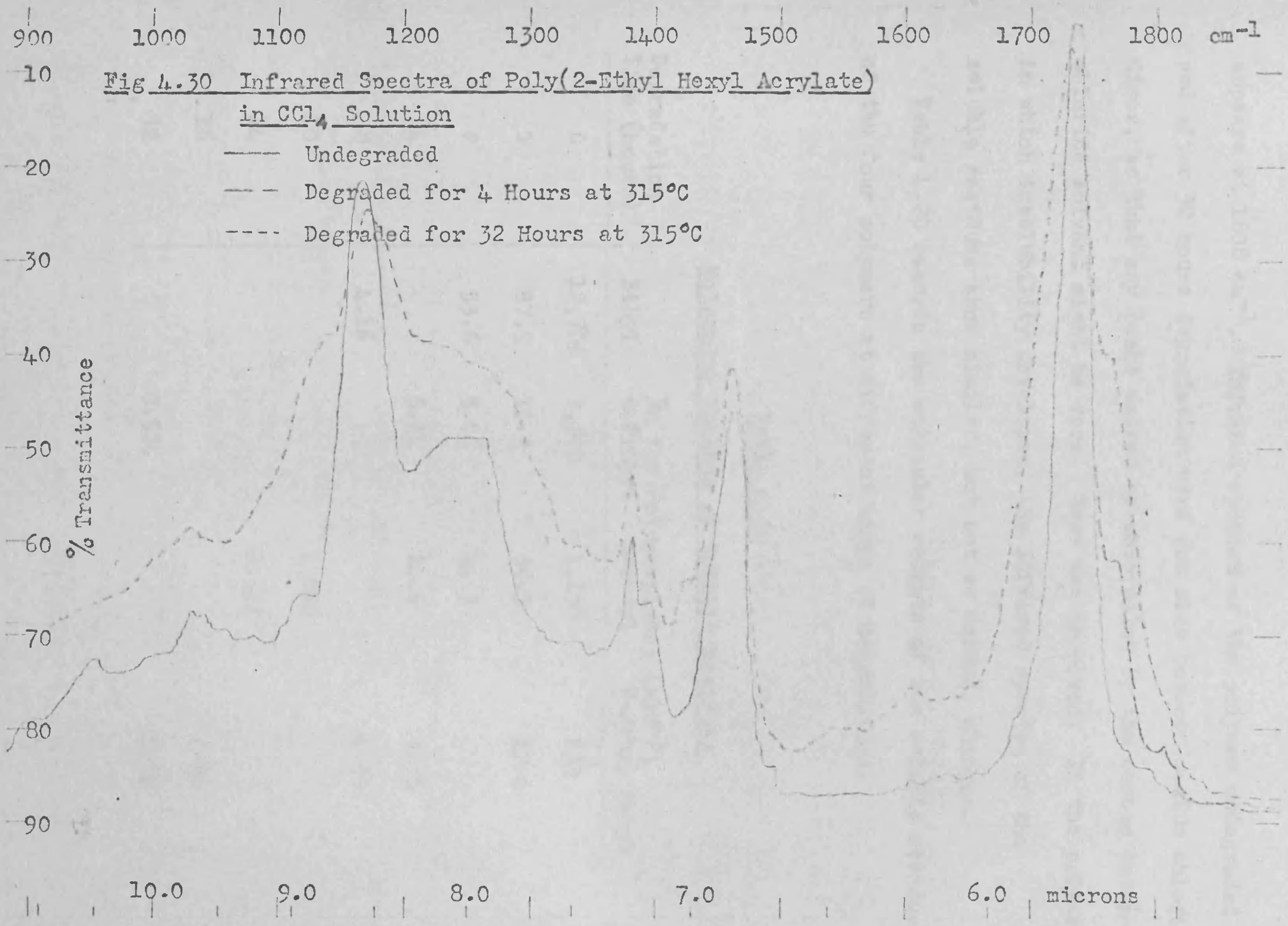


Fig 4.30 Infrared Spectra of Poly(2-Ethyl Hexyl Acrylate) in CCl_4 Solution

appears at 1603 cm^{-1}. Infrared spectra of the polymer undegraded and after 32 hours degradation were run also between sodium chloride discs, so that any peaks masked by absorption by the carbon tetrachloride solvent might be seen. None was observed. In the polymers in which insolubility developes, the infrared spectra of the soluble residues show similar, but not so marked, changes.

Table 4.20 records the molecular weights of the soluble residues of the four polymers at different times of degradation.

Table 4.20

Molecular Weights of Soluble Residues

Degradation Time (hours)	$\overline{M}_n$ for Polyacrylates ($x10^{-3}$)			
	Ethyl	n-Propyl	n-Butyl	2-Ethyl Hexyl
0	12,700	2,300	1,150	253
1	87.5	11.2	36.5	17.0
2	53.6	5.06	24.9	
4		5.14	21.6	9.70
8	4.16			4.80
10			1.082	
14			0.672	
16				2.80
32		0.524		1.02

The values for poly(2-ethyl hexyl acrylate) are plotted on fig 4.31

This data may be used to calculate the number of chain scissions occurring at any given time of degradation as follows:

If a polymer which degrades by random scission of bonds has initial molecular weight M, the initial chain length is given by $M/m = CL_o$ where m is the molecular weight of the monomer unit. After N chain scissions, the chain length becomes CL where

$$N = \frac{CL_o}{CL} - 1$$

If a fraction x is lost as volatile products, and provided that no complete molecules are lost by depropagation, then

$$N = \frac{(1-x)CL_o}{CL} - 1$$

$$\text{or } n = \frac{(1-x)}{CL} - \frac{1}{CL_o}$$ where n is the number of scissions per monomer unit

$$\text{or } n/m = (1-x)/Mt - 1/M_o \quad .$$

Fig 4.32 is a plot of n/m against time of degradation. The rate of chain scission is fast in the early stages of the reaction, but it soon changes to a slower rate, uniform throughout the remainder of the degradation.

D. Insoluble Residue Analysis

The insoluble residue is the most difficult fraction of the degradation products to analyse. It is not soluble in any common organic solvent nor in 0.1 M sodium hydroxide solution even after

Fig 4.31 Molecular Weight (Number Average) against Time of Degradation for Poly(2-Ethyl Hexyl Acrylate)

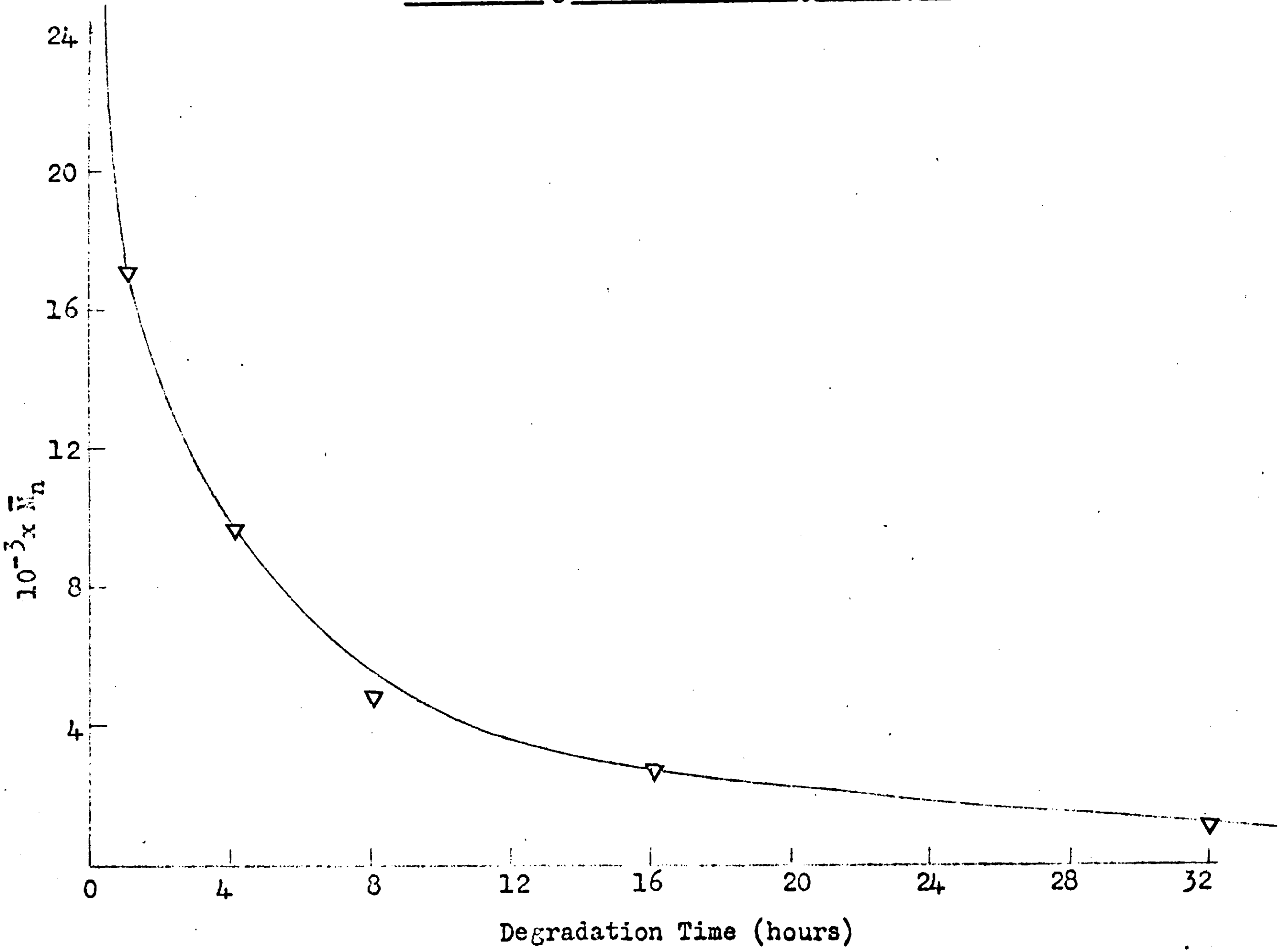
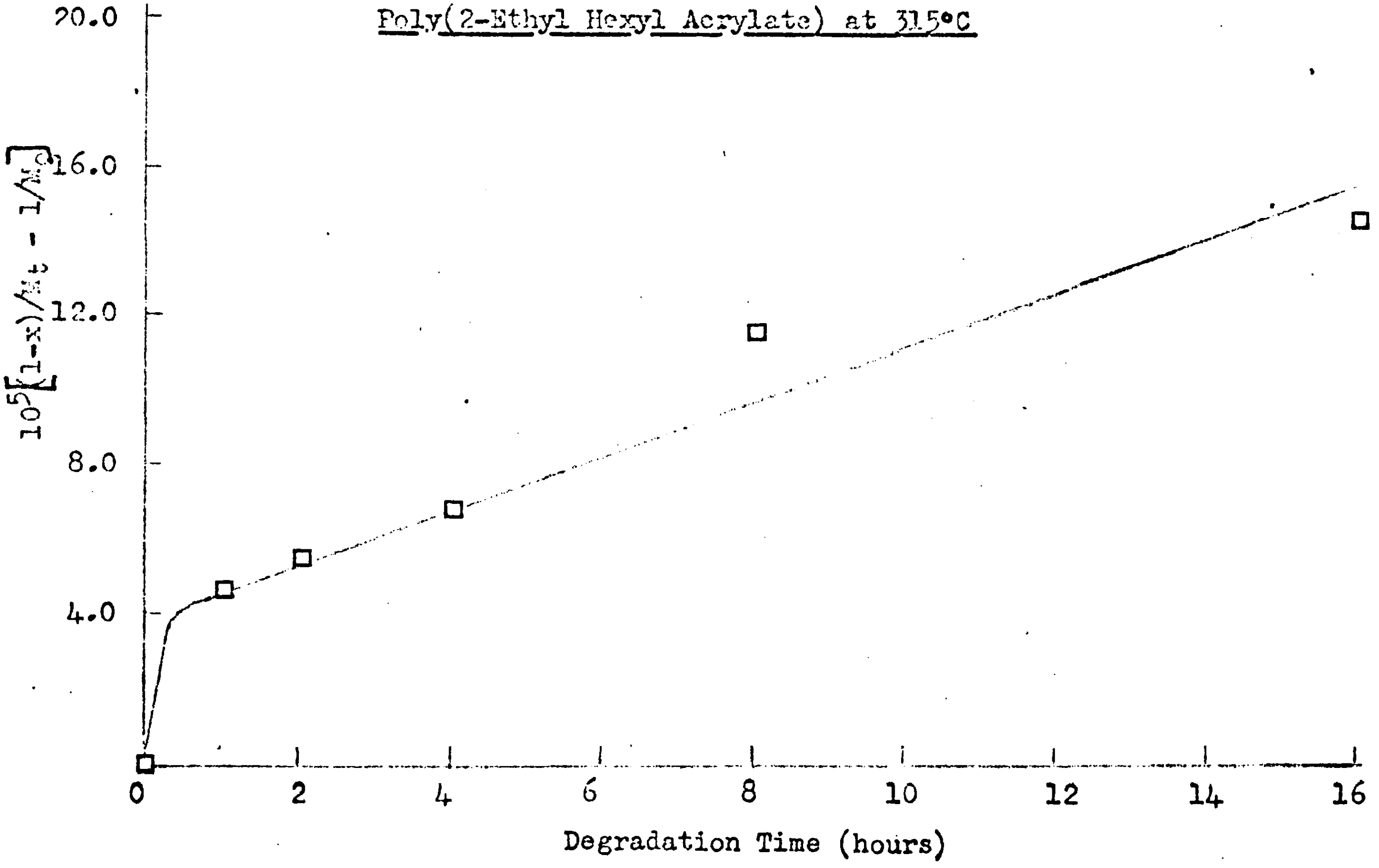


Fig 4.32 $[(1-x)/M_t - 1/M_o]$ against Time of Degradation for Poly(2-Ethyl Hexyl Acrylate) at 315°C



prolonged treatment.

Microanalysis was the only technique used and table 4.21 gives figures for the carbon, hydrogen and oxygen (found by difference) content for the three polymers which showed insolubility. A test run was also carried out with samples of undegraded polymer and figures close to the theoretical were obtained.

Table 4.21

Microanalyses of Insoluble Residues

Polyacrylate	Degradation Time (hours)	% C	% H	% O
Ethyl	0	59.99	8.05	31.96
Ethyl	4	61.19	7.52	31.29
Ethyl	32	73.51	5.85	20.64
n-Propyl	0	63.14	8.83	28.03
n-Propyl	32	71.29	5.75	22.96
n-Butyl	0	65.60	9.44	24.97
n-Butyl	24	73.76	6.93	19.31

In all three cases the carbon content rises, and the hydrogen and oxygen content falls with time of degradation and the changes become less marked when the polymer has a longer alkyl group.

4(vii) Other Possible Products

All the major degradation products have been analysed and, as the mass-balance tables (tables 4.5-4.8) show, they account for nearly all of the total initial weight of polymer. There remains the portion described as 'remaining liquids' still to be accounted for. The most likely substance to avoid detection, and yet be weighed in this fraction is water. The tables show maximum yields in this column as 4.6 %, 4.5 % and 8.9 % of the initial sample of poly(ethyl-), (n-propyl-) and (n-butyl acrylate) respectively. No test for water was applied and therefore the yield of water remains uncertain although it should be less than the figures given above. There is, however, no smooth relationship between the yield and time of degradation, as appears in the other entries in these tables. A likely explanation for a least some of this portion is that part of the material distilled over may be short chain fragments. The amount of short chain fragments which distilled would depend on such variables as the temperature of distillation and the pressure in the vacuum line and, hence, the yield/time of degradation curve for this fraction would not be smooth.

4(viii) Ratios of Products

As described in 4(ii), 4(iv) and 4(v) there are differences in rates of evolution between the different types of volatile products. Tables 4.9-4.12 give the yield of carbon dioxide, olefin and alcohol in molecules per monomer unit. Corresponding figures for short chain fragment production can be read directly from the mass balance tables, tables 4.5-4.8, assuming that the short chain fragments are low molecular weight polymer. Figs 4.33-4.36 plot the molar ratios of each of these products to olefin against time of degradation for each of the polymer systems. Except in the case of poly(2-ethyl hexyl acrylate), the carbon dioxide/olefin ratio begins below 1 and converges to between 1.2 {poly(ethyl acrylate)} and 2.0 {poly(n-butyl acrylate)}. In poly(2-ethyl hexyl acrylate) degradation, the ratio begins above 1 and converges to 0.8. The alcohol/olefin ratio is similar in all four cases, beginning at about 0 and increasing rather slowly to about 2.3. The ratio of gram monomer units of short chain fragments to moles of olefin increases as the length of the alkyl group increases. After 32 hours it is 0.9, 1.3, 1.4 and 4.5 for poly(ethyl-), (n-propyl-), (n-butyl-) and (2-ethyl hexyl acrylates), respectively.

4(ix) Summary

Chapter 4 gives a thorough analysis of the degradation products of four poly(primary acrylates) at 315°C. Olefin and alcohol are produced, presumably in separate ester decomposition reactions. Carbon dioxide production might be expected to occur concurrently with or subsequent to olefin production, but, since carbon dioxide production generally exceeds that of olefin, there is probably a third ester decomposition mechanism operating. Cross-linking is

Fig 4.33 Ratios of Degradation Products to Ethylene against Time of Degradation for Poly(Ethyl Acrylate)

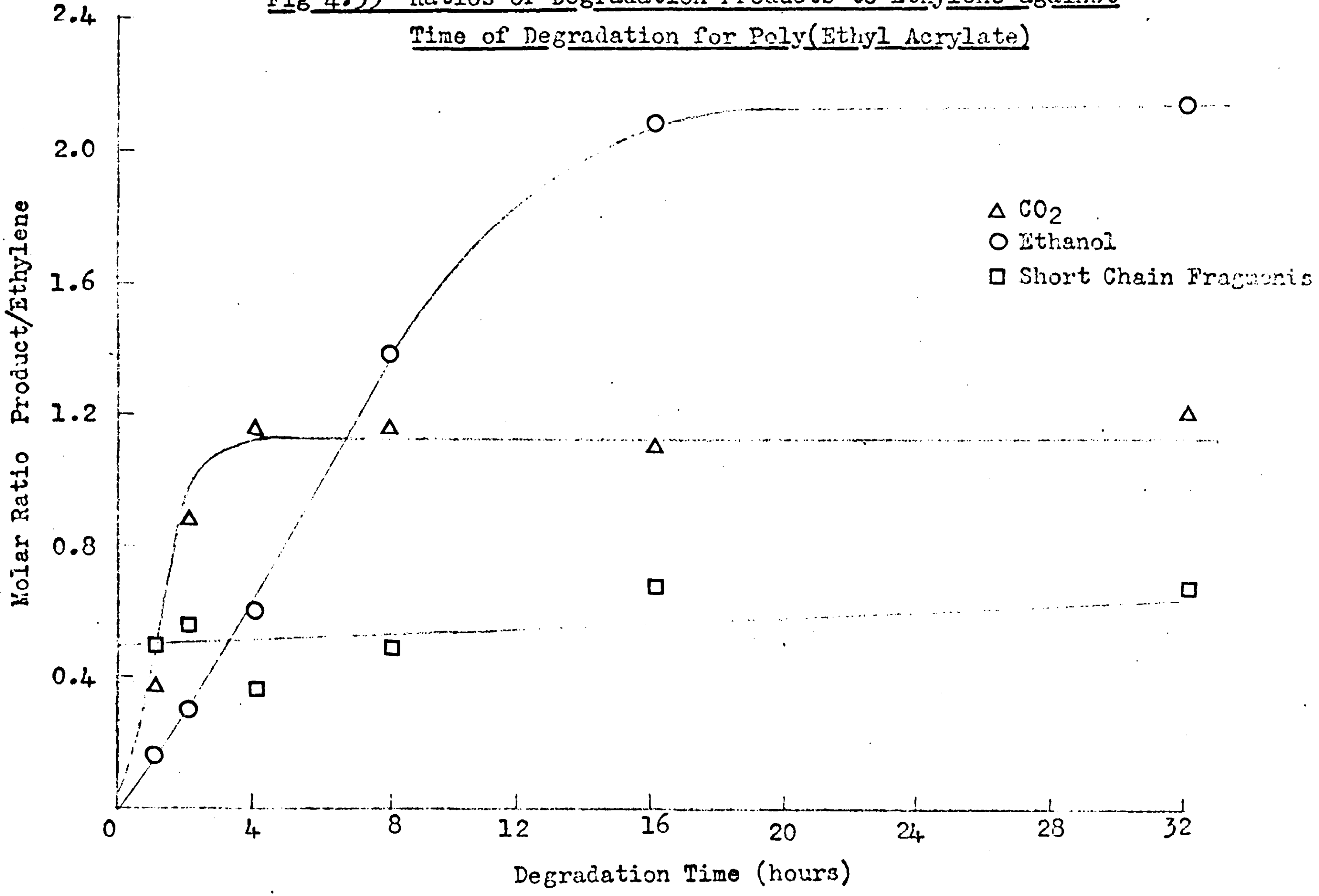


Fig 4.34 Ratios of Degradation Products to Propylene against Time of Degradation for Poly(n-Propyl Acrylate)

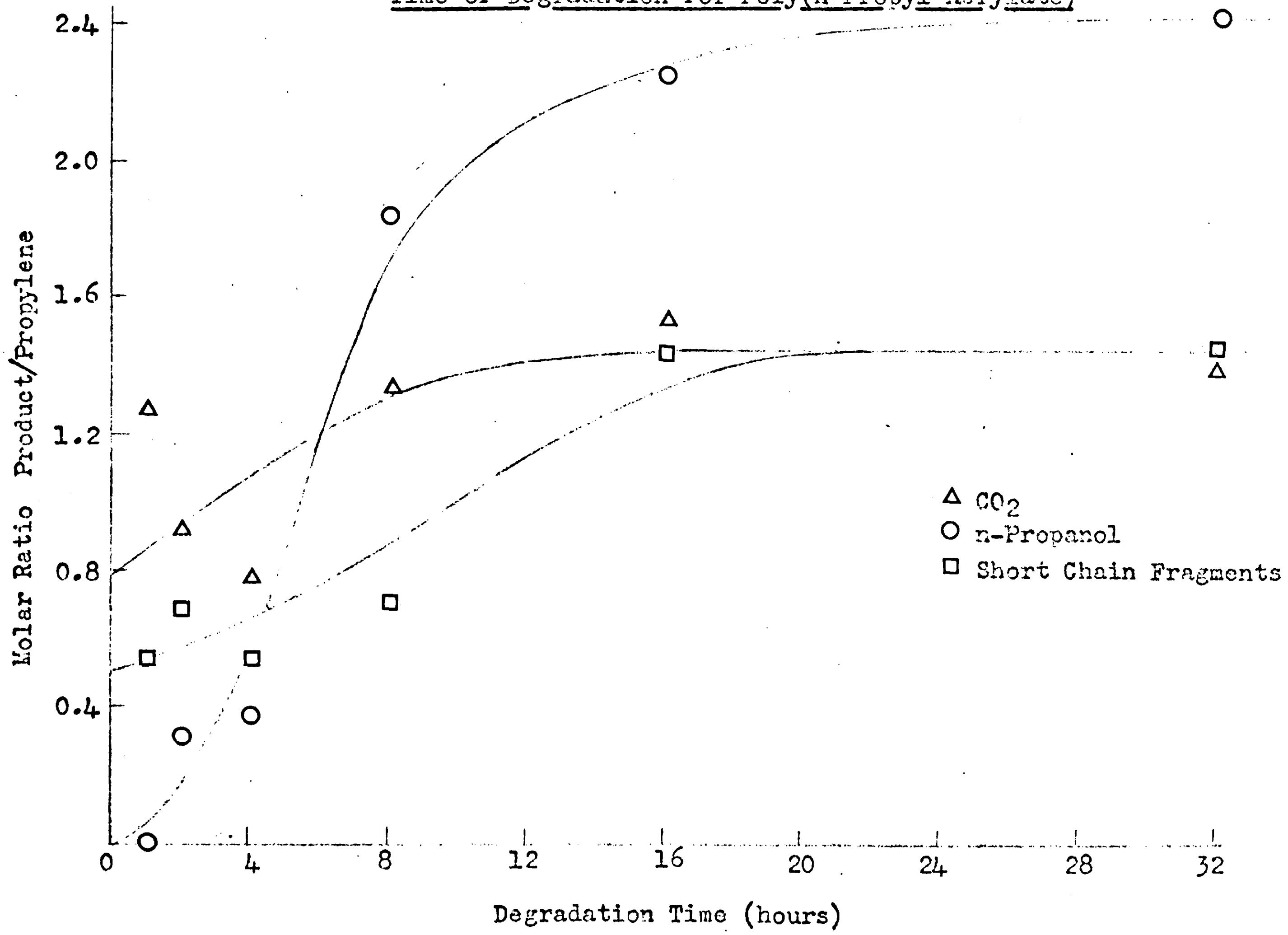


Fig 4.35 Ratios of Degradation Products to 1-Butene against Time of Degradation for Poly(n-Butyl Acrylate)

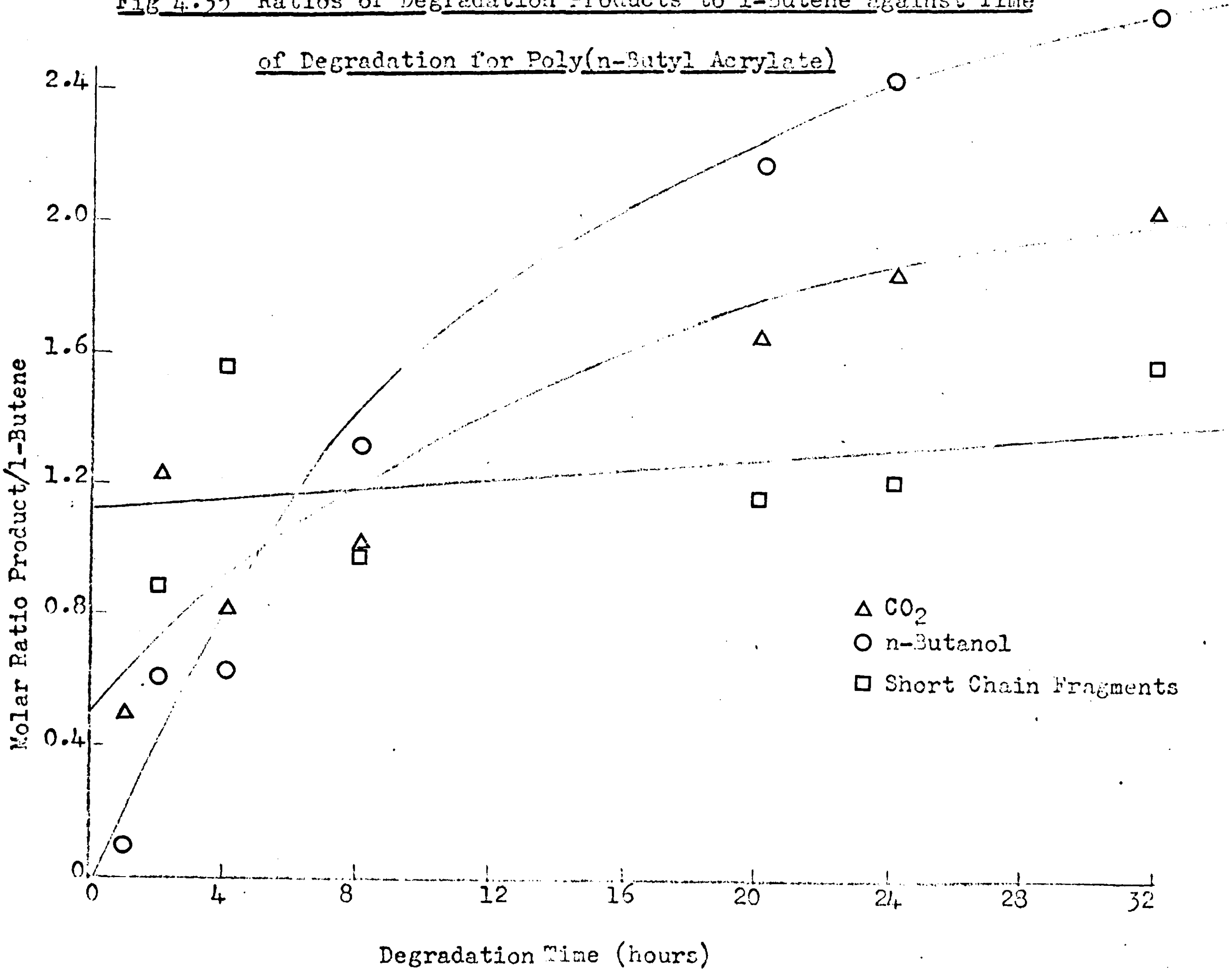
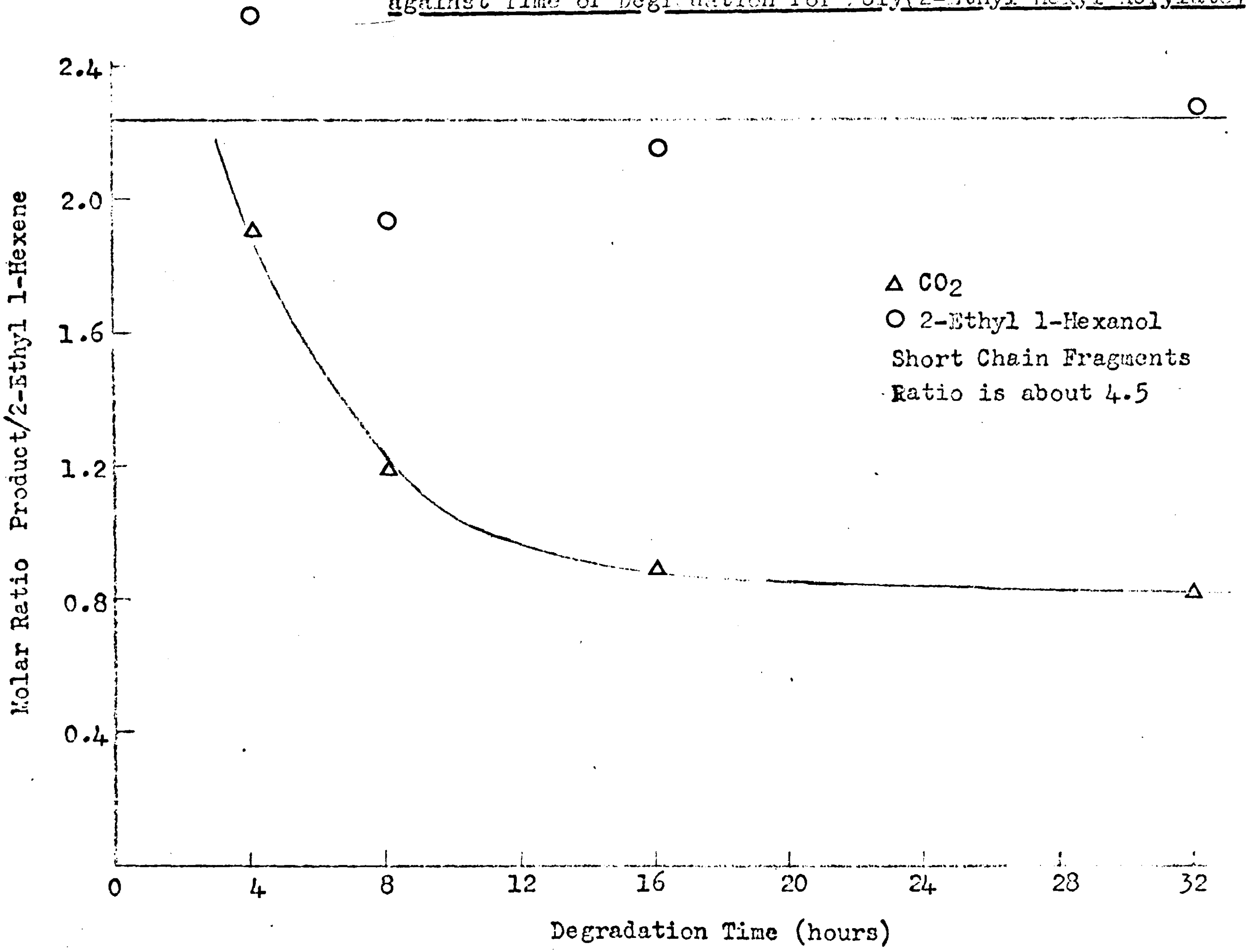


Fig 4.36 Ratios of Degradation Products to 2-Ethyl 1-Hexene against Time of Degradation for Poly(2-Ethyl Hexyl Acrylate)



found in three of the four polymers, although, as the size of the ester group increases, the rate of cross-linking appears to decrease. Chain scission occurs simultaneously and one of the major products of degradation is short chain fragments. Coloration developes and there are several minor products such as carbon monoxide, monomer and methacrylate.

