THE THERMAL DEGRADATION OF COPOLYMERS OF n-BUTYL ACRYLATE AND METHYL METHACRYLATE

A thesis submitted to the University
of Glasgow for consideration of the
award of the degree of Doctor of
Philosophy

by

J. D. Fortune
M.Sc.

Chemistry Department

October 1969

SUMMARY

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This study of the thermal breakdown of copolymers of n-butyl acrylate and methyl methacrylate represents a further contribution to the establishment of a comprehensive picture of the degradation of acrylate - methacrylate copolymer systems.

A series of copolymers covering the whole composition range was synthesised. Degradations were carried out under vacuum either in a dynamic molecular still or using a new technique developed in these laboratories. Thermal methods of analysis such as thermogravimetric analysis (T.G.A.) and thermal volatilization analysis (T.V.A.) showed that the copolymers became more stable to thermal breakdown as the acrylate content was increased. These techniques allowed a suitable temperature range to be chosen in which to

study the decomposition isothermally. The gaseous degradation products, liquid products, chain fragments and residue were each examined separately, using, among other techniques, infra-red spectroscopy, gas-liquid chromatography, mass spectrometry and combined gas chromatography - mass spectrometry. The complex nature of the pyrolysis of this copolymer system is reflected by the great variety of products obtained. The main gaseous products were found to be carbon dioxide and but-1-ene, while the most important liquid products are methyl methacrylate and n-butanol. Quantitative measurements enabled the build up of these products to be followed as degradation proceeds, and mass balance tables were drawn up for each copolymer studied. Pyrolysis was carried out mainly at 313°C but in order to investigate the relationship between carbon dioxide formation and chain scission, a lower temperature, 237°C, was chosen so that this study would not be complicated by large scale volatilization processes. The chain fragments were only briefly examined. Molecular weight measurements on the residue indicated that breakdown by random scission processes becomes more important relative to breakdown by depolymerization processes as the acrylate content was increased. An overall degradation scheme is presented and mechanisms are postulated to account for the formation of all of the important products, although no really satisfactory route for alcohol evolution has been found.

ACKNOWLEDGEMENTS

The work described in this thesis was carried out in the period October 1966 to September 1969 at the University of Glasgow, in the Department of Physical Chemistry, which is under the direction of Professor J. M. Robertson,C.B.E.,F.R.S.

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My thanks are due to the U.S. Air Force(Department of Aerospace Research) for the award of a research scholarship, during the tenure of which this work was carried out.

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The sol-gel analysis data were obtained by J. N. Shaw,B.Sc. and are described in his B.Sc. thesis(Glasgow University 1969), otherwise the work was carried out by

myself.

For the sake of completeness, two earlier papers are included at the end of this thesis.

October 1969 J. D. Fortune

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

In the macromolecular field the term "degradation" is usually defined so that it includes any process which brings about a permanent chemical or physical change in the structure of a polymer. This change may be brought about by many agencies such as heat, light, mechanical strain or oxygen, acting either singly or in combination. Commercially it is important to understand how the properties of a material are affected by a combination of such agencies, and as a first step to this end it is reasonable to study each kind of process in isolation. In this investigation "degradation" implies thermal degradation under vacuum.

Originally, as in the work of Staudinger [1,2] who demonstrated the head to tail arrangement of the monomer units comprising the polystyrene chain, degradation was used to obtain information about polymer structure. With the increasing use of polymeric materials in industry it was often found that the addition of a second component could improve the degradation characteristics of a material when neither the mode of action of this stabilizer, nor, in some cases, the mechanism of breakdown, was known. In commercial poly(methyl methacrylate) small quantities of ethyl acrylate are incorporated into the chain during polymerization to enhance its thermal stability [3], a practice which has been used for many years, while the mechanism of degradation of methyl methacrylate - ethyl acrylate copolymers has only recently been examined [4]. A knowledge of the fundamental processes of polymer breakdown, however, is required before any systematic improvements upon existing materials or new materials for use under specific conditions can be made. Degradation processes in polymers have therefore been the subject of a number of books and monographs [5-10].

Before considering the thermal breakdown of copolymers of methyl methacrylate and n-butyl acrylate it would be pertinent to examine the degradation of the homopolymers of both components of this system and to review current ideas on the decomposition of some relevant copolymer systems.

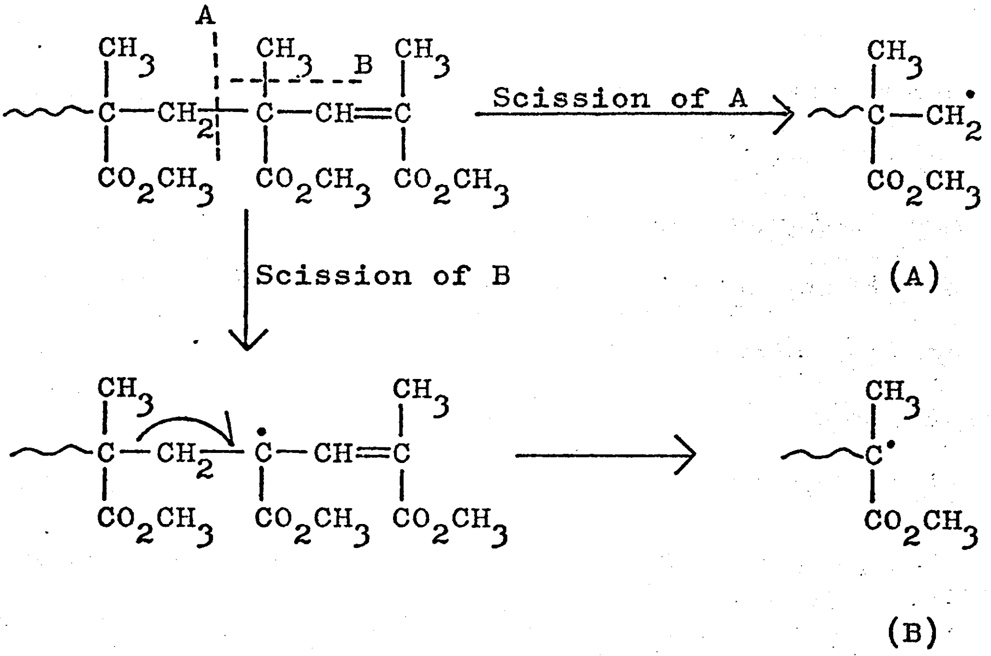
1.2 Degradation of Poly(methyl methacrylate)

Poly(methyl methacrylate) was one of the first polymers found to yield monomer almost exclusively on thermal degradation [11,12]. Investigations were made by Votinov et al [13] who interpreted their results according to the theory of random scission processes developed by Kuhn [14]. Molecular weight measurements made by Grassie and Melville, who carried out a thorough examination of the thermal breakdown of the polymer,[11,15] showed that this interpretation was erroneous, degradation in fact involving reverse polymerization. The expression of this process in mathematical terms by Simha, Wall and Blatz [16], gave satisfactory agreement with the experimental findings of Grassie and Melville.

The radical nature of the chain breaking process was demonstrated by work carried out with a radical inhibitor. To decide where the initial break occurs, measurement of monomer production is useful. In the extreme cases, initiation may be considered to occur solely at chain ends or solely at random in the chain. For the first case the total number of initiation points is inversely proportional to the molecular weight of the polymer, while in the second instance there is no dependence on molecular weight. For molecules whose chain length is less than the zip length of depolymerization, no termination step will take place during degradation, so that the amount of monomer produced per chain scission will be proportional to molecular weight. Thus the overall rate of monomer production will be independent of molecular weight for chain end initiation and directly proportional to it for initiation at random. Experimentally, at 220°C, it has been found that up to initial molecular weights of about 200,000 the rate of monomer production is independent of molecular weight. With the zip length about 2,000 units, confirmation that initiation is from chain ends comes from the fact that after a polymer of initial molecular weight 725,000 had been degraded to just about 50°/o conversion, the same number of molecules was present before as after reaction.

Not all chain ends, however, are equally vulnerable, for at 220°C only 50°/o of a sample prepared using benzoyl peroxide as catalyst was degradable. The disproportionation termination reaction in polymerization [17] introduces equal numbers of two kinds of chain ends, saturated and unsaturated. If one of these types of structure is more thermally stable than the other, then this would account for the experimentally observed result. By using a photo-initiated sample of poly(methyl methacrylate) the fraction of polymer molecules possessing at least one unsaturated end can be increased [11], while by carrying out polymerizations in benzene, a mild transfer agent, the relative number of unsaturated chain ends can be decreased [18]. The percentage of a sample which was degradable at 220°C was found to be just that percentage of molecules which were terminated by at least one unsaturated structure, showing that, in agreement with suggestions based on theoretical grounds [19], these unsaturated ends are the least thermally stable.

At higher temperatures the breakdown appears to follow a different pattern. Brockhaus and Jenckel [20], working at 300°C obtained quantitative amounts of monomer and were able to separate the reaction into stages, the first, a very fast reaction, producing about 50°/o monomer followed by a second slower reaction which goes to 100°/o conversion to monomer. These results have been interpreted in terms of a depolymerization process initiated during the first stage at chain ends and during the second stage at random. The molecular weight measurements of Hart [21] at temperatures over 300°C agree with a random initiation step while programmed work supports the idea of a two stage decomposition as in Fig.1.1 [3,22].



a) Scission at chain ends.

RANDOM SCISSION ⟶ (A) and (B) type radicals.

b) Scission at random in the chain.

Fig.1.1. Scission in poly(methyl methacrylate). [Radicals of type (A) and (B) depolymerize to monomer.]

1.3 Degradation of Polyacrylates

The degradation of homopolymers of the other component of the copolymer system to be studied in this thesis has received much less attention than has poly(methyl methacrylate) degradation. The acrylates in general stand out as a group of polymers whose thermal degradation has been little investigated till recently[23-29]. This may be due in part to the large number of products obtained, which in turn implies a very complex breakdown pattern [12]. In view of the fact that no published review of acrylate degradation is extant, it would seem to be of relevance to this investigation to examine the information available to date on their thermal breakdown. This information is summarised in table 1.1.

(a) Production of Chain Fragments

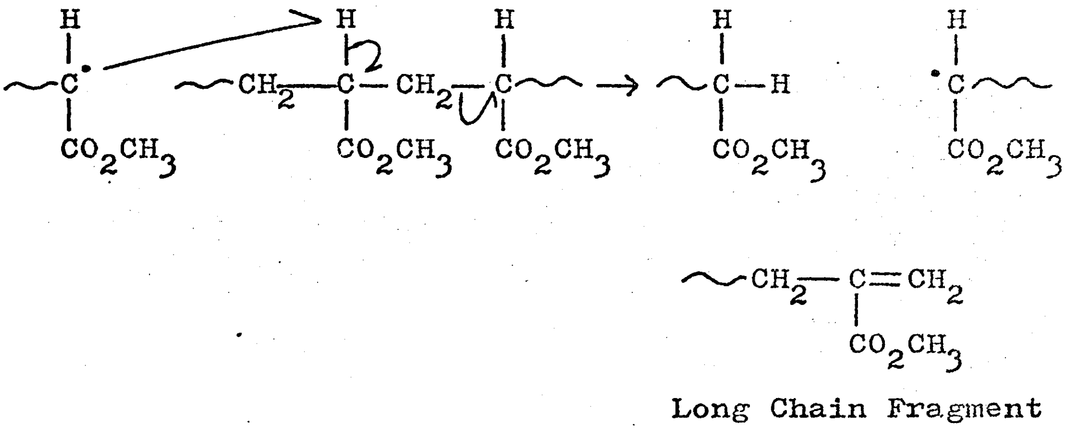
Madorsky [12] was among the first to suggest, on the basis of low monomer yield and the presence, among a variety of products, of chain fragments of molecular weight about 600 in high yield, that the pyrolytic decomposition of acrylates is a random process, involving transfer reactions, the radical nature of which has been demonstrated by Cameron and Kane [27]. Both inter- and intra-molecular transfer take place, the latter being descriptively termed "unbuttoning", and result in the production of long and short chain fragments respectively. Breakdown of the polymer chains by such reactions would introduce terminal double bonds in half of the newly formed chain fragments. Nuclear Magnetic Resonance measurements of these fragments from poly(methyl acrylate)

Table 1.1

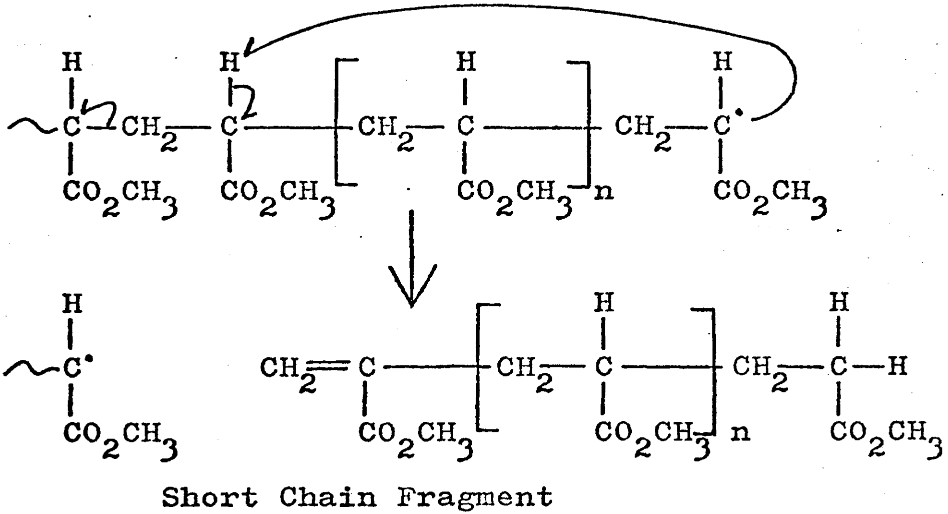
Pyrolysis Products of Polyacrylates

Type of Polyacrylate	Weight Percent Total Volatiles				Temp. °C	Refs.
	Chain Fragments	Alcohol	Carbon Dioxide	Olefin		
Methyl	90	3	5	-	290	12,23,26, 27.
Ethyl	26	28	27	13	315	29.
n-Propyl	26	34	20	14	315	29.
n-Butyl	36	30	15	17	315	29.
Benzyl	50	40	5	-	300	28.
2-Ethyl Hexyl	65	21	5	9	315	29.
iso-Propyl	0	1	32	64	265	29.
tert-Butyl	0	-	3	86	180	24,25.

(Monomer and permanent gases are both less than one percent on the above scale).

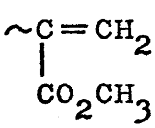


a) Intermolecular transfer.



b) Intramolecular transfer. ("unbuttoning")

Fig.1.2 Transfer reactions in poly(methyl acrylate).

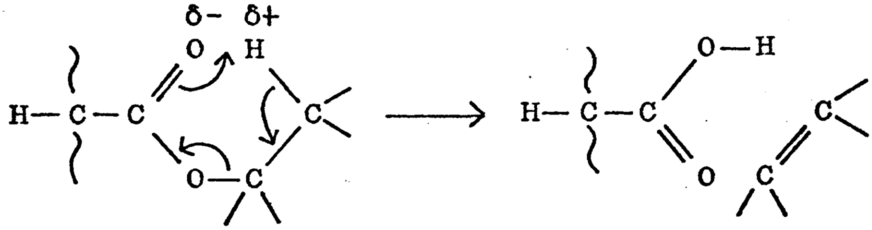
degradation showed two new peaks not found in the undegraded material, characteristic of the terminal methylene structure  $\sim\underset{\displaystyle CO_2CH_3}{\underset{|}{C}}=CH_2$ [30]. Molecular weight measurements and rate of volatilization data for a number of acrylate homopolymers support a random decomposition process [28,29]. Unlike the methacrylate series, end initiated degradation is unimportant.[27]

(b) Ester Decomposition Reactions

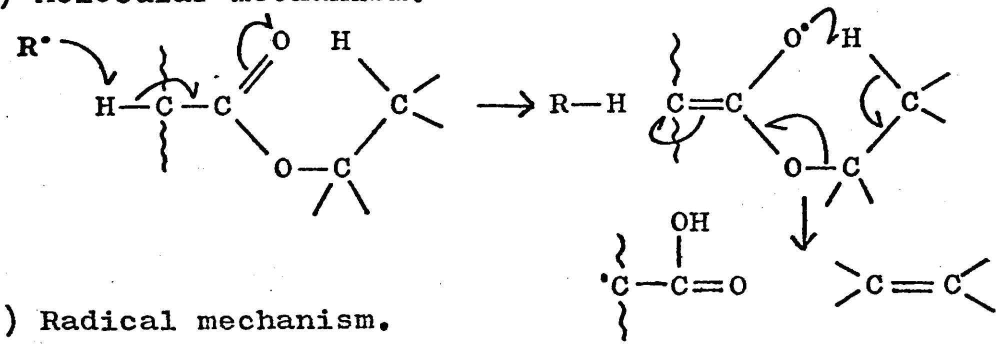
The stability of the acrylate esters is in the expected order primary > secondary > tertiary [31], which may be easily verified from the temperatures chosen in table 1.1 at which to study their breakdown.

Ester decomposition to olefin and acid depends upon the availability of a β hydrogen atom in the alkyl group of the ester [32,33]. This reaction occurs to the exclusion of transfer in secondary and tertiary acrylate esters, but is of much less consequence in primary polyacrylates.

Mechanistically it has been written both as a radical reaction, as in the decomposition of poly(n-butyl acrylate) [29] and as a molecular reaction, as in poly(t-butyl acrylate) degradation [24]. The addition of a radical scavenger to poly(t-butyl acrylate) did not inhibit isobutene formation which displayed autocatalytic behaviour being accelerated by the acid residues from units already decomposed [25]. In contrast to this no autocatalysis has been reported in the evolution of olefin from any of the primary polyacrylates studied [29]. Grassie and MacCallum [34] found that poly(n-butyl methacrylate) can undergo ester decomposition at a temperature very much lower than that found for primary esters decomposing molecularly and suggested that a radical mechanism was involved. The elimination of olefin from poly(iso-propyl acrylate), a polymer with a secondary ester group is catalyzed to only a limited extent by neighbouring acid residues [29]. This behaviour is to be expected since acid groups are being extensively lost as carbon dioxide, hence less are available to catalyze further decompositions. It would appear that as the ester group considered is changed from tertiary, through secondary to primary, so the mechanism of breakdown becomes more radical in nature.



a) Molecular mechanism.



b) Radical mechanism.

Fig.1.3 Ester decomposition in acrylates.

(c) Production of Carbon Dioxide

Carbon dioxide is to be found among the products of degradation of all of the acrylate polymers so far examined. It could be produced by decarboxylation of acid residues remaining on the main chain after ester decomposition has occurred, but the fact that it is also present when materials such as poly(methyl acrylate), which cannot undergo ester decomposition to olefin and acid, are pyrolyzed [27], means that the ester group must be able to degrade in some other fashion to evolve this gas. Decomposition of anhydride units formed when adjacent acid residues eliminate water is a possible third route to carbon dioxide production but cannot account for significant amounts of the gas under the conditions employed [29]. Cameron and Kane [27] have shown by inhibitor experiments that the process involved is a radical one and have suggested a possible route, similar to the scheme proposed by Fox et al [35] and invoked by Grassie and Torrance [36], Fig.1.4. Such a mechanism introduces methyl methacrylate units into the poly(methyl acrylate) chain which may, by unzipping, account for the small amounts of this compound found in the degradation products, although other routes have been put forward [27].

If this were the only way in which the acrylates

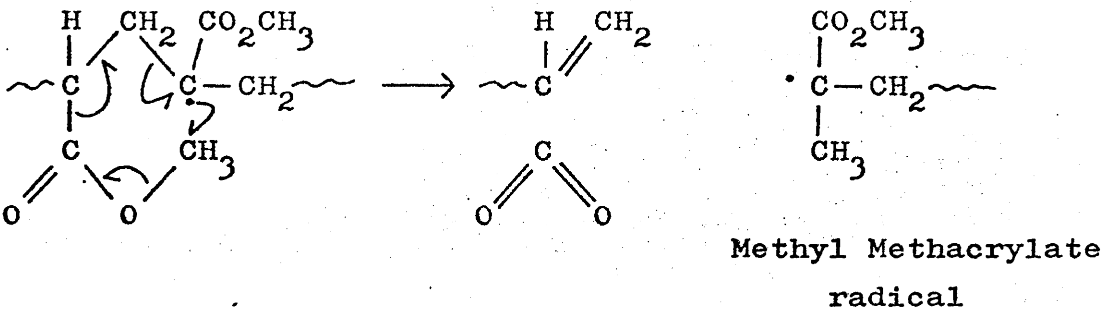


Fig.1.4 Elimination of carbon dioxide from poly(methyl acrylate).

could eliminate carbon dioxide then it would be reasonable to expect to find, in the breakdown products of any poly(alkyl acrylate), traces of the corresponding monomeric alkyl acrylate substituted in the α position by the same alkyl group as in the ester part of the molecule. As these materials have never been reported, there appears to be another route involved such as decarboxylation.

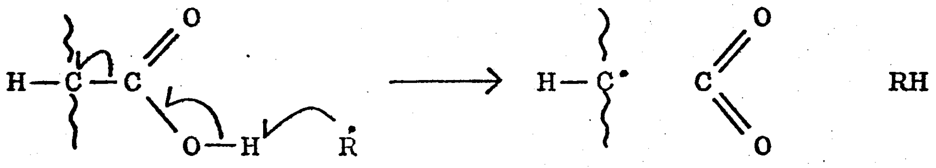


Fig.1.5 Decarboxylation of a carboxylic acid residue.

(d) Production of Alcohol

For the production of alcohol the most straightforward route would seem to be scission of the acyl-oxygen bond [27].

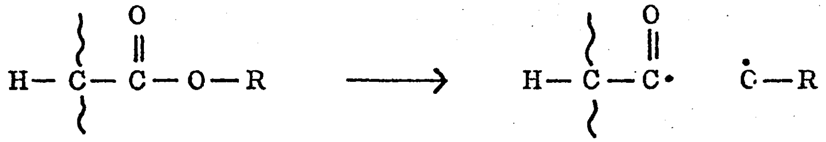


Fig.1.6 Acyl-oxygen fission in acrylates.

This finds no support experimentally, however, because carbonyl radicals are known to be unstable [37], decomposing rapidly into carbon monoxide, which is found in only trace amounts, in no way equimolar to the amount of alcohol produced. In addition a radical inhibitor would not prevent formation of alkoxy radicals by this scheme, but could only prevent these radicals from abstracting hydrogen to form alcohol. Since alcohol formation as outlined is not a chain reaction the inhibitor would soon be used up, the rate of alcohol production returning quickly to its non-inhibited value, but inhibitor experiments on poly(methyl acrylate) have indicated that a trace is sufficient to affect methanol production markedly [27]. The mechanism of Fig.1.6 also implies that alcohol evolution is a property of individual acrylate units whereas work on copolymer systems has shown that sequences of these units are necessary [36,38]. Block copolymers of ethylene and methyl acrylate yield more methanol than do random copolymers of the same overall composition, the quantity of alcohol evolved being a measure of the extent of block formation [38]. To comply with these requirements the following route has been suggested, involving participation of more than one acrylate unit [27].

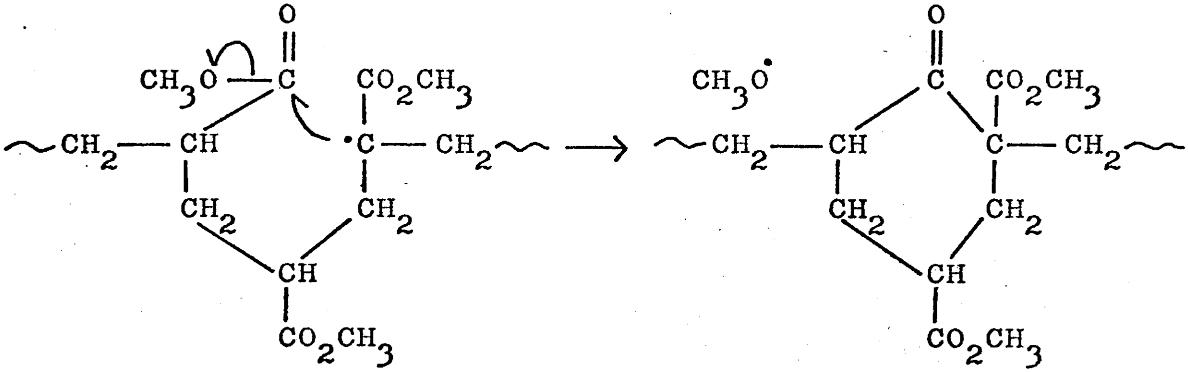
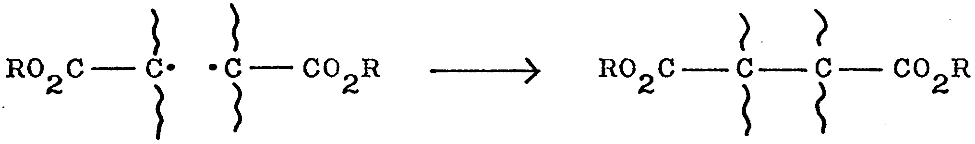


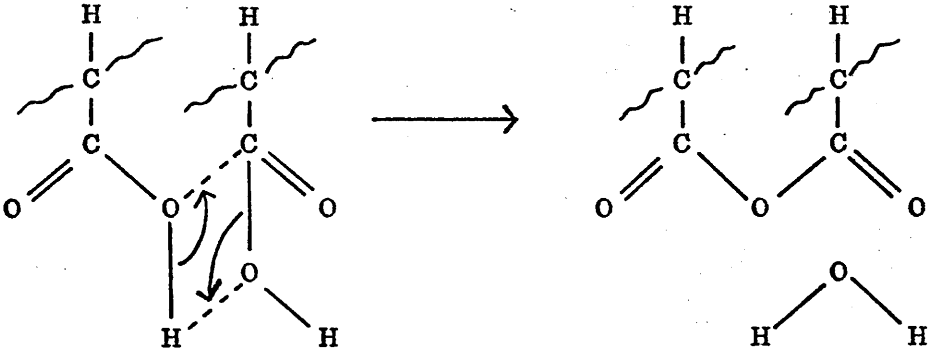
Fig.1.7 Elimination of methanol from poly(methyl acrylate).

(e) Investigation of the Residue

In the acrylate series, the residue remaining after pyrolysis is generally found to be insoluble in non-polar solvents in which the polymer could be dissolved before degradation [29]. This means either that cross-linking has taken place or that rigid structures such as anhydride groups formed by intramolecular condensation reactions are preventing solution. In the latter case the residue would be soluble in polar solvents such as dimethyl formamide [39]. None of the polymeric residues examined were soluble in this compound but both poly(iso-propyl acrylate) [29] and poly(t-butyl acrylate)[25] residues were soluble in reagents capable of hydrolyzing anhydride units, such as alkaline solutions, indicating that to a large extent insolubility is associated with intermolecular anhydride formation. Other types of cross links must be involved to account for the insolubility of primary polyacrylates [27].



a) Cross linking in primary polyacrylates.

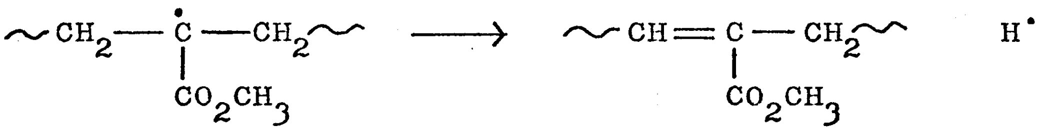


b) Cross linking in non-primary polyacrylates.

Fig.1.8 Cross linking in polyacrylates.

Spectroscopic measurements have confirmed the presence of anhydride functional groups in poly(iso-propyl acrylate) [29] and in poly(t-butyl acrylate) [25] residues.

The coloration observed on degradation of acrylate polymers has been ascribed to the production of conjugated double bond systems. Infra-red and ultra-violet studies support this hypothesis. The initial double bond can be visualised as being formed by a process such as that illustrated in Fig.1.9 [27].



$$\sim CH_2-\underset{\displaystyle CO_2CH_3}{\overset{\bullet}{C}}-CH_2\sim \longrightarrow \sim CH=\underset{\displaystyle CO_2CH_3}{C}-CH_2\sim \qquad H^{\bullet}$$

Fig.1.9 Formation of a double bond in a polyacrylate chain.

The presence of this double bond will tend to weaken the carbon-hydrogen bond in the β position thus rendering it more susceptible either to thermal scission or to attack by a free radical. Scission of this bond followed by abstraction of a hydrogen atom from the adjacent methylene group can give rise to molecular hydrogen, and this has been detected in the products of degradation of poly(benzyl acrylate). Such a process gives rise to a conjugated system of double bonds in the polymer chain.

(f) Production of Permanent Gases

The evolution of hydrogen has been dealt with in the previous section.

Carbon monoxide may be formed by the breakdown of carbonyl radicals formed as in Fig.1.6. Decomposition of

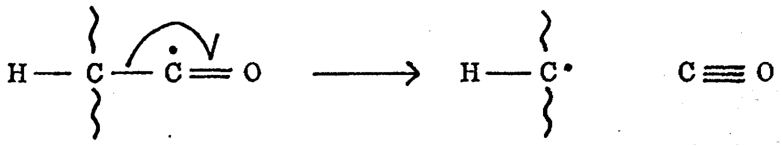


Fig.1.10 Production of carbon monoxide.

anhydride groups with evolution of this gas may also be involved.

1.4 Degradation of Copolymers

A great deal of work has been carried out on copolymer systems with methyl methacrylate as one of the components [40]. The addition of even a small amount of a second component can modify the degradation characteristics of the copolymer quite markedly from those observed in pure poly(methyl methacrylate). In some cases neighbouring group interactions result in a mode of breakdown not found in degradation of the homopolymers of either of the comonomers [41]. For example methyl methacrylate - vinyl chloride copolymers when heated to temperatures as low as 150°C evolve methyl

Comonomer	Degradation Characteristics
Acrylonitrile	Side group reactions
Ethyl methacrylate	Depolymerization
Styrene	Depolymerization and transfer
Methyl acrylate	Random scission and transfer

Table 1.2 Classification of degradation mechanisms.

chloride in almost quantitative yields, but otherwise appear to be quite stable, not undergoing the coloration reaction usually associated with poly(vinyl chloride)[42]. It is most convenient to classify methyl methacrylate copolymers according to the mechanism of degradation of the comonomer as in table 1.2.

(a) Degradation of Acrylonitrile - Methyl Methacrylate Copolymers

Grassie and Farish[43] have studied the degradation of a series of acrylonitrile - methyl methacrylate copolymers which contained less than 13 mole percent acrylonitrile. Materials with greater amounts of acrylonitrile are difficult to handle since polyacrylonitrile itself decomposes by reaction of its nitrile substituents to yield an insoluble, crosslinked, coloured residue[44]. The homopolymer is more thermally stable than poly(methyl methacrylate) losing less than 30°/o of its weight by 300°C[45]. Two temperatures, 220°C and 280°C have been used to study the copolymers.

At the higher temperature, molecular weight data showed that the amount of weight loss per chain scission is constant throughout the composition range dealt with. This weight loss corresponds to the weight of the liquid volatiles which g.l.c. and infra-red showed to be methyl methacrylate and acrylonitrile. The thermal stability of the copolymers increases, while the rate of molecular weight drop decreases, with increasing acrylonitrile content.

At the lower temperature, the production of liquid volatiles shows an inhibition period which becomes less well defined the lower the methacrylate content [11]. During this period the molecular weight of the polymer fell drastically. The rate of monomer evolution reaches a maximum after two to three hours.

It was originally supposed that the acrylonitrile units act as "weak links" at or near which scission can occur, but the rate of molecular weight drop data rule this out. At the lower temperature, methyl methacrylate degrades from chain ends, unzipping until the first acrylonitrile unit is reached, through which this depolymerization cannot pass. Random scission may be imagined to occur slowly in the methacrylate chain at this temperature, being followed by a disproportionation step, producing one saturated and one unsaturated end. As the concentration of chain ends increases so will monomer production, unzipping taking place from the unsaturated ends. This process can account for the rate maximum found for methyl methacrylate evolution. In poly(methyl methacrylate) itself this scission reaction must be obscured by the much faster chain end initiated breakdown.

At 280°C random initiation occurs in the methyl methacrylate chain producing radicals which can immediately depropagate to monomer. These radicals must be able, at this temperature, to unzip through acrylonitrile units since the molecular weight versus percentage volatilization curves are identical for all of the copolymers and acrylonitrile appears among the liquid products.

(b) Degradation of Ethyl Methacrylate - Methyl Methacrylate Copolymers

Since ethyl methacrylate degrades by the same mechanism as does methyl methacrylate it would be reasonable to expect very little, if any, interference with the initiation or propagation steps, and this has been experimentally verified [3].

(c) Degradation of Styrene - Methyl Methacrylate Copolymers

In this well studied system of copolymers [3,46,47], it has been established that the number of "weak links" is proportional to the styrene content, and that "weak link" properties are exhibited by copolymers where as much as 87°/o of the styrene units present are isolated. Grassie, Kerr and Cameron [48-50] postulated that "weak links" involved the reaction of a polystyryl radical in one of its alternative canonical forms, formulating a breakdown mechanism which called for the presence of two adjacent styrene units. This scheme, however, can be modified to fit the experimental finding that only one styrene unit need be involved [46].

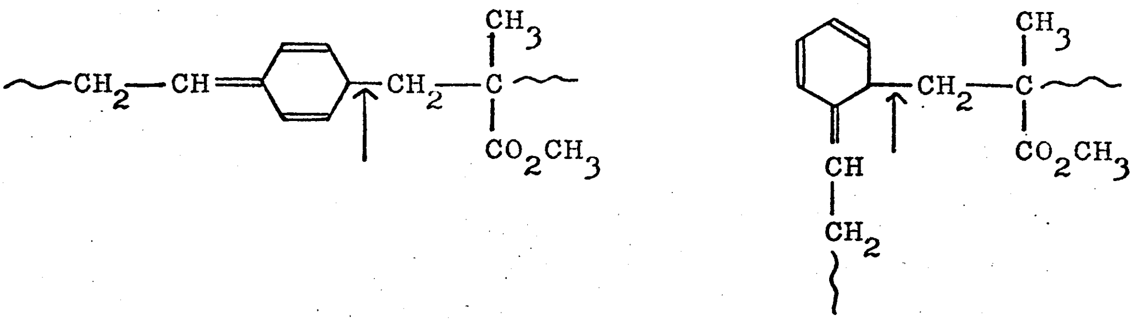


Fig.1.11 Possible structures of "weak links"[arrowed].

There is at present a great deal of controversy surrounding the topic of "weak links" [51-54].

From a copolymer containing 20 mole percent methyl methacrylate the weight ratio of styrene monomer to non-monomer among the products is 12:1 compared with approximately 1:1 in pure polystyrene. Thus small amounts of methyl methacrylate greatly affect the transfer process. The experimental ratio of 12:1 is only realised when it is assumed that sequences of up to ten styrene units yield only monomer.

The initial rate of depolymerization of an 80 mole percent methacrylate copolymer at 300°C is about half that of pure poly(methyl methacrylate) at 260°C which means that replecement of 20°/o of the methyl methacrylate by styrene has increased the thermal stability by a factor of about twenty. This disproportionate increase in stability may be accounted for by two effects:-[3]

i) The number of susceptible unsaturated methyl methacrylate chain ends has been drastically reduced by a cross termination step involving combination being predominant in the polymerization reaction. Measurements made on a 17 mole percent styrene copolymer showed that only 8°/o of the termination steps involved disproportionation [17].

ii) Styrene blocks the unzipping methacrylate radical in much the same way as does acrylonitrile, because of the stability of the styryl radical [3]. As in other copolymer systems, these will not degrade until temperatures are attained at which polystyrene itself will decompose [55].

(d) Degradation of Acrylate - Methyl Methacrylate Copolymers

(d.1) Copolymers of Methyl Acrylate with Methyl Methacrylate

Grassie and Torrance [36] examined copolymers in the composition range 0.01 to 33 mole percent acrylate. As the acrylate content is increased, the thermal stability also improves. This enhancement of stability may be attributed, as before, to the blocking effect of comonomer units, in this case acrylate, and to the introduction of a cross termination step in the polymerization which involves combination [56].

The rapid decrease in the molecular weight during degradation suggests that a random process is involved. The products of breakdown, carbon dioxide, chain fragments, monomers and a permanent gas fraction which is principally hydrogen, are much as might be predicted from a knowledge of the decomposition of the homopolymers. No methanol has been reported, which seems to be at variance with the results of Strassburger et al [57] who found this alcohol in the degradation products of a methyl methacrylate - methyl acrylate copolymer containing only 20 mole percent acrylate. In this latter case, however, polymerization was taken to a very high degree of conversion, so that long sequences of acrylate units must have become incorporated into some of the chains. Since it has already been pointed out that alcohol production from acrylates is a function of sequence length the above results are not incompatible.

Spectroscopic measurements show that the coloration which occurs on prolonged heating is due to conjugated carbon-carbon unsaturation in the polymer backbone.

It has been reported that a 1:1 correspondence exists between the amount of carbon dioxide produced per polymer molecule and the number of chain scissions in the temperature range 270°C to 325°C [36], so that measurement of carbon dioxide production can be used to determine the number of chain scissions which have taken place. Using this relationship it was found that the zip length of depolymerization decreased from 173 to 34 as the acrylate content rose from 0.01 to 33 mole percent.

In order to fit the experimentally determined kinetics, it has been suggested that transfer reactions occur involving not only tertiary hydrogen atoms, but also those of the methylene groups. The radicals so formed must then eliminate carbon dioxide in any scission reaction in which they take part, to preserve the 1:1 chain scission:carbon dioxide relationship.

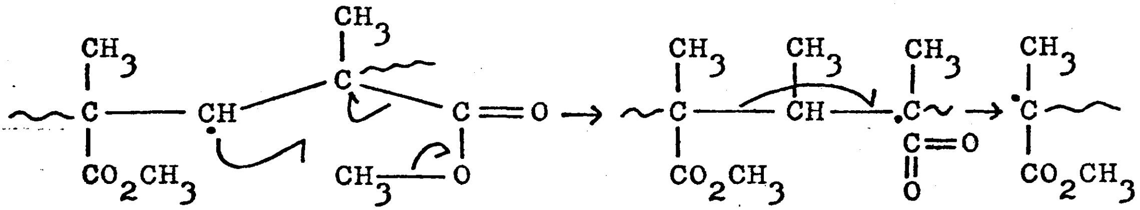


Fig.1.12 Carbon dioxide elimination after hydrogen abstraction from a methylene group.

A comprehensive reaction scheme has been presented for this system [36].

(d.2) Copolymers of other Acrylates with Methyl Methacrylate

The thermal breakdown of acrylate - methyl methacrylate copolymers has been studied uding pyrolysis-g.l.c. [58]

The amount of ethyl acrylate monomer evolved from a 25 mole percent ethyl acrylate - methyl methacrylate copolymer was more than twice that evolved by the acrylate homopolymer, although the amount of ethyl acrylate in the copolymer is one quarter that in the homopolymer. This type of effect was found to be general in the acrylate - methyl methacrylate series. A constant ratio was found between the relative amounts of methyl methacrylate and acrylate in the copolymer and in the degradation products.

1.5 Summary

The overall picture presented by the previous work on homopolymers and copolymers of acrylates and methacrylates may be briefly summarised as follows.

The degradation characteristics of a polymer are governed largely by the availability of suitable atoms to take part in transfer reactions and the stability of the degrading radical. In the poly(n-butyl acrylate) chain, every second carbon atom has a tertiary hydrogen attached to it, and since the relative reactivity of primary to secondary to tertiary hydrogen atoms is about 1:3:33 [5], transfer is an important process. Polymers of α,α disubstituted monomers tend to produce stable degrading species so that depolymerization , as opposed to transfer, is favoured. Methyl methacrylate is just such a monomer, and since its polymer chain has no tertiary hydrogen atoms, depolymerization predominates.

The behaviour of the methyl methacrylate copolymers examined can be explained generally by the comonomer unit blocking the unzipping of methacrylate radicals and by the appearance of a cross termination step in the polymerization involving combination.

1.6 Aims of the Present Work

It is clear from the above discussion that a good deal of work has been done in the field of the thermal degradation of homopolymers and copolymers of acrylates and methacrylates and a coherent overall picture is beginning to emerge. The thermal degradation reactions which occur in homopolymers of acrylates and in the methyl acrylate - methyl methacrylate copolymer system have been clarified. As a further contribution to the establishment of a comprehensive picture of this field of polymer degradation it was considered useful to investigate further acrylate - methacrylate copolymer systems. The n-butyl acrylate - methyl methacrylate system was chosen in particular so that the effect of the replacement of a methyl group by a butyl group in the acrylate component might be observed. This change in structure should allow a slightly wider spectrum of reactions to occur, in particular the type of ester decomposition process which is impossible in methyl esters.

CHAPTER 2

EXPERIMENTAL

2.1 Synthesis of Copolymers

(a) Purification of Monomers

Methyl methacrylate (B.D.H. Ltd.) and n-butyl acrylate (Koch-Light Laboratories Ltd.) were washed with a 10°/o solution of caustic soda to remove inhibitor, and then with distilled water. They were dried over calcium hydride for at least twenty four hours and were stored at -18°C. Before use they were thoroughly degassed and distilled twice on a vacuum line, the first and last 10°/o of each distillation being discarded. The monomers were distilled into graduated reservoirs in this second distillation.

(b) Purification and Introduction of Initiator

The initiator, 2,2'-azo-bis-isobutyronitrile (Kodak Ltd.) was recrystallised from absolute alcohol (m.pt.104°C) and made up as a standard solution in Analar benzene. 5ml. of this solution were added to a 100ml. dilatometer, and the benzene removed under vacuum. The initiator concentration used was 0.17°/o weight/volume.

(c) Preparation and Purification of Copolymers

The volume of each of the comonomers required to obtain a copolymer of a given composition was calculated using the published values of the reactivity ratios, namely 1.8 for methyl methacrylate and 0.37 for n-butyl acrylate [59]. These calculated volumes were then distilled into a dilatometer from the graduated reservoirs referred to above.

Polymerizations were carried out in bulk at 60°C and taken to a maximum of 8°/o conversion. With copolymers of high acrylate content only 3 or 4°/o conversion could be reached because of the high viscosity of the reaction mixture. The polymerizations were stopped by quenching in liquid nitrogen. The dilatometers were then cut open, the contents taken up in Analar toluene and the polymer precipitated by addition to excess Analar methanol. The copolymer was filtered and dried under vacuum. This procedure was repeated three times. Those polymers with a high methacrylate content precipitated as a fine powder, while acrylate rich samples came down as rubbery solids. All of the copolymers were finally freeze-dried from benzene solution. Thermal Volatilization Analysis [60] (2.5a) showed that the copolymers of high methacrylate content still retained traces of solvent, but it was not found possible to remove this.

In addition to seven copolymers covering the whole composition range, a methyl methacrylate homopolymer was

Table 2.1

Copolymer Composition and Molecular Weight Data

Composition (mole percent n-butyl acrylate)	Number Average Molecular Weight, $\overline{M}_n$
0	421,000
0.4	361,000
3.9	337,000
16.3	422,000
50.0	100,000
52.4	1,330,000
82.2	52,500
93.4	76,500

synthesised. Homopolymers of n-butyl acrylate were also available so that it was possible to examine the degradative behaviour of the entire composition range.

Copolymer composition and molecular weight data (2.4) are summarised in table 2.1.

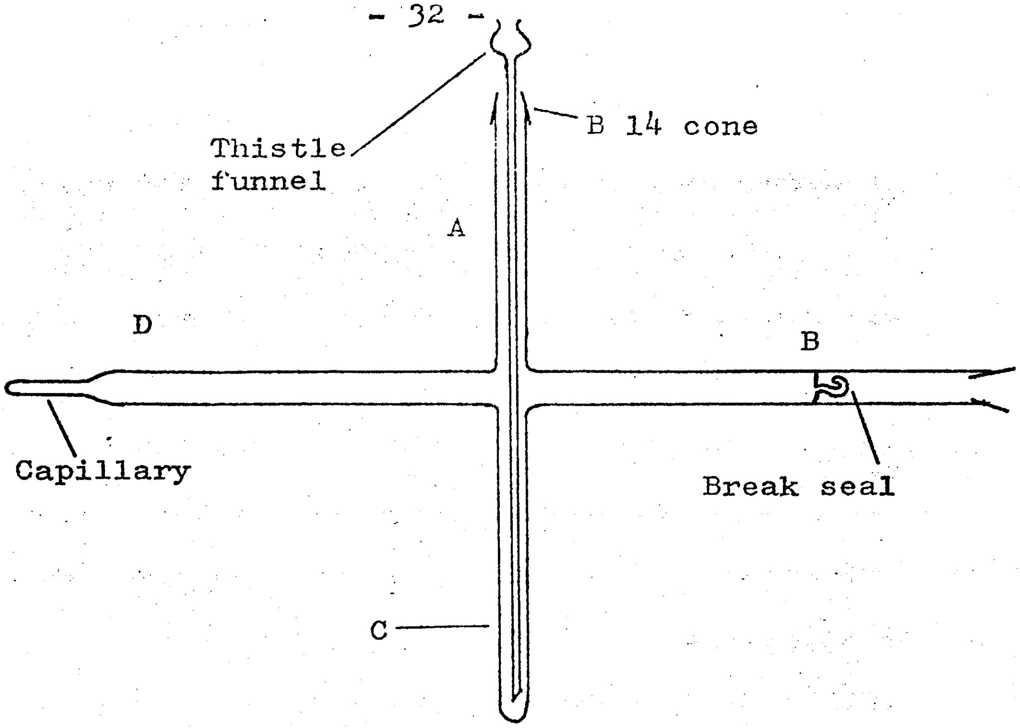
2.2 Degradation Apparatus

During this investigation two types of degradation apparatus were used, namely the sealed tube and the glass still. These are dealt with in the sections following.