The significance of the results described is further discussed in Chapter 8. Results of infrared studies on the polymer residues after degradation at 315°C are given in Chapter 6.

Table 4.1

Weights of Gases from Poly(Ethyl Acrylate)

Run No.	ST11E	ST12E	ST61E	ST62E	ST63E	ST64E
Time (hours)	1	2	4	8	15	30
W_{CO_2}	1.3	5.1	8.4	12.3	12.8	15.4
W_{olefin}	2.4	3.8	4.6	6.7	7.3	8.1
W_{total}	3.7	8.9	13.0	19.0	20.1	23.5
$W_{N.C.}$	0.1	0.1	0.2	0.4	1.1	1.1
$W_{I.P.}$	196.8	196.8	126.8	126.8	126.8	126.8

Table 4.2

Weights of Gases from Poly(n-Propyl Acrylate)

Run No.	ST31P	ST32P	ST83P	ST33P	ST81P	ST84P	ST34P
Time (hours)	1	2	4	6.5	10	16.5	30
W_{CO_2}	4.0	4.8	3.8	9.9	10.3	11.0	23.4
W_{olefin}	3.1	5.0	4.6	6.8	5.4	6.8	16.0
W_{total}	7.1	9.8	8.4	16.7	15.7	17.8	39.4
$W_{N.C.}$	0.1	0.1	0.1	1.7	0.3	0.6	1.3
$W_{I.P.}$	203.2	203.2	113.6	203.2	113.6	113.6	227.2

Table 4.3

Calculation of Weights of Gases from Poly(n-Butyl Acrylate)

Run No.	ST21B	ST22B	ST17B	ST23B	ST19B	ST20B	ST24B
Time (hours)	1	2	4	6.5	10	14	30
P_{total}	4.39	9.72	12.21	19.16	26.51	28.40	39.40
P_{CO_2}	1.48	6.31	6.50	9.82	18.22	19.06	31.20
P_{olefin}	2.58	5.26	7.74	10.24	14.95	17.10	15.35
$C.P._{CO_2}$	1.60	5.30	5.57	9.37	14.57	14.97	26.38
$C.P._{olefin}$	2.78	4.43	6.64	9.78	11.94	13.43	12.98
$P_{N.C.}$	0.02	0.00	0.04	0.07	0.12	0.17	0.19
$10^4 x\ n_{CO_2}$	0.26	0.88	0.92	1.55	2.41	2.48	4.37
$10^4 x\ n_{olefin}$	0.46	0.73	1.10	1.62	1.98	2.22	2.15
$10^4 x\ n_{N.C.}$	0.05	0.00	0.09	0.16	0.28	0.39	0.44
W_{CO_2}	1.1	3.9	4.0	6.8	10.6	10.9	19.2
W_{olefin}	2.6	4.1	6.2	9.1	11.1	12.4	12.0
W_{total}	3.7	8.0	10.2	15.9	21.7	23.3	21.2
$W_{N.C.}$	0.1	0.0	0.3	0.4	0.8	1.1	1.2
$W_{I.P.}$	200.0	200.0	200.0	200.0	200.0	200.0	200.0

Table 4.4

Weights of Gases from Poly(2-Ethyl Hexyl Acrylate)

Run No.	ST91H	ST92H	ST93H	ST94H	ST95H	ST96H
Time (hours)	1	2	4	8	16	32
W_{CO_2}	0.8	0.9	4.0	7.3	9.2	8.4
$W_{N.C.}$	0.2	0.3	0.0	1.0	3.2	3.9
$W_{I.P.}$	435.0	393.0	450.0	393.5	453.5	400.0

In tables 4.1-4.4, P, C.P., n and W have the significance mentioned on page 61, and units of cm.Hg., cm.Hg., no units and mg, respectively.

The subscripts 'total', 'CO_2', 'olefin', 'N.C.' and 'I.P.' signify total gas, carbon dioxide, olefin, non-condensibles and initial polymer respectively.

Tables 4.5-4.8

Mass-Balance Tables for the Degradation of the Polymers at 315°C

Table 4.5 Poly(Ethyl Acrylate)

Degradation Time (hours)	1	2	4	8	16	32
Weight of -						
Initial Polymer	100.0	100.0	100.0	100.0	100.0	100.0
Residue	98.0	92.9	83.4	67.2	45.4	38.0
Insol. Res.	44.2	31.1	39.0	12.8	33.1	30.1
Sol. Res.	49.8	60.8	45.6	50.8	7.2	5.1
Short Chain Fragments	2.1	3.8	4.7	9.3	14.3	15.3
Distillable Liquids	0.4	1.0	6.3	15.0	25.4	26.7
Alcohol	0.3	0.9	3.5	12.0	20.2	22.4
Monomer	0.00	0.02	0.18	0.19	0.26	0.32
Methacrylate	0.00	0.02	0.05	0.08	0.11	——
Remaining Liquids	0.1	0.1	2.6	2.7	4.6	3.7
Total Gases	1.9	4.5	10.3	15.0	16.1	18.5
CO_2	0.7	2.6	6.6	9.7	10.2	12.1
Olefin	1.2	1.9	3.6	5.3	5.9	6.4
Non-Condensibles	0.1	0.1	0.2	0.3	0.9	0.9
Sum of Products	98.5	101.3	106.1	103.2	97.0	96.6
Volatiles	4.5	9.4	21.5	39.6	56.7	61.4

Table 4.6 Poly(n-Propyl Acrylate)

Degradation Time (hours)	1	2	4	8	16	32
Weight of -						
Initial Polymer	100.0	100.0	100.0	100.0	100.0	100.0
Residue	99.2	95.0	84.5	67.5	34.9	24.8
Insol. Res.	31.7	12.9	21.6	12.8	16.9	24.7
Sol.Res.	66.3	73.7	58.9	56.5	20.0	0.0
Short Chain Fragments	2.2	4.6	6.0	8.7	23.4	27.4
Distillable Liquids	0.5	6.2	4.8	14.1	22.2	29.2
Alcohol	0.0	1.1	2.2	12.1	19.3	24.3
Monomer	0.00	0.00	0.02	0.08	0.18	0.23
Methacrylate	0.00	0.00	0.01	0.05	0.11	0.20
Remaining Liquids	0.5	5.1	2.6	1.9	2.6	4.5
Total Gases	3.5	4.8	7.4	11.7	15.7	17.3
CO_2	2.0	2.4	3.3	6.4	9.4	10.3
Olefin	1.5	2.5	4.1	4.6	5.9	7.0
Non-Condensibles	0.0	0.0	0.1	0.6	0.5	0.6
Sum of Products	104.2	102.2	98.8	104.4	98.7	99.2
Volatiles	6.2	15.6	18.3	35.1	61.8	74.5

Table A.7 Poly(n-Butyl Acrylate)

Degradation Time (hours)	1	2	4	8	20	24	32
Weight of -							
Initial Polymer	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Residue	90.3	84.6	74.6	67.2	55.8	35.2	33.9
Insol. Res.	5.3	6.0	5.6	13.1	29.6	33.6	33.9
Sol. Res.	85.0	78.6	69.0	54.1	26.2	1.6	0.0
Short Chain Fragments	7.7	4.1	11.1	11.5	16.3	17.1	21.7
Distillable Liquids	0.4	2.2	10.6	9.8	19.8	28.7	29.6
Alcohol	0.2	1.6	2.6	9.0	17.6	19.6	20.7
Monomer	0.00	0.04	0.08	0.10	0.16	0.20	—
Methacrylate	0.00	0.00	0.03	0.04	0.05	0.03	—
Remaining Liquids	0.2	0.6	7.9	0.7	2.0	8.9	8.4
Total Gases	1.8	4.0	5.1	9.4	14.8	15.4	15.5
CO_2	0.5	1.9	2.0	4.1	7.9	8.9	9.6
Olefin	1.3	2.0	3.1	5.1	6.1	6.1	6.0
Non-Condensibles	0.1	0.0	0.2	0.5	1.1	1.1	1.2
Sum of Products	100.3	94.9	101.6	98.4	106.8	97.5	101.9
Volatiles	10.0	10.7	27.0	31.2	52.0	62.3	68.0

Table 4.8 Poly(2-Ethyl Hexyl Acrylate)

Degradation Time (hours)	1	2	4	8	16	32
Weight of -						
Initial Polymer	100.0	100.0	100.0	100.0	100.0	100.0
Residue	84.0	78.1	69.4	57.2	41.1	15.8
Short Chain Fragments	14.7	19.7	23.8	27.3	36.2	57.6
Alcohol	0.0	0.9	3.6	9.1	14.3	17.3
Olefin	0.0	0.0	1.2	4.1	5.7	6.6
CO_2	0.2	0.2	0.9	1.9	2.0	2.1
Non-Condensibles	0.0	0.1	0.0	0.3	0.8	1.0
Sum of Products	98.9	99.0	98.9	99.9	99.1	100.5
Volatiles	14.9	20.9	29.5	42.7	58.0	84.7

Tables 4.9-4.12

Gaseous Degradation Products as Moles/Gram Monomer Unit

Table 4.9 Poly(Ethyl Acrylate)

Degradation Time (hours)	1	2	4	8	15	16	30	32
CO_2	0.016	0.059	0.150	0.220	0.230		0.275	
Ethylene	0.043	0.068	0.129	0.189	0.207		0.228	
Ethanol	0.007	0.020	0.076	0.261		0.439		0.487

Table 4.10 Poly(n-Propyl Acrylate)

Degradation Time (hours)	1	2	4	6.5	8	10	16	30	32
CO_2	0.052	0.062	0.086	0.127		0.236	0.251	0.267	
Propylene	0.041	0.068	0.111	0.090		0.130	0.163	0.190	
n-Propanol	0.000	0.021	0.042		0.230		0.367		0.462

Table 4.11 Poly(n-Butyl Acrylate)

Degradation Time (hours)	1	2	4	6.5	8	10	14	20	24	32
CO_2	0.015	0.055	0.058	0.099		0.154	0.160			0.279
1-Butene	0.030	0.046	0.071	0.105		0.128	0.142			0.137
n-Butanol	0.003	0.028	0.045		0.156			0.304	0.339	0.362

Table 4.12 Poly(2-Ethyl Hexyl Acrylate)

Degradation Time (hours)	1	2	4	8	16	32
CO_2	0.008	0.008	0.038	0.080	0.084	0.088
2-Ethyl 1-Hexene	0.000	0.000	0.020	0.067	0.094	0.108
2-Ethyl 1-Hexanol	0.000	0.013	0.051	0.129	0.202	0.246

Tables 4.14-4.17

Liquid Degradation Product Analysis

Table 4.14 Poly(Ethyl Acrylate)

Sample	Degradation	Degrad Time (Hrs)	A_a	A_s	W_s	f	W_a	$W_{I.P.}$
Ethanol	ST401E	1	5.0	8.2	1.2	1.049	0.77	275.5
Ethanol	ST402E	2	0.561	1.000	3.8	1.049	2.24	255.5
Monomer	ST402E	2	3.2	193	3.8	1.000	0.06	255.5
Methacrylate	ST402E	2	20.7	1930	3.8	1.000	0.04	255.5
Ethanol	ST403E	4	0.545	1.000	16.5	1.049	9.42	265.6
Monomer	ST403E	4	8.1	274	16.5	1.000	0.49	265.6
Methacrylate	ST403E	4	19.9	2740	16.5	1.000	0.12	265.6
Ethanol	ST404E	8	0.761	1.000	39.4	1.049	31.45	262.1
Monomer	ST404E	8	17.0	1330	39.4	1.000	0.50	262.1
Methacrylate	ST404E	8	13.8	2660	39.4	1.000	0.20	262.1
Ethanol	ST405E	16	0.971	1.000	43.8	1.049	44.55	221.6
Monomer	ST405E	16	22.4	1690	43.8	1.000	0.58	221.6
Methacrylate	ST405E	16	9.6	1690	43.8	1.000	0.25	221.6
Ethanol	ST406E	32	1.030	1.000	53.4	1.049	57.60	256.6
Monomer	ST406E	32	17.5	1140	53.4	1.000	0.82	256.6

Table 4.15 Poly(n-Propyl Acrylate)

Sample	Degradation	Degrad Time (Hrs)	A_a	A_s	W_s	f	W_e	$W_{I.P.}$
n-Propanol	ST411P	1	—	—	—	—	0.00	—
n-Propanol	ST412P	2	1.000	6.67	8.2	0.941	1.16	111.2
n-Propanol	ST413P	4	1.000	1.579	5.2	0.941	3.10	139.1
Monomer	ST413P	4	4.3	854	5.2	1.000	0.04	139.1
Methacrylate	ST413P	4	21.2	8540	5.2	1.000	0.02	139.1
n-Propanol	ST414P	8	1.000	1.154	22.5	0.941	18.36	152.1
Monomer	ST414P	8	18.4	2360	22.5	1.000	0.18	152.1
Methacrylate	ST414P	8	30.8	5890	22.5	1.000	0.12	152.1
n-Propanol	ST415P	16	1.000	1.017	30.1	0.941	27.87	144.7
Monomer	ST415P	16	7.8	665	30.1	1.000	0.37	144.7
Methacrylate	ST415P	16	25.7	3330	30.1	1.000	0.23	144.7
n-Propanol	ST416P	32	1.000	1.035	42.9	0.941	39.03	160.5
Monomer	ST416P	32	17.5	1270	42.9	1.000	0.59	160.5
Methacrylate	ST416P	32	31.2	2530	42.9	1.000	0.52	160.5

Table 4.16 Poly(n-Butyl Acrylate)

Sample	Degradation	Degrad Time (hrs)	A_a	A_s	W_s	f	W_a	$W_{I.P.}$
n-Butanol	ST421B	1	0.53	30.5	20.0	1.065	0.37	200.0
n-Butanol	ST422B	2	1.00	1.209	7.2	1.065	6.34	399.0
Monomer	ST422B	2	16.7	812	7.2	1.000	0.15	399.0
n-Butanol	ST423B	4	1.00	4.51	14.1	1.065	3.83	147.6
Monomer	ST423B	4	13.6	1600	14.1	1.000	0.12	147.6
Methacrylate	ST423B	4	8.0	3200	14.1	1.000	0.04	147.6
n-Butanol	ST424B	8	1.000	0.936	35.0	1.065	39.81	444.7
Monomer	ST424B	8	14.2	998	35.0	1.000	0.50	444.7
Methacrylate	ST424B	8	19.4	4990	35.0	1.000	0.14	444.7
n-Butanol	ST425B	20	1.000	1.077	26.3	1.065	26.02	147.6
Monomer	ST425B	20	8.7	986	26.3	1.000	0.23	147.6
Methacrylate	ST425B	20	31.2	9860	26.3	1.000	0.08	147.6
n-Butanol	ST426B	24	0.768	1.000	43.6	0.866	29.02	147.6
Monomer	ST426B	24	9.7	1430	43.6	1.000	0.30	147.6
Methacrylate	ST426B	24	5.3	5700	43.6	1.000	0.04	147.6
n-Butanol	ST427B	32	6.91	5.73	32.2	1.065	41.4	200.0

Table 4.17 Poly(2-Ethyl Hexyl Acrylate)

Sample	Degradation	Degrad Time (hrs)	A_a	A_s	W_s	f	W_a	$W_{I.P.}$
Olefin	ST91H	1	0.0	—	—	0.797	0.00	435.0
Alcohol	ST91H	1	0.0	—	—	1.045	0.00	435.0
Olefin	ST92H	2	78	47000	45.0	0.797	0.1	393.0
Alcohol	ST92H	2	35.0	470.0	45.0	1.045	3.7	393.0
Olefin	ST93H	4	17.2	417.5	161.8	0.797	5.3	450.0
Alcohol	ST93H	4	40.2	417.5	161.8	1.045	16.3	450.0
Olefin	ST94H	8	29.2	329.0	226.0	0.797	16.0	393.5
Alcohol	ST94H	8	50.2	329.0	226.0	1.045	36.0	393.5
Olefin	ST95H	16	34.7	193.0	180.0	0.797	25.8	453.5
Alcohol	ST95H	16	66.6	193.0	180.0	1.045	65.0	453.5
Olefin	ST96H	32	23.6	172.0	242.4	0.797	26.5	400.0
Alcohol	ST96H	32	47.1	172.0	242.4	1.045	69.5	400.0

In tables 4.14 - 4.17, the symbols used are as follows:

A_a - Area of sample peak

A_s - Area of solvent peak

W_s - Weight (mg) of solvent added to liquids

f - Sensitivity factor

W_a - Weight (mg) of sample

$W_{I.P.}$ - Weight (mg) of initial polymer

Chapter 5 Degradation Reactions of Poly(iso-Propyl Acrylate) at 265°C

5(i) Introduction

In this chapter, the analysis of the degradation products of poly(iso-propyl acrylate), by similar techniques to those used for the study of the poly(primary acrylates), is described. The products of degradation are found to resemble those from the poly(primary acrylates), but there are some considerable differences. In Chapter 3 it was shown that poly(iso-propyl acrylate) evolves gaseous material 50°C below the poly(primary acrylates). It was decided to study the thermal degradation of poly(iso-propyl acrylate) at 265°C. One series of degradation experiments was carried out at that temperature and all the degradation products from it were analysed and measured.

As in Chapter 4, tables of results are placed at the end of the chapter unless they are of immediate relevance to the text.

5(ii) Analysis of Major Gaseous Products

The yields of carbon dioxide and propylene from poly(iso-propyl acrylate) were found in the same way as those from poly(n-propyl acrylate) described in 2(xiv) and 4(ii).

The total gas pressure was measured on the constant volume manometer and quantitative infrared analysis of the gases was used to find the ratio of pressures of carbon dioxide and propylene. The weights of gases are shown in table 5.1. These are shown as weight percentages of the initial polymer sample in table 5.2 and curves of weight percent against time of degradation are drawn in fig 5.1. These results are shown also as molecules of gas evolved per monomer unit in table 5.3. Fig 5.2 illustrates this table and fig 5.3 shows how the molar ratio of carbon dioxide to olefin varies with time of degradation. The carbon dioxide/olefin ratio begins at a low value and converges to 0.6 in the later stages of degradation.

There appears to be some autocatalysis in the olefin elimination reaction. However this effect is small in poly(iso-propyl acrylate) compared with the same effect in poly(t-butyl acrylate)[4,53]. The calculation of kinetic data is complicated by autocatalysis; nevertheless, because of its apparently slight extent, a rate constant and the initial rate for the propylene elimination reaction could be found as described below.

Similar values were obtained for carbon dioxide production. However, in this case, the reaction kinetics are complicated by the dependence of the reaction on the olefin elimination reaction and also by the competing anhydride forming reaction{see 8(ii)}, so that both the reaction order and the rate constant found below are only apparent values and probably not true values.

For a reaction which obeys second-order kinetics,

Rate of reaction = $-d[A]/dt = k[A]^2$ where A is a reagent and k is the rate constant.

Fig 5.1 Gas Evolution from Poly(iso-Propyl Acrylate) at 265°C

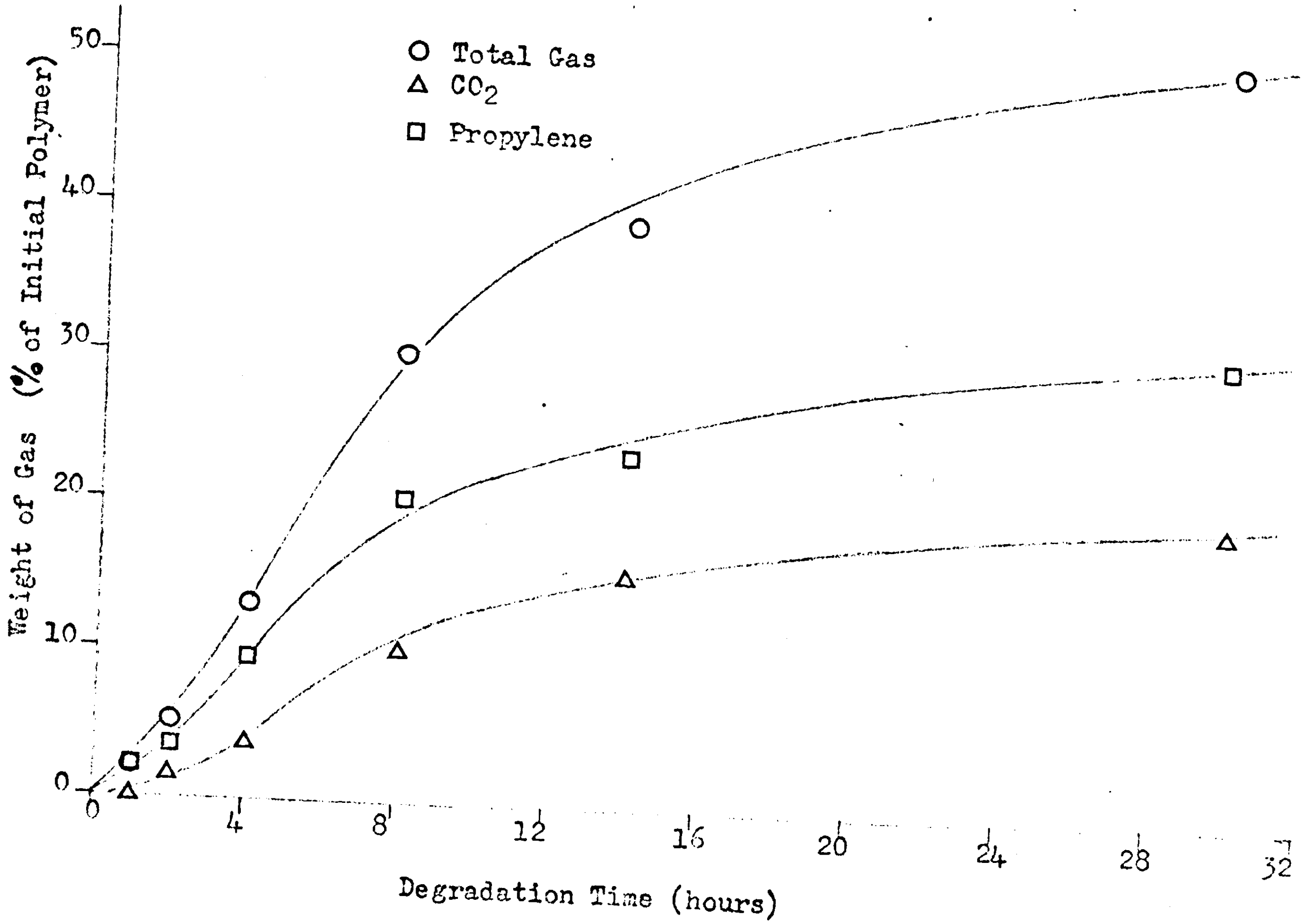


Fig 5.2 Number of Molecules of Gas Evolved per Monomer Unit against Time of Degradation for Poly(iso-Propyl Acrylate)

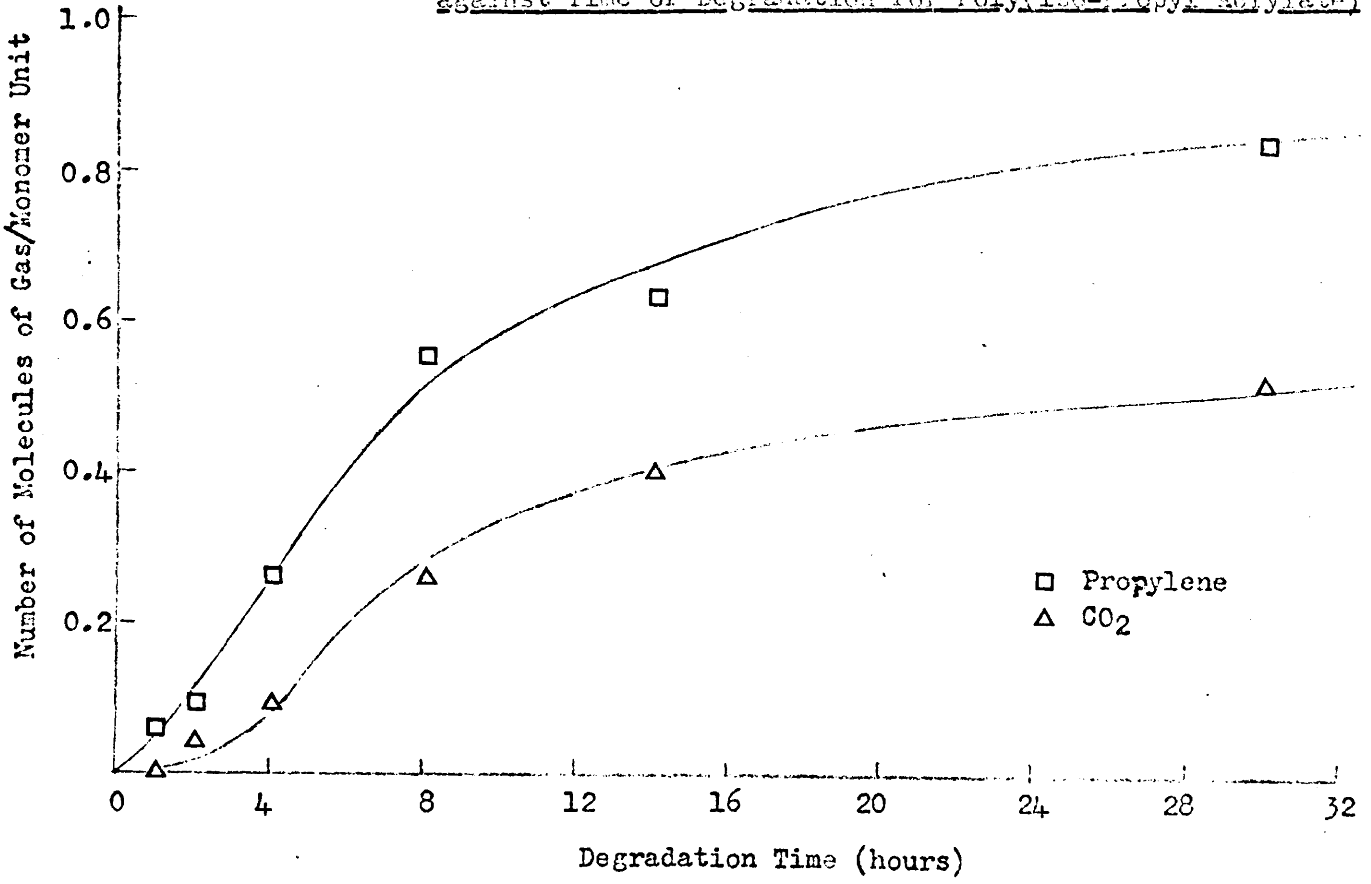
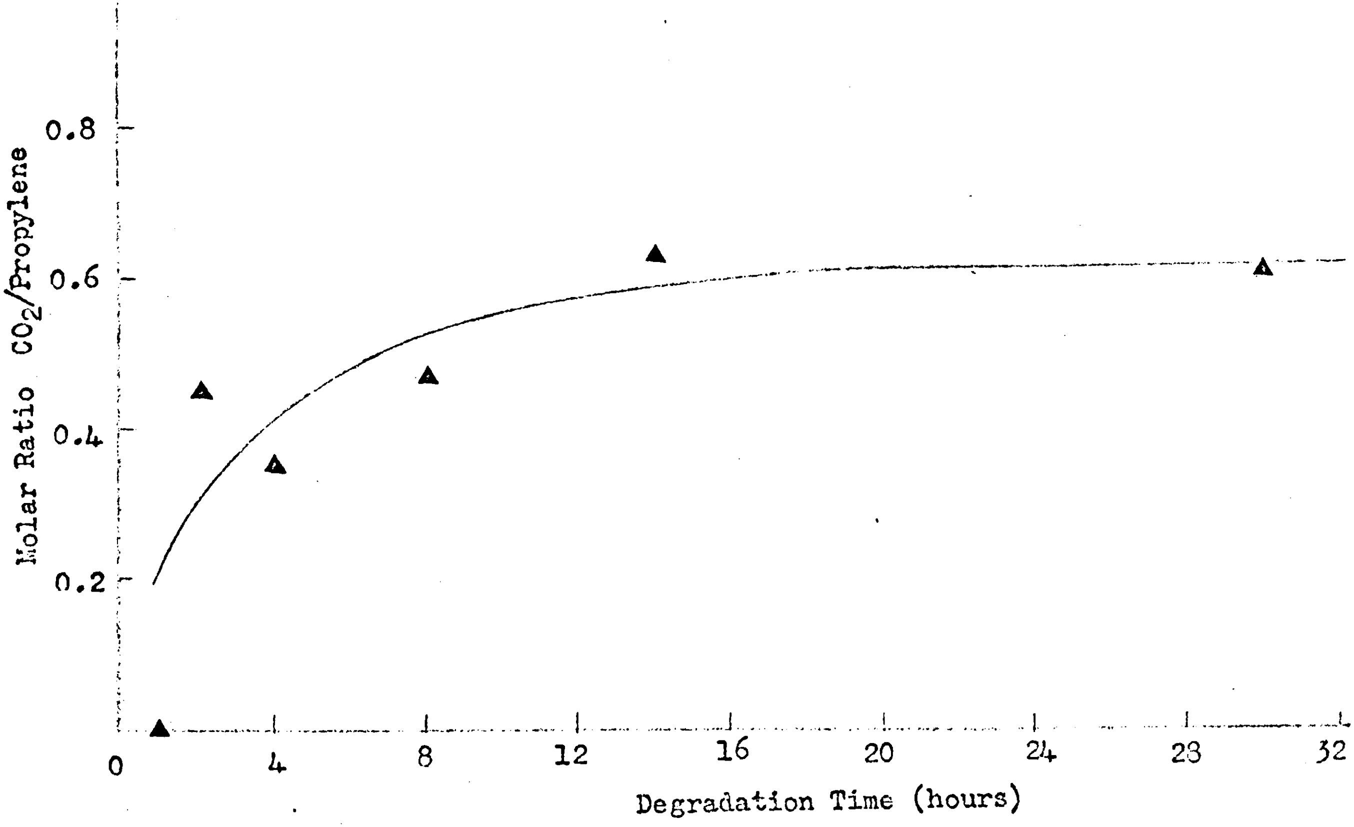


Fig 5.3 Ratio of Carbon Dioxide to Propylene against Time of Degradation for Poly(iso-Propyl Acrylate)



If x represents the amount of reaction at time t and a, the amount of reaction at infinite degradation time, then the above equation can be written as follows:

$$\text{Rate} = dx/dt = k(a-x)^2$$

$$\int_0^x dx/(a-x)^2 = kdt$$

$$\therefore \quad \left[1/(a-x)\right]_0^x = kt$$

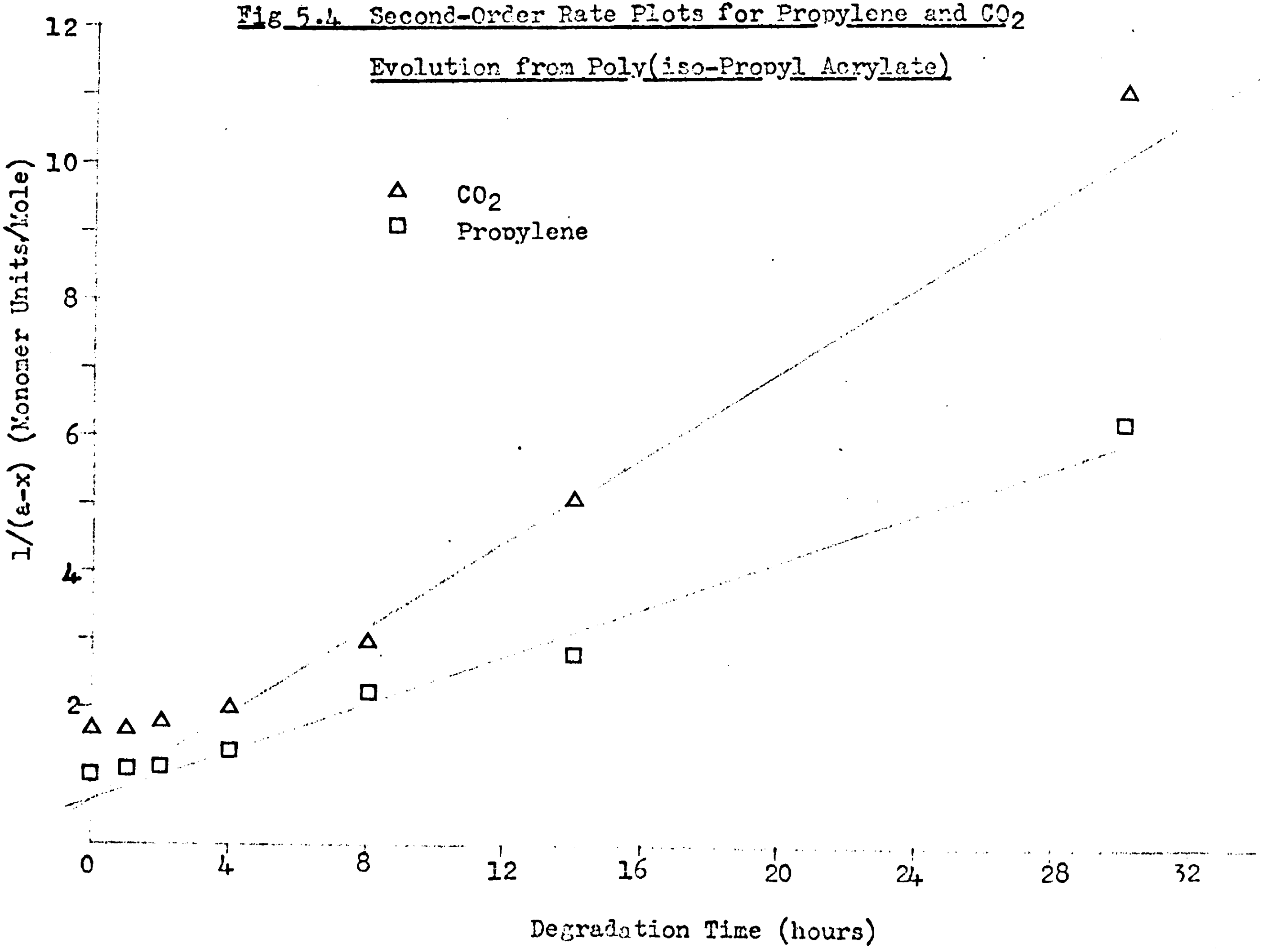
$$\therefore \quad 1/(a-x) - 1/a = kt$$

$$\text{or} \quad 1/(a-x) = kt + 1/a$$

A graph of 1/(a-x) against t will give a straight line of gradient k. In the present case, a, the extent of reaction at infinite degradation time, was taken as 100 % in the case of the olefin elimination reaction and 60 % in the case of the carbon dioxide elimination reaction since the molar ratio of carbon dioxide to propylene is close to 0.6 : 1.0 at later stages of degradation (see fig 5.3).