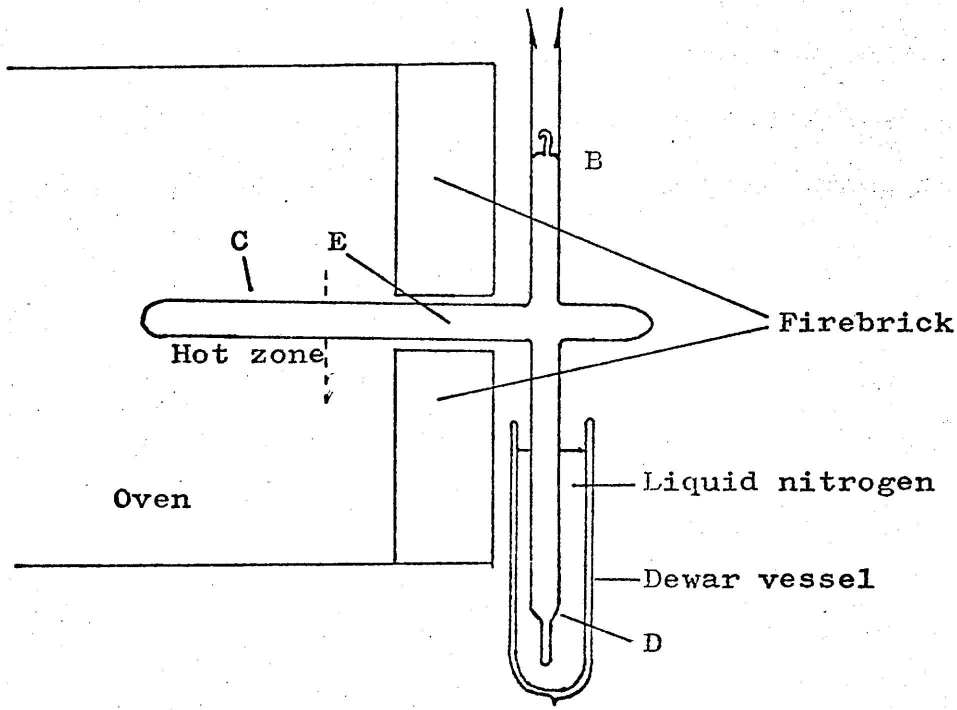
(a) The Sealed Tube

(a.1) Experimental Conditions

Fig.2.1 shows a diagram of a sealed tube.



(a) Filling sealed tube.



(b) Degradation by the sealed tube technique.

Fig.2.1 The sealed tube technique.

Copolymer solutions in Analar toluene (50mg. per ml.) were pipetted into limb C. The toluene was removed under vacuum so that a film of copolymer was deposited on the walls of the tube at C. When all the solvent had been removed the tube was sealed off at A under sticking vacuum. Limb C was then placed in an oven at the required degradation temperature, while limb D was immersed in liquid nitrogen. Degradation products leaving the hot zone condensed either on the part of the tube passing through the furnace fire-brick E or in limb D depending upon their volatility. When the degradation had proceeded for the required time, the sealed tube was removed from the furnace and stored at -18°C until required. The oven was a Catterson-Smith G31LX Electric Furnace controlled by an Ether Transitrol Controller, and its temperature could be maintained to ±1°C. This temperature was monitored throughout the degradation by a thermocouple sealed into an evacuated tube similar to the one containing the polymer sample and placed symmetrically with respect to it within the furnace. The thermocouple output was fed into a Honeywell Brown recorder so that any deviation of the furnace temperature from that required could be quickly noted and rectified.

The sample size degraded by this method normally ranged from 100 to 500mg., but when analysis of the small amount of permanent gases evolved was required, much larger samples up to 1.5g. were necessary. The fact that only small amounts of non-condensable material is produced renders invalid one criticism often levelled at degradation systems which are not continuously pumped, namely that diffusion of degradation products from the hot zone is inhibited by the increase in pressure in the system thus encouraging secondary reactions to take place. The sealed tube technique is particularly useful when the examination of decomposition products, including chain fragments, is to be carried out [29].

(a.2) Product Analysis

In this work the terms "gaseous products" and "gases" mean gases condensable at liquid nitrogen temperature, and do not normally include the permanent gases, which were found to be present in only very small quantities.

For the analysis of degradation products the sealed tube containing degraded polymer is attached to a vacuum line at B, and the capillary on limb D in which the liquid degradation products have collected is cooled in an ice-water bath. The break seal is then broken using a glass covered metal weight, and the gaseous decomposition products are distilled for exactly one minute into a suitable receiver cooled in liquid nitrogen. This technique involving distillation of product gases for a set time was made necessary, especially in copolymers of high methacrylate content, by the volatility of some of the liquid degradation products. The normal procedure followed was to distil the gases firstly into the constant volume manometer (2.3a) to make pressure measurements. From there they were distilled into an infra-red gas cell (2.9a) and then, a spectrum having been run, they were sealed in a glass sample vessel. This container was fitted with a break seal to enable the gases to be withdrawn for further examination if required, while avoiding the possibility of leaks or of the contents being absorbed on tap grease.

To obtain samples of the permanent gases produced in degradation a different procedure was used. The capillary part of the sealed tube was immersed in liquid nitrogen and the products remaining gaseous were collected in a sample bulb using a Topler pump.

The residue, chain fragments and liquid volatiles were separated by cutting the sealed tube in the appropriate places as they all collected in different parts at C, E and D respectively, Fig.2.1. The liquids were weighed, transferred to a suitable container by a Pasteur pipette, and stored at -18°C until required.

(b) The Glass Still

This apparatus is shown in Fig.2.2. It was used to examine molecular weight changes and gas evolution at low extents of volatilization and to obtain spectra of polymers at various stages of their degradation. It was more convenient than the sealed tube for such applications since every degradation carried out by this latter technique required a new tube.

Polymer films were deposited on the flat base of the flange by pipetting in 4ml. of an approximately 50mg./ml. solution of polymer in Analar toluene and removing the solvent under vacuum. The glass still was then assembled as in Fig.2.2 and pumped down to sticking vacuum, the trap being cooled in liquid nitrogen. The electric mantle was heated to give the required degradation temperature then jacked onto the flange, and tap T_2 was closed. When the degradation was completed tap T_1 was closed and the heating mantle removed. Pressure measurements were then made using the McLeod Gauge as in (2.3b). The flange was removed from the vacuum line and the residue dissolved in Analar toluene for molecular weight measurements (2.4).

The electric heater used was an Electrothermal MB602 mantle modified to incorporate two thermocouples. One,

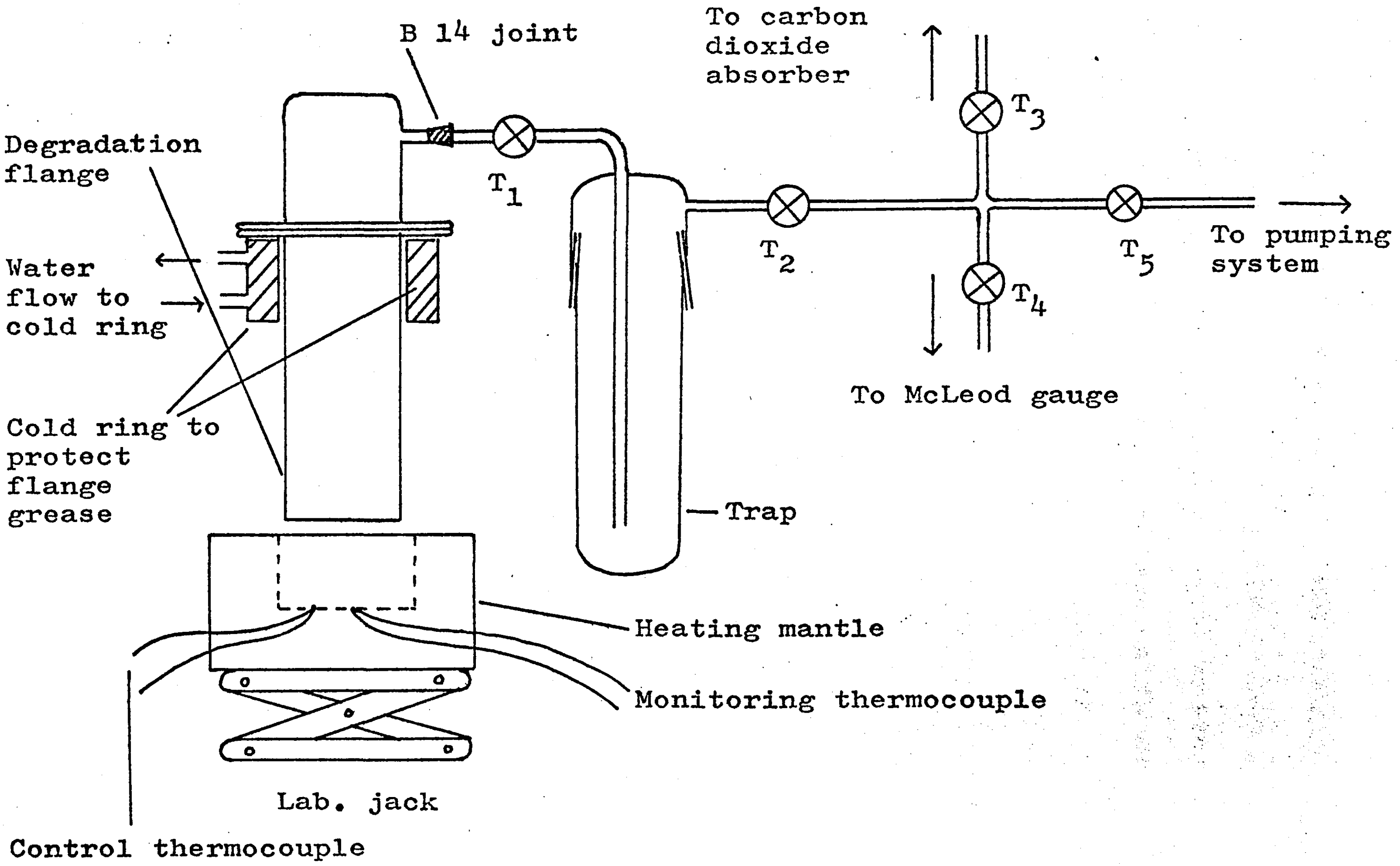


Fig.2.2 The glass still.

the control thermocouple, was connected to an Ether Transitrol Controller while the other, a monitoring thermocouple was connected to a Doran thermocouple potentiometer. The temperature gradient across the bottom of the reaction tube was found by carrying out calibrations in which a third thermocouple was pressed onto the inside surface of the tube where the sample is degraded. This thermocouple was coated with a little Apiezon L grease to simulate the conditions of polymer degradation. For the temperatures used the lag was of the order of 20°C, temperature control being better than ± 2°C.

2.3 Pressure Measurement

Two pressure measuring devices, a constant volume manometer and a McLeod gauge suitable for use in different pressure ranges were used in this work. When data on gas evolution at low percentage conversions were required, as in the investigation of the relationship between carbon dioxide production and chain scission, involving measurement of pressures of the order of 10^{-2}cm. the McLeod gauge was used. On the other hand, when polymers were degraded to higher conversions so that the pressures attained were of the order of several centimetres, use of the constant volume manometer was indicated.

(a) Constant Volume Manometer

The constant volume manometer [61] is shown in Fig.2.3. On the left hand limb, A, of the manometer there was a constant volume mark M. Before any reading was taken it was necessary to adjust the mercury level to this mark. The pressure in the constant volume manometer is given by the difference in height of the mercury columns in limbs A and B. These limbs must be wide enough to avoid any capillary effects.

Before any measurement is made, the manometer is pumped out to sticking vacuum with the mercury all contained in the reservoir. By opening tap T_2 and controlling the pressure above the mercury in the reservoir by suitable adjustments of taps T_3 and T_4 the mercury is brought into limbs A and B. T_2 is now closed and the sample of gas whose pressure is to be measured is distilled into the cold finger which is immersed in liquid nitrogen. Tap T_1 is now closed and the liquid nitrogen removed and replaced by a water bath at 20°C. After equilibrium is attained the mercury level in A is adjusted so that the meniscus is at M, and the pressure read off.

In order to measure absolute quantities of gas the constant volume of the manometer must be known. This was measured by admitting a little nitrogen into the

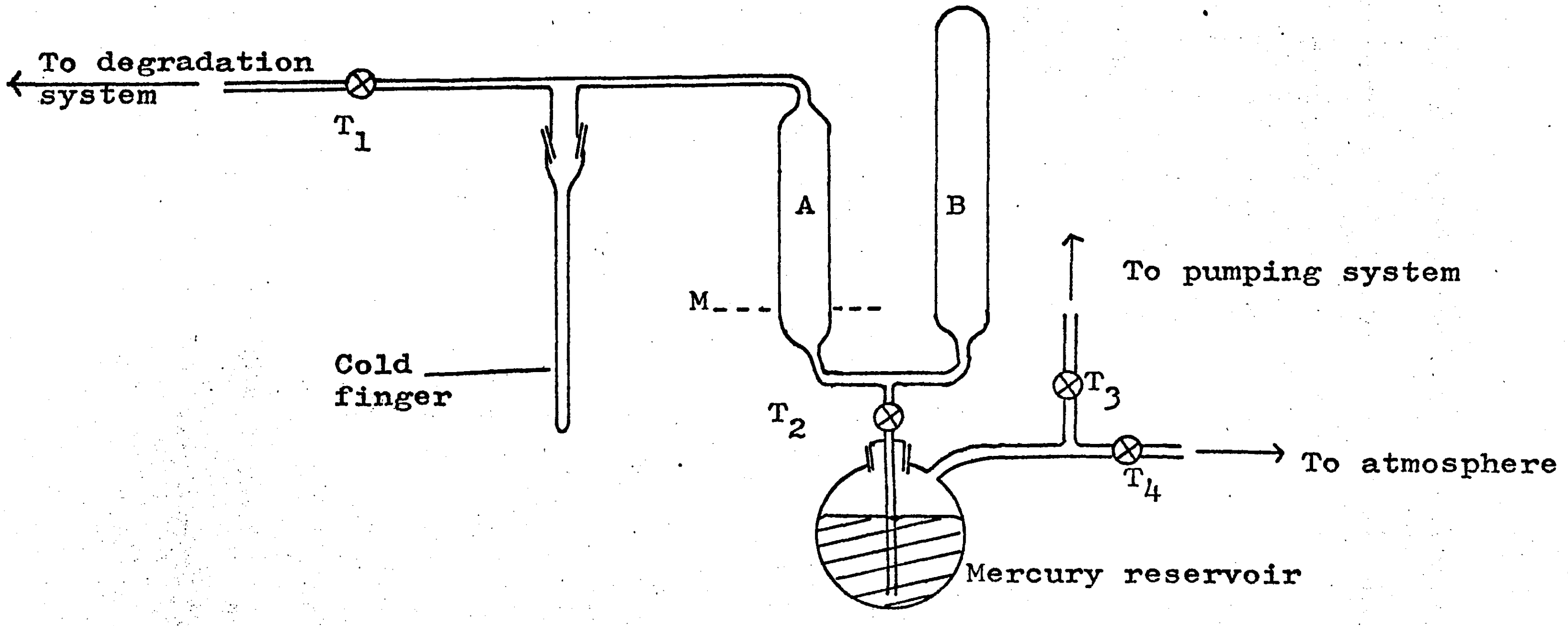


Fig.2.3 Constant volume manometer.

constant volume. A series of pressure versus volume difference readings was then taken on the nitrogen sample, the internal diameter of A being measured by a cathetometer before assembly.

Let V_o be the constant volume of the manometer.

Let V be the volume occupied by the nitrogen sample.

ΔV may be defined such that $V = V_o + \Delta V$.

$pV =$ a constant, where p is the pressure of the gas.

Therefore $p(V_o + \Delta V) =$ a constant.

Therefore $\Delta V = \text{constant}(1/p) - V_o$.

Let r be the internal radius of the limb A.

Let Δh be the height of the mercury in A below mark M.

Then, $\Delta V = \pi r^2.\Delta h$

Therefore $\pi r^2.\Delta h = \text{constant}(1/p) - V_o$.

Therefore

$$\Delta h = \frac{\text{constant}}{\pi r^2}.\frac{1}{p} - \frac{V_o}{\pi r^2}$$

This is of the form $y = mx + c$ so that the plot of Δh versus $1/p$ will have a gradient of $(\text{constant}/\pi r^2)$. From the gradient, V_o may be found since $V_o = (\text{constant}/p_{h=0})$. The results of this calibration are shown in Fig.2.4.

(b) McLeod Gauge

Fig.2.5 is a diagram of the capillary section of a

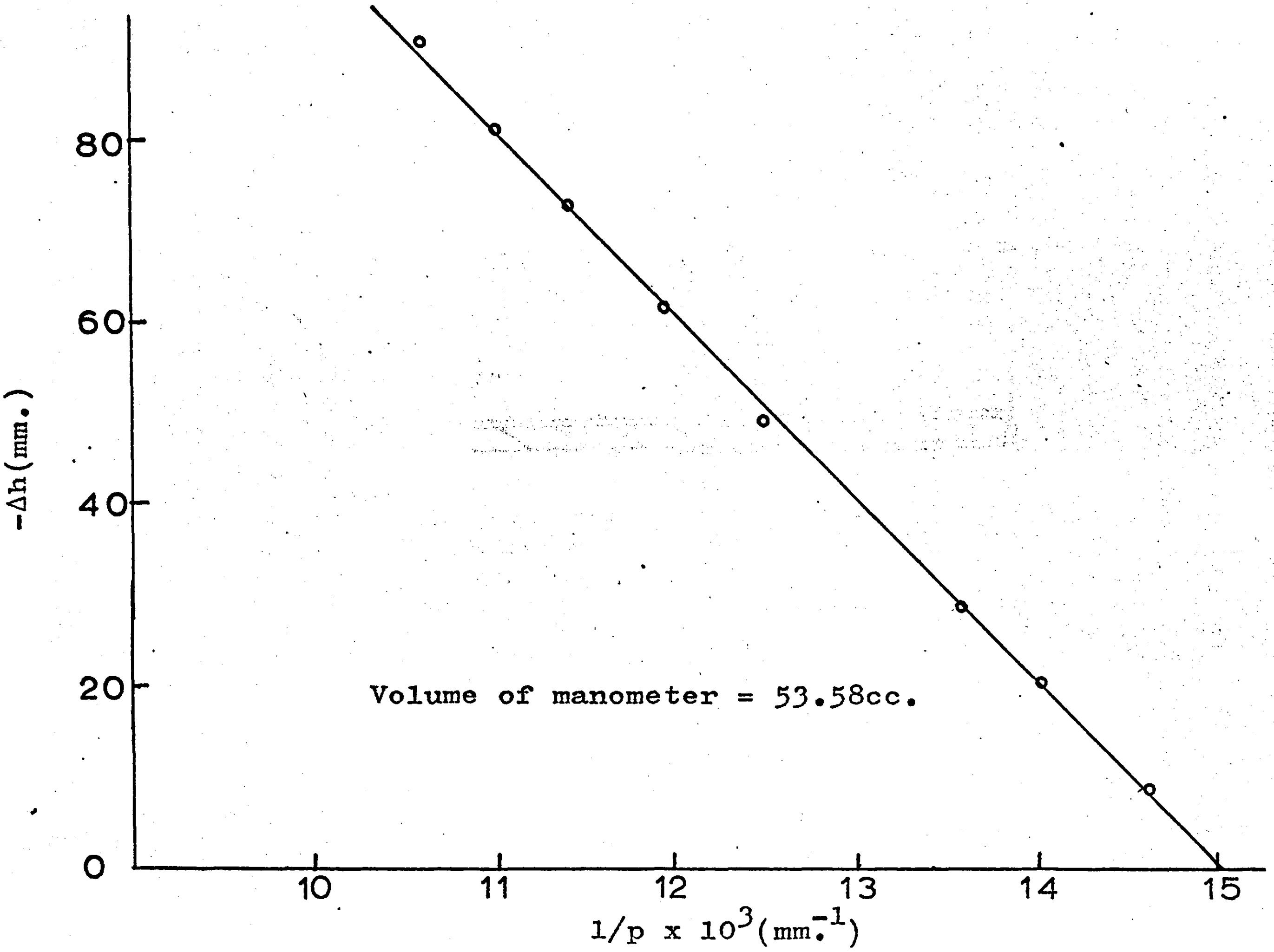


Fig.2.4 Calibration plot for the constant volume manometer.

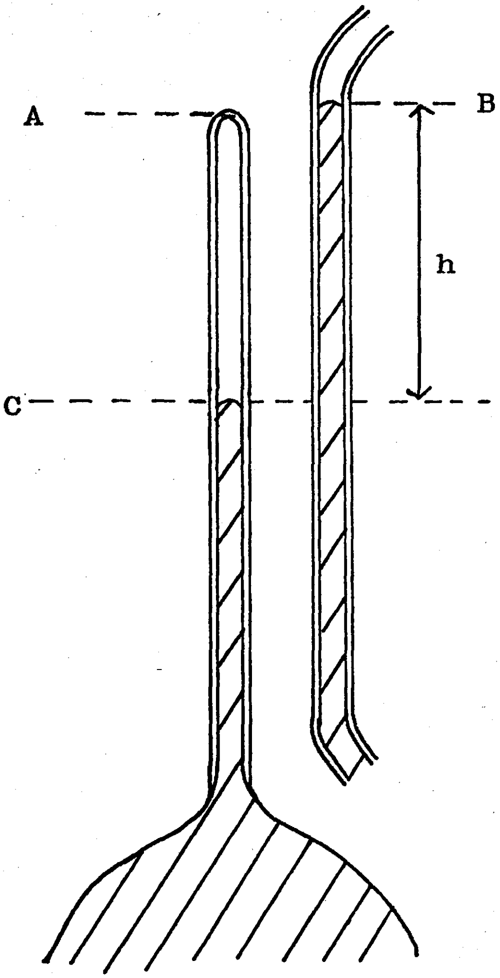


Fig.2.5 Capillary section of a McLeod gauge.

McLeod gauge. The diameter of the Veridia Precision Bore Tubing used to construct the gauge was measured before assembly with a travelling microscope.

Each time the mercury in the gauge was raised to estimate the quantity of gas in the enclosed capillary three readings were taken on a cathetometer:-

(A) the top of the closed capillary.

(B) the top of the mercury meniscus in the open capillary.

(C) the top of the mercury meniscus in the closed capillary.

In addition the temperature T was noted.

After compression the volume of the gas trapped in the closed capillary is given by $(A - C)\pi r^2$, where r is the radius of the capillary, with two corrections. These corrections take account of the facts that:-

(i) the top of the closed capillary is hemispherical and not flat.

(ii) the mercury meniscus is not flat.

This amounts to an addition of $\frac{1}{3}\pi r^2.d - \frac{1}{3}\pi r^3$, where d is the height of the mercury meniscus in the closed column. Taking account of these factors the volume of gas after compression, V_c, is given by

$$V_c = \pi r^2(A - C) + \frac{1}{3}\pi r^2.d - \frac{1}{3}\pi r^3.$$

$$V_c = \pi r^2[(A - C) + \tfrac{1}{3}d - \tfrac{1}{3}r]$$

If measurements are made in centimetres,

$$V_c = \pi r^2[(A - C) - 0.019]$$

The pressure of gas after compression is given by $(B - C) = h$. The volume of the gauge itself was found by filling with water and weighing, and gives the volume of the gas before compression as 134.8cc. From the above data the pressure of gas before compression, P_b, at the standard temperature of 20°C may be shown to be given by,

$$P_b = \frac{[(A - C) - 0.019][(B - C)]}{T} \cdot \frac{293\pi r^2}{134.8}$$

$$= \frac{[(A - C) - 0.019][(B - C)]}{T} \cdot 0.0572 \quad ....(1)$$

Samples of gas from degrading polymers were collected in a trap system Fig.2.2 so that if the volume bounded by taps T_1, T_3 and T_5 were known, given that the pressure before compression had been found, the total amount of gas present could be determined. The volume of the above system was found by pumping the gauge and the section of the glass still, bounded by the taps listed, down to sticking vacuum, then introducing a suitable quantity of nitrogen. Three values of V_c, h, and T were taken each time to test reproducability. With the mercury in the gauge raised, the gas in the trap system was pumped away. The mercury was then lowered, and the gas trapped in the closed capillary allowed to expand into the volume bounded by taps T_1, T_3 and T_5. Three readings were once again noted for V_c, h and T. This procedure of expanding the gas in the capillary into the trap system was repeated three times. It follows that for each set of measurements the quantity V_ch/T should be a constant. The results are shown in table 2.2. Using the nomenclature of this table,

$$E = \frac{E_0}{E_1} = \frac{E_1}{E_2} = \frac{E_2}{E_3} = \frac{\text{vol. of gauge + vol. of trap system}}{\text{vol. of gauge}}$$

Since the average value of E is 1.986 and the volume of the gauge is 134.8cc. the volume of the trap system is 132.9cc. From the fact that the total volume of the McLeod gauge and the trap system is 267.7cc. it can be calculated that at 20°C one m.mole of gas in the apparatus would have a pressure of 6.83cm. Thus by dividing the pressure in cm. calculated using equation (1) by 6.83 the number of m.moles of evolved material is found.

Typically the gauge was used to measure the pressure of total gas and of carbon dioxide produced when a polymer was degraded to low percentage conversion in the glass still,Fig.2.2. Such an experiment has been described as far as the isolation of the product gases (2.2b). To measure the pressure of these gaseous products the liquid

Table 2.2

Calibration of McLeod Gauge.

Expansion	A(cm.)	B(cm.)	C(cm.)	A–C (cm.)	$\frac{V_c}{\pi r^2}$	h=B–C (cm.)	$\frac{1}{\pi r^2} \cdot \frac{V_c h}{T}$	$T^o K$
0	38.921	38.902	25.917	13.004	12.985	12.985	0.5703	295.9
	38.906	38.790	25.829	13.077	13.058	12.961	0.5720	295.8
	38.910	38.890	25.868	13.042	13.023	13.022	0.5724	295.9
						Average	0.5716	$=E_o$
1	38.927	38.919	29.667	9.260	9.241	9.252	0.2883	296.4
	38.903	38.946	29.708	9.195	9.176	9.238	0.2856	296.8
	38.917	38.824	29.613	9.304	9.285	9.211	0.2878	297.1
						Average	0.2872	$= E_1$
2	38.917	38.941	32.376	6.541	6.522	6.565	0.1440	297.2
	38.922	38.883	32.275	6.647	6.628	6.608	0.1449	298.1
	38.930	38.935	32.274	6.656	6.637	6.661	0.1487	297.3
						Average	0.1465	$= E_2$
3	38.906	38.900	34.258	4.648	4.629	4.642	.07228	297.2
	38.922	38.930	34.277	4.645	4.626	4.653	.07243	297.2
	38.929	38.681	34.146	4.783	4.764	4.535	.07264	297.4
						Average	.07245	$= E_3$

nitrogen was exchanged for a water bath at 20°C. Tap T_5 was shut and three determinations of the pressure P_o in the evacuated gauge were made. T_3 was then shut and T_2 opened to allow the gas to fill the gauge. Again three separate sets of measurements were made of P_t, the pressure of the total evolved gas. The gas was now allowed to come in contact with sodium hydroxide pellets, which react with carbon dioxide, by opening T_3. Pressure determinations were made at ten minute intervals until there was no further absorption noted. The unreacted gases were then redistilled under liquid nitrogen into the trap, T_3 closed, the coolant exchanged once again for a 20°C water bath and the system allowed to attain equilibrium. As before three readings were taken of the unabsorbed gas pressure, P_u. Thus,

Total gas pressure = $P_t - P_o$.

Carbon dioxide pressure = $(P_t - P_o) - P_u$.

To check that carbon dioxide was being efficiently removed, mass spectra (2.7) were run of the product gases before and after absorption. These showed no peak attributable to carbon dioxide after absorption.

2.4 Molecular Weight Measurements

In degradation work molecular weight data can often throw light upon the mechanism of breakdown [11]. Two types of osmometer were used covering different molecular weight ranges.

(a) Vapour Phase Osmometer

If a drop of solution and a drop of solvent are suspended, side by side, in a closed thermostatted system saturated with solvent vapour, then because of the lower vapour pressure of the solution with respect to the solvent, a differential mass transfer will occur between the two drops and the solvent phase, resulting in greater condensation on (or lower evaporation from) the solution drop than from the solvent drop. Such a transfer will cause a temperature difference between the drops because of the heat of condensation of the solvent, this difference being proportional to the vapour pressure lowering, ΔP, and therefore proportional to the solute concentration c. Since this temperature shift is a colligative effect, depending solely upon the number of dissolved molecules per unit weight solvent, n, and being independent of their nature, this effect may be used to determine the number average molecular weight, $\overline{M}_n$ of polymeric materials.[62,63]

In the instrument used a Model 301A Vapour Pressure Osmometer (Mechrolab Inc.) a drop of pure solvent is placed on one thermistor bead and a drop of solution on a second thermistor bead. The difference in resistance, ΔR, between these thermistor beads is proportional to their temperature difference, ΔT, hence,

$$\Delta R \propto \Delta T \propto \Delta P$$

Since $\Delta P \propto n \propto c/\overline{M}_n$

$$\Delta R = k_1(c/\overline{M}_n) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where k_1 is a constant. The value of the constant k_1 is obtained by calibrating the instrument with a standard substance of known molecular weight, benzil being used here. Equation (2) refers to ideal solutions but since even dilute polymer solutions are non-ideal it was necessary to extrapolate the results obtained at finite concentrations to infite dilution. The theory of polymer solutions developed by Flory and Huggins [64] shows that for polymeric materials it is more accurate to write equation (2) as,

$$\Delta R/c = k_1(1/\overline{M}_n) + Ac + \ldots\ldots \text{ higher terms in c}..(3)$$

where A is a constant. Neglecting powers of c greater than two, equation (3) means that plots of $\Delta R/c$ versus c should be straight lines, which can easily be extrapolated to find $(\Delta R/c)_{c=0}$, the value of $\Delta R/c$ at infinite dilution, where equation (2) applies. Thus the number average molecular weight of the sample may be calculated.

The Vapour Phase Osmometer was used to measure molecular weights up to about 20,000 with an accuracy of the order of 5°/o, the determinations being carried out in Analar toluene at 65°C.

(b) Membrane Osmometer

The basic equation relating osmotic pressure to number average molecular weight, $\overline{M}_n$, is the expression of van't Hoff,

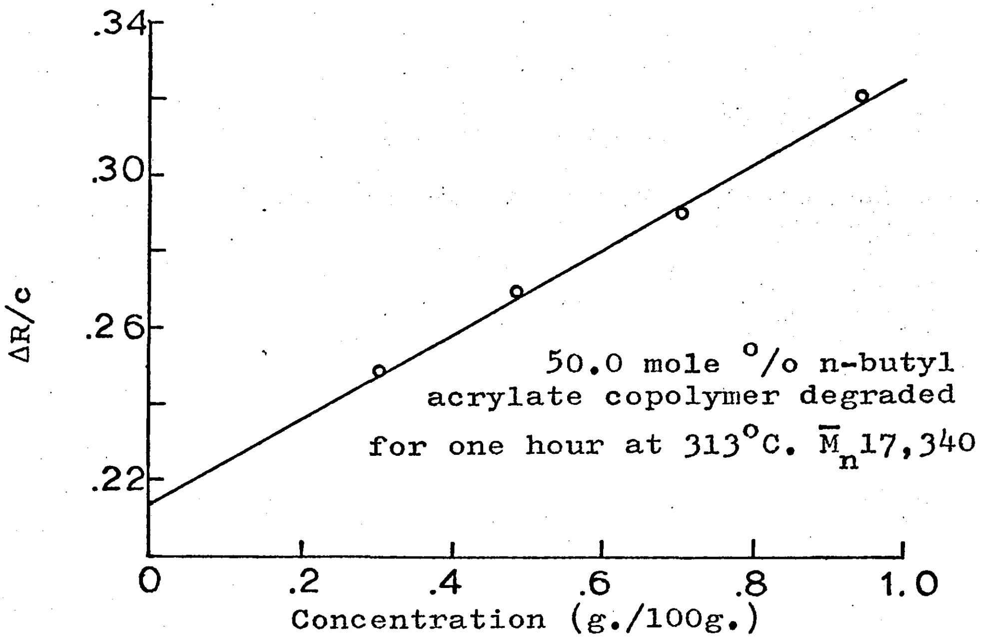
$$\pi = (RT)\frac{c}{\overline{M}_n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where R and T have the usual significance. This equation is of the same form as equation (2) since the product RT is a constant at constant temperature. Applying the same reasoning as before, plots of (π/c) versus c were extrapolated to find $(\pi/c)_{c=0}$, the value of (π/c) at infinite dilution where equation (4) applies.

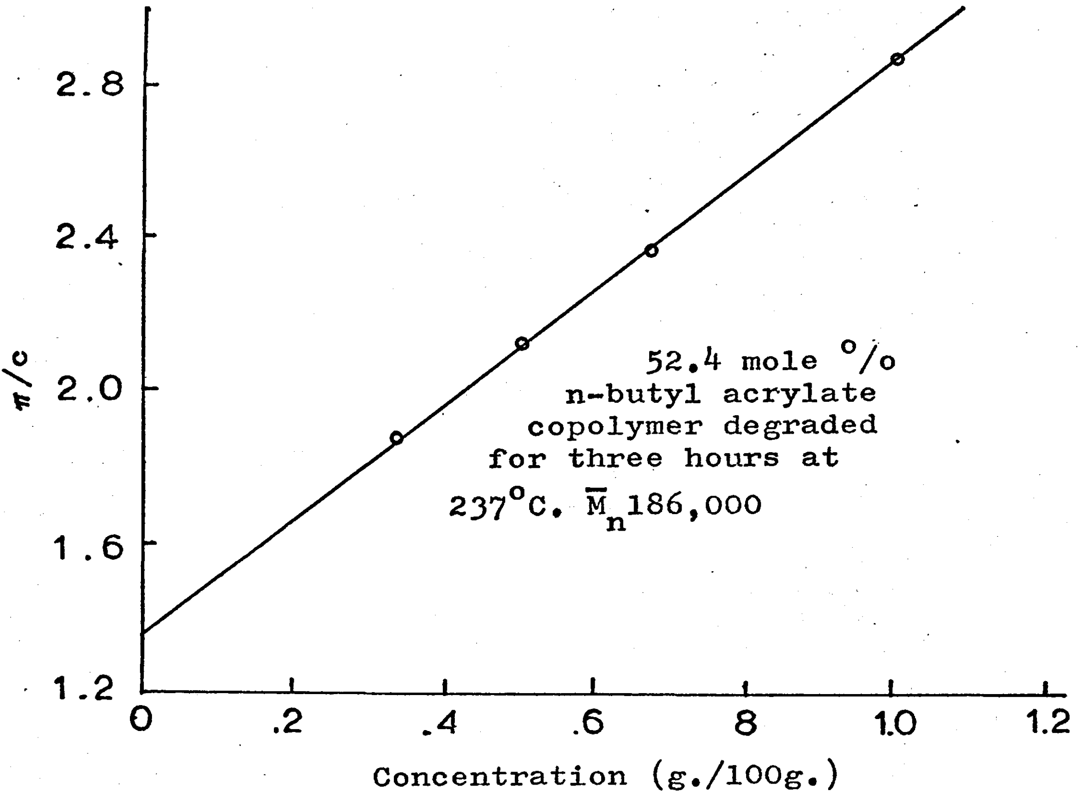
Molecular weights down to 20,000 were measured in Analar toluene solution at 25°C using a Mechrolab Model 501 High Speed Osmometer. Cellophane membranes were used and molecular weight determinations were accurate to about 5°/o in the range 20,000 to 1,000,000.

(c) Molecular Weight Results

In the foregoing the term c, the concentration of solute should be expressed in weight of solute per unit weight solvent, for example as grams of solute per 100g solvent, but concentrations are more conveniently



(a) Vapour Phase Osmometer Plot.



(b) Membrane Osmometer Plot.

Fig.2.6 Molecular weight plots.

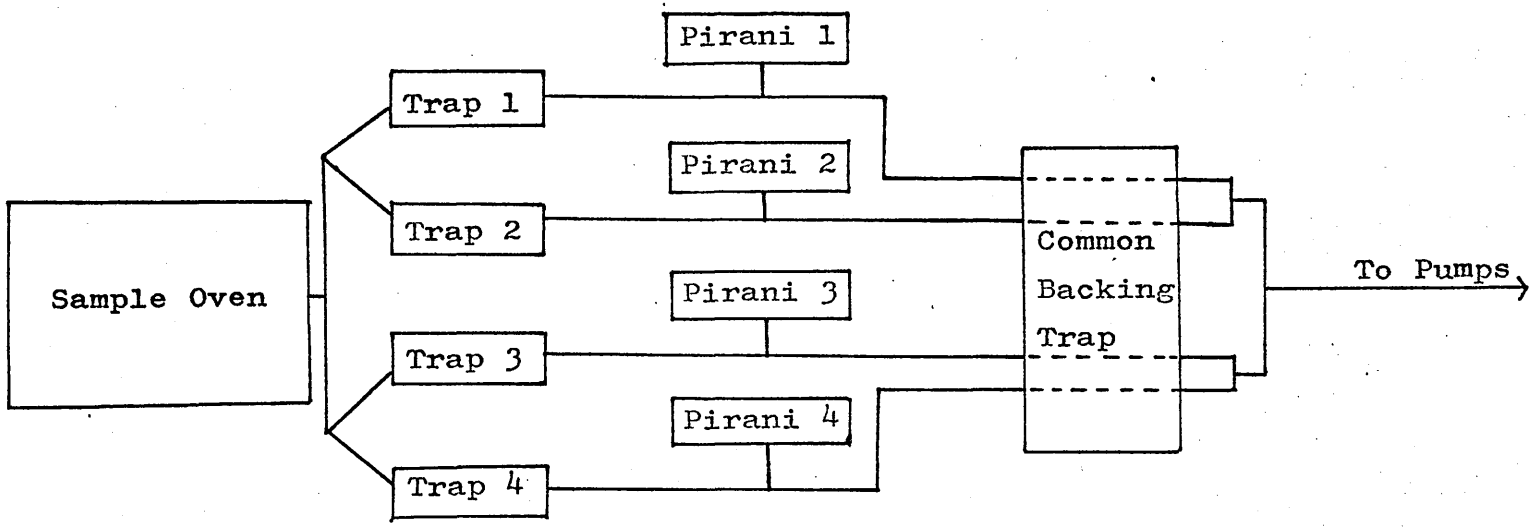
expressed in practice as grams of solute per 100g. solution. At high dilution the difference between these quantities is not great. Typical molecular weight determinations for both osmometers are shown in Fig.2.6.

2.5 Thermal Methods of Analysis

Thermal methods of analysis may be defined to include those techniques in which some physical parameter of a sample is measured continuously while it is being subjected to thermal treatment. A great number of such techniques have been used and many books and review articles have appeared dealing specifically with this subject [65-67].

(a) Thermal Volatilization Analysis (T.V.A.)

Thermal Volatilization Analysis (T.V.A.) is a technique devised by McNeill [60] which measures the thermal conductivity of the volatile material evolved from a heated polymer sample which is being continuously pumped. The Differential Condensation T.V.A. apparatus (D.C.T.V.A.) Fig.2.7 is a modification of the original equipment which employs a series of traps maintained at different temperatures After each trap is placed a Pirani gauge which measures the transient pressure of material not condensed by that particular trap. The Pirani outputs are fed into a multipoint recorder so that the traces produced are of Pirani response, which is a measure of the rate of



Normal working temperatures :-

Trap 1	-100°C
Trap 2	-75°C
Trap 3	-45°C
Trap 4	0°C

Fig.2.7 Schematic Diagram of the Differential Condensation T.V.A.(D.C.T.V.A.)

volatilization, against time. The trace obtained is thus of a differential nature. A separate temperature versus time trace is also recorded so that when a linear temperature programme is used, as is normal practice, any deviations of the heating rate from linearity may be checked.

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

Thermogravimetry has been defined as the science and art of weighing substances while they are being heated. It has developed in two directions. On the one hand studies have been made by following the weight change with time of a sample heated at constant temperature, isothermal T.G.A., while on the other hand in dynamic T.G.A. weight loss is measured as the sample is being heated according to some pre-determined programme, usually linear with time. Typically the trace produced is of weight loss versus time or temperature and is integral in nature.

Many theoretical treatments have been put forward in order to derive kinetic parameters from T.G.A. data.[68-70] The validity of the results obtained, especially where programmed data are involved, have been questioned by some workers.

The Du Pont 950 T.G.A. used employs a null type balance in which any weight change in the sample is opposed by an equal restoring force applied to the beam. This restoring force is then a measure of the change in weight of the sample. Samples may be programmed at any heating rate from 0.5 to 30.0 degrees per minute, the maximum working temperature being 1,200 °C.

(c) Differential Thermal Analysis (D.T.A.)

In this technique [71] the sample temperature is continuously compared with that of an inert reference material, their temperature difference, ΔT, being plotted as a function of furnace temperature.

In the Du Pont 900 D.T.A. the furnace and sample holder consists of an aluminium block, sample and reference material being placed in glass tubes located symmetrically about the heater cartridge. Thermocouples are inserted into the samples through the top of the open glass tubes, the whole assembly being covered by a bell jar to permit a controlled atmosphere.

2.6 Gas-Liquid Chromatography

For the most part g.l.c. data were obtained using a Microtek G.C.2,000R Research Gas Chromatograph equipped with a flame ionization detector. Since gases such as carbon monoxide and hydrogen cannot be detected by such flame ionization devices, analysis of the permanent gas fraction was carried out on a modified Gallenkamp chromatograph which had a thermal conductivity detector. A list of the columns employed and the conditions under which they were used is given in table 2.3.

(a) <u>Gas Sampling Apparatus</u>

Gases were introduced into the G.C.2,000R chromatograph using the apparatus shown in Fig.2.8. This apparatus was first evacuated and tap T_1 closed. The gaseous products of thermal breakdown were distilled from the degradation section into the cold finger under liquid nitrogen and tap T_2 closed. The coolant was then removed from round the cold finger and when the whole had attained equilibrium the pressure was made up to atmospheric with nitrogen gas taken from a cylinder. Samples could then be withdrawn through the septum by means of a gas syringe and injected into the chromatograph in the usual way.

The distillation step involved in the above procedure makes it unsuitable for application to the analysis of the permanent gas fraction. Since the thermal conductivity detector employed is sensitive to air, this means that air must be rigorously excluded if interference with identification and measurements of the permanent gases is to be avoided. To this end the type of sampling system shown in Fig.2.9 was constructed. The sample bulb containing

Table 2.3

G.L.C. Columns Used for Investigation of Degradation Products.

Column	Programme	Use	Detector
10ft. 1/4inch diameter, 30-60 mesh silica gel	Isothermal at 40°C for 3 mins., then programme at 5°C/min. to 250°C.	General gas column	Flame ionization
24ft. 1/8inch diameter 40^{o}/o benzyl cyanide-silver nitrate	Isothermal at room temperature	Separation of C_4 olefins.	Flame ionization
20ft. 1/4inch diameter, 30-60 mesh silica gel	Isothermal at room temperature	Permanent gas investigation.	Thermal Conductivity
10ft. 1/4inch diameter 1^{o}/o S.E.30 on 100-120mesh embacel. (S.E.30 is a silicone gum)	Isothermal for 6 mins. at 40°C, then programme at 5°C/min. to 250°C.	Liquid volatiles and short chain fragments.	Flame ionization
10ft. 1/4inch diameter 10^{o}/o di-nonyl phthalate on 100-120 mesh embacel	Isothermal at 80°C.	Liquid volatiles.	Flame ionization.

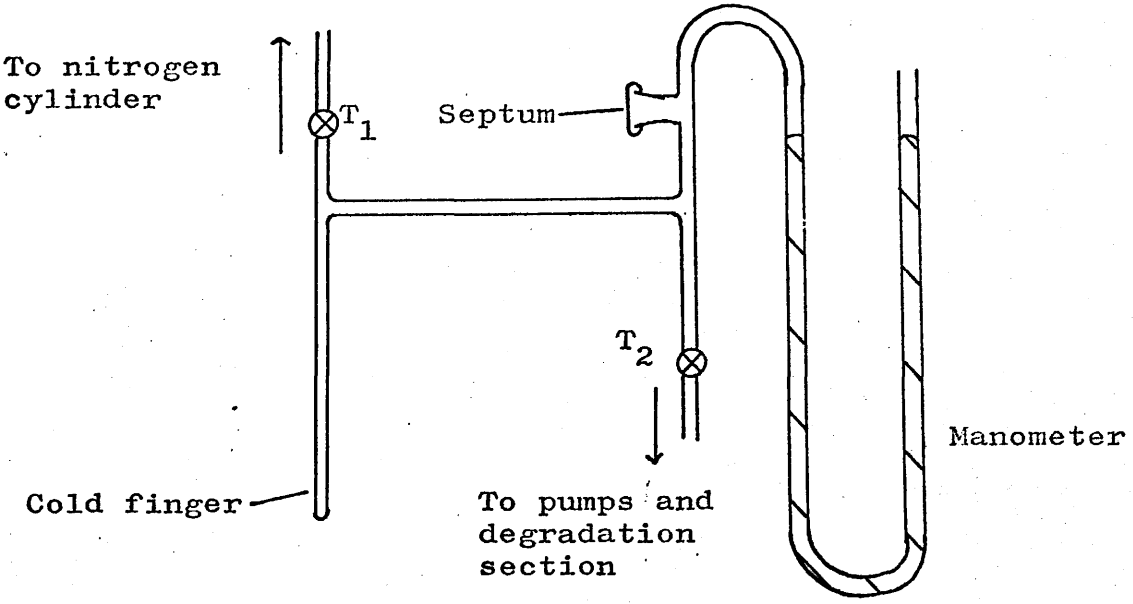


Fig.2.8 Gas sampling system

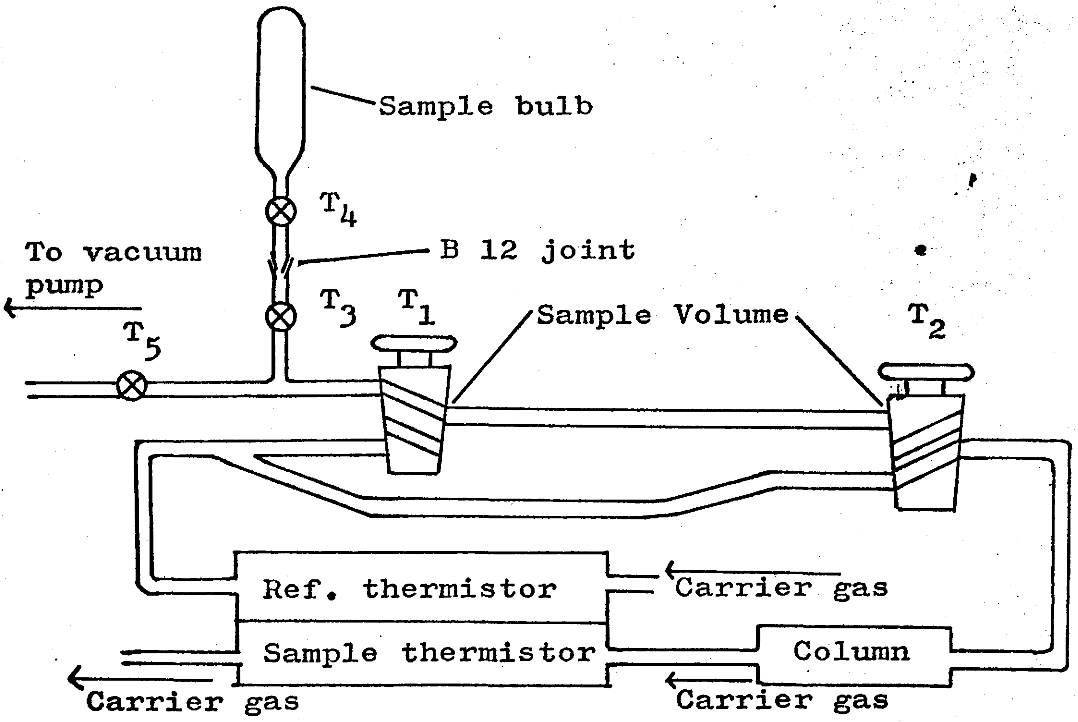


Fig.2.9 Inlet system and schematic diagram of thermal conductivity G.L.C.

the permanent gas fraction obtained as described in (2.2) was attached to the socket with taps T_3 and T_5 open and taps T_1 and T_2 set as shown. The carrier gas, argon, was now by-passing the sample volume. To fill this with gas tap T_5 was closed and T_4 and T_3 opened. The sample was introduced by shutting T_3 and reversing the positions of T_1 and T_2 so that the carrier gas now flushed the sample into the g.l.c. column.