Fig 5.4 shows second-order rate plots for propylene and carbon dioxide. For each gas, the points for 4 hours degradation and thereafter lie close to a straight line. The points for early degradation times do not lie on these straight lines because of the autocatalysis effect. Similar plots for other reaction orders can be drawn but give curves rather than straight lines. This suggests that the true reaction order for the olefin elimination reaction and the apparent order for carbon dioxide elimination reaction are close

Fig 5.4 Second-Order Rate Plots for Propylene and CO_2 Evolution from Poly(iso-Propyl Acrylate)



to 2. Table 5.4 gives the second-order rate constants and initial rates of production for the two gases calculated from fig 5.4.

Rates of evolution of gases are plotted against percent volatilisation in fig 5.5. The initial rates of carbon dioxide and propylene production are obtained by extrapolating the curve back from the maximum. The values thus obtained for the initial rates are also shown in table 5.4. They are rather lower than the values obtained from the second-order rate plot because the linear extrapolation of the rate of volatilisation against percent volatilisation curve method for obtaining initial rates is, strictly speaking, only valid for first order reactions.

Table 5.4

Kinetic Data for Poly(iso-Propyl Acrylate) Degradation

	CO_2	Propylene
From fig 5.4		
Rate constant(g.m.u)(moles)$^{-1}$(hour)$^{-1}$	0.320	0.178
Initial rate(moles)(g.m.u)$^{-1}$(hour)$^{-1}$	0.115	0.178
Initial rate(wt % of initial polymer)(hr)$^{-1}$	4.44	6.56
From fig 5.5		
Initial rate(wt % of initial polymer)(hr)$^{-1}$	4.07	5.50

Fig 5.5 Rate of Volatilisation against Percent Volatilisation Curve for Poly(iso-Propyl Acrylate) Volatilisation at 265°C

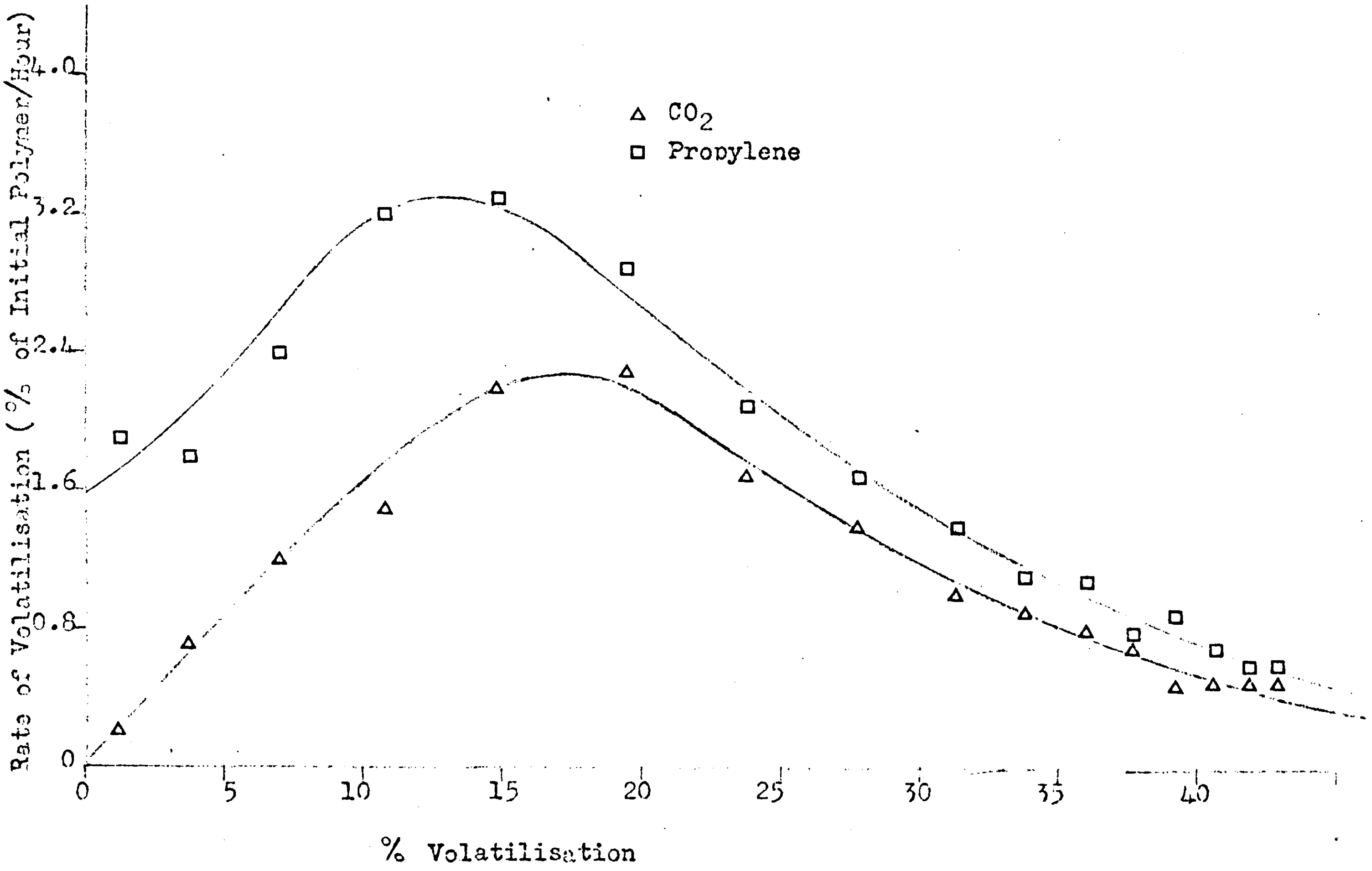


Fig 5.5 shows that the initial rate of olefin production exceeds that of carbon dioxide, but that the rates converge in the later stages of degradation

5(iii) Minor Gaseous Products

A small amount of material not condensible at -196°C is produced. Analysis by mass spectrometry gave similar results to those obtained for the non-condensibles from poly(n-propyl acrylate) and the main component of this fraction is therefore carbon monoxide.

5(iv) Liquid Degradation Products

A trace of liquid material was recovered in limb I of the sealed tube (fig 2.10) after the degradation of 100 mg samples of poly (iso-propyl acrylate) for 8 hours or more at 265°C. n-Propyl acetate was added in weighed amount and gas-liquid chromatograms obtained of the mixture. Only two peaks could be found with both the dinonyl phthalate and carbowax 20M columns mentioned in 2(xv)B. One peak corresponds in retention time to iso-propanol and the second to the n-propyl acetate solvent. The amount of iso-propanol is found by comparing peak areas as described in 2(xv)B. Table 5.5 gives these results and uses the symbols mentioned in 2(xv)B. The sensitivity factor for this analysis was not found accurately, but was assumed to be 1.00.

Table 5.5

Weight of iso-Propanol from Poly(iso-Propyl Acrylate) Degradations

Degradation Time (hours)	A_a	A_s	W_s	f	W_a
8	0.095	1.000	2.6	1.00	0.25
14	0.107	1.000	3.0	1.00	0.32
30	0.118	1.000	2.2	1.00	0.26

The weights of liquids found are given in table 5.2. There remains a substantial amount of liquid not accounted for by G.L.C. analysis. There is no chain fragment fraction to affect the weight of liquid, and therefore this discrepancy is probably caused by the presence of water. No specific test for water was applied to this fraction.

5(v) Analysis of the Residue

Table 5.2 gives weight percent of soluble and insoluble residue at various times of degradation. The polymer rapidly becomes insoluble and brittle on degradation and, as degradation proceeds, a yellow coloration developes. The weight loss can be accounted for almost completely by the carbon dioxide and propylene evolved. After 1 and 2 hours degradation, there is still some soluble residue, the amounts and molecular weights are given in table 5.6

Table 5.6

Data on Soluble Residues

Degradation Time(hours)	Weight(% Residue)	No.Av. Molecular Weight x 10^{-3}
0	100	650
1	69.5	1,140
2	21.2	——

Thereafter the residue becomes completely insoluble. Infrared and N.M.R. spectra show that the soluble residue after these short degradation times does not change significantly.

As with the poly(primary acrylates), an elemental analysis was carried out on the insoluble residue. The results are shown in table 5.7.

The yields of carbon dioxide and propylene after 30 hours degradation (see table 5.3) enable the composition of the residue to be estimated. After 30 hours degradation, the monomer units should be made up as follows:

51.0 %	ethylene
33.1 %	acrylic acid
15.9 %	unreacted iso-propyl acrylate

This ignores any formation of anhydride by elimination of water from acrylic acid units. The composition of the residue based on this estimate is also shown in table 5.7.

Table 5.7

Microanalyses of Poly(iso-Propyl Acrylate) Residues

Degradation Time (hours)	% C	% H	% O (by difference)
0	63.14	8.82	28.03
8	57.44	7.24	35.32
30(measured)	64.60	6.01	29.39
30(calculated)	63.3	8.8	27.9

If carbon dioxide and propylene are evolved with a molar ratio (CO_2/C_3H_6) of 0.6 throughout the degradation then the elemental composition of the residue should change very little. Thus, after 30 hours degradation, when this ratio is in fact close to 0.6, the composition of the residue is close to that of the original polymer. At earlier stages, however, the ratio is less than 0.6 (see fig 5.3) and the oxygen content after 8 hours degradation is correspondingly higher, as table 5.7 shows. The low hydrogen content at long degradation times is surprising, but may be related to the development of coloration (see 8(iii)).

A sample of the residue after 30 hours degradation was shaken with a benzene/0.1 M sodium hydroxide solution mixture. The residue dissolved slowly in the aqueous layer, colouring this layer yellow.

5(vi) Summary

A thorough analysis of the products of degradation of poly(iso-propyl acrylate) at 265°C shows that the main reaction occurring is an ester decomposition process which evolves propylene quantitatively and up to about 60 % of the theoretical yield of carbon dioxide. The cross-linking reaction occurs simultaneously, resulting in insolubility in the residue. All other reactions proceed to a neglible extent at this temperature, in contrast to the behaviour of poly(primary acrylates) degrading at 315°C.

Further investigations of the degradation by infrared analysis of the residue at various times of degradation is described in Chapter 6. The results are discussed in greater detail in Chapter 8 and Chapter 7 includes a study of the low temperature degradation of poly (iso-propyl acrylate).

Table 5.1

Weight of Gases from Poly(iso-Propyl Acrylate)

Run No.	ST57I	ST52I	ST58I	ST59I	ST55I	ST60I
Degradation Time (hours)	1	2	4	8	14	30
P_{Total}	5.80	7.17	18.72	43.0	55.7	62.1
P_{CO_2}	0.00	2.48	5.23	12.40	22.52	24.35
P_{Olefin}	2.96	5.93	14.78	25.35	36.18	40.33
$C.P._{CO_2}$	0 00	2.12	4.89	14.45	21.37	23.39
$C.P._{Olefin}$	2.96	5.05	13.82	29.54	34.33	38.72
$P_{N.C.}$	0.01	0.01	0.02	0.03	0.04	0.06
$10^4 x\ n_{CO_2}$	0.00	0.35	0.81	2.39	3.54	3.88
$10^4 x\ n_{Olefin}$	0.49	0.84	2.29	4.89	5.68	6.41
$10^4 x\ n_{N.C.}$	0.02	0.02	0.05	0.07	0.09	0.14
W_{CO_2}	0.0	1.5	3.6	10.1	15.6	17.1
W_{Olefin}	2.1	3.5	9.6	20.5	23.8	26.9
W_{Total}	2.1	5.0	13.2	30.6	39.4	44.0
$W_{N.C.}$	0.1	0.1	0 1	0.2	0.3	0.4
$W_{I.P.}$	100.8	100.8	100.8	100.8	100.8	86.8

The symbols in column 1 have the same significance as the symbols used in tables 4.1 - 4.4.

Table 5.2

Mass-Balance Table for the Degradation of Poly(iso-Propyl Acrylate) at 265°C

Degradation Time (hours)	1	2	4	8	14	30
Weight of -						
Initial Polymer	100.0	100.0	100.0	100.0	100.0	100.0
Total Residue	96.2	95.7	87.3	71.5	59.2	47.7
Insol.Residue	29.3	75.4	87.3	71.5	59.2	47.7
Sol.Residue	66.7	20.3	0.0	0.0	0.0	0.0
Distillable Liquids	0.0	0.0	0.0	1.4	1.6	1.6
Alcohol	0.0	0.0	0.0	0.3	0.3	0.3
Remaining Liquids	0 0	0 0	0.0	1.1	1.3	1.3
Total Gases	2.1	5.0	13.1	30.1	39.3	50.7
CO_2	0.0	1.5	3.6	10.1	15.6	19.7
Olefin	2.1	3.5	9.5	20.4	23.7	31.0
Non-condensibles	0.1	0.1	0.1	0.2	0.3	0.4
Sum of Products	98.4	100.8	100.5	103.2	100.4	100.4
Volatiles	2.2	5.1	13.2	31.7	41.2	52.7

Table 5.3

Gaseous Degradation Products as Molecules/ Monomer Unit

Degradation Time (hours)	1	2	4	8	14	30
CO_2	0.000	0.039	0.093	0.262	0.404	0.510
Propylene	0.057	0.095	0.258	0.554	0.643	0.841

Chapter 6 Infrared Spectral Studies on the Polymer Residues

6(i) Introduction

As was shown in Chapters 4 and 5, a considerable proportion of the alkyl groups present in the initial polymer are lost either as olefin or alcohol during degradation. Table 6.1 shows the percentage of the initial monomer units which lose alkyl groups after 30 hours degradation at 315°C (for the poly(primary acrylates)) or at 265°C (for poly(iso-propyl acrylate)).

Table 6.1

Percentage of the Initial Alkyl Groups Lost after 30 Hours Degradation

Polyacrylate	Ethyl	n-Propyl	iso-Propyl	n-Butyl	2-Ethyl Hexyl
% Alkyl Groups Lost	71.5	65.2	70.8	49.9	35.4
% Volatilisation	61.4	74.5	51.8	68.0	84.7

This means that the residue of poly(ethyl acrylate) after 30 hours degradation must have few ester groups remaining and that of poly(2-ethyl hexyl acrylate) must have only about half the initial number, since material is also being lost as short chain fragments. It is remarkable, therefore, that the infrared spectrum of poly(2-ethyl hexyl acrylate) residue after 30 hours degradation at 315°C shows so little change from the spectrum of the undegraded polymer (fig 4.30). In the cases of the other three poly(primary acrylates), more marked changes would be expected since the alkyl groups are lost at a faster rate. It is not possible, however, to find the infrared spectra of these polymers under similar conditions since they develope insolubility.

The experimental technique used to find the infrared spectra of the polymer residues is described in 2(xviii). The polymer in these studies is degrading between sodium chloride discs, and it is therefore in a rather different environment from that of the polymer degrading on the glass surface of the sealed tube in the work described in Chapters 4 and 5. For this reason care must be taken in comparing the results of the two sets of degradations. However, as far as can be judged, the weight losses appear to be comparable and the changes in the spectra can be related to the loss of volatiles, as found in Chapters 4 and 5.

The only exception to this occurs when water is absorbed by the sodium chloride discs. Because of the design of the degradation apparatus, glass blowing had to be carried out rather close to the sodium chloride discs. Water tended to condense round about the hot glass and unless great care was taken, it was absorbed by the sodium chloride. This water is not driven off the sodium chloride at 300°C under high vacuum and as described below (6(v)) appears to affect the infrared spectrum of the degraded polymer. The water can be detected in the spectra by a broad band around 3400 cm^{-1}, and its presence may, in fact, help in interpreting the spectra.

6(ii) The Infrared Spectra of the Residues from Poly(n-Butyl Acrylate)

The infrared spectrum of a film of undegraded poly(ethyl acrylate) between sodium chloride discs is shown in fig 6.1. The spectrum covers the region 4000-625 cm^{-1}. The assignment of some of the peaks to the various types of molecular vibration is also shown in this figure. The spectrum of undegraded poly(n-butyl acrylate) is generally similar. The peaks are broader than those shown for poly(2-ethyl hexyl acrylate) solution in carbon tetrachloride in fig 4.30. This is due to restricted molecular vibrations in the solid phase compared with the much freer vibrations in solution.

Fig 6.2 compares the infrared spectrum in the region 1900-900 cm^{-1} of undegraded poly(n-butyl acrylate) to the spectrum of the same sample degraded for 16 hours at 315°C. The main changes are the development of a clear shoulder on the carbonyl peak at 1760 cm^{-1}, a general increase in absorption between 1650 cm^{-1} and 1550 cm^{-1}, and the appearance of a new peak at 1563 cm^{-1}. There is a shift in the maximum peak height in the carbonyl region from 1730 cm^{-1} to 1720 cm^{-1} and in the C-O stretch region from 1165 cm^{-1} to 1175 cm^{-1}. Outwith the region 1900 cm^{-1} to 900 cm^{-1}, there is no significant change in peak shape and no new peaks appear. No peak developes for water with this polymer sample and it is assumed that dry conditions were obtained throughout the handling of the sample. Fig 6.3 shows

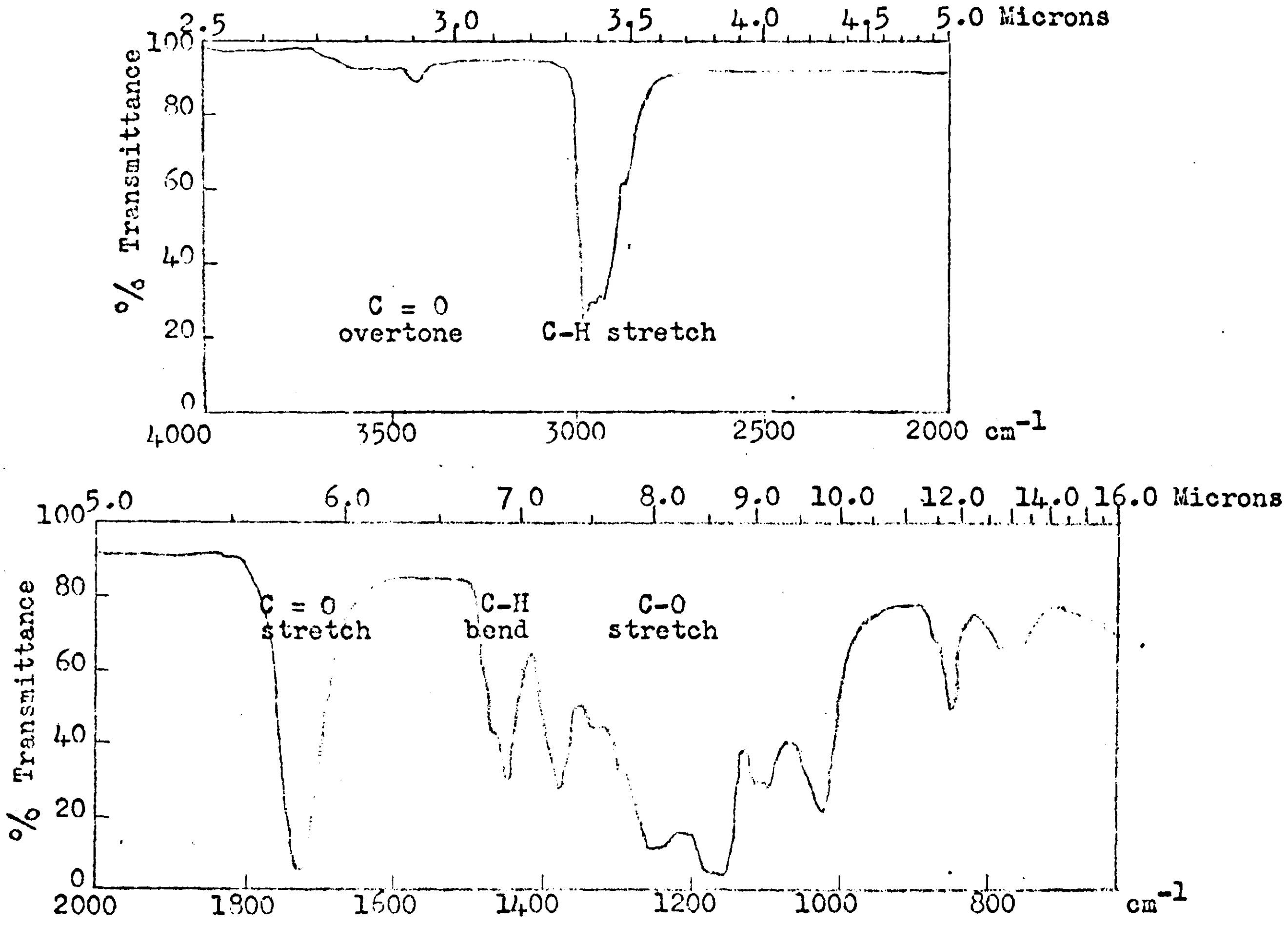


Fig 6.1 Infrared Spectrum of Undegraded Poly(Ethyl Acrylate)

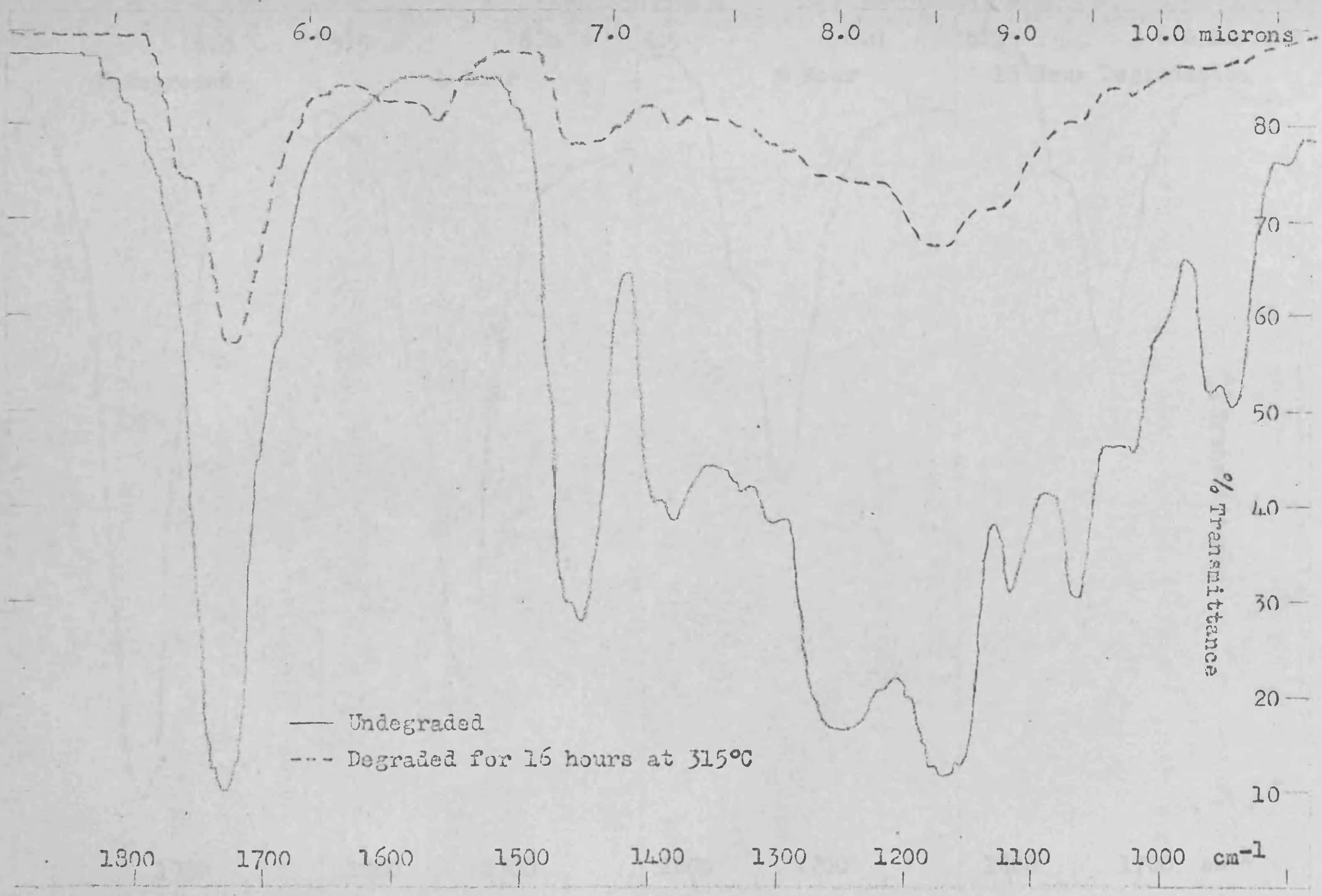


Fig 6.2 Infrared Spectra of Poly(n-Butyl Acrylate)

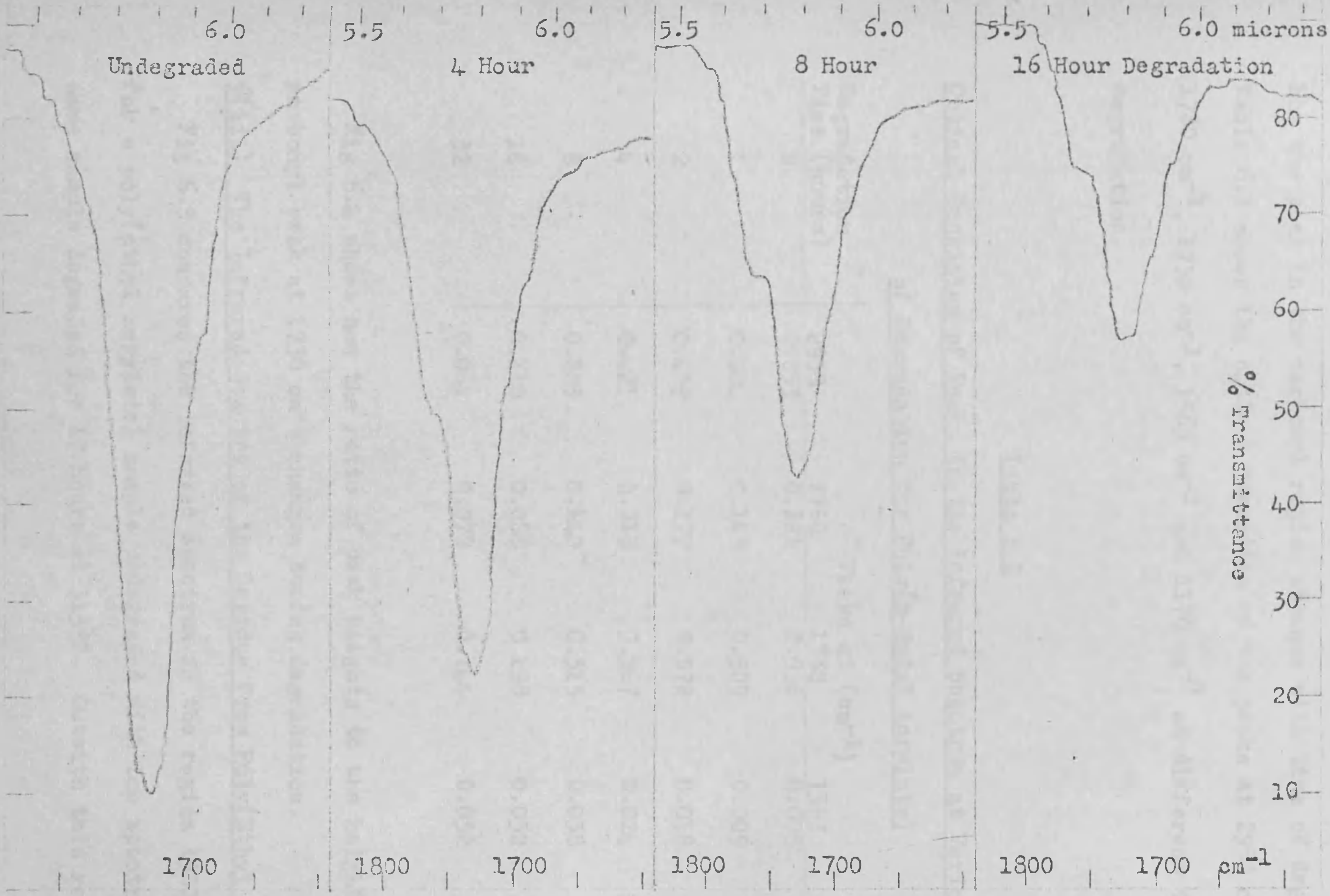


Fig 6.3 Changes in the Carbonyl Region of the I.R. Spectrum of Poly(n-Butyl Acrylate)

how the peak in the carbonyl region changes with time of degradation. Table 6.2 shows the optical densities of the peaks at 2958 cm^{-1}, 1760 cm^{-1}, 1730 cm^{-1}, 1563 cm^{-1} and 1170 cm^{-1} at different times of degradation.