(b) Quantitative Gas-Liquid Chromatography

Quantitative measurements were made on the liquid volatiles by adding a known weight of a suitable material as internal standard to a weighed quantity of liquid products. Several mixtures of pure samples of each of the products were made up with known amounts of the internal standard and run on the chromatograph to determine the sensitivities of the product compounds relative to the standard. Measurement of peak areas on g.l.c. traces was carried out by planimetry since the peak area for a particular substance is proportional to the weight present. If the sensitivity factor, k, for any product Y is defined as the ratio of the peak areas of product to standard when equal weights of both are considered, then the percentage by weight of Y in G grams of sample is given by,

$$^{o}/_{o}Y = \left(\frac{\text{peak area of Y}}{\text{peak area of standard}}\right)\left(\frac{100}{\text{G / weight of standard}}\right)\left(\frac{1}{k}\right)$$

A similar procedure was followed to determine the amounts of the various gases present, mixtures being made up by pressure rather than by weight, but as no internal standard was used in these cases, only relative, rather than absolute measurements were possible.

2.7 Mass Spectrometry

Mass spectra were run on an A.E.I. M.S. 12 Mass Spectrometer.

2.8 Combined Gas Chromatography - Mass Spectrometry

A schematic diagram of the L.K.B. 9,000A Gas Chromatograph - Mass Spectrometer is shown in Fig.2.10. In this instrument where the mass spectrometer is used as the detector for the g.l.c., the sample and helium carrier gas having passed through the g.l.c. column are fed directly through a helium separator into the ion source of the mass spectrometer. This molecule separator strips off the carrier gas before the sample enters the ion source, thus considerably increasing the sensitivity of the spectrometer. Mass spectra may be recorded from any chemical compounds having sufficient volatility and stability to be separated by g.l.c. An ultra-violet recorder capable of a fast scan is used to obtain the

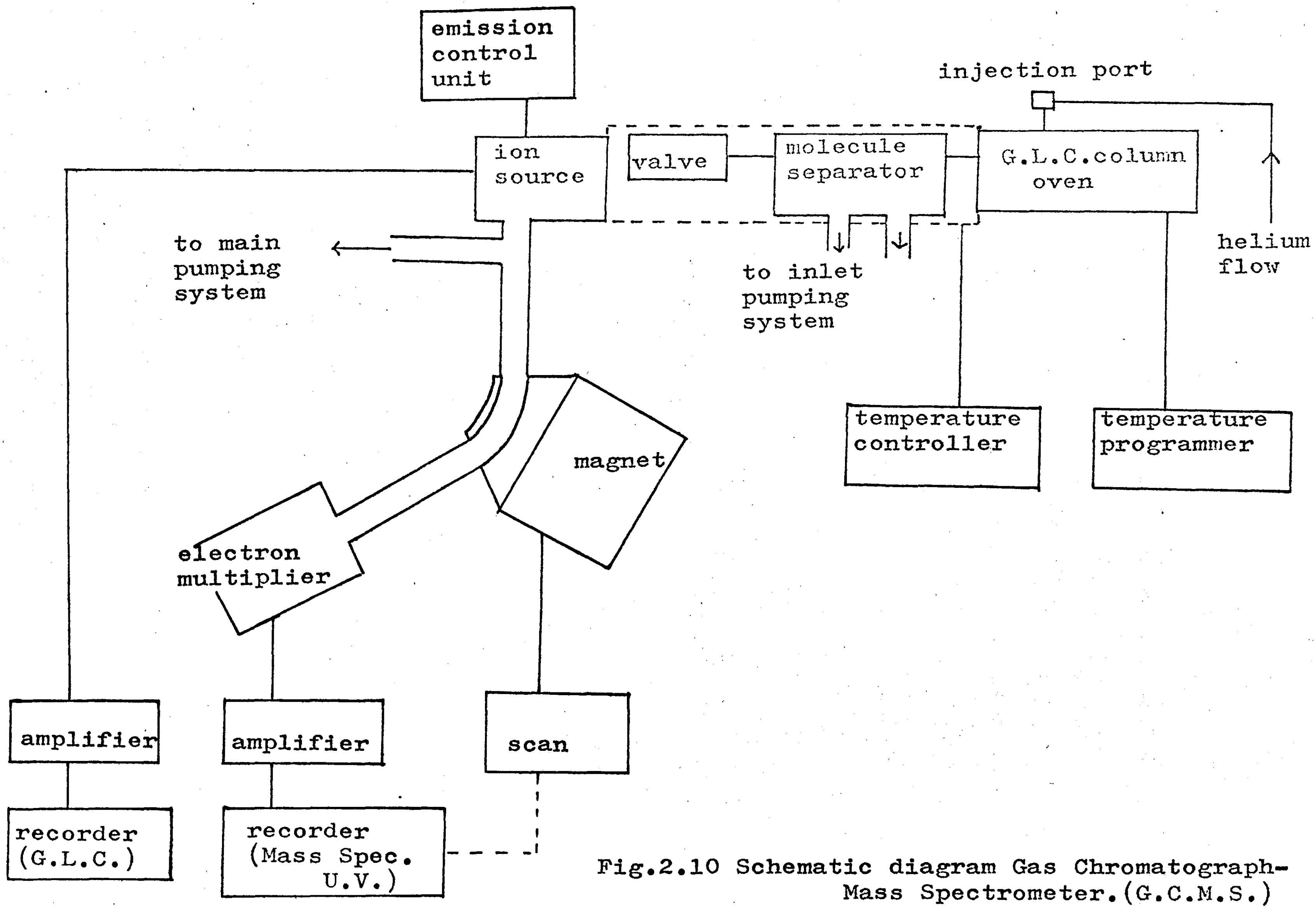


Fig.2.10 Schematic diagram Gas Chromatograph-Mass Spectrometer.(G.C.M.S.)

mass spectra while a pen recorder is used for the g.l.c. traces.

Before examining the liquid degradation products they were first fractionated in order to remove high molecular weight materials which would contaminate the apparatus. This was done by distillation under high vacuum from a container at room temperature to a receiver cooled in liquid nitrogen.

A 10ft. quarter inch diameter 1°/o S.E.30 column was used for the separation of the liquid products, run isothermally at 50°C.

2.9 Spectroscopic Measurements

(a) Infra-red

Infra-red spectra of the gaseous decomposition products were obtained on a Perkin Elmer 257 Grating Infra-red Spectrophotometer.

Once the pressure of the gaseous decomposition products had been measured as in (2.3) they were distilled under liquid nitrogen into an infra-red gas cell of path length 12cm. An identical cell pumped down to sticking vacuum was placed in the reference beam of the spectrophotometer. Prior to making any measurements the infrared detector was flushed with nitrogen so that quantitative analysis of the carbon dioxide present would not be interfered with by the presence of this gas in the atmosphere. The optical densities of the characteristic absorptions of the gases were measured. Known pressures of pure samples of each of the product gases were measured by using the constant volume manometer, and infra-red spectra obtained over a wide pressure range. The optical density of the appropriate peaks was then plotted against pressure of the pure gas so that these traces could be used to determine the composition of the gaseous products of polymer breakdown.

All other infra-red spectra presented were run on this same type of instrument.

(b) U.V.-Visible

A Unicam SP 800 Spectrophotometer was used for measurements in this region of the spectrum.

(c) N.M.R.

N.M.R. spectra were obtained on a Perkin Elmer R 10 60 Mc/s spectrometer, in carbon tetrachloride solution.

2.10 Sol-gel Analysis

The material remaining when copolymers of methyl methacrylate and n-butyl acrylate of high acrylate content, or homopolymers of n-butyl acrylate itself, are degraded is not completely soluble in organic solvents such as benzene in which it could be dissolved before decomposition.

Sol-gel analysis was carried out on this residue using a Soxhlet extractor. Degradations were carried out by the sealed tube technique (2.2) after which the portion of the tube containing residue was cut into short sections about one inch long. These were weighed and placed in a weighed glass sinter of porosity three. The whole assembly was then positioned in a Soxhlet extractor such that the solvent could wash, and drain easily from, every piece of the tube. Analar benzene (b.pt. 80°C) was used as solvent and the extraction continued for a standard time of twenty hours. At the end of this time the tube pieces and glass sinter were removed, drained for a few minutes, then dried in a vacuum oven at 60°C for three hours, after which they were allowed to cool and were reweighed. The difference in weight of the sinter, ΔS, gives the weight of any insoluble material trapped, while the difference in weight of the tube pieces, ΔP, less ΔS, gives the weight of soluble residue. This latter weight was also determined by distilling off benzene from the solvent reservoir after extraction, and determining the concentration of a known volume of this solution. The sealed tube sections were immersed in soap solution overnight, cleaned of all insoluble material, dried and reweighed. The difference in weight before and after this last operation, ΔQ, when added to ΔS is the weight of the insoluble residue. Thus the total weight of residue, the weight of soluble residue and the weight of insoluble residue have been found and are given by $(\Delta P+\Delta Q)$, $(\Delta P-\Delta S)$, and $(\Delta Q+\Delta S)$ respectively.

CHAPTER 3

THERMAL METHODS OF ANALYSIS

3.1 Introduction

The techniques dealt with in this chapter may be generally applied to a polymer as a preliminary to a thorough investigation of its breakdown. From the results of such investigations an overall picture of the decomposition pattern of the n-butyl acrylate - methyl methacrylate copolymers was obtained and a temperature range selected in which to examine their degradation in some detail under isothermal conditions.

3.2 Thermal Volatilization Analysis

(a) Collection of T.V.A. Data

The apparatus is shown in Fig.2.7 and described in section 2.5a. All samples were run as films cast from 1ml. of a 50mg./ml. Analar toluene solution and heated at 10°C/min. from ambient to 500°C. The traces obtained are shown in Figs.3.1-3.8 and the temperatures at which rate maxima occur are listed in table 3.1.

It is clear that the position of the lowest temperature peak (A) is independent of the n-butyl acrylate content of the copolymer and that it decreases in size relative to the main peak (B) as the acrylate content of the copolymer increases, becoming a point of inflection

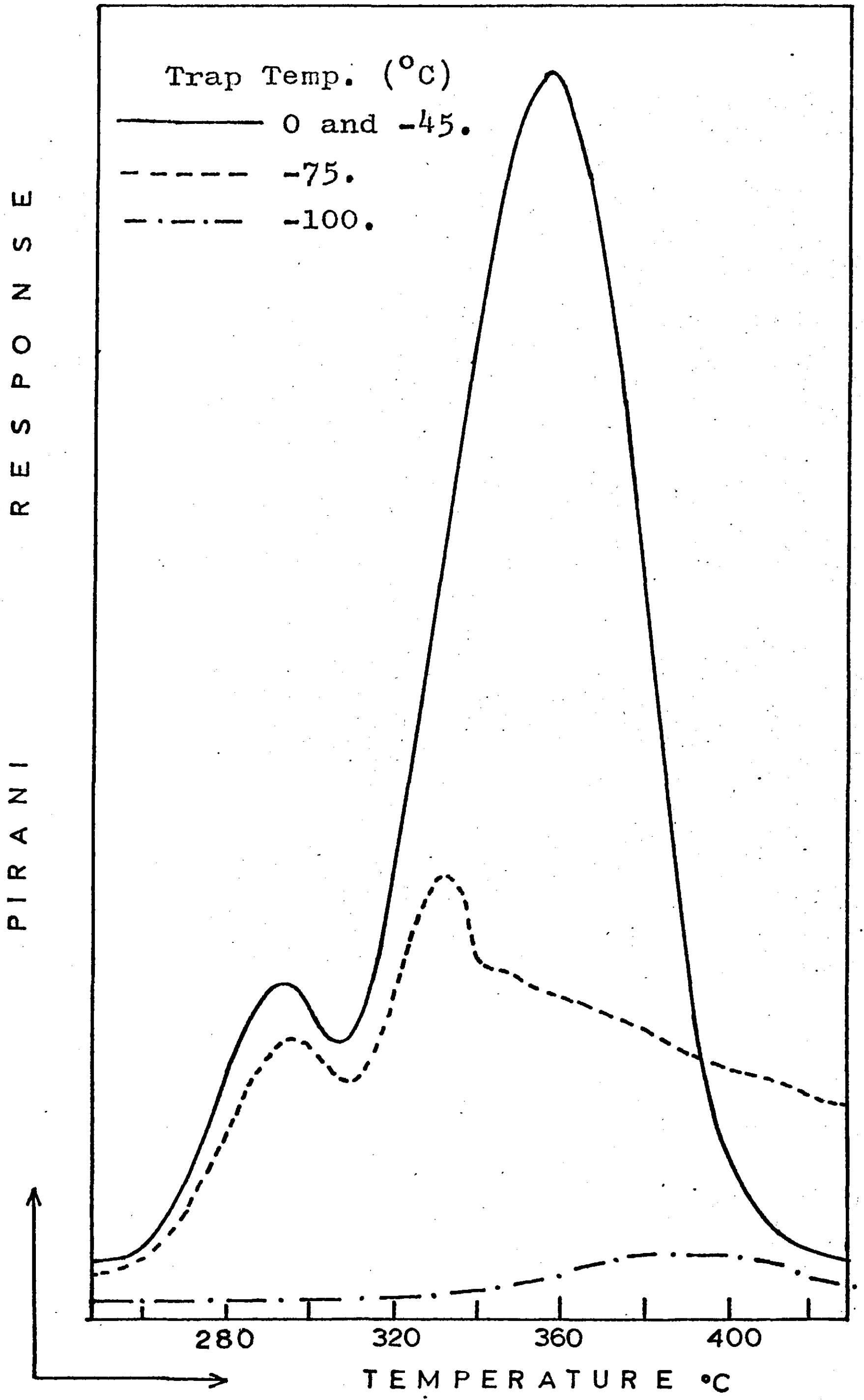


Fig.3.1 D.C.T.V.A. of a polymethylmethacrylate standard.

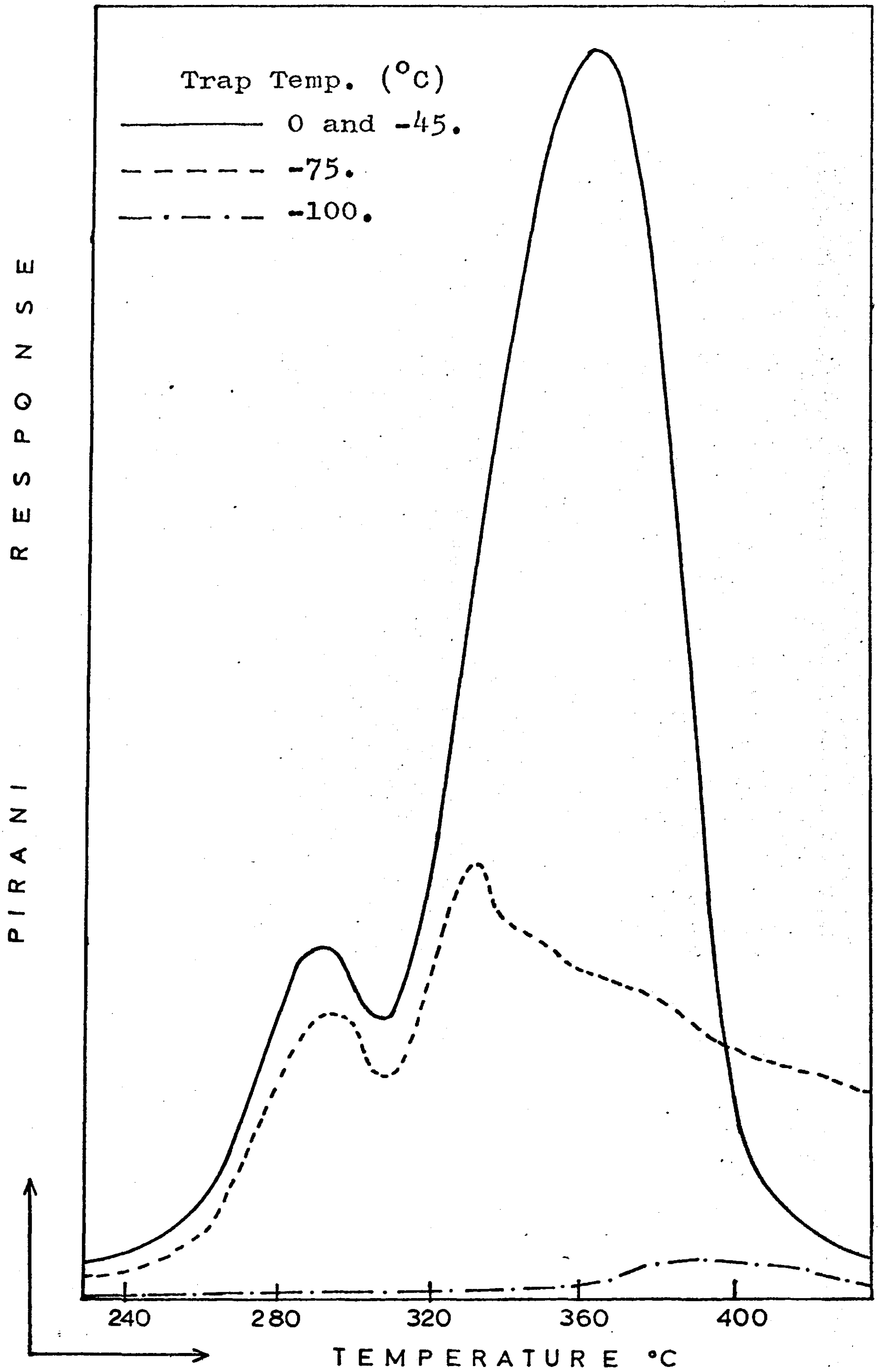


Fig.3.2 D.C.T.V.A. of a 0.4 mole percent n-butyl acrylate copolymer.

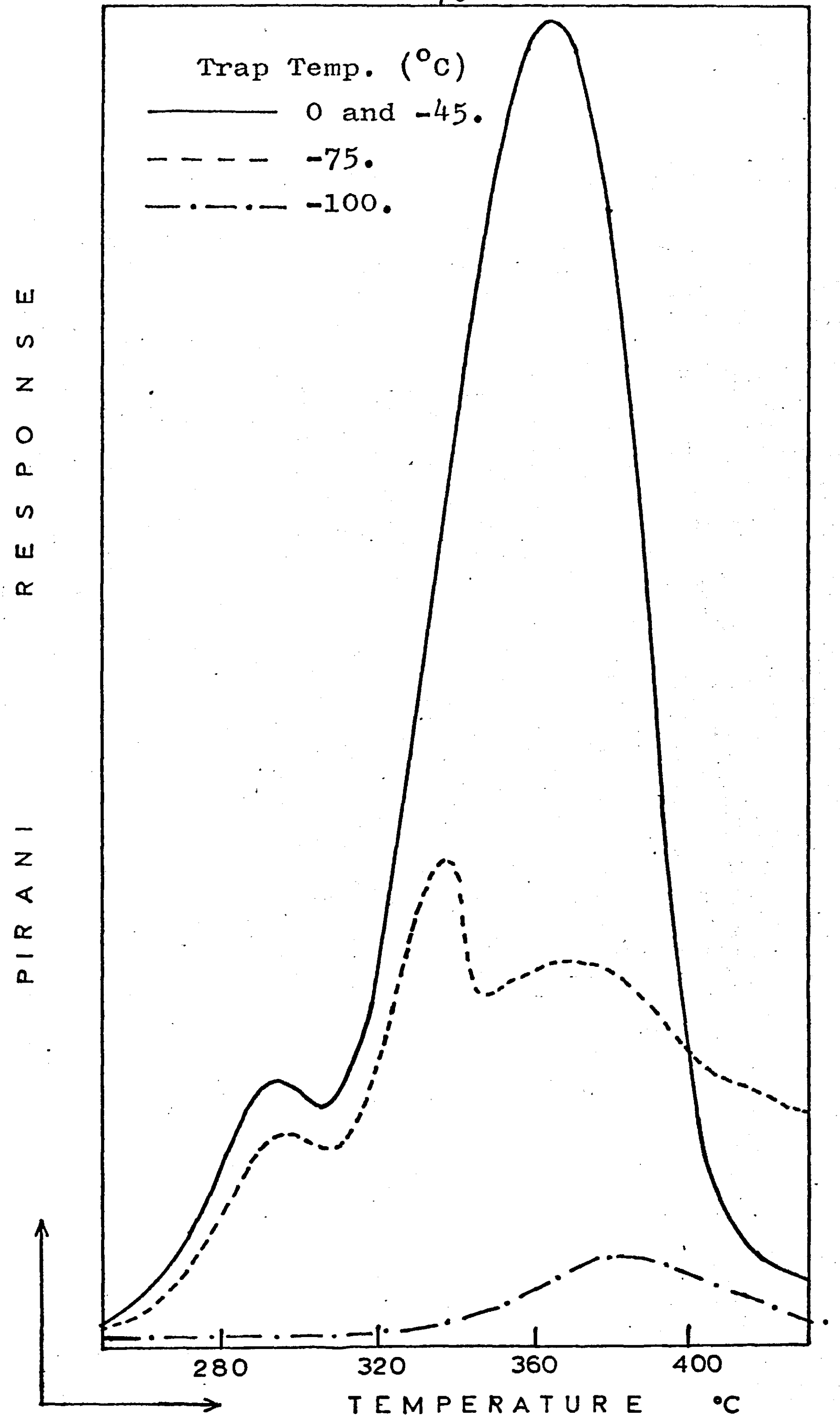


Fig.3.3 D.C.T.V.A. of a 3.9 mole percent n-butyl acrylate copolymer.

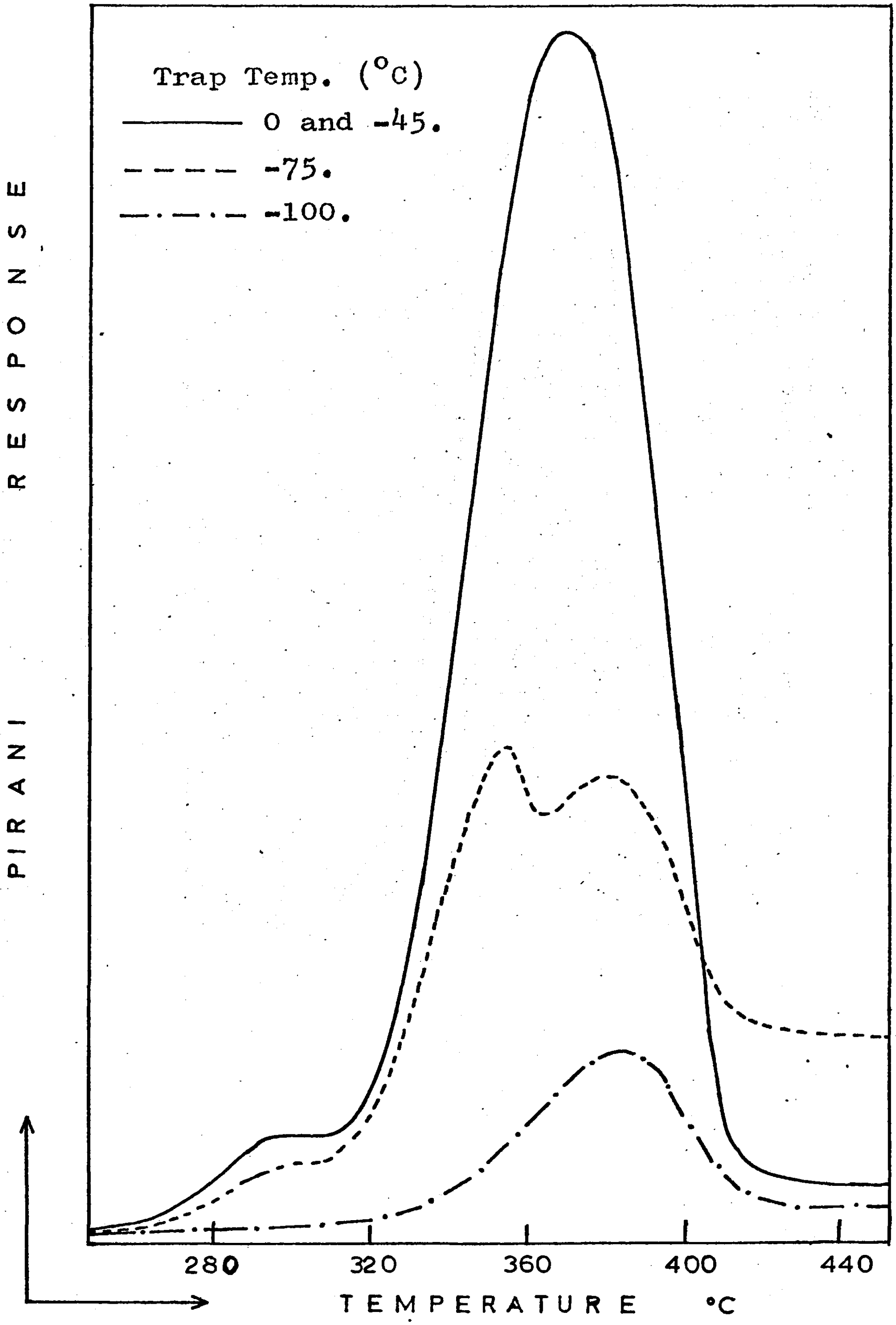


Fig.3.4 D.C.T.V.A. of a 16.3 mole percent n-butyl acrylate copolymer.

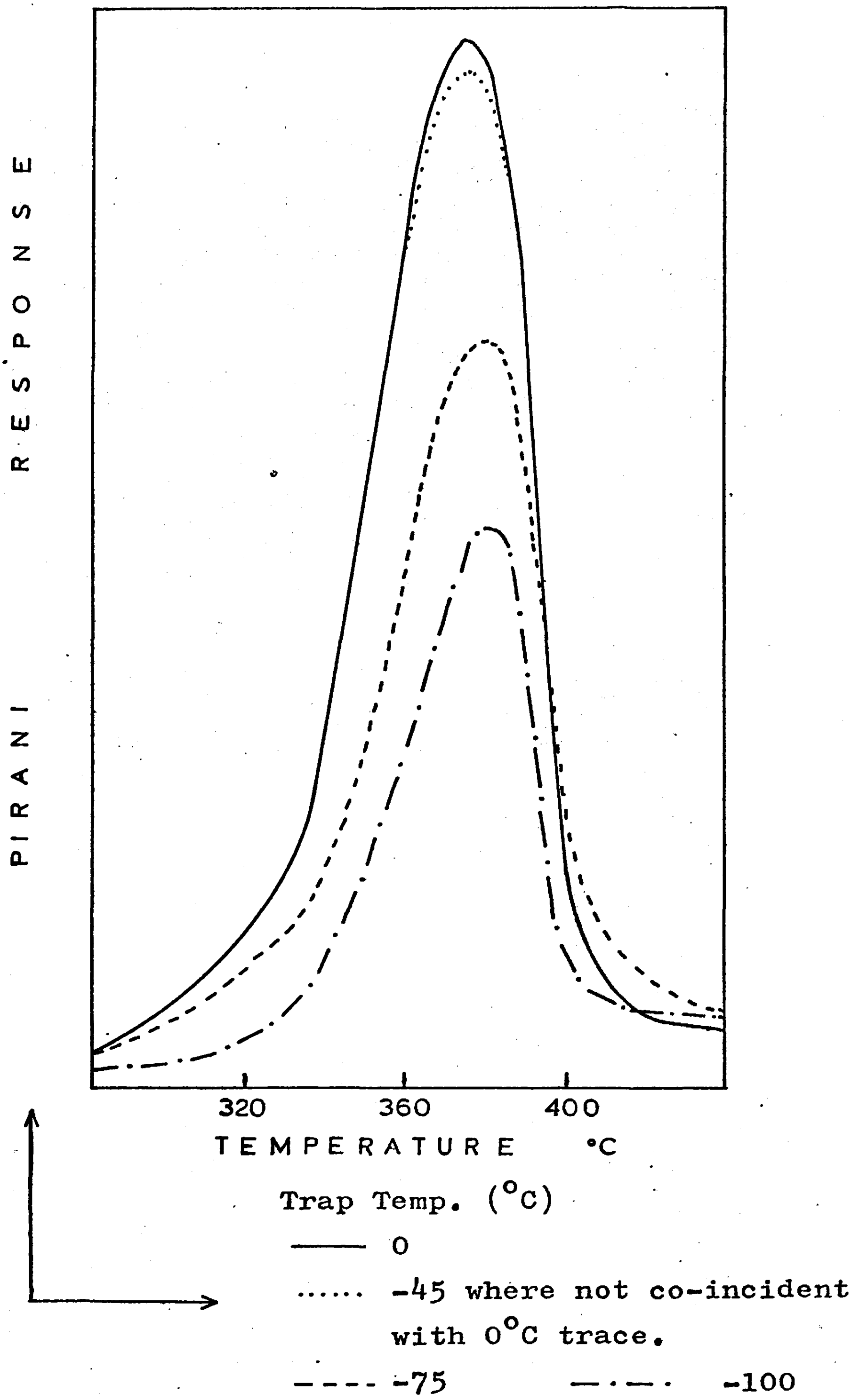
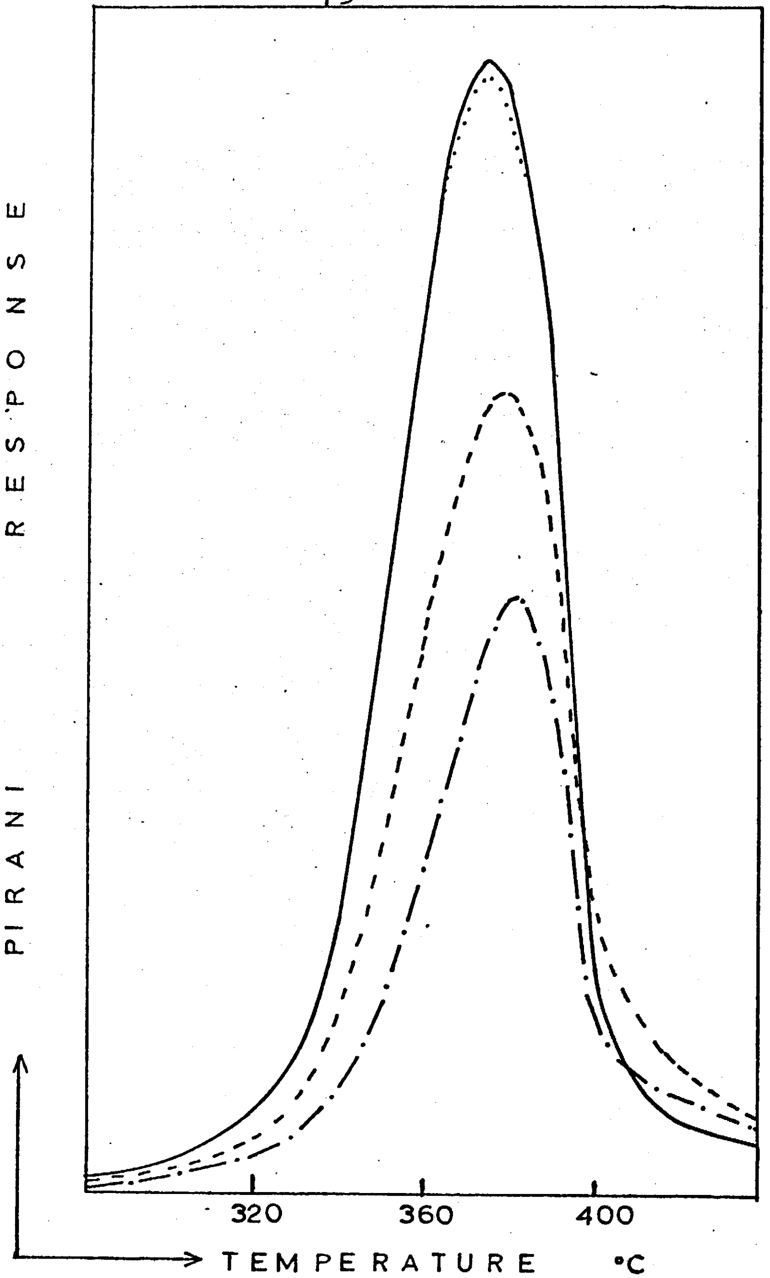


Fig.3.5 D.C.T.V.A. of a 50.0 mole percent n-butyl acrylate copolymer.



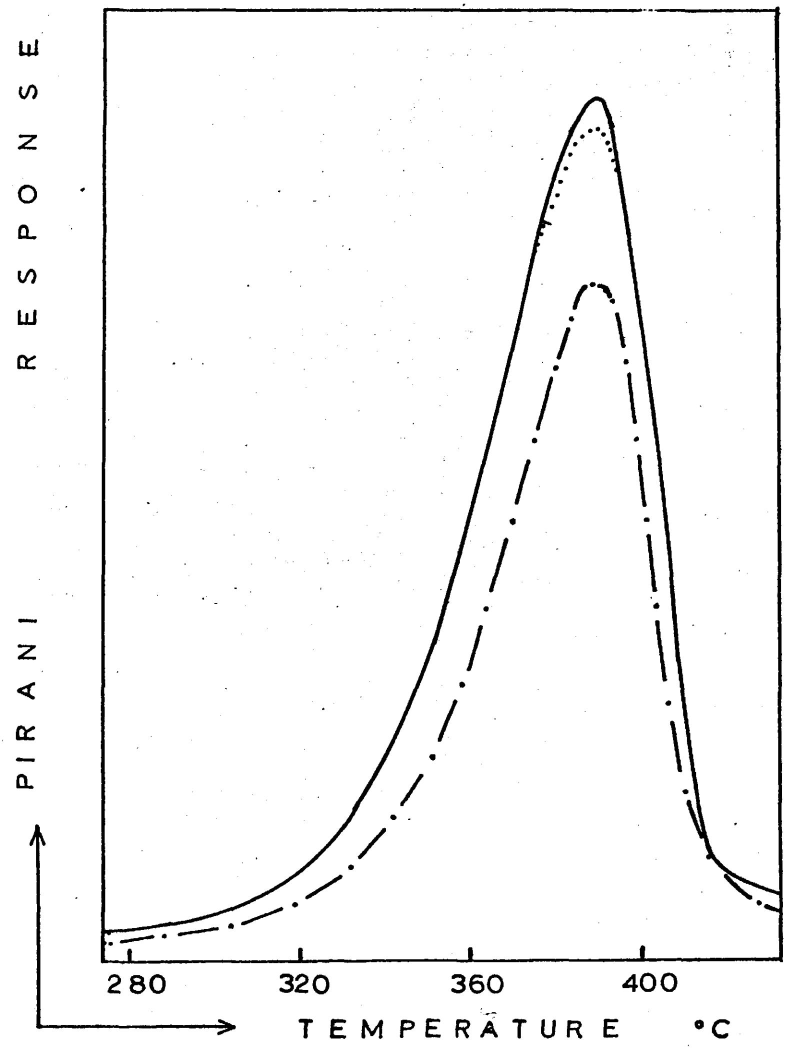
Trap Temp. (°C)

—— 0

····· -45 where not co-incident with 0°C trace.

---- -75 —·—· -100

Fig.3.6 D.C.T.V.A. of a 52.4 mole percent n-butyl acrylate copolymer.



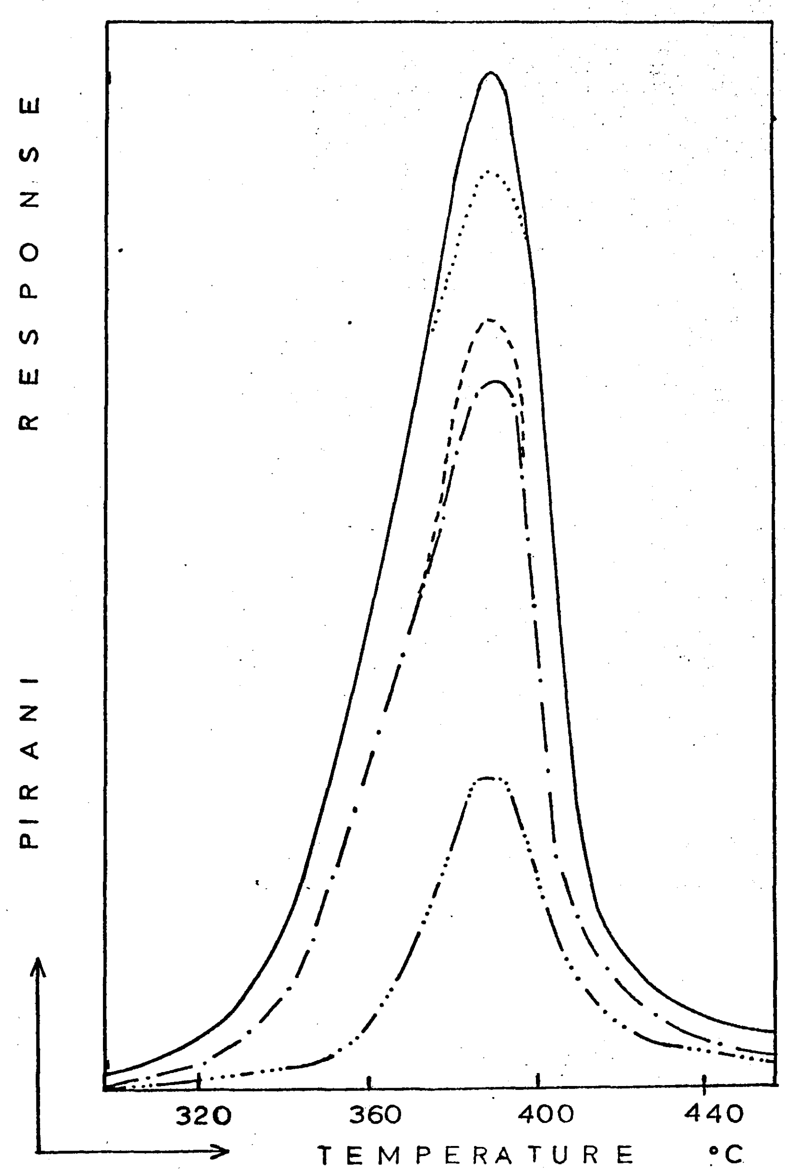
Trap Temp. (°C)

—— 0

..... -45 where not co-incident with 0°C trace.

—·—· -75 and -100

Fig.3.7 D.C.T.V.A. of an 82.2 mole percent n-butyl acrylate copolymer.



Trap Temp. (^{o}C)

——— 0 —···—··· -196 —·—· -100

····· -45 where not co-incident with 0^{o}C trace.

- - - - -75 where not co-incident with -100^{o}C trace.

Fig.3.8 D.C.T.V.A. of a 93.4 mole percent n-butyl acrylate copolymer.

Table 3.1

Polymer Composition (mole °/o n-butyl acrylate)	Temp. in °C for Rate Maxima Attributable to		
	(A) Chain End Initiated Degradation	(B) Degradation Initiated by Random Scission	(C) Products Non-Condensable at -100°C
0	292	359	385
0.4	292	360	385
3.9	292	364	385
16.3	292	367	383
50.0 $\overline{M}_n$ 100,000	-	371	381
52.4 $\overline{M}_n$ 1,330,000	-	371	381
82.2	-	388	389
93.4	-	389	389

when the acrylate content is 16.3 mole percent and disappearing altogether at 50 mole percent n-butyl acrylate. This low temperature peak may be ascribed to the products of depolymerization from unsaturated methacrylate chain end structures [3,22].

The second and main peak (B) moves to higher temperatures as the n-butyl acrylate content of the copolymer is increased. It is associated with depolymerization initiated by random scission of the main polymer chain.

The position of peak (C) appears to be composition independent but it is difficult to locate the exact position of this peak maximum for some of the copolymer samples. This peak is due to materials not condensable at -100°C in a flow system and could be attributed to gases such as carbon monoxide, methane, hydrogen and carbon dioxide. Peak (C) increases in size with increasing acrylate content. A further T.V.A. trace, shown in Fig.3.8, was obtained from the 93.4 mole percent n-butyl acrylate copolymer with one of the traps at liquid nitrogen temperature. Some material passes through this trap, which demonstrates that permanent gases are formed in the degradation process in addition to carbon dioxide which would be condensed at this temperature.

It is not possible to obtain quantitative information from these traces about the relative amounts of material condensable at the various trap temperatures since,

i) Pirani response is not linear with pressure, and

ii) Pirani response depends upon the substance giving rise to that response.

The trace from the trap at -75°C is interesting in that for samples of high methacrylate content three peaks occur, Fig.3.3, the middle one of which does not correspond to any of the other peaks noted in table 3.1. Its presence may be explained in terms of a nucleation effect, which occurs when a considerable quantity of a material which is only partially condensed at that temperature enters the trap rather than by any explanation involving the mechanism of polymer breakdown. Thus the first surge of material passes through the trap. Later, nucleation takes place in the trap, and thereafter condensation is more efficient so less material reaches the Pirani gauge.

The results for the high and low molecular weight 50 mole percent copolymers, Figs.3.5 and 3.6 are identical showing that in the molecular weight range 100,000 to 1.330,000 chain length has no effect on degradative behaviour at least as far as the production of volatile materials is concerned.

From these investigations it would appear that the temperature range 270-340°C should be suitable for studying the degradation reaction isothermally. The principal results may be listed as follows. With increasing acrylate content,

1) The lowest temperature peak, ascribed to chain end initiated breakdown, becomes smaller although its position remains unchanged.

2) The main peak moves to higher temperatures showing that the main polymer chain is becoming more stable to breakdown.

3) Production of chain fragments which condense immediately above the reaction zone increases with acrylate content, and they become deeper in colour (pale yellow to brown).

4) The residue becomes more abundant and darker in colour as in 3).

(b) Interpretation of T.V.A. Data

(b.1) Discussion of Results 1) and 2)

The decrease in importance of degradation initiated at unsaturated methyl methacrylate chain ends may be ascribed to a combination of effects. As the acrylate content of the copolymers increase,

i) The relative amount of methacrylate available to form susceptible chain ends decreases.

This is the most straightforward explanation of the lessening importance of peak (A) but cannot itself explain the fact that when only 16.3 mole percent of n-butyl acrylate is present, this first peak is reduced to a point of inflection.

ii) A new cross termination step in the polymerization reaction results in methacrylate radicals taking part in combination, rather than disproportionation, termination reactions.

The unsaturated methacrylate chain ends are produced in disproportionation termination reactions. Chaudhuri et al [56] found that in a methyl methacrylate - methyl acrylate copolymer containing 45.9 mole percent methacrylate crossed termination was predominant, and that 67°/o of the termination steps in which a methacrylate radical took part occurred by combination, thus drastically reducing the number of unsaturated chain ends. It seems reasonable to suppose that a similar mechanism could operate in the n-butyl acrylate - methyl methacrylate system.

iii) The zip length of depolymerization decreases because of the "blocking" effect of acrylate units.

This effect of acrylate content on zip length is demonstrated by molecular weight measurements reported in a later section, and has been observed in other related copolymer systems [36]. It has already been discussed in section 1.4.

In randomly initiated degradation the ease with which the initial break occurs depends upon acrylate content, since acrylate-acrylate bonds are more difficult to rupture than methacrylate-methacrylate bonds, but in chain end initiated degradation the initial process is independent of acrylate content. Thus the temperature shift shown to occur for peak (B) in table 3.1 is a consequence of randomly initiated breakdown.

(b.2) Discussion of Results 3) and 4)

The chain fragments may be explained by the increasing importance of transfer reactions over depolymerization with increasing acrylate content because of the reactivity of the acrylate radical and the availability of tertiary hydrogen atoms. Coloration is due to conjugated sequences of double bonds formed as in Fig.1.9. This reaction is further investigated in a later section.

3.3 Thermogravimetric Analysis

T.G.A. experiments were carried out in an atmosphere of nitrogen, since the Du Pont 950 Thermogravimetric Analyzer cannot be used under conditions of high vacuum. The rate of gas flow was 70cc./min. and the sample size was about 10mg. Programmed work was carried out using a heating rate of 5°C/min., the sample being heated from ambient to 500°C. Typical traces obtained for the degradation of a number of copolymers are shown in Fig.3.9. As the acrylate content of the copolymer examined increases the T.G.A. trace moves to higher temperatures, showing that the copolymer is becoming more stable to weight loss. At high methacrylate content a two stage decomposition takes place, the higher temperature process accounting for the bulk of the weight loss. These observations are in agreement with the data obtained from T.V.A., although because of the different conditions used, these techniques are not strictly comparable.

(a) Determination of Kinetic Parameters from T.G.A.

While it is difficult to determine reaction kinetics by the use of T.V.A. many methods of obtaining kinetic parameters from T.G.A. measurements have been advocated[66,68]. It was considered possible that activation energies found in this way could make some contribution towards an understanding of the thermal breakdown of the copolymer system under investigation.