Table 6.2

Optical Densities of Peaks in the Infrared Spectrum at Various Times of Degradation for Poly(n-Butyl Acrylate)

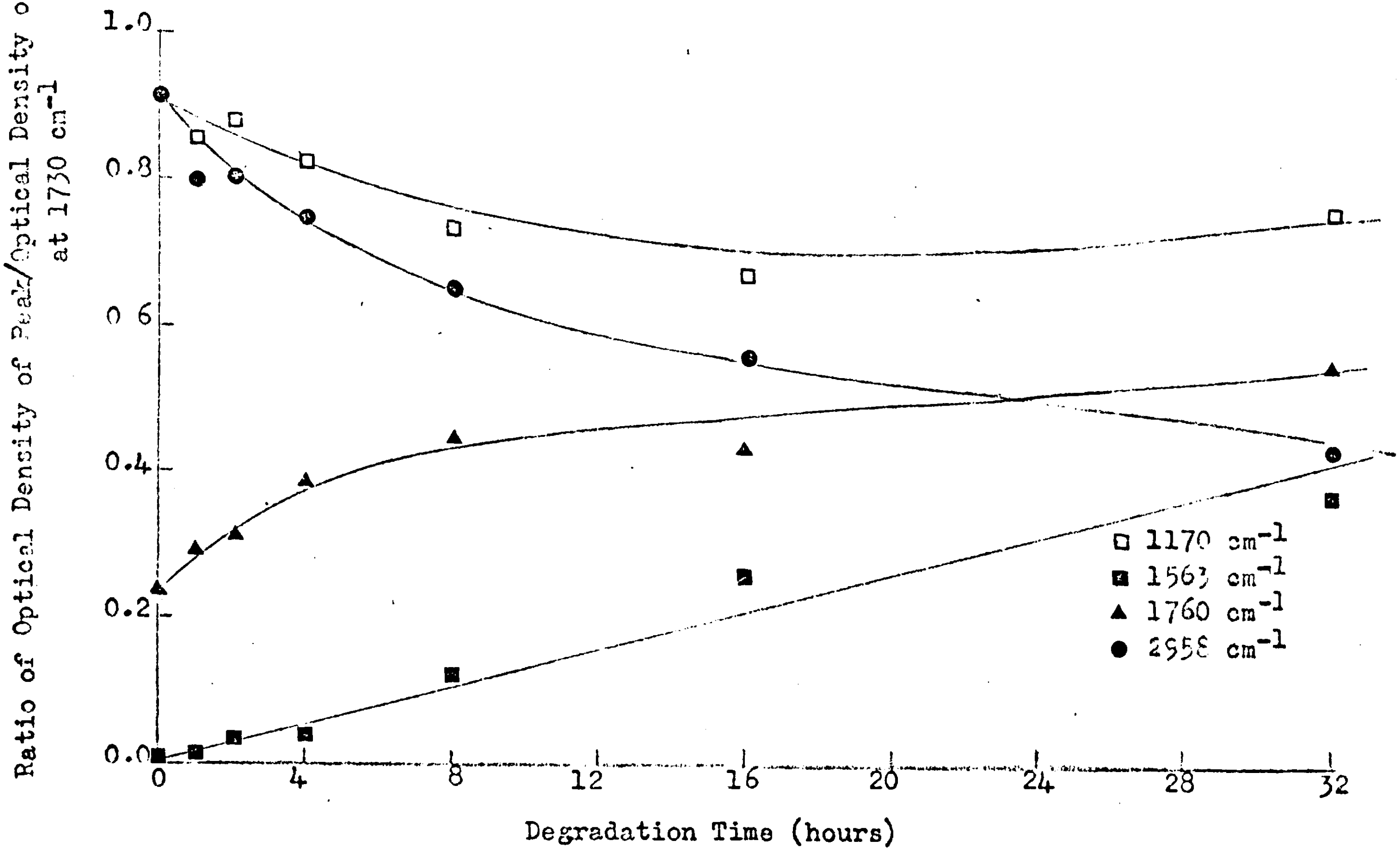
Degradation Time (hours)	Peaks at (cm^{-1}) 2958	1760	1730	1563	1170
0	0.853	0.221	0.936	0.008	0.859
1	0.404	0.148	0.509	0.005	0.437
2	0.459	0.177	0.572	0.018	0.502
4	0.421	0.218	0.567	0.024	0.467
8	0.203	0.140	0.313	0.038	0.231
16	0.110	0.086	0 198	0.052	0.133
32	0.062	0.078	0.144	0.052	0.109

Fig 6.4 shows how the ratio of peak heights to the height of the carbonyl peak at 1730 cm^{-1} changes during degradation.

6(iii) The Infrared Spectra of the Residue from Poly(Ethyl Acrylate)

Fig 6.5 compares the infrared spectrum in the region 1900-900 cm^{-1} for a poly(ethyl acrylate) sample undegraded with the spectrum of the same sample degraded for 17 hours at 315°C. Outwith this region the

Fig 6.4 Ratios of Infrared Peak Heights to Height of the Peak at 1730 cm^{-1} in the Spectrum of Degrading Poly(n-Butyl Acrylate)



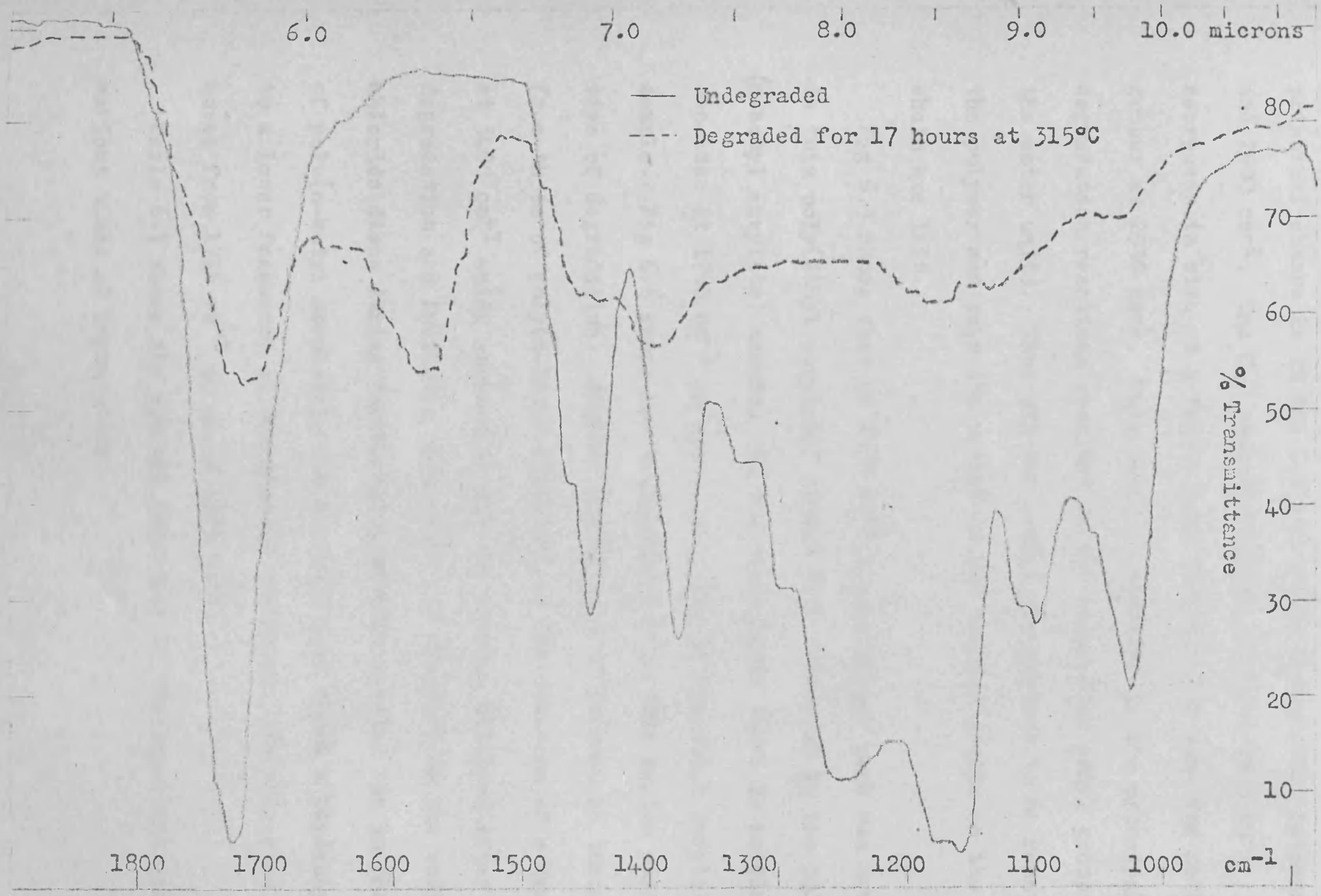


Fig 6.5 Infrared Spectra of Poly(Ethyl Acrylate)

principal change is in the C-H stretching frequencies between 3000 cm^{-1} and 2900 cm^{-1}. The C-H peak for methyl groups at 2978 cm^{-1} decreases in size at a faster rate than the C-H peak for methylene groups at 2930 cm^{-1}. This would be expected if the principal degradation reactions resulted in the removal of ethyl groups from the ester units. Thus all the methyl groups tend to be removed from the polymer and only the methylene and methine groups on the polymer chain are left.

Fig 6.5 shows that at 1570 cm^{-1} a much larger peak has developed in this poly(ethyl acrylate) sample than developed in the poly (n-butyl acrylate) sample. On the other hand, there is no clear shoulder at 1760 cm^{-1} as appeared in the poly(n-butyl acrylate) sample. Fig 6.6 shows how the absorption in this region changes with time of degradation. Another significant difference in these spectra from those of poly(n-butyl acrylate) is the presence of a broad peak at 3400 cm^{-1} which appears in all the spectra obtained after 2 hours degradation and indicates that water was absorbed on the sodium chloride discs during the handling of this sample. As in the case of poly(n-butyl acrylate), the carbonyl peak shows a tendancy to move to a lower frequency as degradation continues. In this case it moves from 1726 cm^{-1} to about 1705 cm^{-1}.

Table 6.3 shows the optical densities of the important peaks at various times of degradation.

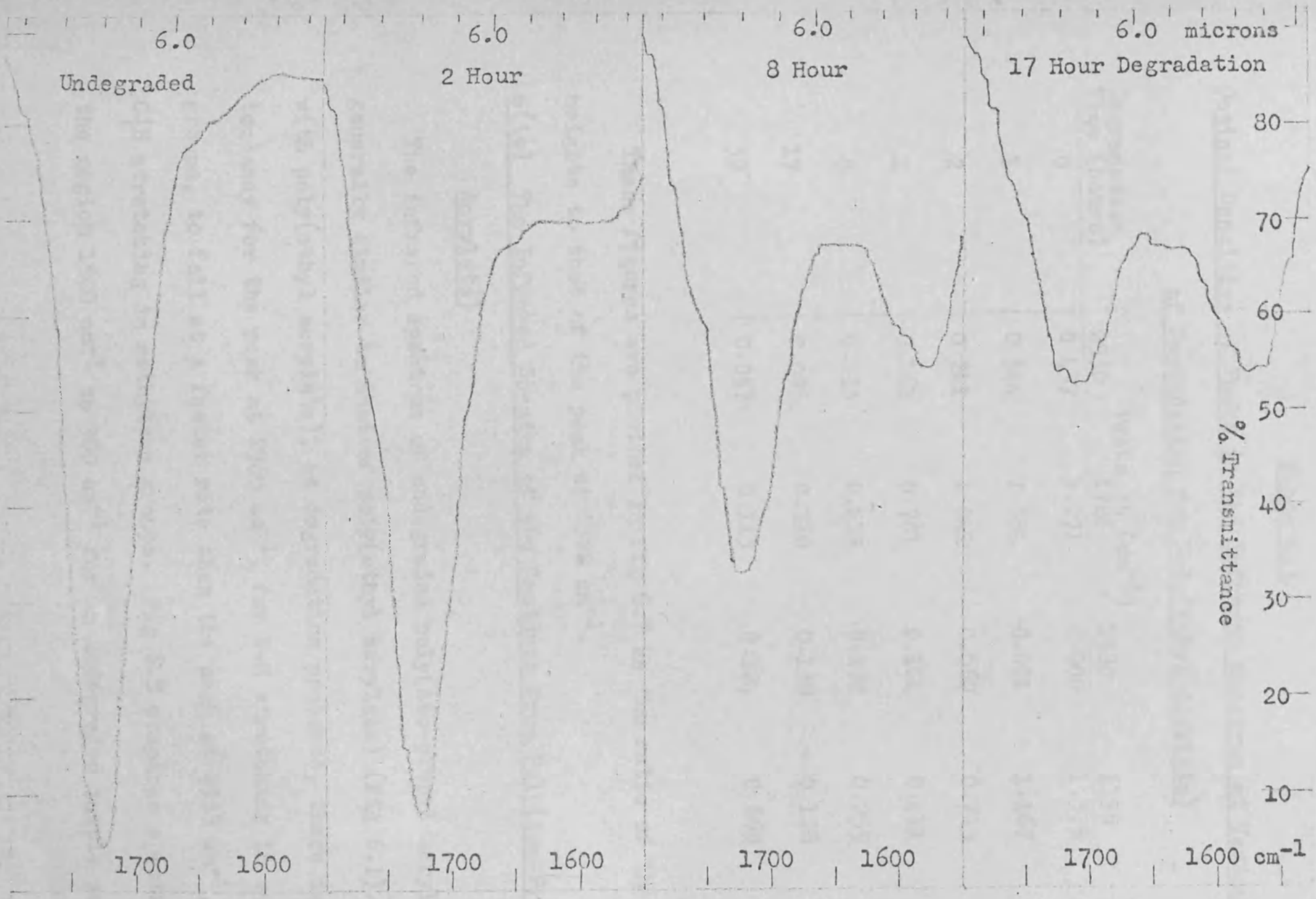


Fig 6.6 Changes in the Carbonyl Region of the I.R. Spectrum of Poly(Ethyl Acrylate)

Table 6.3

Optical Densities of Peaks in the Infrared Spectrum at Various Times of Degradation for Poly(Ethyl Acrylate)

Degradation Time (hours)	Peaks at (cm^{-1}) 2930	1726	1580	1158
0	0.497	1.271	0.000	1.376
1	0.344	1.334	0.021	1.167
2	0.241	1.041	0.060	0.713
4	0.161	0.701	0.124	0.411
8	0.133	0.419	0.178	0.255
17	0.095	0.210	0.178	0.126
32	0.057	0.113	0.124	0.069

These figures are plotted in fig 6.7 as the ratio of the peak heights to that of the peak at 1726 cm^{-1}.

6(iv) The Infrared Spectra of the Residues from Poly(iso-Propyl Acrylate)

The infrared spectrum of undegraded poly(iso-propyl acrylate) is generally similar to that of poly(ethyl acrylate) (fig 6.1). As with poly(ethyl acrylate), as degradation proceeds, there is a tendancy for the peak at 2980 cm^{-1}, for C-H stretching in methyl groups, to fall at a faster rate than the peak at 2938 cm^{-1}, for C-H stretching in methylene groups. Fig 6.8 compares spectra in the region 1900 cm^{-1} to 900 cm^{-1} for an undegraded sample and the

Fig 6.7 Ratios of Infrared Peak Heights to the Height of the Peak at 1726 cm^{-1} in the Spectrum of Degrading Poly(Ethyl Acrylate)

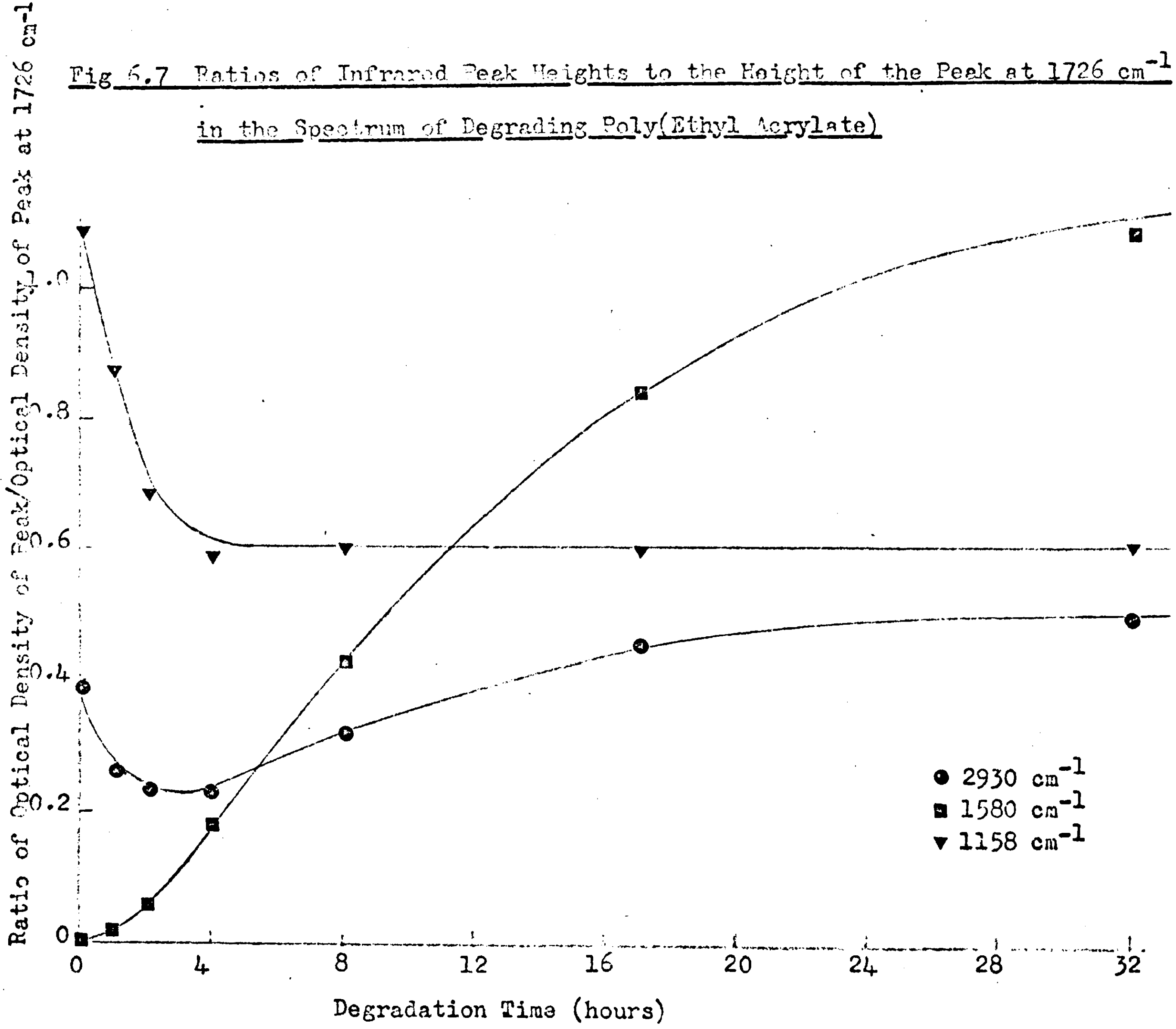
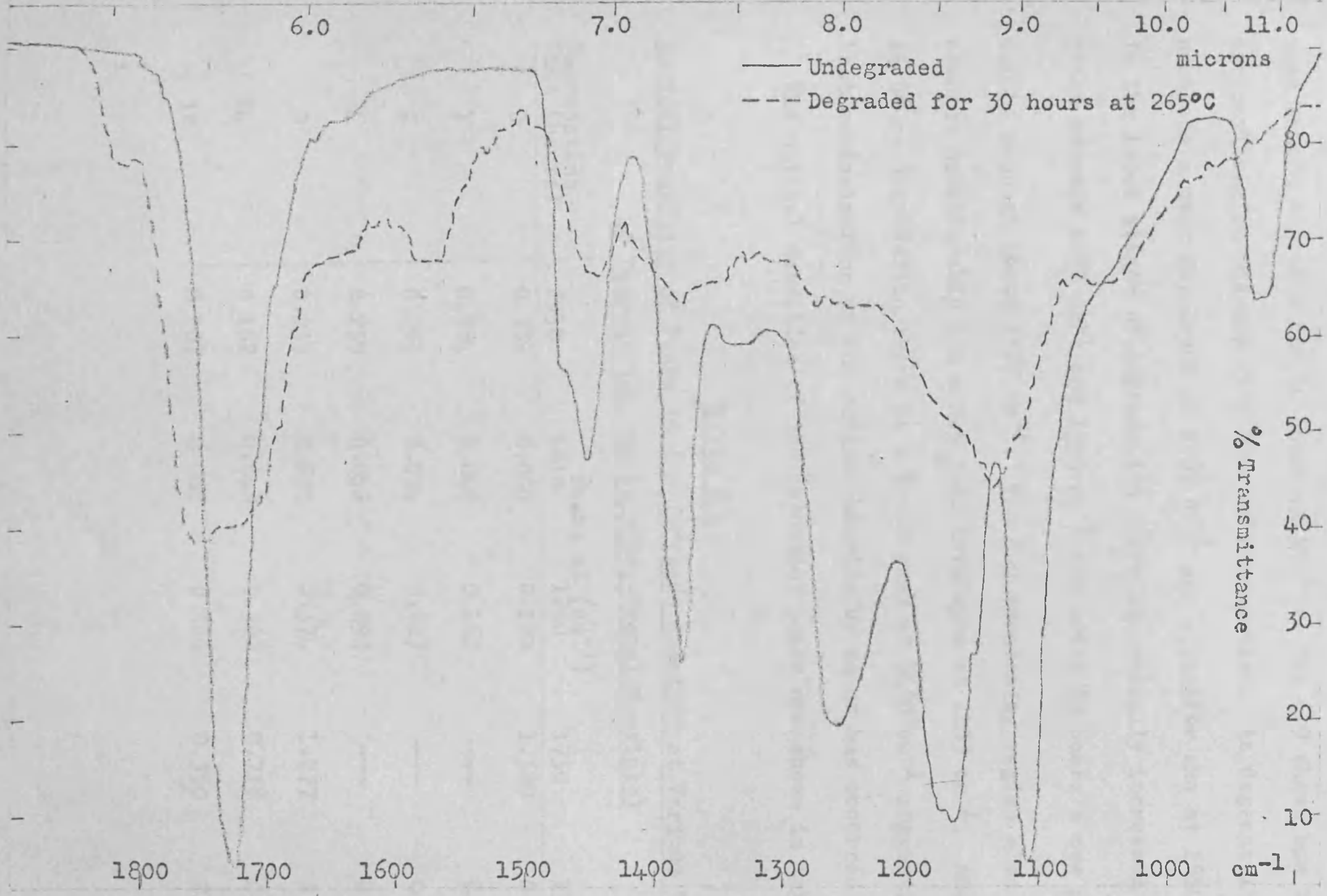


Fig 6.8 Infrared Spectra of Poly(iso-Propyl Acrylate)



same sample degraded for 30 hours at 265°C. Fig 6.9 shows how the carbonyl region changes with time of degradation. As degradation proceeds a peak developes at 1762 cm^{-1} and a smaller one at 1810 cm^{-1}. In the later stages of degradation there is generally increased absorption between 1650 cm^{-1} and 1550 cm^{-1} and after 30 hours a new peak can be seen at about 1575 cm^{-1}. The C-O stretching region also changes considerably and a new peak developes at 1135 cm^{-1}. After 14 hours degradation there is a broad peak at 3400 cm^{-1} suggesting that contamination of the sodium chloride by water has occurred.

The optical densities of the important peaks are shown in table 6.4

Table 6.4

Optical Densities of Peaks in the Infrared Spectrum at Various Times of Degradation for Poly(iso-Propyl Acrylate)

Degradation Time (hours)	Peaks at (cm^{-1})				
	2938	1810	1760	1730	1575
0	0.338	0.000	0.100	1.320	0.020
1	0.324	0.048	0.162	—	0.013
2	0.299	0.054	0.217	—	0.020
4	0.259	0.042	0.298	—	0.020
8	0.233	0.030	0.374	1.277	0.039
14	0.162	0.048	0.392	0.718	0.071
32	0.107	0.066	0.366	0.350	0.126

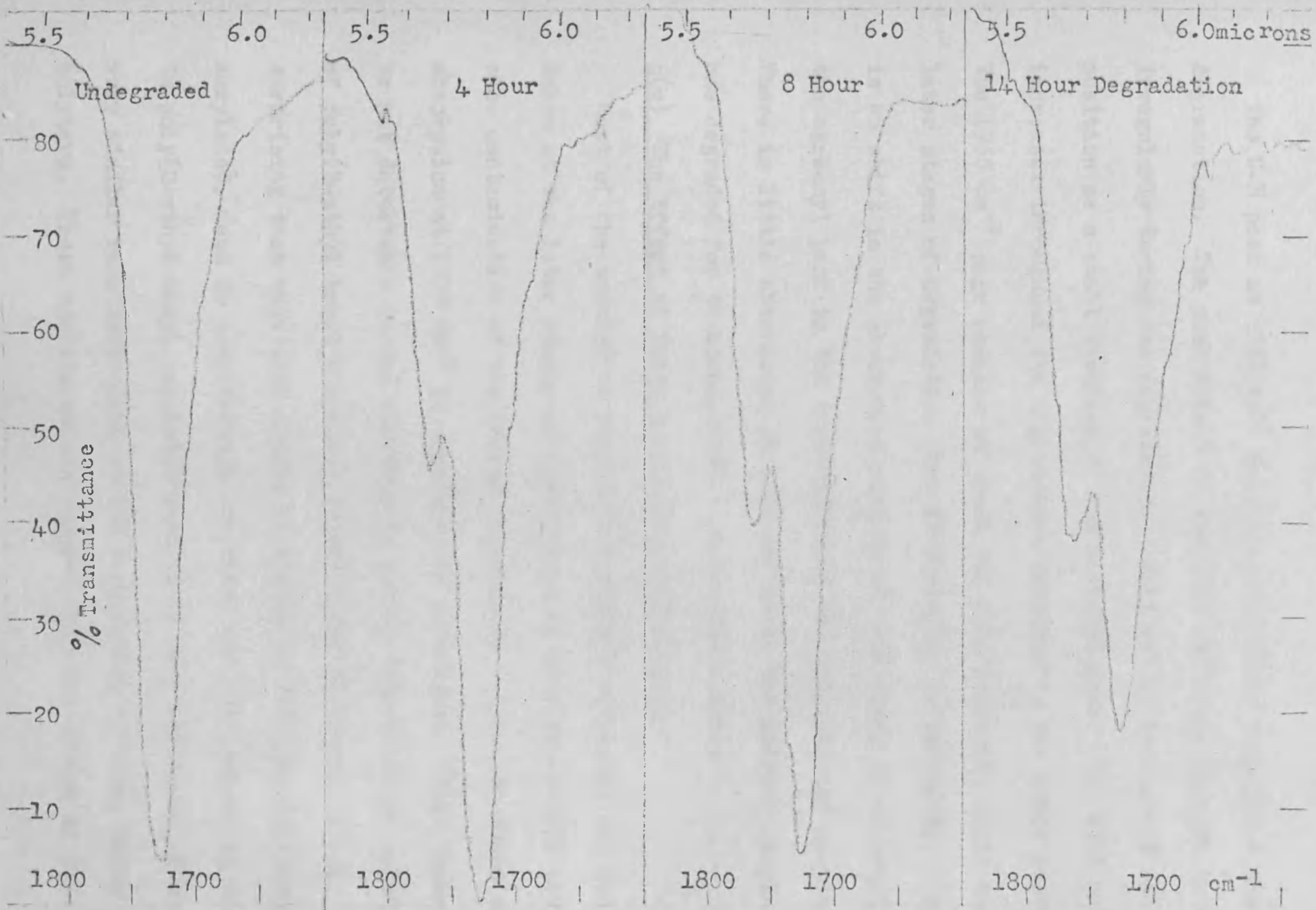


Fig 6.9 Changes in the Carbonyl Region of the I.R. Spectrum of Poly(iso-Propyl Acrylate)

The C-H peak at 2938 cm^{-1} decreases uniformly throughout the degradation. The peak height of the 1810 cm^{-1} peak appears to vary irregularly during the degradation. This may be because of its position as a small shoulder of the carbonyl peak. The 1760 cm^{-1} increases throughout the degradation relative to the other peaks. The 1730 cm^{-1} peak remains at about the same intensity until the later stages of degradation when it decreases in intensity. There is no shift in the absorption maximum of this peak, in contrast to the carbonyl peak in the degradation of the poly(primary acrylates). There is little absorption at 1575 cm^{-1}until the polymer sample has degraded for 30 hours, when a peak appears here.

6(v) The Effect of Water on the Infrared Spectra

Most of the spectra of degraded poly(ethyl acrylate) and those taken at the later stages of degradation of poly(iso-propyl acrylate) show contamination of the sodium chloride by water. In these spectra, absorption at 1570 cm^{-1} is particularly pronounced. This absorption is not detectable in the spectrum in carbon tetrachloride solution of poly(2-ethyl hexyl acrylate) degraded for 32 hours. It is surprising that this peak should be strong in degraded poly(ethyl acrylate), weak in poly(n-butyl acrylate) and not present at all in poly(2-ethyl hexyl acrylate) when it is known (Chapter 4) that very similar reactions occur in the degradation of these three polymers. These considerations suggest that the action of water on the degrading polymer may produce the peak at 1570 cm^{-1}.

Water itself gives a broad peak between 1750 and 1580 cm^{-1} with a maximum intensity at 1640 cm^{-1} [82]. This peak is not the right shape and does not occur at the right frequency to account for the absorption at 1570 cm^{-1}. Of the chemically feasible groups, the only ones which normally absorb at this frequency are enolisable β-diketones, carboxylate ions and, possibly, but not very likely, conjugated carbon - carbon double bonds[83]. Cameron and Kane proposed a mechanism for elimination of methanol from poly(methyl acrylate) in which the end product was a β-ketoester (fig 1.14)[3].

Enolisable β-ketoesters absorb at 1650 cm^{-1}, but when the enolic form is impossible, as in this case, they will absorb as isolated ester and ketone groups around 1730 and 1710 cm^{-1}, respectively. Conjugated carbon - carbon double bonds normally absorb between 1660 cm^{-1} and 1580 cm^{-1} and it is difficult to suggest any mechanism in which the presence of water would catalyse the formation of sequences of carbon - carbon double bonds along the polymer chain.

The most likely explanation, therefore, for the appearance of this peak in the spectra of the polyacrylate degradation residues in the presence of water is that it is due to the carboxylate ion. It is known[82] that carboxylic acid groups are liable to some ionisation by the alkyl halide used as a support in the measurement of infrared spectra; a peak occurs between 1610 and 1540 cm^{-1}

associated with the carboxylate ion, along with the peak between 1720 cm^{-1} and 1700 cm^{-1} associated with the unionised acid. Poly(iso-propyl acrylate) degradation may produce acid groups by elimination of olefin (see Chapter 8). The presence of acid groups in the degradation residue from the poly(primary acrylate) has not been proposed, however. It may be that when water contaminates the sodium chloride to form a strongly ionising medium, ester or anhydride linkages in the polymer residue may be hydrolysed on heating and the resulting acid groups ionised.

To test this, a disc of polymerised propiolactone in potassium bromide was made up. The potassium bromide was not specially dried and contained a trace of water. The infrared spectrum of the disc was obtained. The disc and contents were then heated to 250°C under high vacuum, the tube broken open and the infrared spectrum measured. A peak appears at 1570 cm^{-1}, confirming that compounds of the ester type are liable to hydrolysis when heated in an ionising medium in the presence of traces of water.

6(vi) Summary

On degradation of poly(primary acrylates), the principal change in the infrared spectrum is the appearance of a shoulder at 1760 cm^{-1} on the carbonyl peak. There is a general broadening of the spectrum in the carbonyl region and also in the C-O stretching region. Some increase in absorption occurs in the carbon - carbon double bond region. The carbonyl peak at 1730 cm^{-1} tends to move by about 20 cm^{-1} towards lower frequency. A tendency to higher frequency is observed in the C-O stretching region.

Poly(iso-propyl acrylate) shows a large shoulder at 1760 cm^{-1} on the carbonyl peak and a smaller shoulder at 1810 cm^{-1}. A new peak appears at 1135 cm^{-1}.