Dynamic T.G.A. has the advantage in theory that a single programmed weight loss curve can yield the same information as a whole set of isothermal traces, but many methods of calculating kinetic data from such programmed

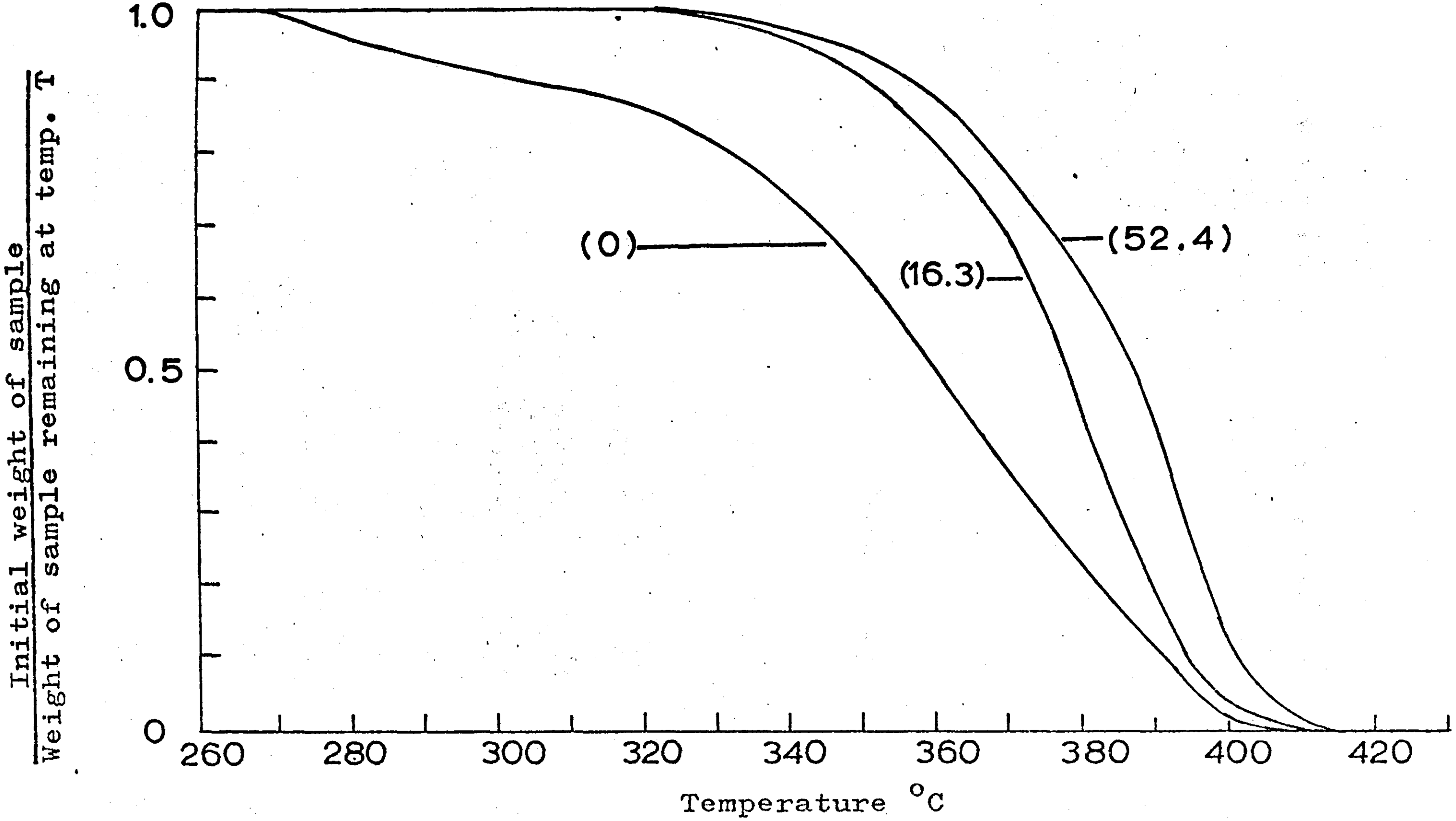


Fig.3.9 Programmed (5°C/min.) T.G.A. traces of a series of copolymers. The figures in brackets give copolymer composition as mole percent n-butyl acrylate.

runs require the original trace to be differentiated, a process which can greatly increase experimental scatter, or require the assumption that a single set of parameters applies over the whole reaction. This assumption is not always justified since the nature of the material being degraded can change drastically in character with increasing conversion. Isothermal methods avoid such complications but in these the sample can undergo considerable reaction while being heated to the temperature of interest. In view these considerations it was decided to carry out both dynamic and isothermal T.G.A. measurements.

(a.1) Dynamic T.G.A.

In the literature many mathematical treatments of polymer degradation processes have been developed. Such treatments [16,53] show that if initiation occurs solely at chain ends or solely at random along the chain, then, in the limits of long and short depolymerization zip lengths, the overall degradation process can be described by an "order" type of equation, as in table 3.2.

Table 3.2

Type of Initiation	Zip Length	"Order" of Reaction
End Initiation	Long	One
	Short	Zero
Random Initiation	Long	One
	Short	None

The particular method used to determine activation energies was that of Coats and Redfern [72]. The appropriate plots of $\log[2.303\log F/T^2]$ versus $1/T$, where F is the fractional weight of material remaining and T is the absolute temperature, are shown in Figs.3.10-3.14. From the gradients of these plots the activation energies listed in table 3.3 were calculated.

Table 3.3

Copolymer Composition (mole °/o n-butyl acrylate)	Activation Energy of Random Initiation (kcal./mole)
0	39
0.4	41
3.9	48
16.3	50
52.4	51

As the acrylate content of the copolymers increases, the end initiated reaction is suppressed, so that it becomes extremely difficult to separate the first decomposition from the randomly initiated one. In view of this, no activation energies are quoted here for this end initiated process. The use of a first order plot is probably less valid for the 52.4 mole percent n-butyl acrylate copolymer than for any of the others in table 3.3 because at this acrylate content the zip length is possibly too short for the degradation to follow first

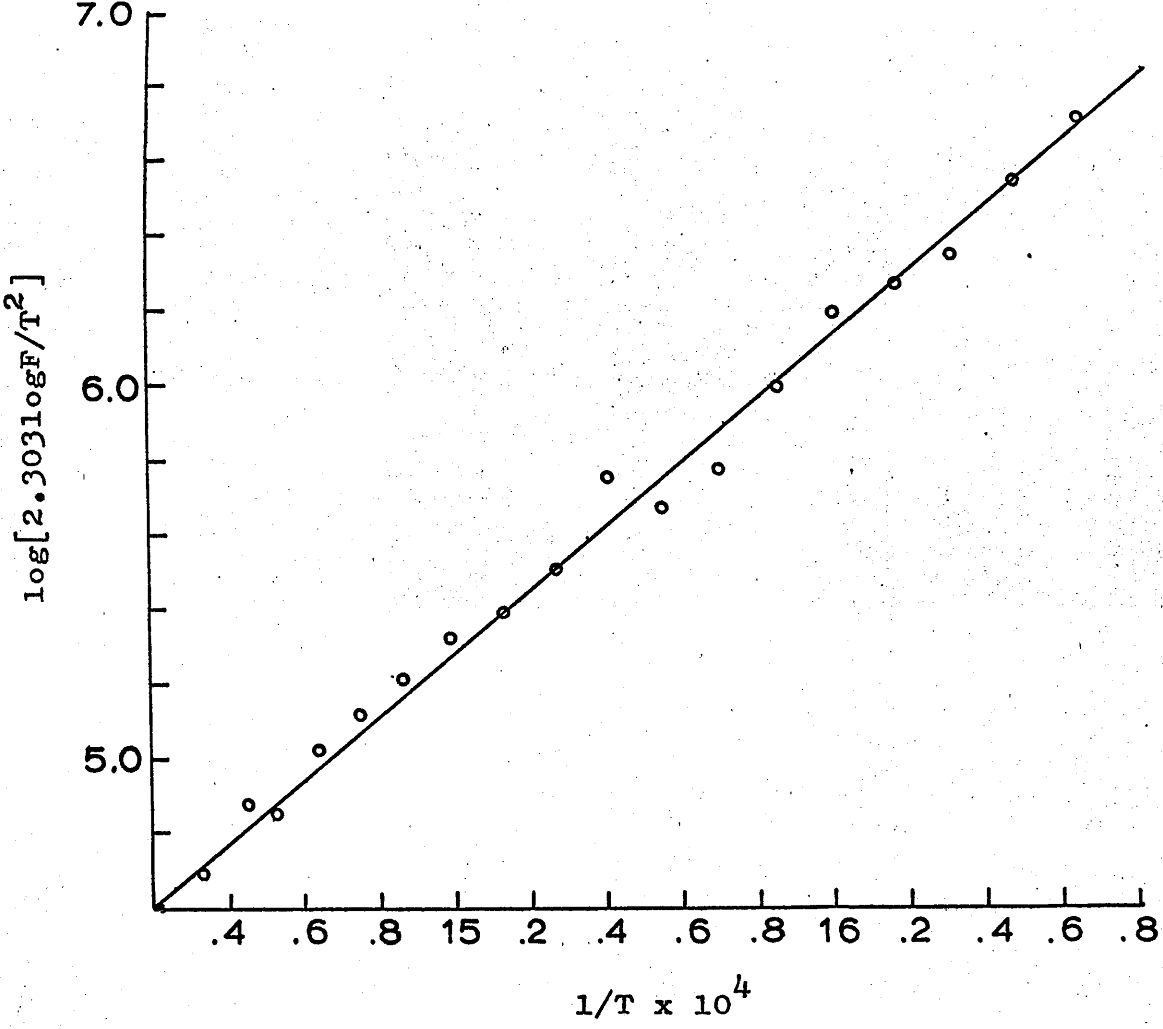


Fig.3.10 First order plot for poly(methyl methacrylate) standard.

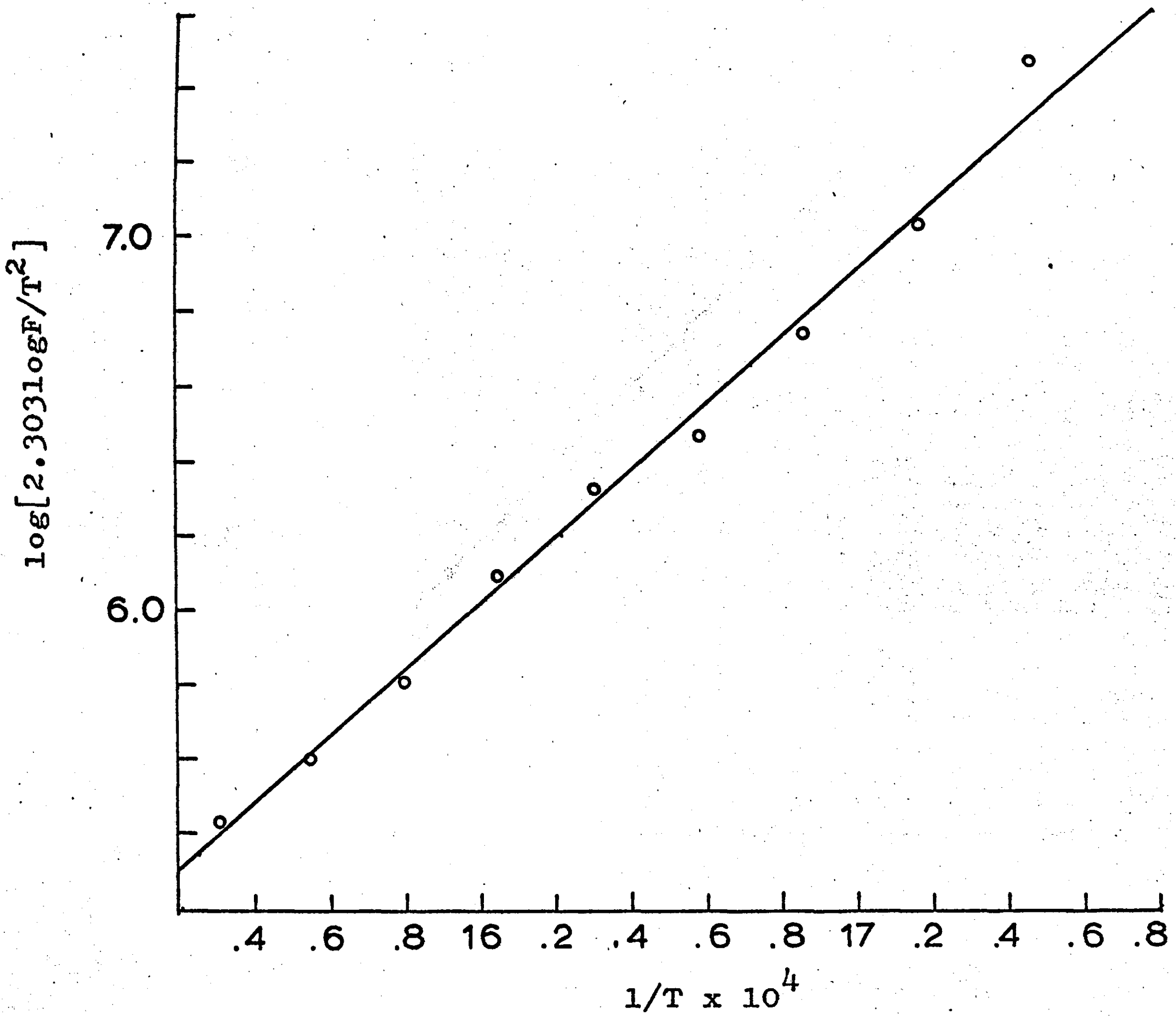


Fig.3.11 First order plot for a 0.4 mole °/o n-butyl acrylate copolymer.

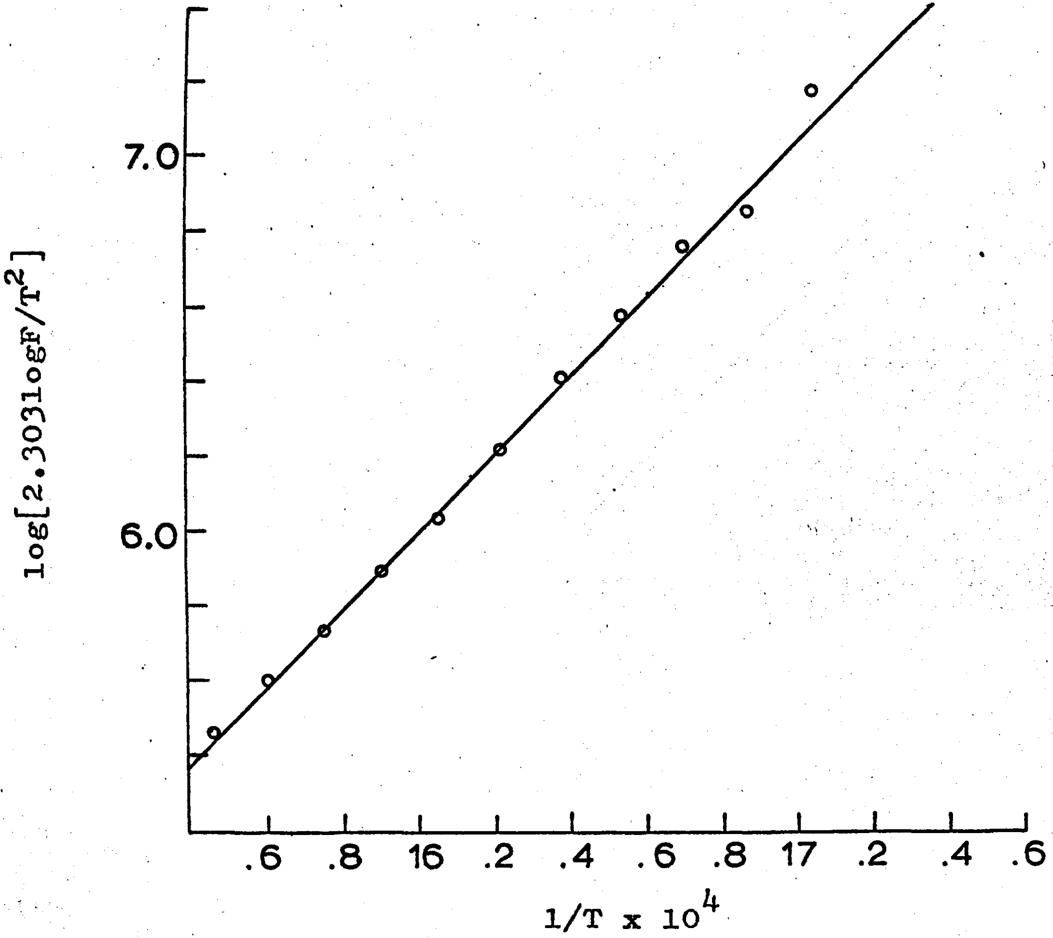


Fig.3.12 First order plot for a 3.9 mole percent n-butyl acrylate copolymer.

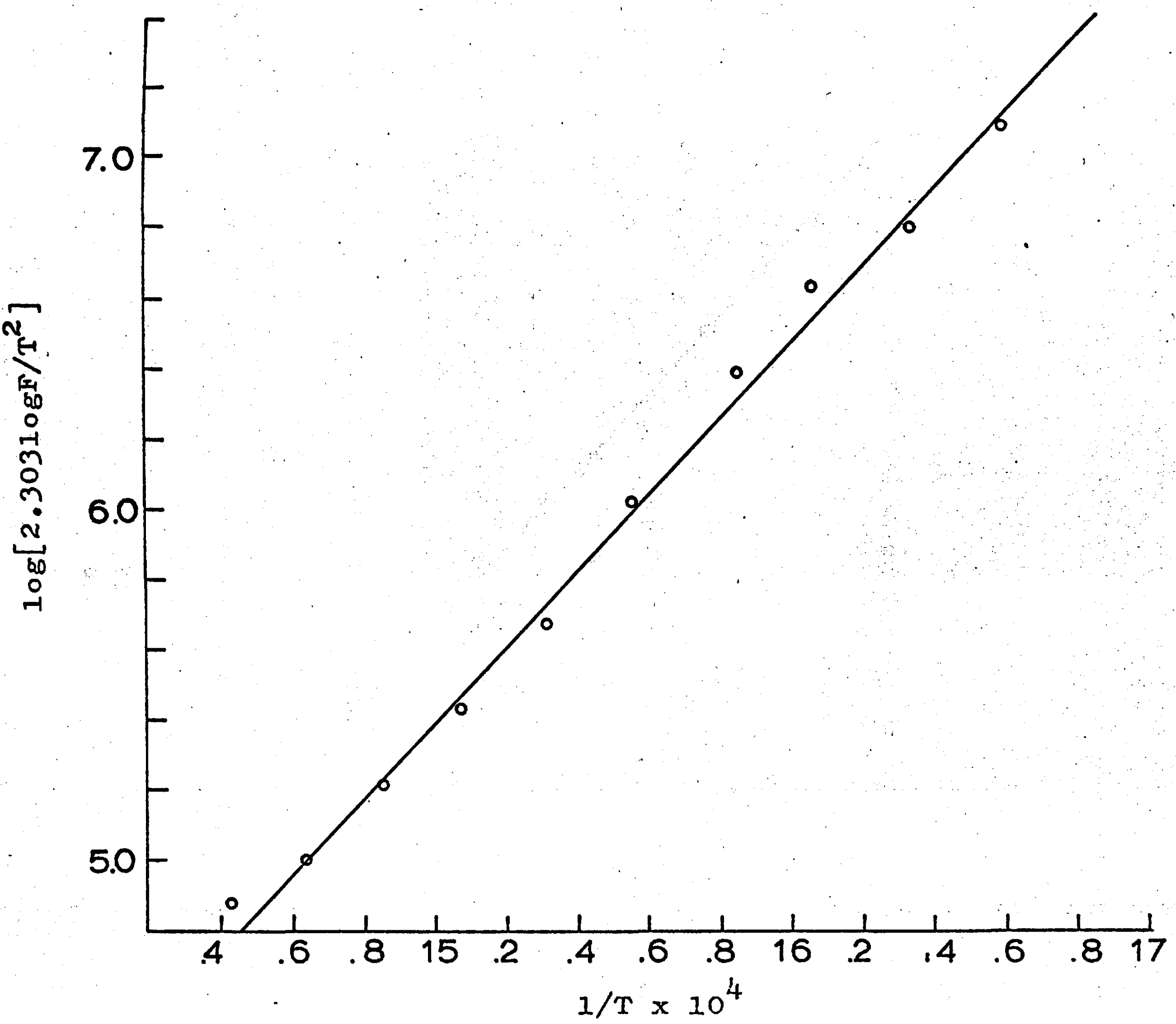


Fig.3.13 First order plot for a 16.3 mole percent n-butyl acrylate copolymer.

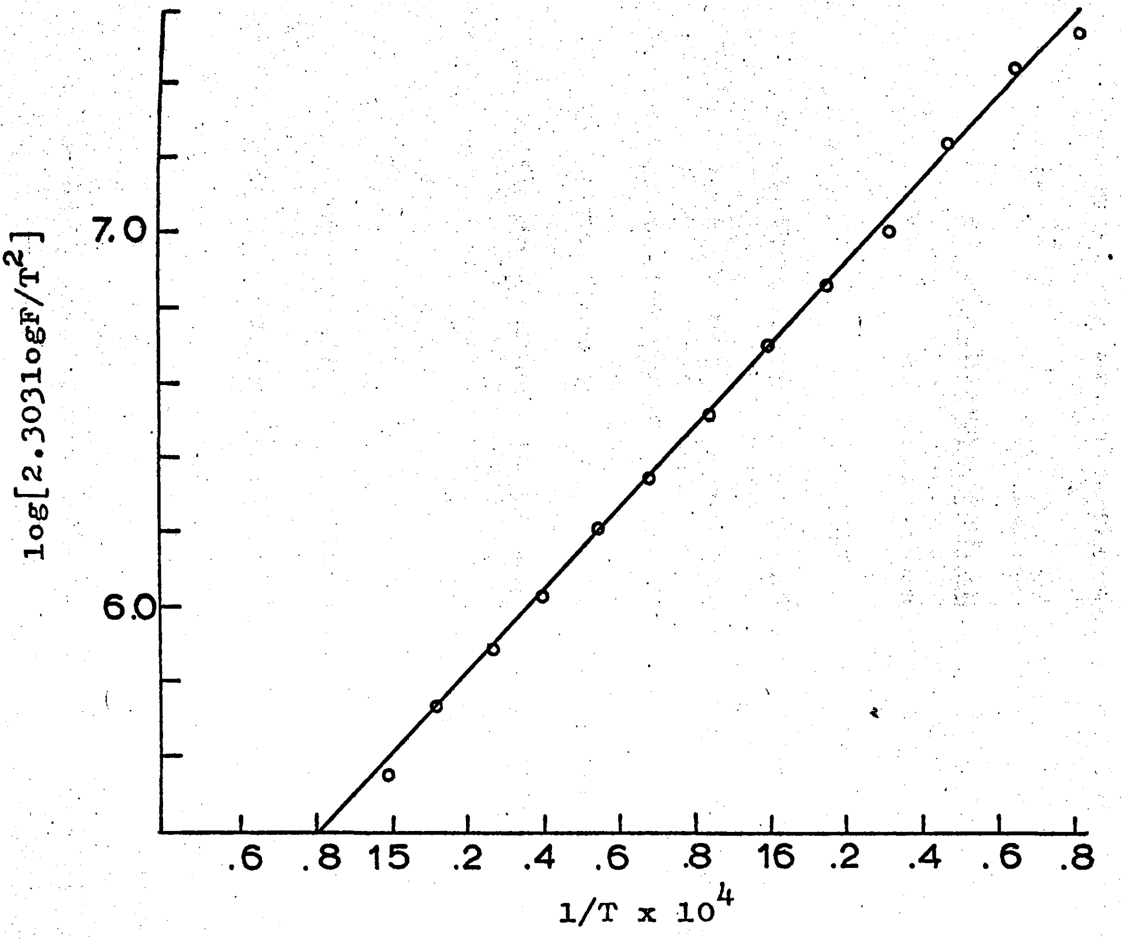


Fig.3.14 First order plot for a 52.4 mole percent n-butyl acrylate copolymer.

order kinetics closely. At still higher acrylate content the degradation cannot be approximated to any "order" type of process. Few published methods of obtaining kinetic parameters from programmed T.G.A. data can deal with random kinetics and those that can involve experimental measurements outwith the scope of the instrumentation available [73].