It should be noted that infrared spectra of samples in the solid phase are broader and less well resolved than the spectra of samples in the liquid phase. The assignment of peaks cannot therefore be made with great precision in the spectra of the solid phase. All figures quoted in this chapter are accurate to ± 5 cm^{-1}.

Chapter 7 Degradation Studies of the Polyacrylates at Lower Temperatures

7(i) Introduction

In chapters 4,5 and 6, all the degradation studies described were carried out at one temperature for each polymer - 315°C in the case of the poly(primary acrylates) and 265°C in the case of poly (iso-propyl acrylate). These studies show that at these temperatures a complex series of reactions occurs. By lowering the temperature of degradation, it was hoped that a simpler degradation pattern might be observed. T.V.A. and T.G.A. thermograms (figs 3.4 and 3.5) show that volatilisation in the polyacrylates occurs mainly in one stage and that the different volatile products are produced concurrently. It was therefore thought to be unlikely that, in the study of the degradations at lower temperatures, one volatilisation reaction would be found unaccompanied by the other such reactions. Rather, it was anticipated that molecular weight changes might be observed and that a cross-linking or chain scission process might be studied unaccompanied by large-scale volatilisation reactions. It is useful, however, to measure such small amounts of volatilisation as do occur. Interesting correlations between evolution of volatile material and changes in molecular weight may be observed in this way[45].

As described in 4(vi)A, it is found that the polymers of ethyl and n-propyl acrylates used in the present work have molecular weights too high to allow the polymer to filter completely through the filter paper used to separate sol and gel fractions. The present studies are therefore confined to poly(n-butyl acrylate), studied at 241°C, and poly(iso-propyl acrylate), studied at 195°C, where this complication does not arise.

7(ii) Measurement of Volatiles

The McLeod Gauge and method of operating it are described in 2(xix)A and Appendix C. Series of degradations of poly(n-butyl acrylate) and poly(iso-propyl acrylate) were carried out and the gases analysed as described in 2(xix) and Appendix C. This gives the number of moles of non-condensible gases ($n_{N.C.}$) in the larger system. The remaining volatile material is condensed into the smaller system and the number of moles ($n_{R.T.}$) found. The number of moles of condensible material (n_C) is found by subtracting the number of moles of non-condensible gas in the smaller system (n_S) from $n_{R.T.}$.

$$n_C = n_{R.T.} - n_S$$

Tables 7.1 and 7.2 show the method of calculation of the number of moles of gas from the two polymers at various times of degradation. These results are plotted as number of molecules of volatiles evolved per monomer unit in figs 7.1 and 7.2. Volatile evolution from poly(n-butyl acrylate) at 241°C seems to be at a uniform rate throughout this early stage of degradation. The non-condensible

Fig 7.1 Volatile Production from Poly(n-Butyl Acrylate) at 241°C

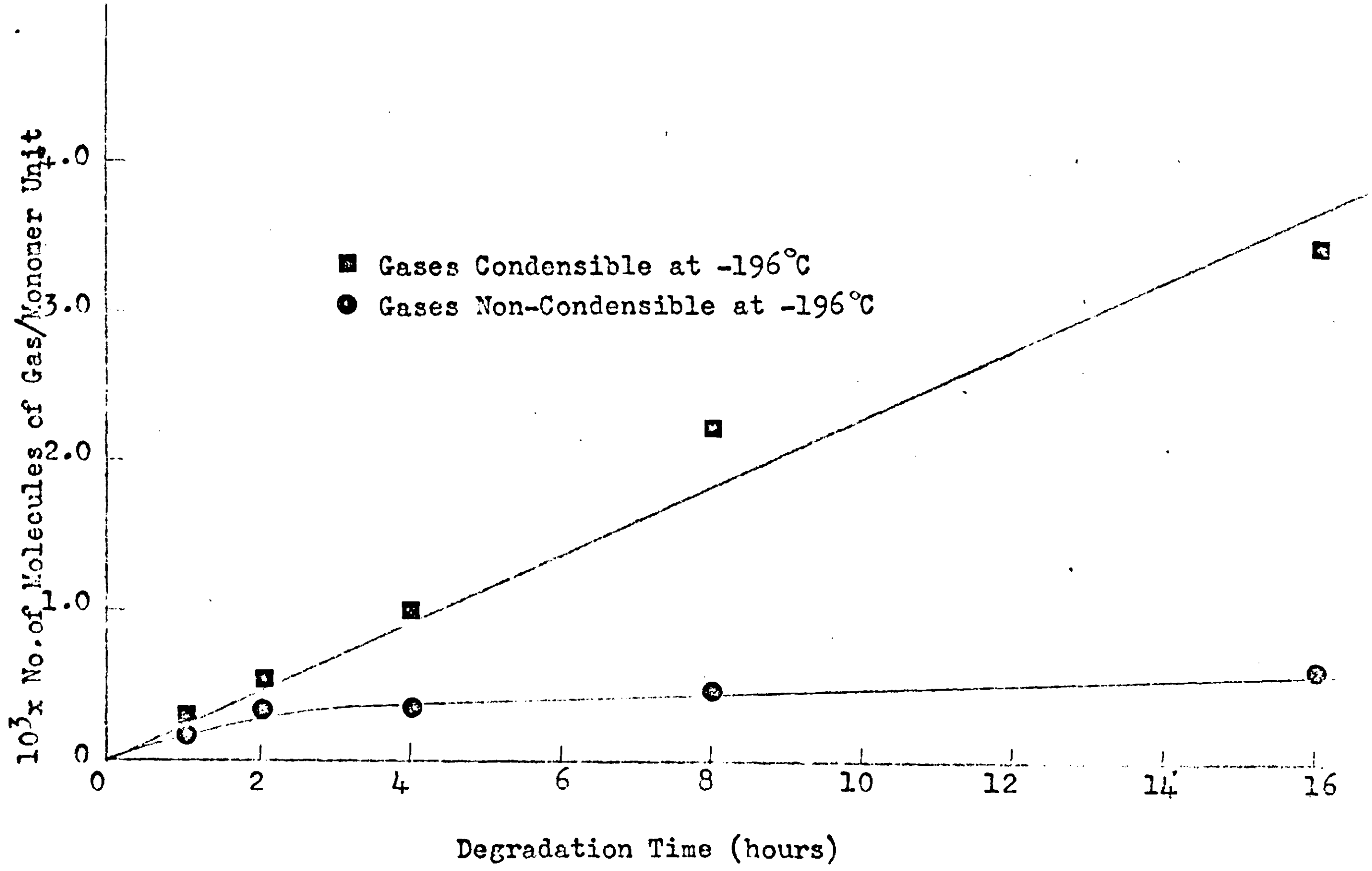
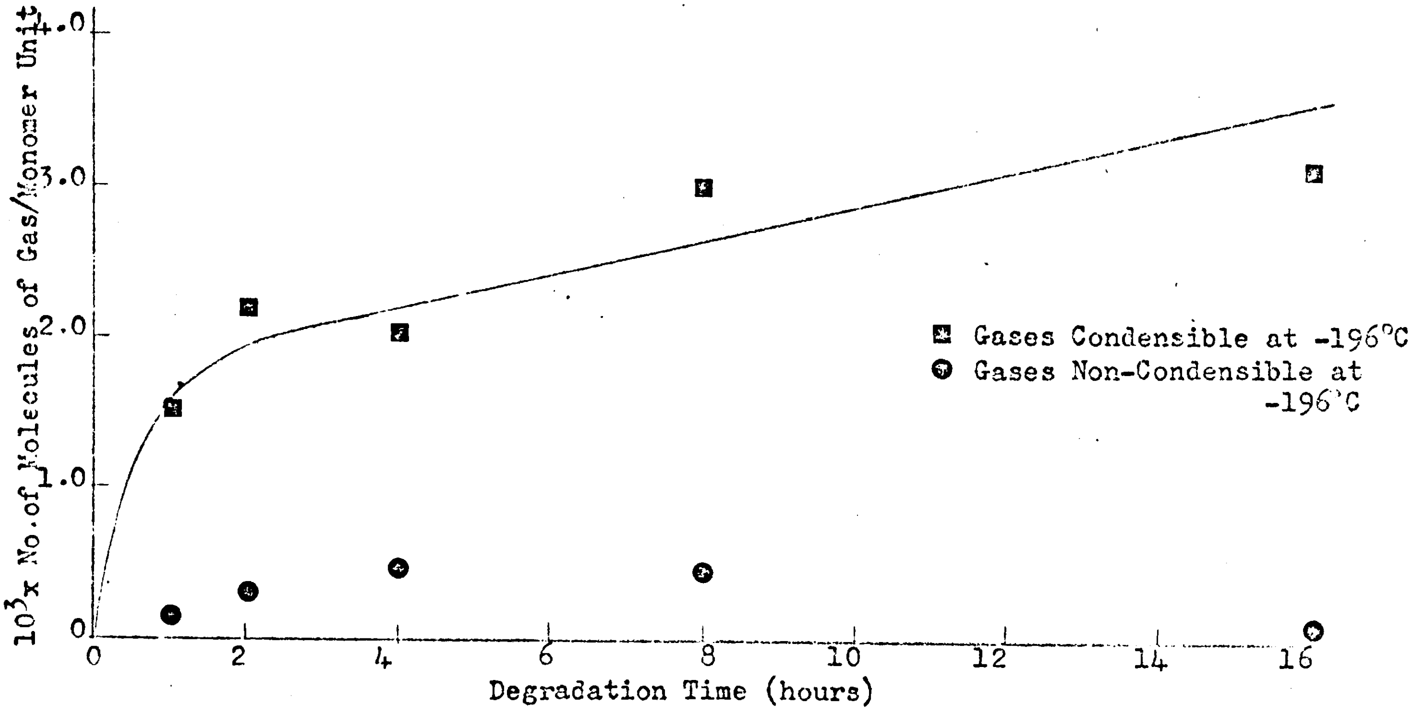


Fig 7.2 Volatile Production from Poly(iso-Propyl Acrylate) at 195°C



gases appear to increase in amount as degradation proceeds. Poly (iso-propyl acrylate) seems to have a fast rate of volatile evolution initially, before settling down to a uniform rate. In this case the non-condensible gases do not give a consistant relationship with time of degradation.

7(iii) Nature of Volatile Products

The mass spectra of the volatile materials from a 32 hour degradation of a 400 mg sample of poly(n-butyl acrylate) at 241°C and from an 8 hour degradation of a 100 mg sample of poly(iso-propyl acrylate) are shown in fig 7.3. Fig 7.3 also shows the mass spectrum of propylene[81]. Fig 3.2 gives mass spectra for carbon dioxide, 1-butene and n-butanol.

The mass spectrum of the degradation products from poly(n-butyl acrylate) corresponds closely to that of a mixture of carbon dioxide and 1-butene, with 1-butene present in rather greater amount than carbon dioxide. At the low pressure of gases inside the sealed tube, the vapour pressure of n-butanol would be expected to be significant. The base peak for n-butanol is at mass number 31, but the peak here (fig 7.3a) is very small. Hence, it can be concluded that there is very little n-butanol in the volatiles from poly(n-butyl acrylate) at 241°C.

The mass spectrum of the degradation products from poly(iso-propyl acrylate) corresponds to that of a mixture of carbon dioxide and

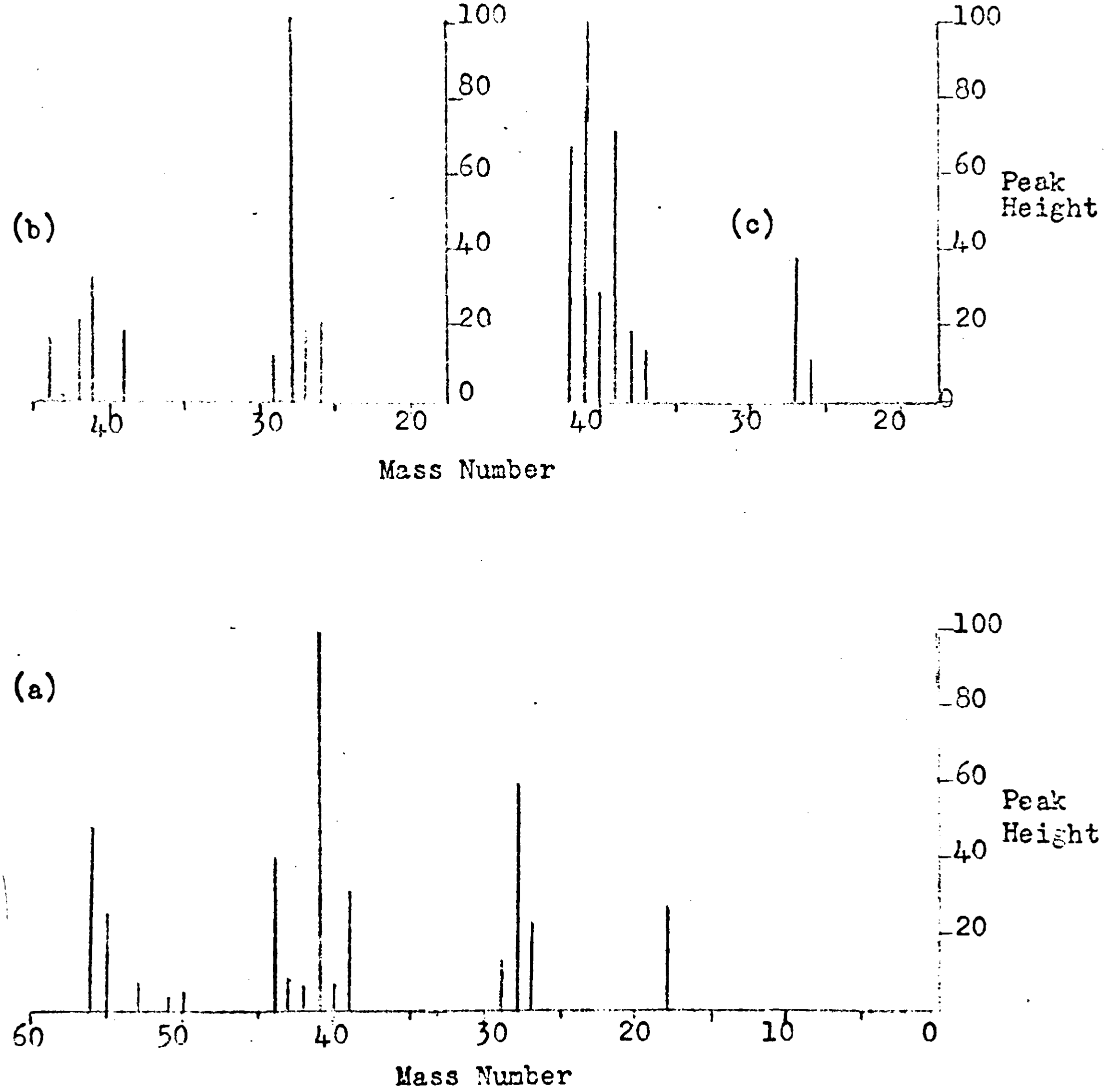


Fig 7.3 Mass Spectra of Volatiles from Low Temperature Degradation of
(a) Poly(n-Butyl Acrylate)
(b) Poly(iso-Propyl Acrylate).
(c) Mass Spectrum of Propylene
all at 70 eV

propylene, with propylene in excess over carbon dioxide. This does not explain the large peak at mass number 28. It is probably caused by nitrogen from the air leaking into the mass-spectrometer. The total pressure of the volatiles in this degradation is very small and the mass-spectrometer is not at full sensitivity at such a pressure. Small amounts of extraneous material, such as air, would therefore affect the spectrum considerably.

The amounts of non-condensibles are irregular in the case of poly(iso-propyl acrylate). This is possibly because air, dissolved in the polymer, is released on heating. The small amounts of non-condensibles recorded for both polymers could also be explained by the residual air sealed into the sealed tube before degradation. Both these factors would be irregular, depending on the polymer sample and on the vacuum conditions under which the degradation tube was sealed.

7(iv) Short Chain Fragments

In the degradations of poly(n-butyl acrylate) at 241°C, care was taken to ensure that any short chain fragments produced would be measured. A very small and irregular amount of material was found and is recorded in table 7.3. This indicates that very few short chain fragments are produced at this temperature.

Since poly(iso-propyl acrylate) produces very few short chain fragments when degraded at 265°C, it was thought to be unlikely that any would be produced at 195°C and no attempt was made to measure this material.

7(v) Analysis of the Residue

The sol and gel portions of the residue were separated by the filtration technique described in 2(xvii) and 4(vi)A. Tables 7.3 and 7.4 give the percentage soluble and insoluble residues at various times of degradation and also the molecular weight of the soluble residue.

The percentage soluble and insoluble residue is shown graphically on figs 7.4 and 7.5. In both cases, some insolubility developes early in the reaction, but this remains at a constant value of about 25 % in the case of poly(n-butyl acrylate) and 35 % in the case of poly(iso-propyl acrylate) for some time thereafter. With the latter polymer, however, there is some sign that the degree of cross-linking continues to increase at long times of heating; this is shown by the increase in molecular weight of the soluble material. With poly(n-butyl acrylate), on the other hand, the molecular weight of the soluble material falls slightly, in spite of the fact that the proportion of soluble material remains almost constant. This suggests that some chain scission is occurring alongside the cross-linking reaction.

7(vi) Summary

The thermal degradation of poly(n-butyl acrylate) at 241°C, apart

Fig 7.4 % Sol and % Gel in Residue from Poly(n-Butyl Acrylate) at 241°C

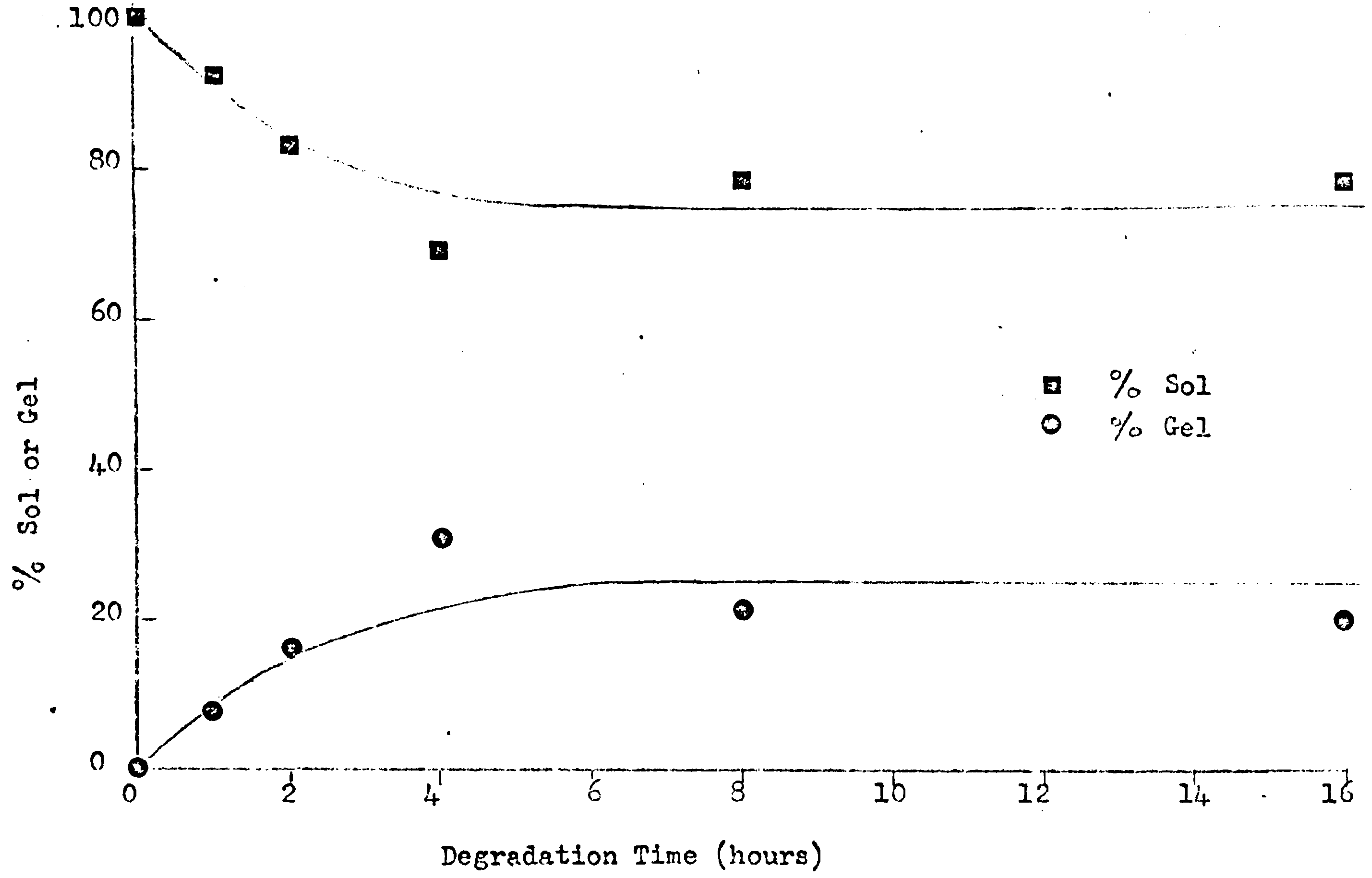
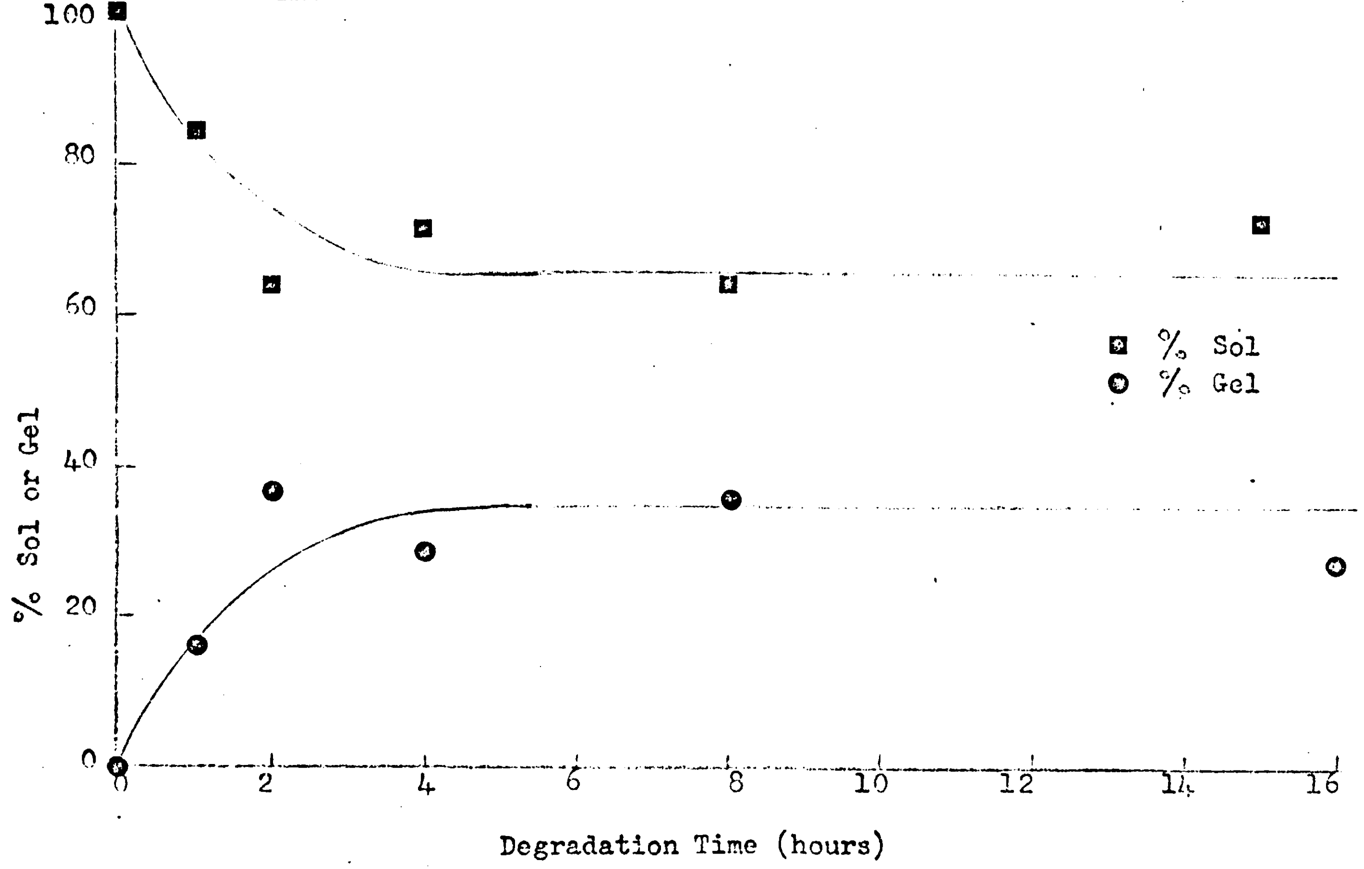


Fig 7.5 % Sol and % Gel in Residue from Poly(iso-Propyl Acrylate) at 195°C



from exhibiting very much slower volatilisation than the degradation at 315°C, also shows some differences in the products. In particular, no n-butanol is detected and the cross-linking reaction sets in at an early stage, but then levels off to give a constant sol/gel ratio. There does not seem to be a close relationship between changes in molecular weight and extent of volatilisation.

Poly(iso-propyl acrylate) appears to give the same volatile products at 195°C as at 265°C. Cross-linking increases slowly at the lower temperature as degradation proceeds. In this polymer, the degree of cross-linking appears to increase with volatilisation.

Table 7.1

Calculation of Number of Moles of Volatiles from Poly(n-Butyl Acrylate) at 241°C

Run No.	ST301B	ST302B	ST303B	ST304B	ST305B
Degradation Time (hours)	1	2	4	8	16
A. Non-Condensibles					
α (cm)	38.113	37.626	37.600	37.637	37.418
β (cm)	38 144	37.568	37.499	37.418	37.544
γ (cm)	35.501	33.826	33.886	33.076	32.320
$x=\alpha-\gamma$ (cm)	2.612	3.800	3.714	4.561	5.098
$(x-0.015)$(cm)	2.597	3.785	3.699	4.546	5.083
$V=(x-0.015).A(cm)^3$	0.0683	0.0996	0.0973	0.1196	0.1337
$P=\beta-\gamma$ (cm.Hg)	2.643	3.742	3.613	4.342	5.224
$P.V.(cm)^3.(cm.Hg)$	0.1806	0.3726	0.3516	0.5193	0.6986
$10^6 n_1=10^6 P.V/R.T$	0.0981	0.2024	0.1910	0.2821	0.3795
$10^6 n_S=10^6 n_1 x 1.991$	0.1953	0.4030	0.3803	0.5617	0.7556
$10^6 n_{N.C.}=10^6 n_1 x 2.566$	0.2517	0.5194	0.4901	0.7239	0.9738
B. Condensibles					
α (cm)	38.113	37.626	37.600	37.637	37.418
β (cm)	38.103	37.671	37.674	37.737	37.353
γ (cm)	33.303	31.110	30.337	25.748	22.682
$x=\alpha-\gamma$ (cm)	4.810	6.516	7.263	11.889	14.736
$(x-0.015)$(cm)	4.795	6.501	7.248	11.874	14.721
$V=(x-0.015).A(cm)^3$	0.1262	0.1710	0.1907	0.3124	0.3873
$P=\beta-\gamma$ (cm.Hg)	4.800	6.561	7.337	11.989	14.671
$P.V\ (cm)^3(cm.Hg)$	0.6056	1.1222	1.3991	3.7454	5.6822
$10^6 n_1=10^6 P.V/R.T$	0.3290	0.6096	0.7600	2.0344	3.0865
$10^6 n_{R.T}=10^6 n_1 x 1.991$	0.6550	1.2137	1.9502	4.0505	6.1452
$10^6 n_C=10^6(n_{R.T}-n_S)$	0 4597	0.8107	1.5699	3.4888	5.3896

Table 7.2

Calculation of Number of Moles of Volatiles from Poly(iso-Propyl Acrylate) at 195°C

Run No.	ST311I	ST312I	ST313I	ST314I	ST315I
Degradation Time (hours)	1	2	4	8	16
A. Non-Condensibles					
α (cm)	37.895	38.114	38.120	38.122	38.070
β (cm)	37.836	38.197	38.144	38.054	38.011
γ (cm)	37.230	35.379	34.708	34.617	37.495
$x=\alpha-\gamma$ (cm)	0.665	2.735	3.412	3.505	0.575
$(x-0.015)$(cm)	0.650	2.720	3.397	3.490	0.560
$V=(x-0.015)A.(cm)^3$	0.0171	0.0716	0.0894	0.0918	0.0147
$P=\beta-\gamma$ (cm.Hg)	0.606	2.818	3.436	3.337	0.516
$P.V$ $(cm)^3(cm.Hg)$	0.0104	0.2017	0.3071	0.3064	0.0076
$10^6 n_1=10^6 P.V/R.T$	0.0056	0.1096	0.1668	0.1664	0.0041
$10^6 n_S=10^6 n_1 x 1.991$	0.0112	0.2182	0.3321	0.3313	0.0081
$10^6 n_{N.C.}=10^6 n_1 x 2.566$	0.0144	0.2812	0.4280	0.4270	0.0105
B. Condensibles					
α (cm)	37.895	38.114	38.120	38.122	38.070
β (cm)	38.253	38.218	38.269	38.261	38.136
γ (cm)	30.956	29.182	29.318	27.623	27.862
$x=\alpha-\gamma$ (cm)	6.939	8.932	8.802	10.499	10.208
$(x-0.015)$(cm)	6.924	8.917	8.787	10.484	10.193
$V=(x-0.015).A(cm)^3$	0.1822	0.2346	0.2312	0.2758	0.2682
$P=\beta-\gamma$ (cm.Hg)	7.297	9.036	8.951	10.638	10.274
$P.V$ $(cm)^3(cm.Hg)$	1.3293	2.1199	2.0694	2.9343	2.7553
$10^6 n_1=10^6 P.V/R.T$	0.7221	1.1515	1.1241	1.5939	1.4966
$10^6 n_{R.T}=10^6 n_1 x 1.991$	1.4377	2.2926	2.2381	3.1735	2.9797
$10^6 n_C=10^6(n_{R.T}-n_S)$	1.4265	2.0744	1.9060	2.8422	2.9716

Table 7.3

Mass Balance for the Degradation of Poly(n-Butyl Acrylate) at 241°C

Run No.	ST301B	ST302B	ST303B	ST304B	ST305B
Degradation Time (hours)	1	2	4	8	16
Weight of -					
Initial Polymer	100.0	100.0	100.0	100.0	100.0
Sol. Residue	92.3	83.2	69.1	78.7	79.0
Insol. Residue	7.6	15.8	30.6	21.4	20.2
Short Chain Fragments	0.2	1.0	0.3	0.0	0.8
$10^{-3} \times \bar{M}n$ Sol. Residue	632	333	316	316	220

Table 7.4

Mass Balance for the Degradation of Poly(iso-Propyl Acrylate) at 195°C

Run No	ST311I	ST312I	ST313I	ST314I	ST315I
Degradation Time (hours)	1	2	4	8	16
Weight of -					
Initial Polymer	100.0	100.0	100.0	100.0	100.0
Sol. Residue	84.0	63.7	71.5	64.3	72.5
Insol. Residue	16.0	36.3	28.6	35.6	27.5
$10^{-3} \times \bar{M}n$ Sol. Residue	281	460	372	903	2,530

Chapter 8 General Discussion

In this chapter, various reaction mechanisms introduced in earlier chapters are discussed. For convenience of reference, Appendix D gives a list of these mechanisms in the order in which they are mentioned in this chapter.

8(i) Overall Characteristics of the Degradation Reactions

Madorsky[10] has suggested that, since little monomer is formed, the mechanisms of the degradation reactions occurring in poly(methyl acrylate) do not involve free radicals. Cameron and Kane[1,2,3], on the other hand, proposed free-radical mechanisms for these reactions and suggested that only a small amount of monomer is formed because of unfavourable factors in the structure of the monomer unit.

Small gaseous organic molecules of the ester type do not normally show bond scission to give free-radicals at temperatures below 400°C [42,84], except in especially favourable circumstances. But in a polymer environment and particularly where a radical stabilised by resonance or inductive effects can be formed, there is overwhelming evidence that free-radical mechanisms may operate below 300°C. Indeed, at temperatures above 280°C, degradation mechanisms other than by radicals are rare. This applies to such widely different polymers as polyesters[42,43], polyethylene[18], and poly(tetrafluoroethylene)[30,31]. Certainly, the variety of products from the degradation of poly(primary acrylates), polyesters or polyethylene, is indicative of participation of radical mechanisms in their formation.

The initial step in the degradation of the poly(primary acrylates) is therefore likely to be the scission of a polymer molecule at a weak link to give two polymer radicals. At least some of these radicals would be of the type

$$\sim\sim\sim CH_2^{\bullet} \qquad \text{I}$$

and would therefore be unstable[21]. Cameron and Kane[1,2,3] suggested that the most likely bond to be attacked by these initial radicals would be that between a tertiary hydrogen and a carbon atom. This would result in a hydrogen atom being removed and a relatively stable radical

II

being formed.

Cameron and Kane proposed that all the major decomposition reactions in poly(methyl acrylate) were initiated by radical II. Evidence to support this theory in the case of other poly(primary acrylates) is provided by the T.V.A. thermograms (fig 3.4) and by the qualitative analysis of the products described in Chapter 3 of this thesis. It is difficult to explain how such a variety of products could be evolved in a one-stage process unless all the reactions have a common initiator, such as radical II.

Poly(iso-propyl acrylate) degrades at a rather lower temperature and in two stages The major degradation product is the olefin and, to this extent, the degradation is analogous to those of poly (t-butyl acrylate)[4,53] and poly(t-butyl methacrylate)[52]. The mechanism proposed for ester decomposition in these last two polymers is non-radical, of the molecular type (fig 1.10). However, in the case of poly(n-butyl methacrylate) degradation, Grassie and McCallum[51] proposed a radical mechanism for the ester decomposition reaction (fig 1.9). No direct evidence is presented in this thesis as to the exact nature of the mechanism of the olefin elimination reaction, but this may well be an example of a reaction where the mechanism varies, being completely molecular at low temperatures in the absence of radicals, and completely radical at high temperatures and where radicals are available from accompanying reactions.

It is very often true that for an ionic reaction mechanism there exists a radical counterpart. It follows that chemical situations may arise where the mechanism is neither entirely ionic nor entirely radical in character, but partly both. The same arguement may be applied to molecular and radical mechanisms in polymers, the elimination of olefin from polyacrylates being a case in point.

Another example of this effect is given by the decarboxylation reaction. In small organic molecules in a polar medium, decarboxylation will generally occur by an ionic mechanism (fig 8.1)[85].

Fig 8.1 Decarboxylation by an Ionic Mechanism

But, in a polymer melt, at high temperatures, a much more likely route is by radical decomposition (fig 8.2). Analogous reaction mechanisms have been proposed for small molecules[86].

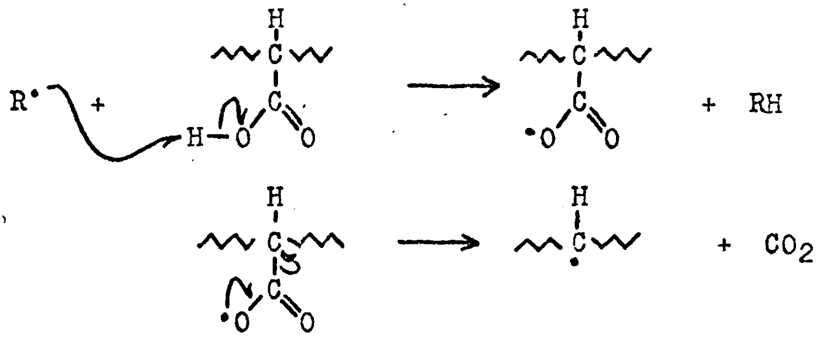


Fig 8.2 Decarboxylation by a Radical Mechanism

8(ii) The Reactions in the Degradation of Poly(iso-Propyl Acrylate)

Poly(iso-propyl acrylate) seems to have the most readily understood degradation pattern of the five polymers studied. As with poly(t-butyl acrylate)[4,53] and poly(t-butyl methacrylate)[52], quantitative yields of olefin are recovered and insolubility develops in the residue.

However, there are considerable differences from the poly (tertiary acrylates). Poly(iso-propyl acrylate) volatilises very slowly at 195°C (fig 7.2), at which temperature poly(t-butyl acrylate) exhibits much faster volatilisation to yield iso-butene and water.

Schaefgen and Sarasohn[53] found a molar ratio of iso-butene to carbon dioxide of about 25:1 in the degradation products of poly(t-butyl acrylate). Poly(iso-propyl acrylate), however, evolves large yields of carbon dioxide. After 30 hours degradation at 265°C, the molar ratio of propylene to carbon dioxide is 1.7 to 1 (see fig 5.3); at this time of degradation 84 % of the alkyl groups have been eliminated as olefin and 51 % of the carboxyl groups, as carbon dioxide (table 5.3). The T.G.A. thermogram (fig 3.5c) shows that the rate of weight loss slows after 59 % volatilisation. This corresponds closely to loss of all the alkyl groups as olefin and 60 % of the carboxyl groups as carbon dioxide. Water is also produced with a yield of about 8.0 mole percent after 30 hours degradation. The yield of water was not obtained directly (see 5(iv)), so this figure is only approximate.

Grant and Grassie[52], Weir[4] and Schaefgen and Sarasohn[53] all observed autocatalytic behaviour in the elimination of olefin from acrylate polymers with tertiary ester groups. They accounted for this by the suggestion that the elimination of olefin was catalysed by neighbouring acid groups (fig 1.10). There appears to be similar behaviour in poly(iso-propyl acrylate) but to a much smaller extent (see figs 5.1 and 5.2). This is not surprising since acid groups are being lost extensively as carbon dioxide and, hence, this molecular chain reaction will be curtailed. Mechanisms for ester decomposition in poly(iso-propyl acrylate) may therefore be suggested as follows: There are three principal routes.

In routes 1 and 2, the initial step will be the elimination of an olefin molecule by the cyclic mechanism shown in fig 1.4 or by the radical equivalent of this mechanism (fig 8.3)

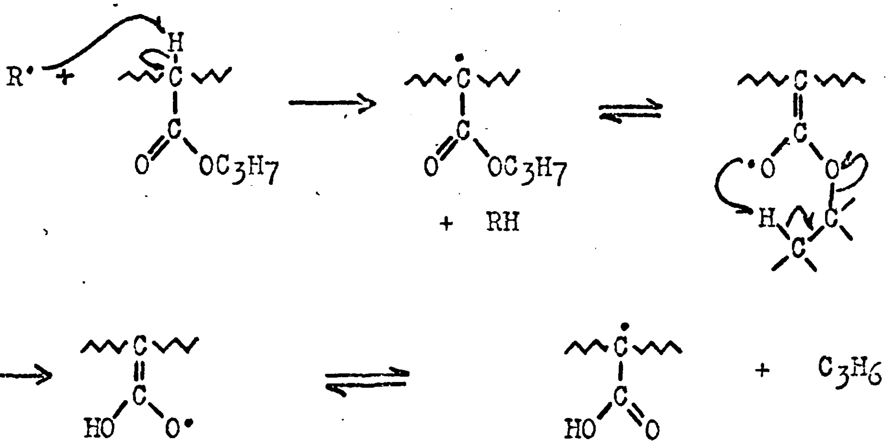


Fig 8.3 Radical Mechanism for the Elimination of Olefin

Thereafter the acid group will catalyse decomposition of a neighbouring ester group as follows:

Route 1 is the molecular reaction shown in fig 1.10 or a similar reaction involving radicals.

Route 2 is the simultaneous elimination of olefin and water to give an anhydride ring[51] (fig 8.4)

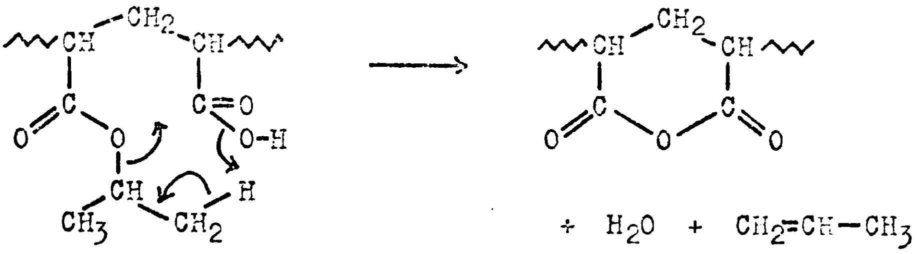


Fig 8.4 Simultaneous Elimination of Propylene and Water to Give Anhydride Groups

Route 3 involves a radical mechanism and results in the simultaneous elimination of carbon dioxide and propylene. (fig 8.5)

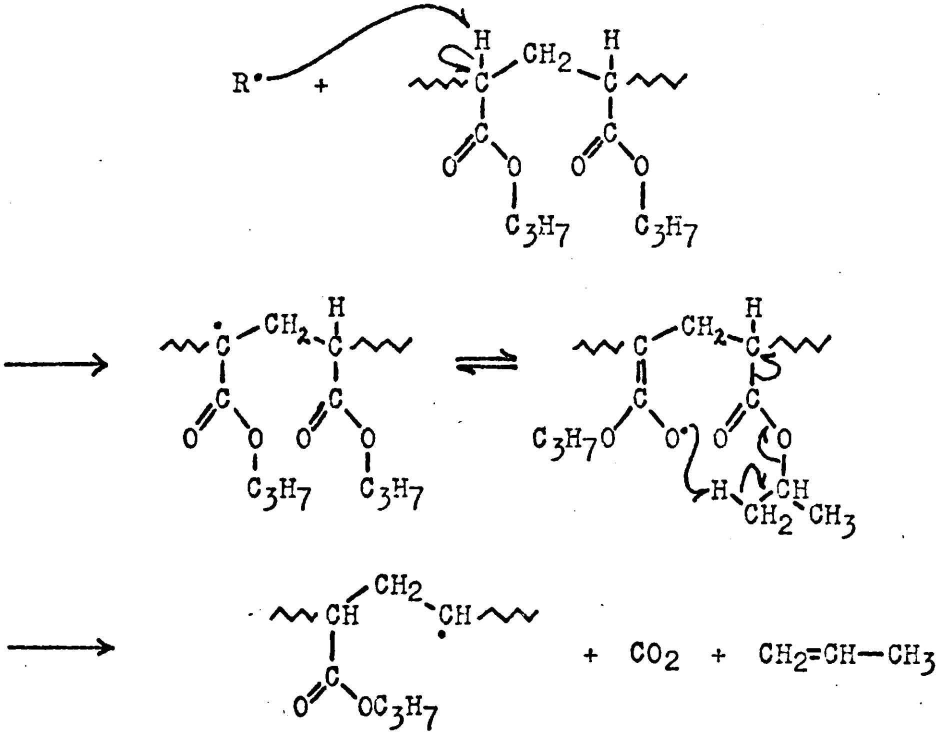


Fig 8.5 Simultaneous Elimination of Propylene and Carbon Dioxide

All these reactions seem chemically feasible. Route 3 ends with a radical which would be rather unstable, but the same radical is formed in all the proposed carbon dioxide producing reactions except one which involves a four membered ring with an sp^2 hybridised carbon atom (fig 8.6) and which would therefore not be sterically favoured.

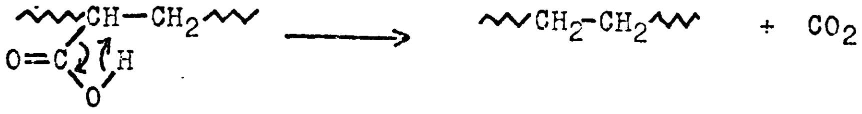


Fig 8.6 Four-Membered Ring Elimination of Carbon Dioxide

Once acid groups are formed by route 1, they may remain unreacted in the residue, decompose to give carbon dioxide (fig 8.2) or couple with other acid groups on the same molecule or another molecule to give anhydride groups (see fig 1.6). If coupling occurs between two separate polymer molecules, a cross-link is formed.

The orders of the olefin elimination and of the carbon dioxide elimination reactions are found to be close to 2 {5(ii)}. As far as the olefin elimination reaction is concerned, this may well be caused by the necessity for two monomer units to be involved in the production of each olefin molecule (see fig 8.5). Thus the rate of production of olefin will depend on the square of the concentration of monomer units.

In the carbon dioxide elimination reaction, the apparent second order behaviour may be spuriously caused by the dependence of this reaction on the olefin elimination reaction. The true reaction order cannot be determined from the present data.

8(iii) The Residue from Poly(iso-Propyl Acrylate) Degradations

The residue dissolves in alkali solution but not in organic solvents. Insolubility in organic solvents suggests either that cross-linking occurs or that the polymer becomes rigid because of the large number of intramolecular anhydride rings. Grant and Grassie[41] showed that poly(methacrylic anhydride) with no cross-links is insoluble in all non-polar organic solvents, but soluble in polar solvents such as dimethyl formamide (D.M.F.). The residue from poly(iso-propyl acrylate) is insoluble in D.M.F. and it was therefore concluded that some cross-linking occurs through anhydride groups.

Poly(iso-propyl acrylate) loses olefin quantitatively, about 60 % of the theoretical yield of carbon dioxide and about 20 % of the theoretical yield of water at 265°C (5(ii) and 5(iv)). After complete degradation at this temperature the residue should therefore contain ethylenic, acrylic acid and acrylic anhydride units. The elemental analysis (5(v)) is in agreement with the composition found by taking into account the products of degradation. After 30 hours degradation, the monomer units are estimated to be made up as follows:

16 %	unreacted iso-propyl acrylate
16 %	1/2(acrylic anhydride)
17 %	acrylic acid
51 %	ethylene

Each acrylic anhydride unit is equivalent to 2 units of the other monomers. The infrared spectrum (fig 6.8) agrees well with this estimation. Grant and Grassie[41] gave the infrared absorption of the carbonyl peaks in both poly(methacrylic anhydride) and degraded poly(methacrylic acid) as 1750 cm^{-1} and 1795 cm^{-1}, whereas glutaric anhydride absorbs at 1756 cm^{-1} and 1802 cm^{-1}. Schaefgen and Sarasohn [53] give figures for the anhydride carbonyl absorption in degraded poly(t-butyl acrylate) as 1725 cm^{-1} and 1807 cm^{-1}. The former figure (1725 cm^{-1}) seems rather low when compared with normal anhydride carbonyl absorption (1840-1800 cm^{-1} and 1780-1740 cm^{-1} [83]). In the present work, absorption attributed to anhydride carbonyl groups is observed at 1762 cm^{-1} and 1810 cm^{-1} and a third peak, attributed to carbon-oxygen single bond stretching is observed at 1135 cm^{-1} (fig 6.8). No reference to this last peak can be found in previous work on polymer degradation, but the carbon-oxygen single bonds in cyclic anhydrides normally absorb in the region 1175 cm^{-1} to 1045 cm^{-1} [83].

The relative intensities of the carbonyl peaks remain to be considered. Grant and Grassie[41] made a thorough investigation of the infrared absorption of the two carbonyl peaks in several anhydride systems, both in small organic molecules and in a polymer environment. They found that in ring systems the lower frequency absorption is the more intense, whereas, in acyclic anhydride structures the higher frequency absorption is the more intense. In degraded poly(iso-propyl acrylate) the lower frequency absorption is the more intense (figs 6.8 and 6.9) and it is concluded that most of the anhydride groups are of the glutaric anhydride type, with a few open anhydride groups forming cross-links.

Acid groups normally absorb in the carbonyl region at 1725-1700 cm^{-1} 83. The acrylic acid units remaining in the polymer would therefore cause part of the broadening towards lower frequency observed in the carbonyl group at 1730 cm^{-1} at long times of degradation. The carboxyl ion peak at 1575 cm^{-1} (fig 6.8) may be caused by ionisation of acid groups by the sodium chloride discs or by hydrolysis of some anhydride or ester groups by traces of water (see 6(v)).

The residue develops a yellow coloration as degradation proceeds. It was found to be very difficult to obtain films suitable for ultraviolet or visible spectroscopy and no significant spectra were obtained for double bond absorption in this region. However, the coloration is thought to be due to a small amount of carbon-carbon double bond conjugation in the polymer chain. A possible mechanism for double bond formation would involve a polymer radical as shown in fig 8.7.

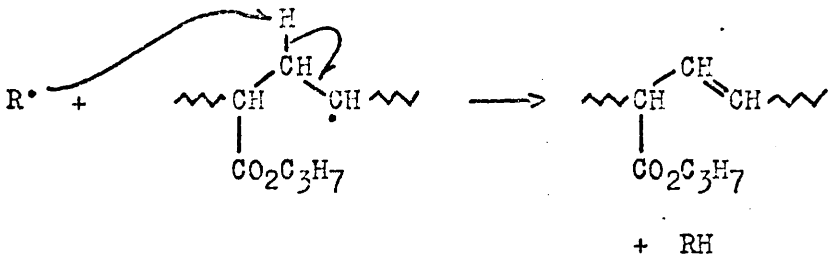


Fig 8.7 Possible Mechanism for Double Bond Formation in Poly(iso-Propyl Acrylate)

Once one such double bond is formed, it will weaken the C-H bonds in the alpha position and hence encourage conjugation. Coloration provides additional evidence for radical involvement in the reaction mechanisms.

The surprisingly small hydrogen content of the residue after 30 hours degradation (see table 5.7) is not in agreement with the products of degradation found (table 5.2). This discrepancy could be caused by:

1/ inaccuracy in the hydrogen analysis

or 2/ non-detection of a degradation product. This is most likely to be molecular hydrogen which might escape by diffusion before a mass-spectral analysis of the non-condensible gases could be made.

The residue degrades further when heated to higher temperatures as T.V.A. (fig 3.4d) and T.G.A. (fig 3.5c) show. From the T.V.A. thermogram it can be deduced that the material given off at this stage is mostly non-condensible at -100°C. Small molecules are therefore evolved. Since the residue contains a large number of polyethylene units, it seems likely that low molecular weight chain fragments are also given off at this stage[18]. This fraction would mainly condense on the cold ring of the T.V.A. apparatus (fig 2.6) and would not be recorded on any of the Pirani Gauges.

8(iv) The Reactions in the Degradation of the Poly(Primary Acrylates)

A. Production of Olefin and Carbon Dioxide

Cameron and Kane[1,2,3] suggested that the degradation reactions in poly(methyl acrylate) occur by mechanisms involving free radicals. Since the poly(primary acrylates) studied in the present work degrade at about the same temperature and give similar products, it is reasonable to suppose that the same reaction schemes may apply.

At low temperatures (7(iii)) and at early stages of degradation (4(ii) and 4(iv)B), carbon dioxide and olefin are evolved from these polymers in a molar ratio close to unity. It seems probable that a reaction mechanism similar to that shown in fig 8.5 is operating.

At 315°C there is no evidence for autocatalytic production of olefin. There appears to be negligible competition to the reaction shown in fig 8.5 from that shown in fig 1.10. Although the reaction in fig 8.5 is shown as being catalysed by a radical on a neighbouring monomer unit, there is no reason why any available radical should not be the initiator.

There appears to be a connection between the number of β-hydrogen atoms on the alkyl group and the production of olefin. Thus the yield of olefin from the four polyacrylates decreases in the order, ethylene > propylene = 1-butene > 2-ethyl 1-hexene (tables 4.9-4.12) and the initial rate of production shows a corresponding trend (table 4.13). This would agree with a mechanism such as that shown in fig 8.5, where the extent of reaction depends on the availability of the β-hydrogen atoms.

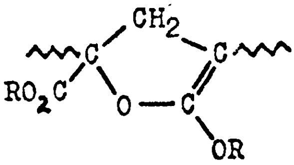
In the infrared spectra of the residues from poly(2-ethyl hexyl acrylate), a small peak can be observed at 1810 cm^{-1} as well as the peak at 1760 cm^{-1}. There may be some tendency for olefin elimination to occur unaccompanied by carbon dioxide production in this polymer. The carboxyl radical formed may then attack neighbouring ester units to produce anhydride rings and eliminate an alkoxyl radical. No other poly(primary acrylate) gives evidence for anhydride formation, but this is presumably a minor reaction.

With the remaining poly(primary acrylates), carbon dioxide production exceeds that of olefin at long degradation times. The most likely mechanism to account for this is one first suggested by Fox and others[48] and later used by Grassie and Torrance[45,47] and Cameron and Kane[1,3] to account for carbon dioxide production in degradation systems involving methyl acrylate units (figs 1.7 and 1.13). It is a rather unusual type of reaction, involving shift of an alkyl group, and it may therefore be thought to become less likely as the size of the alkyl group increases. This may explain why in the present work it is only observed at later stages of degradation and only in polymers which have developed insolubility. The restrictions on the movement of the side group which extensive cross-linking produces may tend to hold the alkyl group close to the polymer radical and hence encourage reaction. In previous papers evidence for this reaction was provided by the existence of methyl methacrylate monomer amongst the degradation products. In the present work, no corresponding α-substituted acrylate monomer was found, yet the methacrylate was still recovered in the volatile degradation products (4(iv)A). The methacrylate found is probably from reactions at chain ends (see 8(iv)E).

B. Production of Alcohol

Cameron and Kane[1,3] have suggested four possible mechanisms for the production of a methoxyl radical from poly(methyl acrylate). Two of these are given in figs 1.12 and 1.14. The other two involve formation of a ketene[1,3] and formation of a vinyl ketone[1]. The ketene forming reaction was discounted because absorption was not detected at 2160 cm^{-1} in the infrared spectrum of the polymer residue. The carbonyl absorption of $\alpha:\beta$ unsaturated ketones occurs at 1695 - 1660 cm^{-1} [83] and since only slight increase in absorption was observed in this region both in the present studies and those by Cameron and Kane, this can also be discounted as a major reaction. There remain the reactions shown in figs 1.12 and 1.14. The former produces a $\gamma:\delta$ unsaturated δ lactone ring system (intramolecular reaction) or an ester (intermolecular reaction) and the latter, a non-enolisable β-ketoester which can be in a 6-membered ring (intramolecular reaction) or acyclic (intermolecular reaction).

Although, at first sight, it seems the less likely of the two reactions, that shown in fig 1.12 receives strong support from the infrared spectra of the degraded polymers. A shoulder develops in the spectra of poly(ethyl acrylate) (6(iii)), poly(n-butyl acrylate) (6(ii) and poly(2-ethyl hexyl acrylate) (4(vi)C) at 1760 cm^{-1}, which is at a higher frequency than most carbonyl absorption. In the absence of an accompanying peak between 1800 cm^{-1} and 1850 cm^{-1} (except for a small peak in the spectrum of degraded poly(2-ethyl hexyl acrylate) (see 8(iv)A)), the most likely cause is a lactone. A $\beta:\gamma$ unsaturated γ lactone (III) might be formed by radical coupling,



III

but this would absorb at rather higher frequency (1805 - 1785 cm^{-1} 83). The normal absorption for δ lactones is 1750 - 1735 cm^{-1} 83, but, with $\gamma:\delta$ unsaturation in the ring, this would move to higher frequency, so that the absorption at 1760 cm^{-1} agrees with the product shown in fig 1.12. Carbon-carbon double bond absorption is normally much weaker than carbonyl absorption. However, in this case, the polarity of the bond will be greater because of the presence of two carbon-oxygen bonds at one end and two carbon-carbon bonds at the other end. This should cause enhanced absorption in the carbon -carbon double bond region between 1680 cm^{-1} and 1620 cm^{-1} [83]. There is a general increase in absorption in this region as degradation proceeds, but no clear peak can be distinguished. However, the carbonyl peak overlaps into this region at later stages of degradation and, therefore no firm conclusions about this structure can be drawn from consideration of carbon-carbon double bond absorption.

The other route for alcohol production suggested by Cameron and Kane (fig 1.14) yields a product which would absorb in the 6-membered cyclic ketone region between 1720 cm^{-1} and 1700 cm^{-1}. This is slightly lower in frequency than the carbonyl absorption from the ester group and the presence of ketones in the degradation residue may explain the shift in the carbonyl peak to shorter frequency as degradation proceeds. This shift is observed in the residuesfrom all three poly(primary acrylates) studied and is most marked in poly (ethyl acrylate) (fig 6.6) which would be expected to lose nearly all of its ester groups (see 6(i)) at long times of degradation.

In conclusion, it can be said that there is strong infrared evidence for lactone formation in the residues from poly(primary acrylate) degradation, whilst the changes in the infrared spectrum agree well with, but do not prove, the formation of ketonic groups.

These reactions both result in the production of alkoxyl radicals. Shaw and Trotman-Dickenson[87] found that methoxyl radicals in the gas phase have a stability between that of a methyl radical and that of a chlorine atom. Therefore, the formation of these radicals in a degrading polymer system at 315°C is not an unreasonable suggestion. It has also been shown[88] that, in the gas phase, the alkoxyl radicals have stabilities in the order $CH_3O^{\cdot} > CH_3CH_2O^{\cdot} > CH_3CH_2CH_2CH_2O^{\cdot} > (CH_3)_2CHCH_2O^{\cdot}$. Thus the alcohol elimination reactions will be less likely in the polymers of acrylates with fewer β-hydrogen atoms and this will account for the decreasing yield of alcohol in the four poly(primary acrylates) in the order : Ethyl > n-propyl > n-butyl > 2-ethyl hexyl (tables 4.9 - 4.12).

McBay and Tucker[89] have shown that, in solution, at temperatures between 110 and 155°C, the alkoxyl radicals can react either by hydrogen abstraction (H.A.) from a solvent molecule to give alcohol or by disproportionation (D.P.) with another alkoxyl radical to give equal yields of alcohol and aldehyde. Rust, Suebold and Vaughan[88] studied the reaction of the alkoxyl radicals with cyclohexene in the gas phase at 195°C. They found that both H.A. and D.P. occurred and that, in the gas phase at 195°C, the ratio H.A./D.P. decreased in the order $CH_3O^\cdot > CH_3CH_2O^\cdot > CH_3CH_2CH_2CH_2O^\cdot > (CH_3)_2CHCH_2O^\cdot$. In the present work, no aldehyde was recovered, but abstraction of a tertiary hydrogen atom from the acrylate polymer chain would, no doubt, occur much more readily than abstraction of a hydrogen atom from cyclohexene, which has no tertiary hydrogen atoms.

One striking feature of the production of alcohol (see figs 4.16-4.18 and 4.20) is that it appears to be autocatalytic in character. Cameron and Kane, on the other hand, make no mention of a similar effect in methanol production from poly(methyl acrylate). The G.L.C. technique used to analyse the liquid degradation products in the present work appears to give rather low values at low yield of product and, hence, spuriously introduce autocatalytic character into yield/time of degradation curves. This can be seen in the production of 2-ethyl 1-hexene from poly(2-ethyl hexyl acrylate) (fig 4.19). However, it is thought that this effect is insufficient to explain the apparently autocatalytic nature of alcohol production. The mechanisms so far proposed for alcohol production are all initiated by the same polymer radical (II) as initiates other degradation reactions. Since no other reaction is autocatalytic, it seems unlikely that the autocatalytic nature of the alcohol elimination reaction is brought about by the removal of alcohol molecules encouraging the formation of radical II. It is also difficult to suggest any other chemical way in which the products of the alcohol elimination reaction can encourage further alcohol production.

The answer may lie in the changes in the physical character of the polymer molecule brought about by alcohol elimination. Both reactions 1.12 and 1.14 involve either formation of a ring (when they occur intramolecularly) or formation of a cross-link (when they occur intermolecularly). These new structures will increase the rigidity of the polymer. A rigid system might be expected to encourage reactions involving 6-membered rings, such as those proposed for alcohol production (figs 1.12 and 1.14), carbon dioxide production alone (figs 1.7 and 1.13) and intramolecular transfer (fig 1.1), whilst discouraging reactions such as the simultaneous olefin and carbon dioxide eliminating reaction (fig 8.5) which involves a 10-membered ring. There does not appear to be any mention in the literature of cases in which reaction rates are altered by increasing rigidity in polymer systems and therefore this explanation for autocatalysis of alcohol production should be regarded as being tentative. On the other hand, in polymer degradations studied in detail in which cross-linking occurs, there have not been competing volatilisation processes which might be selectively influenced by the cross-linking. In this respect the polyacrylates should be regarded as a novel system.

C. Production of Short Chain Fragments and Chain Scission

The large amounts of short chain fragments produced and the rapid decrease in molecular weight of poly(2-ethyl hexyl acrylate) are probably the result of a considerable degree of chain transfer (fig 1.1). Cameron and Kane[1,2] suggested that intramolecular transfer predominates in the degradation of poly(methyl acrylate) as this favours the formation of small chain fragments. They termed the process whereby a radical moves along the polymer chain eliminating small polymer molecules 'unbuttoning' to compare it with the so-called 'unzipping' process which results in high monomer yields from poly (methyl methacrylate) (fig 1.2).

The main feature of interest in the unbuttoning reaction, as it occurs in the polymers studied in the present work, is that it increases in extent relative to the ester decomposition reactions as the size of the alkyl group increases. There are probably two reasons for this.

1/ Table 4.18 shows that the molecular weight of the short chain fragment fraction increases with the length of the alkyl group on the polymer. This would mean that higher molecular weight material can volatilise from degrading poly(octyl acrylate) more readily than from degrading poly(ethyl acrylate). Material which would remain in the degradation zone in the case of poly(ethyl acrylate) and be liable to ester decomposition would be lost as short chain fragments from poly(octyl acrylate). As the length of the alkyl group increases, the polymer becomes less polar and hence the attractive forces between neighbouring polymer chains, or between segments of the same chain, become smaller. Thus, with the higher homologues, larger chain fragments can volatilise.

2/ Both the olefin elimination reaction (see 8(iv)A) and the alcohol elimination reactions (8(iv)B) become less likely as the availability of the β-hydrogen atoms in the ester group decreases. This effect will increase the short chain fragment/ester decomposition product ratio, as the number of β-hydrogen atoms on the ester group decreases.

Fig 4.32 shows that for poly(2-ethyl hexyl acrylate) after an initially fast rate of bond scission, the rate throughout the rest of the degradation is constant The faster initial rate may be explainedby the presence of weak links in the polymer, although this effect is surprisingly large.

For a polymer degrading only by random scission of polymer chain, Simha and Wall[90] have calculated that the rate of volatilisation against percent volatilisation curve should show a maximum rate at about 26 % volatilisation. Thereafter the curve should follow a straight line to meet the percent volatilisation axis at 100 %. This curve is shown for poly(2-ethyl hexyl acrylate) in fig 4.28d. It does not agree with the calculations of Simha and Wall and it must be concluded that other volatilisation reactions are masking the chain scission process. The initial rate of volatilisation is fast and linear and this changes at about 30 % conversion to give a second approximately linear relationship. With so many volatilisation reactions occurring plus, indeed, the possibility that a small amount of cross-linking may take place with this polymer, as in the other poly(primary acrylates), it is perhaps unwise to attempt to interpret this curve and the corresponding curves for the other poly(primary acrylates) (fig 4.28a-c) before more extensive studies of the degradations are carried out. They may, however, represent the sum of three curves: one for weak link scission, one for random chain scission and one for the volatilisation of ester decomposition products.

D. The Cross-Linking Reactions

Cross-linking occurs in at least three of the poly(primary acrylates) studied (4(vi)). Cameron and Kane[1,3] suggested that the cross-linking reactions might be radical coupling between polymer chains (fig 1.11) or intermolecular forms of the alcohol elimination reactions (figs 1.12 and 1.14). The residue is insoluble in alkali solution which would be expected to cause hydrolysis of the ester formed in the reaction shown in fig 1.12. It can therefore be said that one of the reactions shown in figs 1.11 and 1.14 must operate.

The development of insolubility in the residue has an induction period in poly(n-butyl acrylate) (figs 4.25 and 4.26) and in this respect parallels the production of n-butanol (fig 4.18). It seems likely, therefore, that the alcohol elimination reactions are responsible for most of the cross-linking. However, since alcohol is also produced from poly(2-ethyl hexyl acrylate), in which no insolubility is observed and since in the other polymers, insolubility develops rather slowly, the intramolecular forms of the alcohol elimination reactions appear to predominate and the intermolecular forms are comparatively minor in extent. A parallel reaction is that of anhydride formation in poly(methacrylic acid)[41] which has been shown to be mostly intramolecular, but with sufficient intermolecular structures to cause insolubility.

Insolubility appears to develop faster in the lower homologues of the polyacrylate series and decrease in rate as the size of the ester group increases. This would appear to be purely steric effect. In polyacrylates with large alkyl groups, polymer molecules are kept so far apart by the bulky ester groups that radicals on the polymer chain cannot attack neighbouring molecules

It is unfortunate that the polymers used in the present study decreased in molecular weight with increase in size of the alkyl group. This might suggest that development of insolubility is a function only of the initial molecular weight of the undegraded polymer. However, insolubility was observed by Kane[1] in the degradation of poly(methyl acrylate) of initial molecular weight as low as 120,000. Also, Fortune[91] has observed insolubility in 15:1 n-butyl acrylate:methyl methacrylate copolymers of molecular weight 76,500; in this system, cross-linking is thought to occur by a similar mechanism to that in the polyacrylate system.

At lower degradation temperatures, there is no alcohol produced from degrading poly(n-butyl acrylate) (7(iii)). The degradation pattern at this temperature is very similar to that of poly(iso-propyl acrylate) at the same temperature (8(ii)). The volatiles consist largely of carbon dioxide and olefin and it seems likely that the insolubility which develops in poly(n-butyl acrylate) at this temperature is caused by anhydride formation. Unlike the insolubility in poly(iso-propyl acrylate) which is complete at 265°C after 4 hours degradation, that in poly(n-butyl acrylate) at 241°C levels off at about 25 % and the molecular weight of the remaining soluble material falls as degradation proceeds. This suggests that a chain scission process is competing with the cross-linking reaction in poly(n-butyl acrylate), but not in poly(iso-propyl acrylate).

At higher temperatures olefin and carbon dioxide elimination appears to be nearly simultaneous. Hence anhydride cross-links cannot form in the poly(primary acrylates) at 315°C and insolubility develops more slowly and by a different route from that taken at 241°C.

E. Minor Degradation Reactions

The residues from poly(primary acrylate) degradation become progressively more intensely coloured as degradation proceeds. Unfortunately, all the good solvents for the polymers absorb in the ultraviolet region and no significant spectra could be found in the visible region. It is presumed, however, that the colour develops from double bond conjugation, involving mainly carbon-carbon double bonds, but possibly also carbonyl groups. Carbon-carbon double bonds will be formed in the polymer molecules by such reactions as chain transfer (fig 1.1) and alcohol elimination (fig 1.12). Once one such bond is formed, it will tend to weaken the carbon-hydrogen bonds on carbon atoms in the α position and hence promote the formation of a double bond between it and the β carbon atom. Thus conjugated sequences may be built up. These sequences do not appear to run to great length as there does not seem to be a bathychromic shift on degradation. Little hydrogen is observed in the degradation products at 315°C (see 4(iii)) and therefore it appears that spontaneous carbon-hydrogen bond fission does not occur. On the other hand, as in poly(iso-propyl acrylate) (see 8(iii)) the hydrogen content of the residue at long degradation times is rather low (table 4.21) and some doubt remains as to whether the amount of hydrogen gas evolved from the degrading polymer is as low as the mass spectrum suggests (4(iii)).

The presence of methacrylate groups in small amounts in the liquid degradation products cannot arise from the formation of methacrylate units in the polymer chain as has been suggested for methyl acrylate polymers[3]. It is more likely that it arises from reactions at chain ends (fig 8.8).

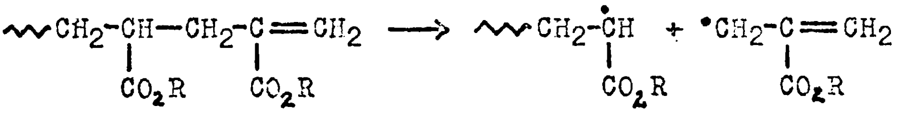


Fig 8.8 Formation of Methacrylate Radical

The bond β to the double bond is particularly vulnerable to scission.

Acrylate is found in rather greater amount than methacrylate. It probably arises from a small amount of depropagation (fig 1.2), although, of course, this reaction is very minor in polyacrylate degradation.

Another minor product identified in poly(primary acrylate) degradation is carbon monoxide. The most likely source of this is homolytic scission of the acyl-oxygen bond of the ester group (fig 8.9).

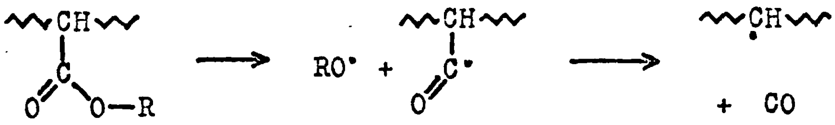


Fig 8.9 Formation of Carbon Monoxide

The carbonyl radical produced is very unstable[92] and will decompose immediately, generally to give carbon monoxide.

8(v) Residue from the Poly(Primary Acrylates)

The infrared studies of the poly(primary acrylates) show that at long degradation times, the principal change is the development of a peak at 1760 cm^{-1} (see 6(ii) and fig 4.30). This has been attributed to lactone formation (see 8(iv)B). The spectrum of poly(ethyl acrylate) at long degradation times, in the presence of traces of water, shows the development of a strong peak at 1570 cm^{-1}. This has been discussed and explained by formation of the carboxyl ion following hydrolysis of ester-type groups (6(v)). Since little ethyl ester remains in the residue at long degradation times (6(i)), it is thought that this peak arises largely from hydrolysis of the lactone rings produced on elimination of alcohol (fig 1.12). The small size of the shoulder at 1760 cm^{-1} in the spectrum of degraded poly(ethyl acrylate) supports this theory. There is, however, still a considerable carbonyl peak, which has shifted in maximum absorption from 1730 cm^{-1} to 1705 cm^{-1}. This is in the region of ketone absorption and is evidence for the existence of the alternative alcohol elimination reaction (fig 1.14).

The development of insolubility in the residue has already been discussed (8(iv)D).

8(vi) Suggestions for Further Work

The degradation pattern of poly(iso-propyl acrylate) seems to be fairly straightforward. There are, however, some unanswered problems;

1/ the elimination of propylene and carbon dioxide may be simultaneous (fig 8.5) or consecutive (fig 1.10 and 8.2). The first of these reactions involves free radicals, while the olefin elimination may be a molecular process. There has been no direct evidence for free radical participation in the degradation of poly(iso-propyl acrylate) and studies of the degradation using a free radical trap such as diaminoanthroquinone may be useful in determining the extent of each of these reactions.

2/ An accurate method of measuring the small amounts of water evolved from the polymer would allow the amount of anhydride formed in the polymer to be calculated. In contrast to the findings of Schaefgen and Sarasohn[53] in the case of poly(t-butyl acrylate), in the present work it was estimated that some acid groups remain in the poly(iso-propyl acrylate) residues at long degradation times. However, the amount of water produced from poly(iso-propyl acrylate) was not measured accurately and the relative amounts of acid and anhydride are not known with certainty.

3/ Studies of the degradation at three or four different temperatures would allow activation energies to be calculated for the ester decomposition reaction. It would be of interest to compare these values for poly(iso-propyl acrylate) with values for other polyacrylates, as an exercise in ester decomposition kinetics. However, the autocatalytic effect in olefin production will complicate calculation of kinetic data.

The poly(primary acrylates) would repay a good deal of attention. There is good evidence that the proposed mechanisms for olefin, carbon dioxide and short chain fragment production are substantially correct. The lactone-forming alcohol elimination reaction (fig 1.12) receives strong support from infrared studies (6(ii), 6(iii) and 8(iv)B), but the existance of its ketone-forming counterpart (fig 1.14) is still not definitely proven. The cross-linking reactions have also not been substantiated by experiment. The following would seem to be the most fruitful areas for further research.

4/ A great deal of work is still to be carried out on the insolubility which develops in the polyacrylates. Kane[1] studied the development of insolubility in degrading poly(methyl acrylate) and concluded that it depends primarily on the temperature of polymerisation. It has also been shown[93] that in the degradation of n-butyl acrylate/ methyl methacrylate copolymers, insolubility depends on the initial molecular weight. It remains to be clarified how cross-linking can be related to such factors as initial molecular weight and molecular weight distrbution, polymerisation conditions, size of the ester group, temperature of degradation and evolution of alcohol from ester decomposition. The filtration method of separating sol and gel is not considered satisfactory (4(vi)A) and a Soxhlet extraction method[93] is to be preferred. The latter is, however, open to objection in that it requires the polymer residues to be refluxed for long periods in a solvent, thus rendering them liable to further breakdown. Studies of the extent of cross-linking by the swelling method[94] should also prove rewarding.

5/ Degradation studies of the poly(primary acrylates) at temperatures other than 315°C might usefully be pursued. For example, Chapter 7 of this thesis contains a description of a brief investigation of the degradation of some polyacrylates at temperatures at which little volatilisation is occurring. Use of the McLeod Gauge in such studies enables the production of small amounts of volatiles to be investigated and, hopefully, related to changes in molecular weight.

6/ Poly(2-ethyl hexyl acrylate) degradation is not complicated by the development of insolubility and a study of this polymer at a suitable temperature (below 315°C) should enable the chain scission reaction in the poly(primary acrylates) to be examined in greater detail. There appears to be a large 'weak-link' effect in this polymer (figs 4.20 & 4.28d) which results in a fast evolution of chain fragments early in the degradation This is rather unusual and not easy to explain. A useful approach to the study of the chain scission reaction might be to attempt the characterisation of preferred species in the short chain fragment fraction, or of the end groups of the molecules in this fraction.

7/ With very careful measurement of initial rates of volatile production, kinetic data and activation energies could be found and corresponding data from the various polymers compared.

8/ Careful choice of other acrylate polymers for comparative degradation studies might well be useful. For example, 2-hydroxy ethyl acrylate monomer is available commercially and a study of the degradation of its polymer should show interesting changes in the ester decomposition reactions.

Appendix A

Calibration of Constant Volume Manometer

The apparatus shown in fig 2.12a for gas analysis includes a constant volume manometer. The constant volume is the volume enclosed by taps C and F and the mercury at level zero in limb L. It was found as follows.

The cross-sectional area of limb L must be found. This was done before assembly of the C.V.M. by partially filling with mercury a length of the glass tubing to be used for making limb L. The mercury level was found by means of a cathetometer. A known weight of mercury was added to the tube and a second cathetometer reading of the mercury level taken. The cross-sectional area of the tube was found as follows:

Table A.1

1st Mercury level	= 26.778 cm	30.084 cm
2nd Mercury level	= 30.095 cm	31.147 cm
Difference	= 3.317 cm	1.063 cm
Weight of mercury added	= 107.96 g	34.49 g
Density of mercury at room temp (25°C)	= 13.5340gcm^{-3}	13.5340gcm^{-3}
Hence, volume of mercury	= 7.9768 cm^3	2.5482 cm^3
Therefore, cross-sectional area of tubing	= 2.405 cm^2	2.397 cm^2

Average cross-sectional area = 2.401 cm^2

With the level of mercury down below tap O, the apparatus was pumped out to high vacuum. Taps C and F were closed and the level of mercury allowed to rise into limbs L and R. A small amount of air was let into limb L and a plot of 1/P against V_a obtained where P is the difference in heights of mercury in the two limbs and V_a is the volume of limb L above the zero mark occupied by mercury. The volume occupied by gas is $V_o - V_a$ where V_o is the constant volume By Boyle's Law,

for a given mass of gas,

$$P(V_o - V_a) = k \quad \text{where k is constant}$$

$$V_o - V_a = k/P$$

$$V_a = -k/P + V_o$$

A plot of V_a vs 1/P should therefore be a straight line of gradient -k which intercepts the V_a axis at V_o. Hence V_o can be found.

Three values for V_o were obtained using different amounts of gas, and the average taken as follows:

Table A.2

	Mercury level in		Pressure	1/P	V_a
	Limb R(cm)	Limb L(cm)	P(cm.Hg)	$(cm.Hg)^{-1}$	(cm^3)
A	9.88	7.20	2.68	0.373	17.29
	8.92	6.55	2.37	0.422	15.73
	7.48	5.49	1.99	0.503	13.18
	6.31	4.57	1.74	0.575	10.97
	4.93	3.41	1.52	0.658	8.19
	3.92	2.48	1.44	0.694	5.95
	2.80	1.51	1.29	0.775	3.63
	1.55	0.39	1.16	0.862	0.94
B	10.21	6.01	4.20	0.238	14.43
	8.96	5.23	3.73	0.268	12.56
	8.00	4.55	3.45	0.290	10.92
	7.19	4.01	3.18	0.314	9.63
	5.86	2.97	2.89	0.346	7.13
	4.89	2.25	2.64	0.379	5.40
	3.41	1.03	2.38	0.420	2.47
	2.23	0.00	2.23	0.448	0.00
C	10.29	5.34	4.95	0.202	12.82
	8.52	4.28	4.24	0.236	10.28
	7.51	3.58	3.93	0.265	8.60
	6.69	3.00	3.69	0.271	7.20
	5.90	2.42	3.48	0.287	5.81
	5.31	1.98	3.33	0.303	4.75
	3.90	0.90	3.00	0.333	2.16
	2.85	0.00	2.85	0.351	0.00

Fig A.1 shows the plots for 1/P against V_a for these three sets of values. The three intercepts on the V_a axis are

A	B	C
30.57	30.52	30.38

The average value of the volume for the constant volume manometer is therefore taken as 30.5 cm^3.

It was found, however, that too much gas was evolved from some of the degradations to be measured on this form of C.V.M.. The constant volume was therefore increased to include the sealed tube and the volume enclosed by taps B and F and the mercury level at the zero mark in limb L. The value of 30.5 cm^3 found above is referred to as the volume of the smaller system and the enlarged volume referred to as the larger system.

The volume of the larger system cannot be found in the same way as that of the smaller system because V_a is very small in comparison. Instead, gas was let into the smaller system and its pressure found. The remainder of the larger system was pumped out to high vacuum. Tap B was closed and the gas allowed to expand into the larger system. A new value for the pressure was obtained,

From Boyle's Law $P_1V_1 = P_2V_2$, hence the volume of the larger system was found. The average of eleven readings shown in table A.3 was taken.

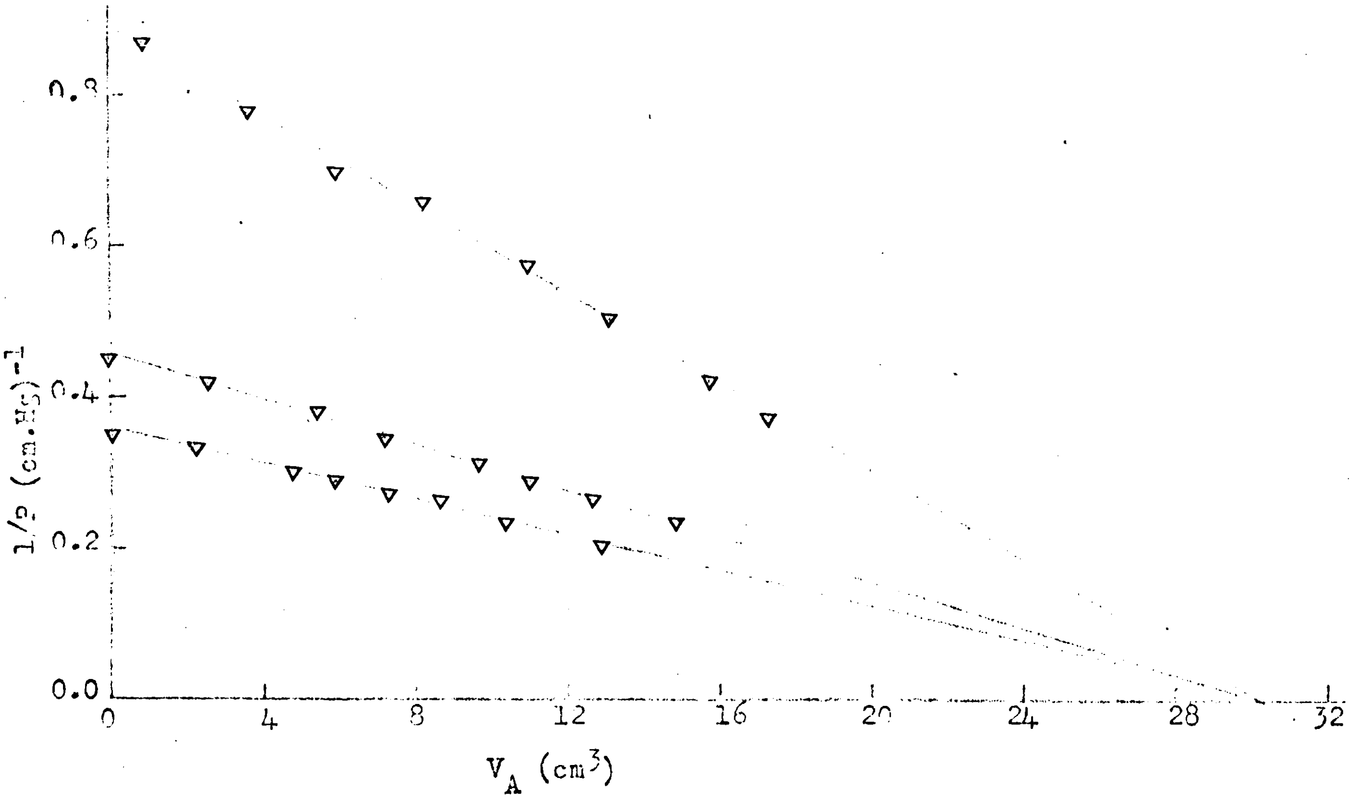


Fig A1 To Find Volume of Constant Volume Manometer (Smaller System)

Table A.3

Pressure in smaller volume	Pressure in larger volume	$\frac{\text{Volume of larger system}}{\text{Volume of smaller system}}$
21.81	1.55	14.07
27.28	1.96	13.92
13.62	0.99	13.76
14.67	1.08	13.58
16.36	1.20	13.63
18.18	1.36	13.37
19.45	1.41	13.79
21.43	1.52	14.10
22.03	1.58	13.94
24.38	1.73	14.09
27.10	1.93	14.04

The average value for $\frac{\text{Volume of larger system}}{\text{Volume of smaller system}}$ is 13.84

$\therefore$ Volume of larger system = 423 cm^3

Appendix B

Determination of Sensitivity Factors in G.L.C.

The Microtek 2000R Research Gas Chromatograph used to analyse the liquid volatiles, has a flame ionisation detector. It is found that the response of the detector depends on the weight of the component being analysed. To check this, standard mixtures were made up of the liquid to be analysed and a suitable solvent. The liquids analysed and the solvents are given in 2(xv)B, as is the method of calculating the sensitivity factor (f).

$$f = (W_a \times A_s)/(W_s \times A_a),$$

where W_a and W_s are the weights of sample and solvent in the standard mixture and A_a and A_s are the areas of the peaks corresponding to sample and solvent.

Commercial reagents were used in making up standard mixtures (except for 2-ethyl 1-hexene). 2-Ethyl 1-hexene was made by refluxing 2-ethyl 1-hexanol with 50 % by weight of p-toluene sulphonic acid. 2-Ethyl 1-hexene distilled off at 119°C and was dried with calcium chloride.

Table B.1

Standard Mixtures

Mixture Number	Polyacrylate	Weight Alcohol (mg)	Weight Olefin (mg)	Acetate Solvent	Weight Solvent (mg)
1	ethyl	23.7		ethyl	27.3
2	ethyl	47.6		ethyl	26.9
3	ethyl	23.5		ethyl	53.8
4	n-propyl	24.6		n-propyl	26.6
5	n-propyl	48.5		n-propyl	26.7
6	n-propyl	24.6		n-propyl	53.7
7	n-butyl	24.5		n-propyl	26.8
8	n-butyl	24.4		n-propyl	53.1
9	n-butyl	48.8		n-propyl	26.1
10	n-butyl	25.6		n-butyl	27.3
11	n-butyl	49.5		n-butyl	26.3
12	n-butyl	24.5		n-butyl	53.7
13	2-ethyl hexyl	29.8	31.5	ethyl benzoate	30.7

Table B.2

Calculation of Sensitivity Factors

A_a	A_s	W_a/W_s	f
Ethanol/Ethyl Acetate			
26.4	33.2	0.868	1.091
33.2	37.0	0.868	0.968
29.6	37.4	0.868	1.097
35.2	47.6	0.868	1.176
31.0	37.2	0.868	1.041
45.4	27.6	1.770	1.077
31.2	19.2	1.770	1.090
79.2	44.0	1.770	0.983
26.8	17.0	1.770	1.123
24.0	56.4	0.437	1.026
32.4	74.8	0.437	1.010
34.4	76.8	0.437	0.976
40.0	83.2	0.437	0.910
14.8	37.8	0.437	1.117

Av. Sens. Factor for ethanol vs ethyl acetate = 1.049

Table B.2 Cont.

A_a	A_s	W_a/W_s	f
n-Propanol/n-Propyl Acetate			
18.8	19.6	0.925	0.941
18.8	19.4	0.925	0.954
13.6	14.0	0.925	0.953
18.6	9.6	1.818	0.938
20.6	10.6	1.818	0.935
34.4	17.2	1.818	0.909
7.95	15.7	0.458	0.905
3.75	8.1	0.458	0.989
10.9	22.0	0.458	0.924

Av. Sens. Factor for n-propanol vs n-propyl acetate = 0.941

Table B.2 Cont.

A_a	A_s	W_a/W_s	f
n-Butanol/n-Propyl Acetate			
20.9	24.4	0.914	1.167
29.0	28.4	0.914	0.896
29.6	23.1	0.914	0.713
22.8	46.8	0.460	0.943
38.5	63.2	0.460	0.754
8.9	14.2	0.460	0.733
36.5	16.0	1.869	0.820
18.9	9.4	1.869	0.930
30.5	13.6	1.869	0.834

Av. Sens. Factor for n-butanol vs n-propyl acetate = 0.866

Table B.2 Cont.

A_a	A_s	W_a/W_s	f
n-Butanol/n-Butyl Acetate			
10.0	11.7	0.938	1.098
12.9	12.6	0.938	0.916
13.0	15.8	0.938	1.140
10.3	6.1	1.882	1.114
13.8	7.3	1.882	0.996
20.6	10.9	1.882	0.996
4.6	10.6	0.456	1.051
8.8	18.2	0.456	0.943
15.8	46.0	0.456	1.328

Av. Sens. Factor for n-butanol vs n-butyl acetate = 1.065

2-Ethyl 1-Hexene/Ethyl Benzoate

56.1	45.0	0.972	0.780
57.0	47.0	0.972	0.801
56.4	47.0	0.972	0.811

Av. Sens. Factor for 2-ethyl 1-hexene vs ethyl benzoate = 0.797

Table B.2 Cont.

A_a	A_s	W_a/W_s	f
2-Ethyl 1-Hexanol/Ethyl Benzoate			
44.6	45.0	1.027	1.033
46.7	47.0	1.027	1.031
45.0	47.0	1.027	1.070

Av. Sens. Factor for 2-ethyl 1-hexanol vs ethyl benzoate = 1.045

Appendix C

McLeod Gauge Calibration

The McLeod Gauge system used in the low temperature degradation studies is shown in fig 2.16. Fig C.1 shows the capillary section on a larger scale.

The capillary was made of Veridia Precision Bore tubing. The internal diameter was measured by means of a cathetometer before the McLeod Gauge was assembled. It was found to be 0.183 cm.

The volume of the bulb plus capillary (the volume of the McLeod Gauge, V) was found by weighing this portion of the gauge empty and then full of distilled water to level H-I (fig 2.16). The temperature of the water was taken and from its weight and density the volume of the McLeod Gauge was found to be 134.8 cm^3.

Each time the pressure of a gaseous sample was measured, three readings were taken:

α - the height of the top of the closed limb

β - the level of the top of the mercury meniscus in the open limb

and

γ - the height of the top of the mercury meniscus in the closed limb

The volume occupied by the gas is a cylinder of diameter the same as that of the inside of the tube and of height x where $x = \alpha - \gamma$

Two corrections have to be made as follows:

1/ The top of the closed limb is taken to be hemispherical, not

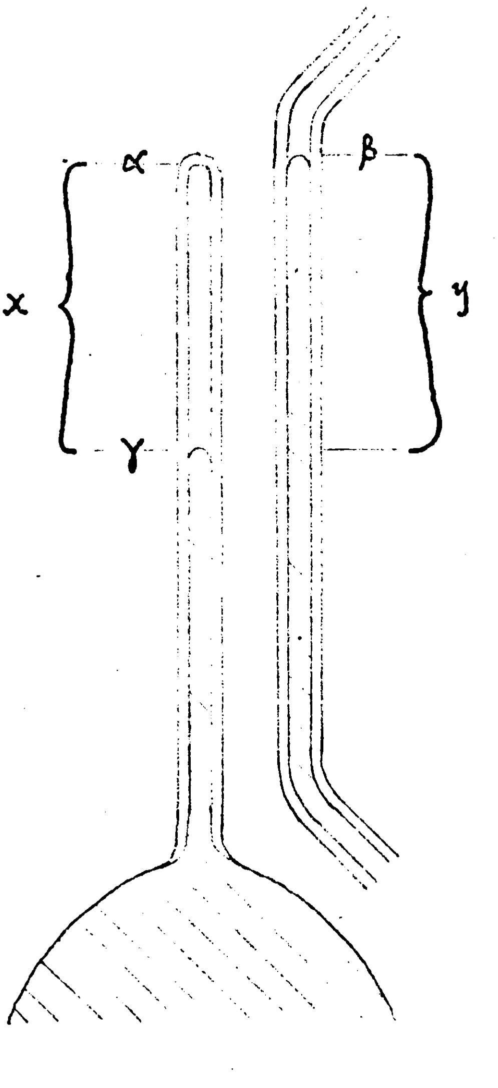


Fig C.1 McLeod Gauge Readings

cylindrical. It therefore has a volume of $2/3.\pi r^3$ instead of πr^3 where r is the radius of the capillary tubing. $1/3.\pi r^3$ is therefore subtracted from x to find the volume of the gas.

2/ The mercury meniscus is taken as being a segment of a sphere. the height, c, of the meniscus was measured. The meniscus occupies a volume $2/3.\pi r^2 c$, and a correction factor of $1/3.\pi r^2 c$ must be added to the volume of the gas in the closed limb.

This, therefore, is taken as

$$\begin{aligned} V &= \pi r^2 x - 1/3.\pi r^3 + 1/3.\pi r^2 c \\ &= \pi r^2 (x - r/3 + c/3) \\ &= \pi r^2 \left[x - (0.0915 - 0.0453)/3\right] \\ &= \pi r^2 (x - 0.015) \text{ cm}^3 \end{aligned}$$

The pressure, P, is given by $y = \beta - \gamma$ (fig C.1)

The initial volume occupied by the non-condensible gases (the 'larger system') (V_1) is bounded by the sealed tube, the trap C, taps A and B and the bulb and capillary of the McLeod Gauge (fig 2.16). The initial volume occupied by the condensible gases (the 'smaller system') (V_2) is bounded by trap C, taps A, E and B and the bulb and capillary of the McLeod Gauge. To find these volumes a small amount of air was allowed to enter the system through tap A. The pressure exerted by the air was found using the McLeod Gauge. With the mercury level still inside the bulb of the gauge, tap B was opened to pump out the 'dead space' to high vacuum. This tap was closed and the air in the bulb and capillary was allowed to expand to fill the volume to be measured. This process was repeated three times and three values for the ratio

$$\frac{\text{Volume of McLeod Gauge + dead space}}{\text{Volume of McLeod Gauge}} = V_1/V \text{ or } V_2/V$$

were found as shown below. Hence V_1 and V_2 were found.

c is defined as $c = PV/AT = kn$ where n is the number of moles of gas,

k is a constant,

T is temperature in °A,

and A is the cross-sectional area of the capillary.

Initially n_o moles of gas are compressed into the McLeod Gauge and c_o measured. This gas is then allowed to expand into the volume V_1. The mercury level is raised into the bulb of the gauge and the air in the dead space is pumped away. The remaining number of moles n_1 is measured to find c_1. n_1 is proportional to the volume of the gauge, V, in the same ratio as the original number of moles, n_o, is proportional to the total volume, V_1

$$n_o/n_1 = c_o/c_1 = \frac{\text{Volume of gauge + dead space}}{\text{Volume of gauge}}$$

For the larger system, V_1

the following table may be drawn up.

Table C.1

Expansion	α	β	γ	Temp	x-0.015	y	$\frac{x-0.015}{T}.y$	
	(cm)	(cm)	(cm)	(°C)	(cm)	(cm)	cm^2deg^{-1}	
0	38.081	38.409	22.841	22.8	15.225	15.568	0.8008	0.7993
	38.033	37.990	22.657	22.8	15.411	15.333	0.7983	
	38.087	38.155	22.738	22.8	15.334	15.417	0.7989	
1	38.085	37.684	28.241	22.4	9.829	9.443	0.3140	0.3124
	38.088	38.082	28.491	22.2	9.582	9.591	0.3111	
	38.087	38.053	28.462	22.0	9.610	9.591	0.3122	
2	38.099	38.067	32.068	21.6	6.016	5.999	0.1224	0.1219
	38.096	38.045	32.070	21.7	6.011	5.975	0.1218	
	38.097	38.031	32.070	21.5	6.012	5.961	0.1216	
3	38.098	37.800	34.177	21.2	3.906	3.623	0.0481	0.0473
	38.100	38.218	34.439	20.9	3.646	3.779	0.0468	
	38.098	38.396	34.515	20.6	3.568	3.881	0.0471	

$c_0/c_1 = 0.7993/0.3124 = 2.559$

$c_1/c_2 = 0.3124/0.1219 = 2.563$

and $c_2/c_3 = 0.1219/0.0473 = 2.577$

The average value is 2.566

Volume of larger system, V_1 = 2.566 x 134.8 cm^3

= 346 cm^3

Volume of dead space = 211 cm^3

For the smaller system (V_2)

Table C.2

Expansion	α (cm)	β (cm)	γ (cm)	Temp (°C)	(x-0.015) (cm)	(x-0.015)y/T ($cm^2\ C^{o\ -1}$)	
0	38.921	38.902	25.917	22.7	12.989	0.5700	0.5719
	38.906	38.790	25.829	22.6	13.062	0.5723	
	38.910	38.890	25.868	22.7	13.027	0.5733	
1	38.927	38.919	29.667	23.2	9.245	0.2886	0.2874
	38.903	38.946	29.708	23.6	9.180	0.2857	
	38.917	38.824	29.613	23.9	9.289	0.2880	
2	38.917	38.941	32.376	24.0	6.526	0.1442	0.1465
	38.922	38.883	32.275	24.9	6.632	0.1465	
	38.930	38.935	32.274	24.1	6.641	0.1488	
3	38.906	38.900	34.258	24.0	4.633	0.0724	0.0725
	38.922	38.930	34.277	24.0	4.630	0.0725	
	38.929	38.681	34.146	24.2	4.768	0.0727	

$c_o/c_1 = 0.5719/0.2874 = 1.990$

$c_1/c_2 = 0.2874/0.1465 = 1.962$

and $c_2/c_3 = 0.1465/0.0725 = 2.021$

The average value is 1.991

Volume of smaller system, V_2 = 1.991×134.8 cm^3

= 268.4 cm^3

Volume of dead space = 133.6 cm^3

When a sample is being measured three readings, α, β and γ (see fig C.1) are taken. The volume of the gas in the capillary

$$V = (\alpha - \gamma - 0.015).A \text{ cm}^3$$

$$= 0.0263(\alpha - \gamma - 0.015)\text{cm}^3$$

The pressure of the gas, $P = \beta - \gamma$ cm.Hg

$$P.V. = 0.0263(\beta - \gamma)(\alpha - \gamma - 0.015)(\text{cm.Hg})(\text{cm}^3)$$

The number of moles of gas in the capillary is calculated as

$$n_1 = P.V/R.T = 1.430 \times 10^{-8}(\beta - \gamma)(\alpha - \gamma - 0.015)$$

Therefore the number of moles of gas evolved from the degradation is $n_1 \times 1.991$ or $n_1 \times 2.566$ depending on whether the gas is enclosed in the smaller or larger system.

Appendix D

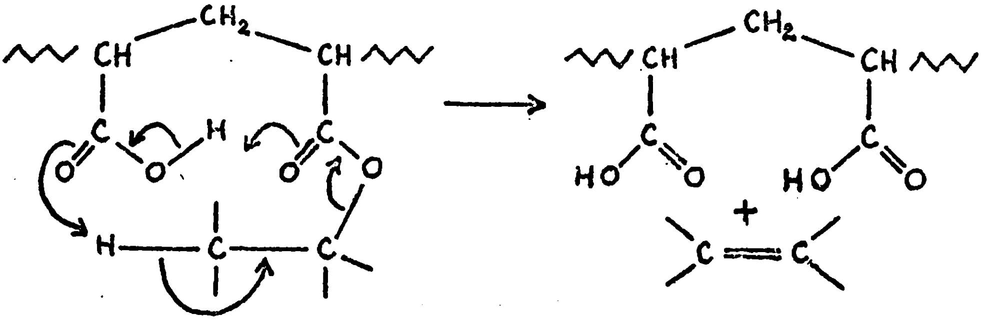
Proposed Reaction Mechanisms in Polyacrylate Degradation

In Chapter 8, the reaction mechanisms shown below have been put forward to account for the degradation products evolved from the polyacrylates. In this appendix, they are collated in the order in which they are mentioned in Chapter 8. Under the heading 'reference' are noted some relevant papers in which the same, or a similar reaction scheme has been discussed.

8(i)

Reference

Fig 1.10 Molecular Mechanism for the Elimination of Olefin 52



Reference

Fig 1.9 Radical Mechanism for the Elimination of Olefin 51

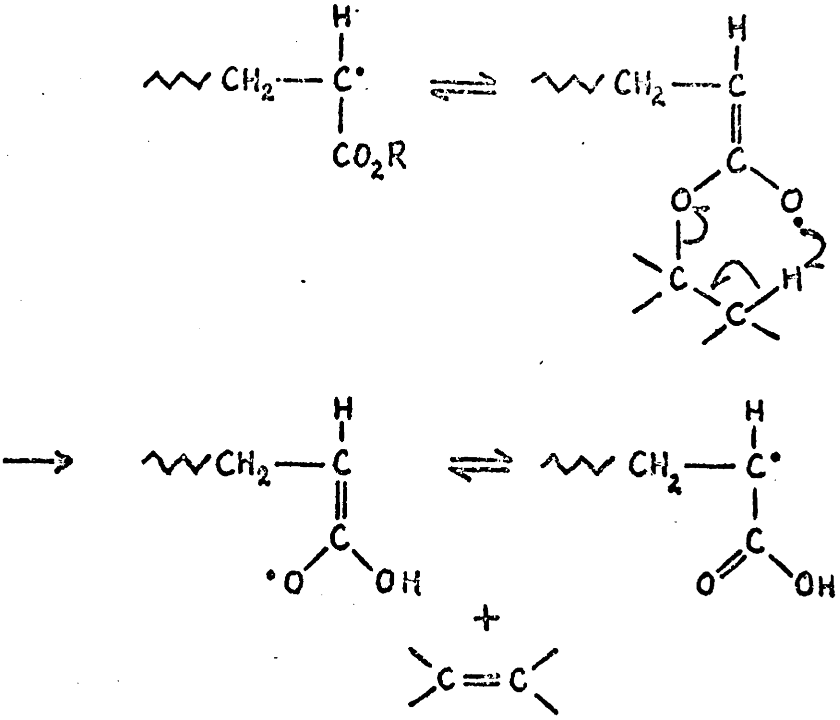
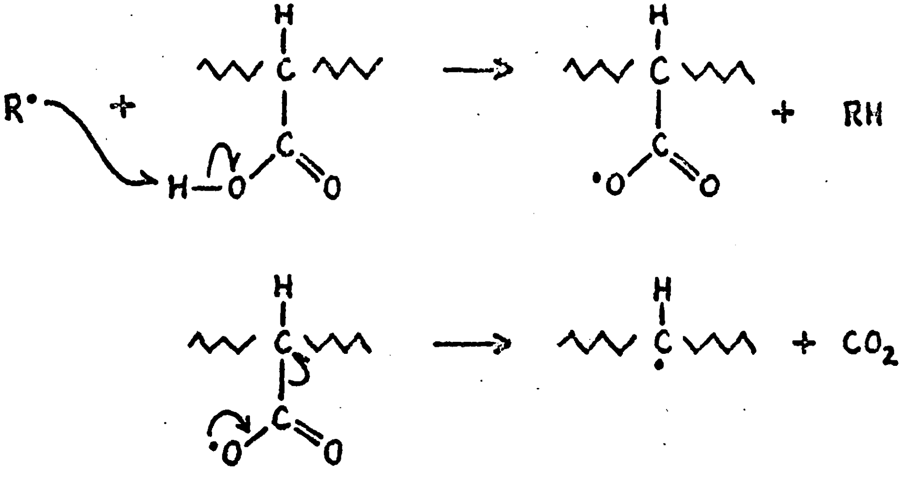


Fig 8.2 Radical Mechanism for Decarboxylation of an Acid Group 86



8(ii)	Reference
Fig 1.10, see above.	
Fig 1.4 Spontaneous Elimination of Olefin	36,37,38

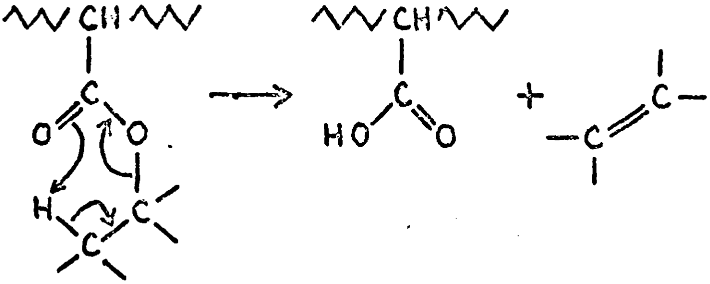


Fig 8.3 Radical Mechanism for Elimination of Olefin Alone	—

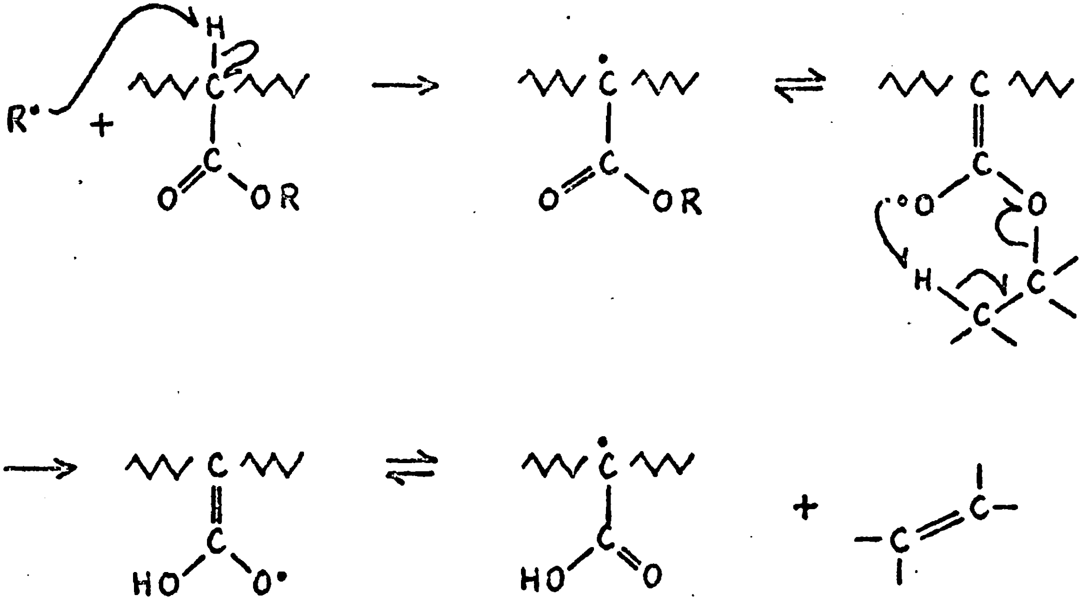


Fig 1.10, see above.

	Reference
Fig 8.4 Simultaneous Elimination of Olefin and Water	51

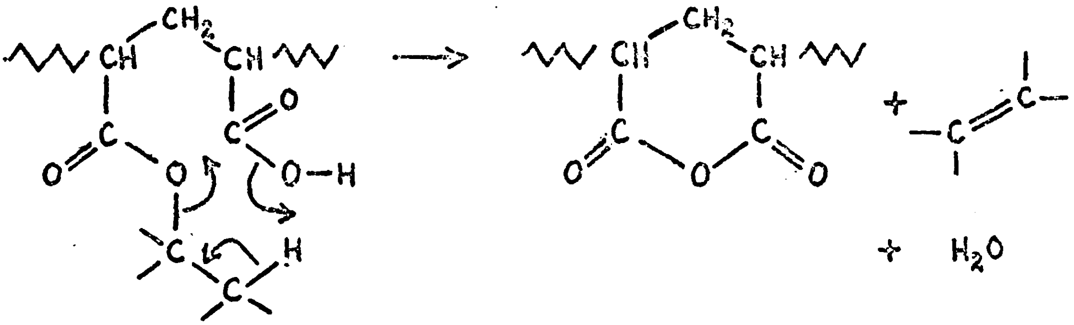


Fig 8.5 Simultaneous Elimination of Olefin and CO$_2$	—

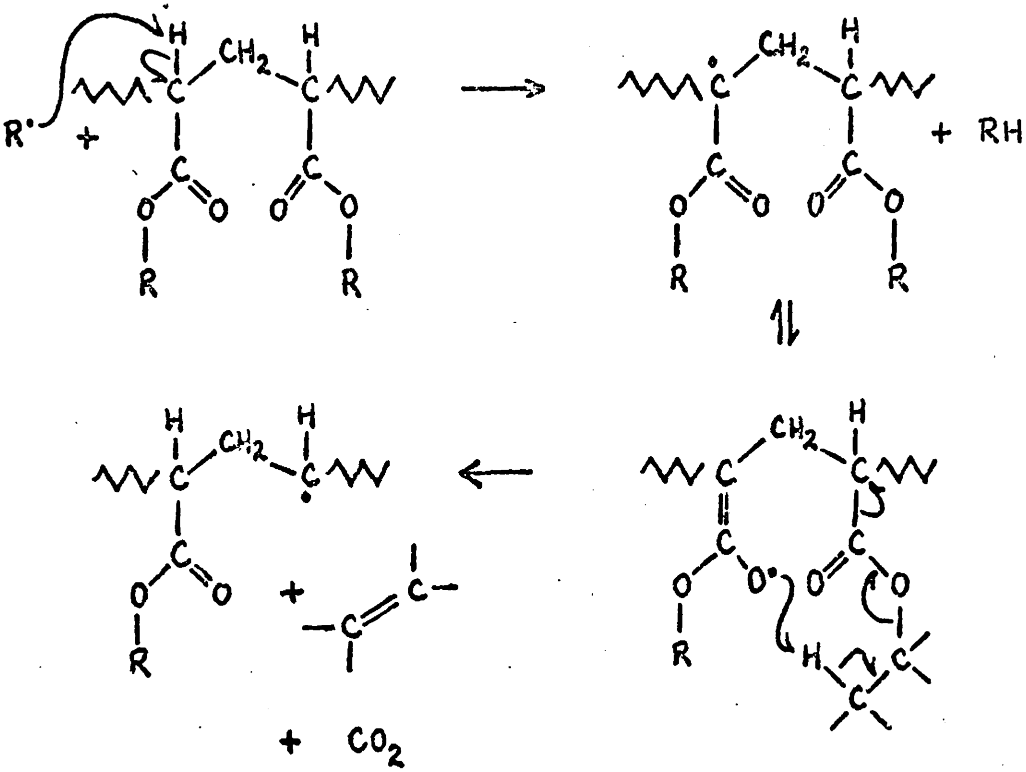


Fig 8.2, see above. **Reference**

Fig 1.6 Elimination of Water between Neighbouring Acid Groups 41

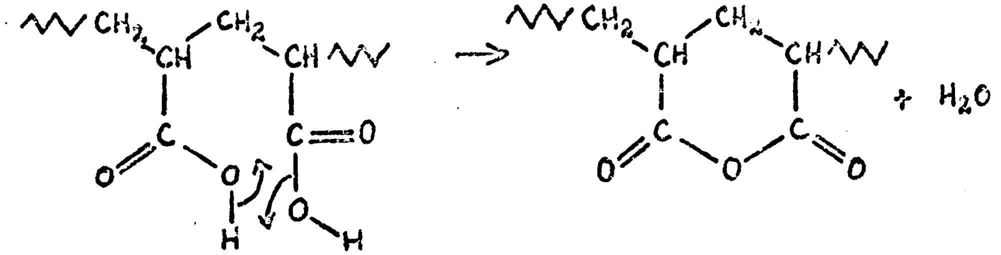
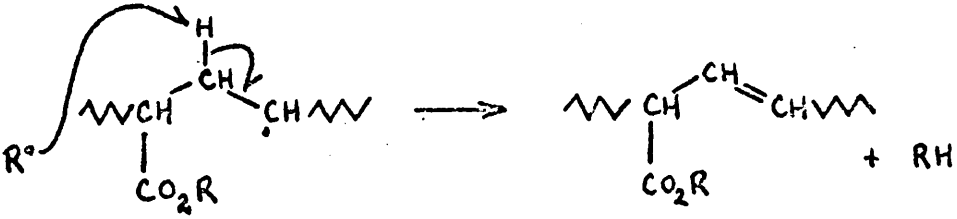


Fig 8.5, see above.

8(iii)

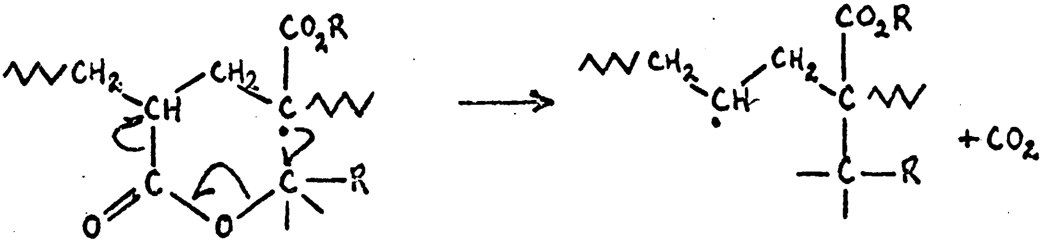
Fig 8.7 Mechanism for Double Bond Formation —



8(iv)A

Figs 8.5 and 1.10, see above

Fig 1.13 Elimination of CO_2 Alone 3,47,48



8(iv)B

Reference

Fig 1.12 Elimination of Alcohol: δ-Lactone Formed 1,3

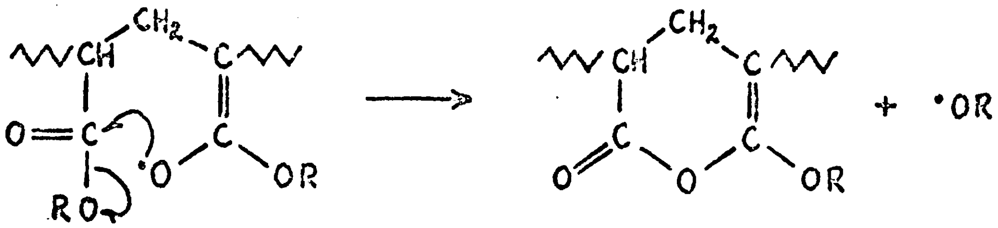
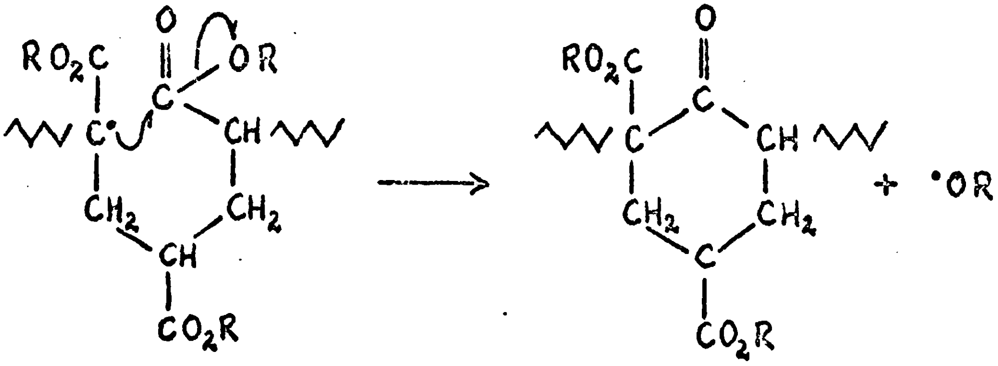


Fig 1.14 Elimination of Alcohol: Ketone Formed 1,3

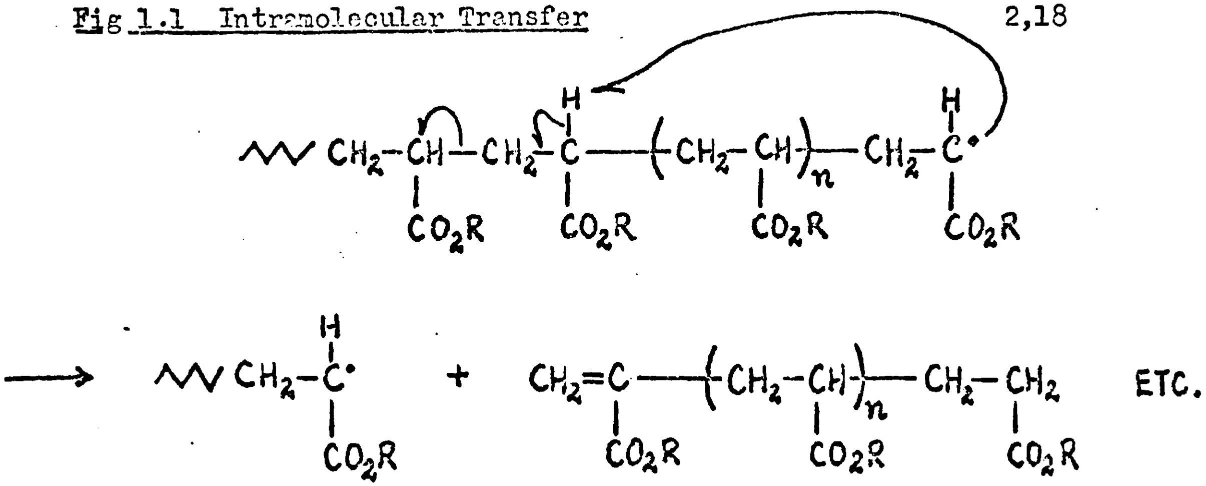


Figs 1.13 and 8.5, see above.

Fig 1.1, see below.

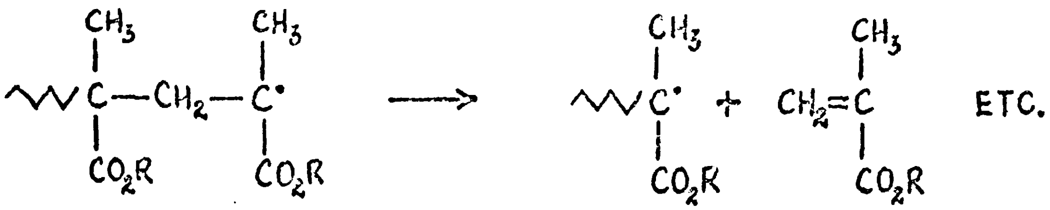
8(iv)C

Fig 1.1 Intramolecular Transfer 2,18



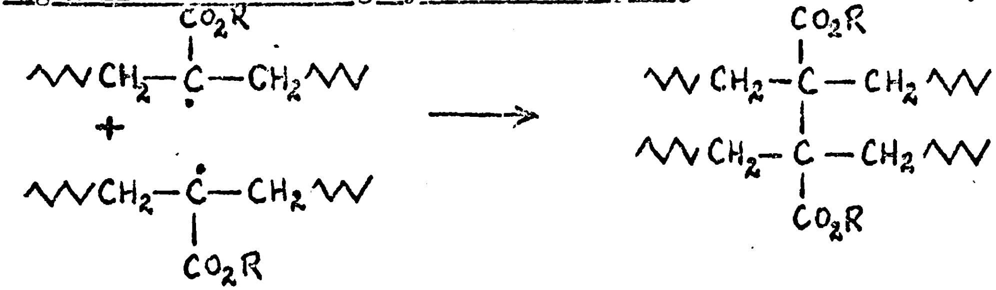
Reference

Fig 1.2 Depropagation Reaction in Polymethacrylates 23



8(iv)D

Fig 1.11 Cross-Linking by Radical Coupling 1,3



Figs 1.12 and 1.14, see above.

8(iv)E

Figs 1.1 and 1.12, see above.

Fig 8.8 Formation of Methacrylate 1,3

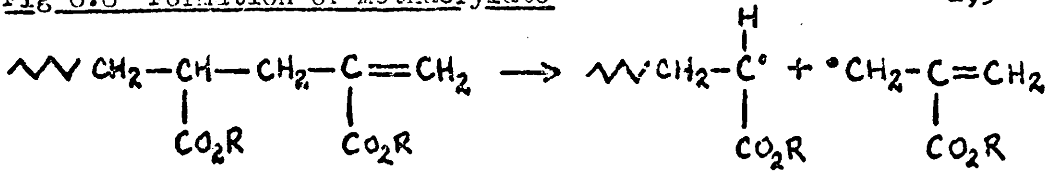
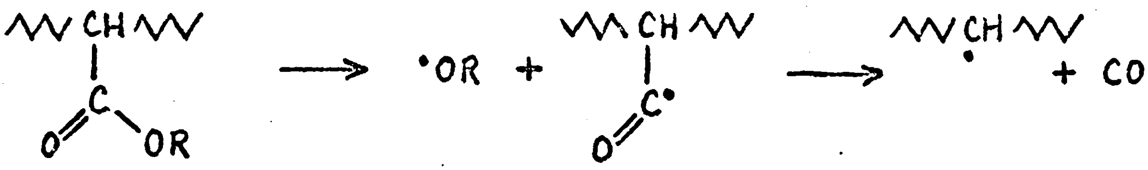


Fig 1.2, see above.

Fig 8.9 Formation of Carbon Monoxide 92



8(v)

Figs 1.12 and 1.14, see above.

References

1. D.R.Kane, Ph.D. Thesis, University of St.Andrews, 1966.

   G.G.Cameron and D.R.Kane, Polymer Letters, 2, 693 (1964).

2. G.G.Cameron and D.R.Kane, Makromol.Chem., 109, 194 (1967).

3. G.G.Cameron and D.R.Kane, Makromol.Chem., 113, 75 (1968).

4. N.Weir, B.Sc. Thesis, University of Glasgow, 1960.

5. 'Polymer Degradation Mechanisms', National Bureau of Standards, Circular 525, Washington, 1953.

6. N.Grassie, 'Chemistry of High Polymer Degradation Processes', Butterworths Scientific Publications, London, 1956.

7. H.H.G.Jellinek, 'Degradation of Vinyl Polymers', Academic Press Inc., New York, 1955.

8. 'Thermal Degradation of Polymers', S.C.I.Monograph No.13, Society of Chemical Industry, London, 1961.

9. N.Grassie, 'Chemical Reactions of Polymers', Ed. E.M.Fettes, Ch.3, Interscience Publishers, New York, 1964.

10. S.L.Madorsky, 'Thermal Degradation of Organic Polymers', Interscience Publishers, New York, 1964.

11. C.G.Williams, Phil.Trans., 150, 241 (1860).

12. H.Staudinger, M.Brunner, K.Frey, P.Garbsch, R.Signer and S.Wehrli, Ber., 62, 241 (1929).

13. H.Staudinger and A.Steinhofer, Ann., 517, 35 (1935).

14. W.Kuhn, Ber., 63, 1503 (1930).

15. R.Simha, J.Appl.Phys., 12, 569 (1941).

16. E.W.Montroll and R.Simha, J.Chem.Phys., 8, 721 (1940).

17. L.A.Wall, J.Res.Nat.Bur.Stand., 41, 315 (1948)..

18. W.G.Oakes and R.B.Richards, J.Chem.Soc., 1949, 2929.

19. H.H.G.Jellinek, Trans.Faraday Soc., 40, 266 (1944).

20. Ref.6, Page 56.

21. A.Kossiakoff and F.O.Rice, J.Am.Chem.Soc., 65, 590 (1943).

22. S.L.Madorsky, J.Res.Nat.Bur.Stand., 62, 219 (1959).

23. N.Grassie and H.W.Melville, Proc. Roy. Soc., 199A, 14 (1949)..

24. N.Grassie and H.W.Melville, Proc.Roy.Soc., 199A, 24 (1949).

25. N.Grassie and H.W.Melville, Proc.Roy.Soc., 199A, 39 (1949).

26. N.Grassie and E.Vance, Trans.Faraday Soc., 49, 184 (1953).

27. R.Simha, L.A.Wall and P.J.Blatz, J.Polymer Sci.,5,615 (1950).

28. S.L.Madorsky, J.Polymer Sci., 11, 491 (1953).

29. D.W.Brown and L.A.Wall, J.Phys.Chem., 62, 848 (1958).

30. E.E.Lewis and M.A.Naylor, J.Am.Chem.Soc., 69, 1968 (1947).

31. S.L.Madorsky, V.E.Hart, S.Straus and V.A.Sedlak, J.Res.Nat. Bur.Stand., 51, 327 (1953).

32. N.Grassie and I.C.McNeill, J.Chem.Soc., 3929 (1956).

33. W.J.Burlant and J.L.Parsons, J.Polymer Sci., 22, 249 (1956).

34. N.Grassie and I.C.McNeill, J.Polymer Sci., 27, 207 (1958).

35. N.Grassie and J.N.Hay, J.Polymer Sci., 56, 189 (1962).

36. C.D.Hurd and F.H.Blunck, J.Am.Chem.Soc., 60, 2419 (1938).

37. J.P.W.Houtman, J.Van Steenis and P.M.Heertjes, Rec.Trav.Chim., 65, 781, (1946).

38. A.Maccoll, J.Chem.Soc., 3398 (1958).

39. N.Grassie, Trans.Faraday Soc., 48, 379 (1952).

40. E.J.Arlman, J.Polymer Sci., 12, 547 (1954).

41. D.H.Grant and N.Grassie, Polymer, 1, 125 (1960).

42. P.D.Ritchie, Ref.8, Page 107.

43. E.P.Goodings, Ref.8, Page 211.

44. I.C.McNeill, European Polymer J., 4, 21 (1968).

45. B.J.D.Torrance, Ph.D. Thesis, University of Glasgow, 1967.

46. N.Grassie and B.J.D.Torrance, J.Polymer Sci., A-1, 6, 3303, (1968).

47. N.Grassie and B.J.D.Torrance, J.Polymer Sci., A-1. 6, 3315, (1968).

48. R.B.Fox, L.G.Isaacs, S.Stokes and R.E.Kagarise, J.Polymer Sci., A, 2, 2085 (1964).

49. J.Strassburger, G.M.Brauer, M.Tryon and A.F.Forziati, Anal. Chem., 32, 454 (1960).

50. J.W.C.Crawford, J.Soc.Chem.Ind., 68, 201 (1949).

51. N.Grassie and J.R.MacCallum, J.Polymer Sci., A, 2, 983 (1964)

52. D.H.Grant and N.Grassie, Polymer, 1, 445 (1960)

53. J.R.Schaefgen and I.M.Sarasohn, J.Polymer Sci., 58, 1049 (1962).

54. S.Straus and S.L.Madorsky, J.Res.Nat.Bur.Stand., 50, 165 (1953).

55, R.T.Conley, Proc.Battelle Symp., 'Thermal Stability of Polymers' Columbus, Ohio, 1963, Jl.

56. C.J.Noel, Am.Chem.Soc., Div.Polymer Chem., Polymer Preprints, 4(1), 378 (1963).

57. H.McCormick, J.Chromatog., 40, 1 (1969).

58. C.E.Rehberg and C.H.Fisher, J.Am.Chem.Soc., 66, 1203 (1944). and C.E.Rehberg, W.A.Faucette and C.H.Fisher, J.Am.Chem.Soc., 66, 1723 (1944).

59. Handbook of Chemistry and Physics, 45th Edition, The Chemical Rubber Co., 1964.

60. J.D.Fortune, B.Sc. Thesis, University of Glasgow, 1965.

61. J.Gemmell, B.Sc. Thesis, University of Glasgow, 1965.

62. M.S.Mathieson, E.E.Auer, E.B.Bevilacqua and E.J.Hart, J.Am. Chem.Soc., 73, 5395 (1951).

63. M.Devaleriola, Bull.Soc.Roy.Sci.Liège, 30, 36 (1961).

64. H.W.Melville and A.F.Bickel, Trans.Faraday Soc., 45, 1049 (1949).

65. Polymer Handbook, Ed. J.Brandrup and E.H.Immergut, Interscience Publishers, New York, 1965, page VIII-2.

66. P.J.Flory, 'Principles of Polymer Chemistry', Ch 7, Cornell University Press, 1953.

67. R.U.Bonnar, M.Dimbat and F.H.Stross, 'Number Average Molecular Weights', Interscience Publishers, New York, 1958.

68. R.H.Müller and H.J Stolten, Anal.Chem., 25, 1103 (1953).

69. B.Enoksson, J.Polymer Sci., 3, 314 (1948).

70. P.E.Slade and L.T.Jenkins, 'Techniques and Methods of Polymer Evaluation', Vol.1 'Thermal Analysis', Arnold, London, 1966.

71. D.A.Anderson and E.S.Freeman, J.Appl.Polymer Sci., 1, 192 (1959)

72. J.H.Flynn and L.A.Wall, J.Res.Nat.Bur.Stand., 70A, 487 (1966).

73. I.C.McNeill, J.Polymer Sci., A-1, 4, 2479 (1966).
European Polymer J., 3, 409 (1967).

74. I.C.McNeill, Second International Conference on Thermal Analysis, Worcester, Massachusetts, 1968.

75. N.Grassie and H.W.Melville, Proc.Roy.Soc., 199A, 1 (1949).

76. D.R.Bain, Ph.D. Thesis, University of Glasgow, 1968.

77. S.Hasegawa, Rev.Phys.Chem.Japan, 19, 141 (1945).

78. N.Grassie, Unpublished Work.

79. A.Servotte and V.Desreux, J.Polymer Sci., C, 22, 367 (1968).

80. R.Ryhage, Arkiv Kemi, 26, 305 (1966).

81. A.Cornu and R.Massot, 'Compilation of Mass Spectral Data', Heydon and Sons, 1966.

82. 'Laboratory Methods in Infrared Spectroscopy', Ed. R.G.J.Miller, Heydon and Sons, London.

83. A.D.Cross, 'Introduction to Practical Infrared Spectroscopy', Butterworths, London, 1964.

84. R.J.P.Allan, H.V.R.Iengar and P.D.Ritchie, J.Chem.Soc., 1957, 2107.

85. E.S.Gould, 'Mechanism and Structure in Organic Chemistry', page 346, Holt,Rinehart and Winston, New York, 1965.

86. M.S.Kharasch, J.L.Rowe and W.H.Urry, J.Org.Chem., 16, 905 (1951)

87. R.Shaw and A.F.Trotman-Dickenson, Proc.Chem.Soc., 1959, 61.

88. F.E.Rust, F.H.Suebold and W.E.Vaughan, J.Am.Chem.Soc., 72, 338 (1950).

89. H.C.McBay and O.Tucker, J.Org.Chem., 19,869 (1954).
and J.Org.Chem., 19, 1003 (1954).

90. R.Simha and L.A.Wall, J.Phys.Chem., 56, 707 (1952).

91. J.D.Fortune, Unpublished Communication.

92. H.W.Anderson and G.K.Rollefson, J.Am.Chem.Soc., 63, 816 (1941).

93. J.Shaw, B.Sc. Thesis, University of Glasgow, 1969.

94. A.Charlesby and S.H.Pinner, Proc.Roy.Soc., A249, 367 (1959).