(a.2) Isothermal T.G.A.

If the rate of decomposition of a sample can be found for the same extent of conversion at a number of temperatures, then an activation energy may be calculated. This value is not an average one, but refers to the particular extent of degradation at which it was calculated. It is convenient to use zero conversion as the point at which to determine activation energy, since this condition of the sample is the most reproducible. It is not possible, because of the time required for the thermobalance to attain equilibrium to find the initial rate of decomposition directly, the technique used here being to extrapolate the rate of weight loss versus time curve back to zero time. The first 3°/o of degradation occurred during heat up and was neglected, the extrapolation being carried out on data obtained for up to 20°/o conversion. Initial rate methods are not strictly applicable where the material decomposes by random scission, since this type of breakdown leads to an initial rate of zero with respect to weight loss. In considering the copolymers in order of increasing acrylate content, as poly(n-butyl acrylate) degrades randomly there must be a point at which initial rate techniques become invalid. This point may be found simply, since "random" processes can be distinguished from "order" processes by the fact that the maximum rate of decomposition does not occur at zero conversion for random breakdown. Hence for random kinetics the T.G.A. trace i.e. weight loss versus time, will exhibit a point of inflection. For copolymers containing up to 52.4 mole percent n-butyl acrylate, no such inflection points were found. Figs.3.15-3.19 show the log(initial rate) versus 1/T plots obtained from the values listed in tables 3.4-3.8 where T is the absolute temperature. The activation energies calculated from the gradients of these plots are given in table 3.9.

In the literature there are many examples of initial rate measurements being made on randomly degrading polymers [8]. This type of measurement not only involves a very inaccurate plot, but attempts to fit the degradation to an erroneous set of parameters, and should be avoided.

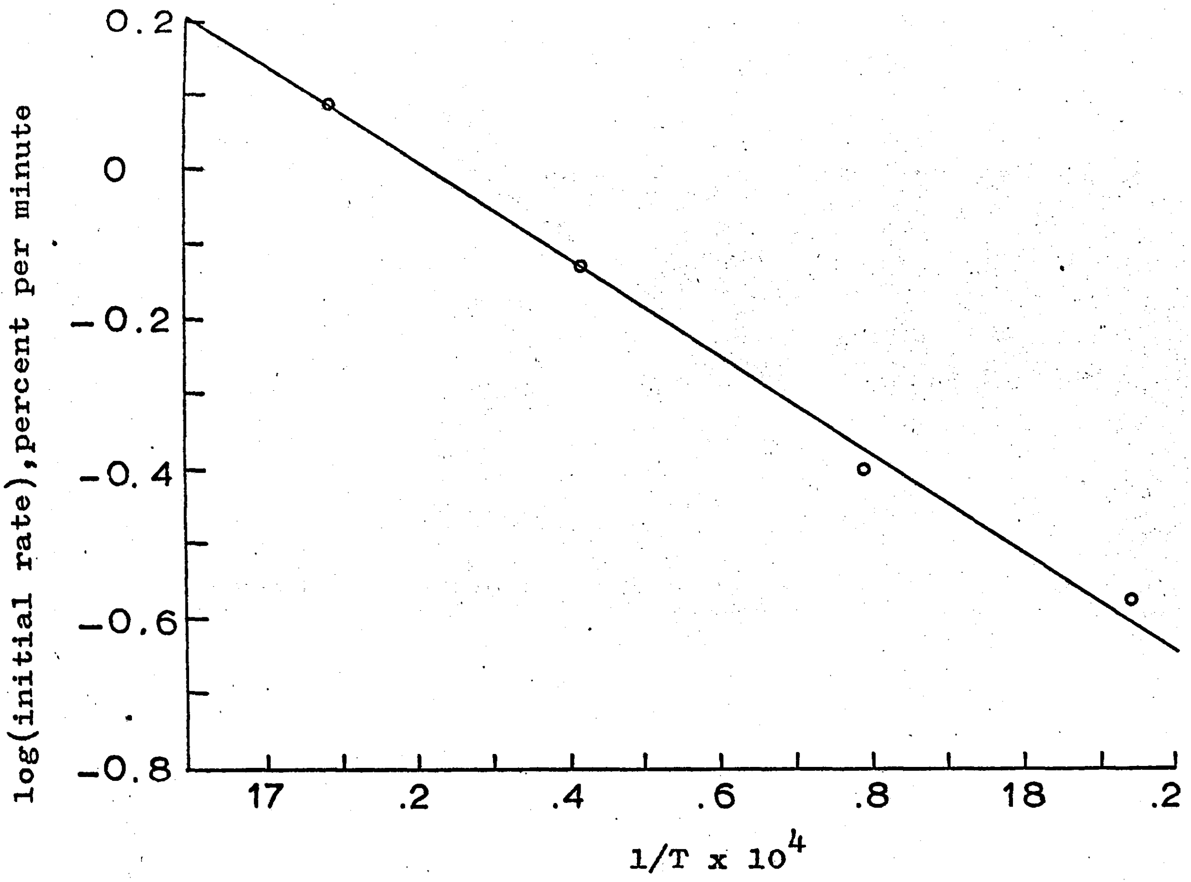


Fig.3.15 Activation energy plot from initial rate data for a poly(methyl methacrylate) standard.

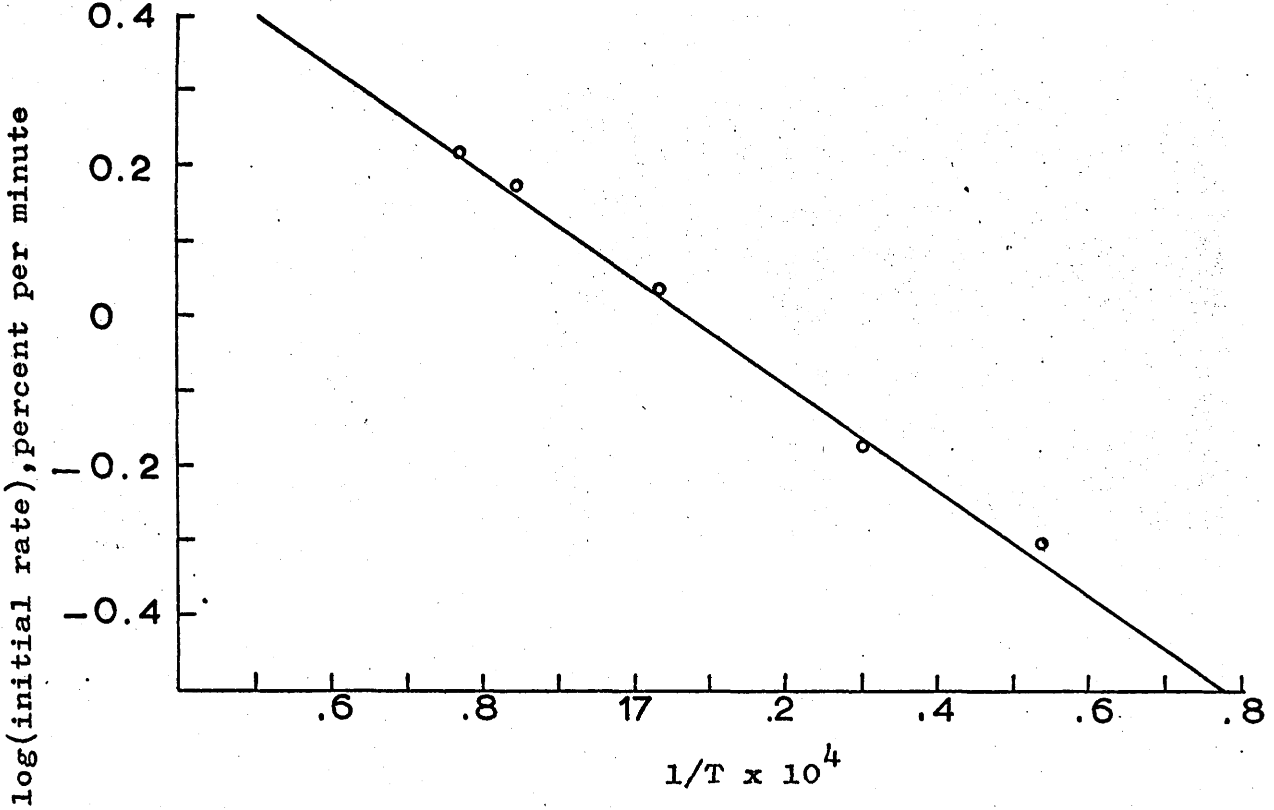


Fig.3.16 Activation energy plot from initial rate data for a 0.4 mole percent n-butyl acrylate copolymer.

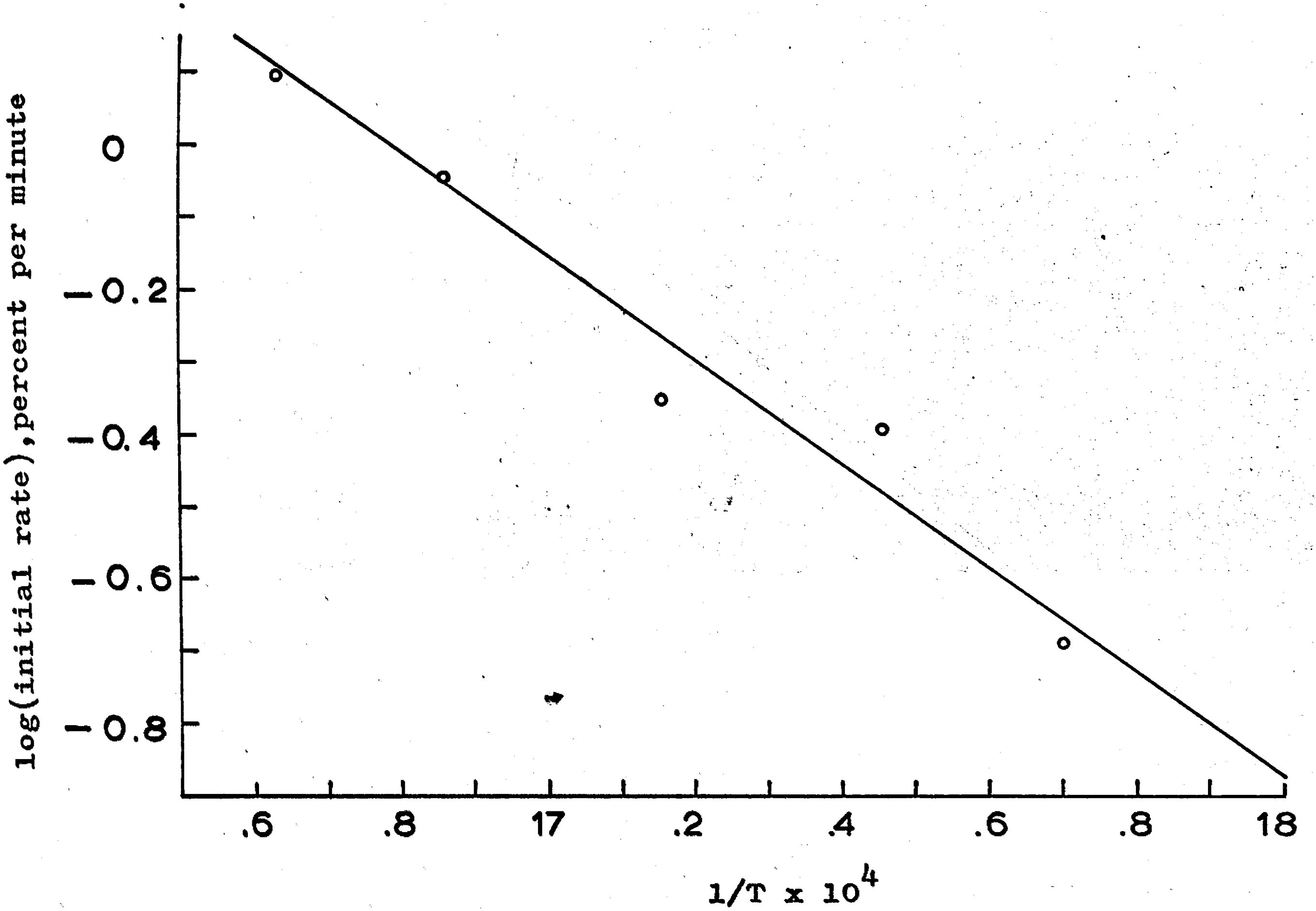


Fig.3.17 Activation energy plot from initial rate data for a 3.9 mole percent n-butyl acrylate copolymer.

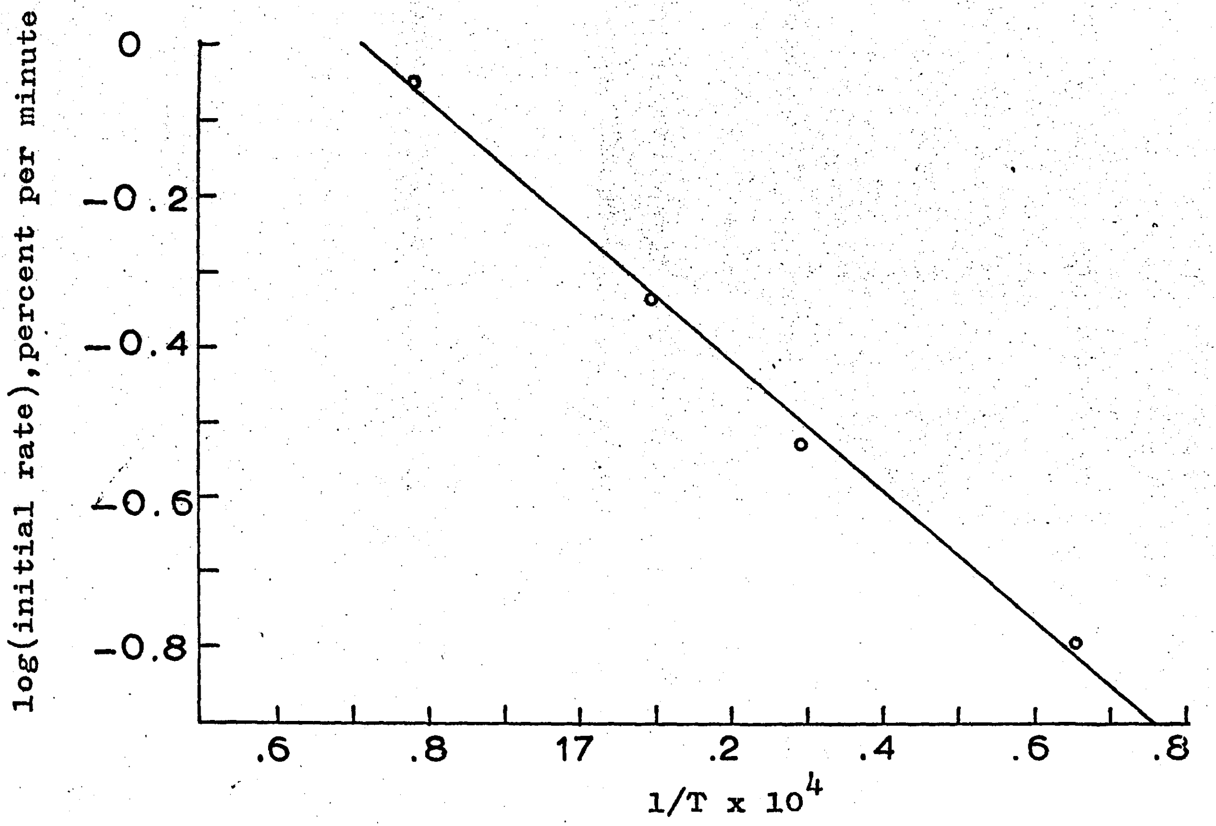


Fig.3.18 Activation energy plot from initial rate data for a 16.3 mole percent n-butyl acrylate copolymer.

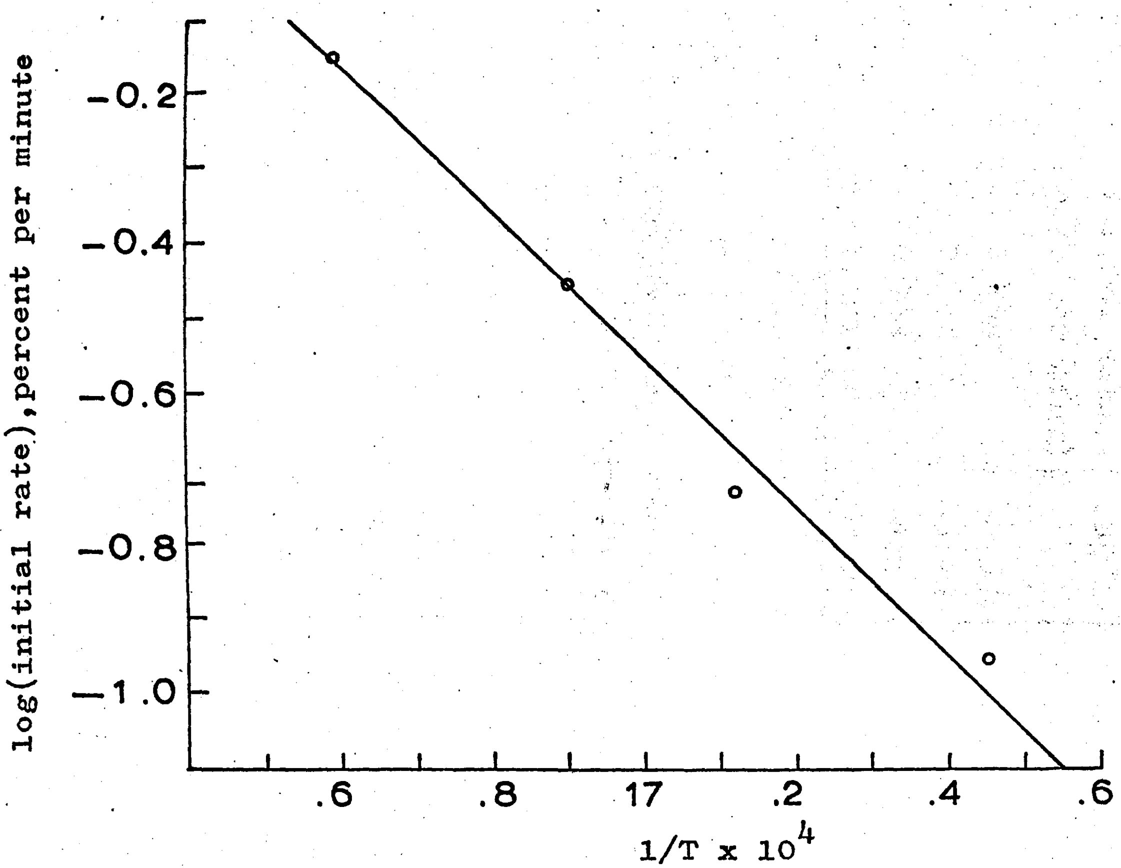


Fig.3.19 Activation energy plot from initial rate data for a 52.4 mole percent n-butyl acrylate copolymer.

Table 3.4

Initial Rate Data for a Poly(methyl methacrylate) Standard.

Initial Rate, I (°/o per min.)	log I	Temp. (°C)	$1/T \times 10^4$
0.264	-0.578	278.0	18.14
0.398	-0.400	289.0	17.79
0.734	-0.134	301.0	17.42
1.221	0.087	312.0	17.09

Table 3.5

Initial Rate Data for a 0.4 Mole Percent n-Butyl Acrylate Copolymer.

Initial Rate, I (°/o per min.)	log I	Temp. (°C)	$1/T \times 10^4$
0.492	-0.308	297.0	17.54
0.662	-0.179	305.0	17.30
1.076	0.032	314.5	17.03
1.479	0.170	320.5	16.85
1.637	0.214	323.5	16.77

Table 3.6

Initial Rate Data for a 3.9 Mole Percent n-Butyl Acrylate Copolymer.

Initial Rate, I (°/o per min.)	log I	Temp. (°C)	1/T x 10^4
0.204	-0.690	292.0	17.70
0.398	-0.400	300.0	17.45
0.441	-0.356	310.0	17.15
0.904	-0.044	320.0	16.86
1.255	0.099	328.0	16.63

Table 3.7

Initial Rate Data for a 16.3 Mole Percent n-Butyl Acrylate Copolymer.

Initial Rate, I (°/o per min.)	log I	Temp. (°C)	1/T x 10^4
0.163	-0.788	293.5	17.65
0.296	-0.529	305.5	17.29
0.458	-0.339	312.0	17.09
0.889	-0.051	323.0	16.78

Table 3.8

Initial Rate Data for a 52.4 Mole Percent n-Butyl Acrylate Copolymer.

Initial Rate, I (°/o per min.)	log I	Temp. (°C)	$1/T \times 10^4$
0.111	-0.953	300.0	17.45
0.184	-0.736	311.0	17.12
0.349	-0.457	319.0	16.90
0.706	-0.151	330.0	16.59

Table 3.9

Activation Energy From Initial Rate Measurements.

Copolymer Composition (mole °/o n-butyl acrylate)	Activation Energy (kcal./mole)
0	30
0.4	32
3.9	34
16.3	39
52.4	46

(b) Discussion of Results

For copolymers of high methyl methacrylate content, the activation energies quoted in table 3.9 are considerably lower than those listed in table 3.3 for the randomly initiated reaction. This may be explained by noting that the values found by the initial rate method will, in this copolymer composition region, refer to the end initiated degradation. In the literature many determinations of the energy of activation for poly(methyl methacrylate) decomposition have been reported [11,20,74-76]. Typical values obtained for the chain end initiated and randomly initiated reactions are 31 and 49 kcal./mole respectively.

The activation energy for poly(methyl methacrylate) degradation is a composite quantity involving contributions from the energies involved in the elementary steps of initiation, depropagation and termination [77,78]. If copolymers of very low acrylate content are considered, it is likely that the initial step in their breakdown will be the same as that in pure poly(methyl methacrylate) and that the energy involved in the termination step, being diffusion controlled because of the high viscosity of the degrading polymer, will not change markedly. This would imply that the increase in activation energy found at this range of copolymer composition with increasing n-butyl acrylate content is due to an increase in the activation energy of depropagation, E_d. Since $E_d = E_p - \Delta H_p$ where E_p is the energy of propagation in polymerization and $(-\Delta H_p)$ the heat of polymerization, and the value of E_p is about 5 kcal./mole for a large variety of polymers [78], any increase in E_d with increasing acrylate content would be reflected by an increase in $(-\Delta H_p)$. In the limiting case this means that $(-\Delta H_p)$ for n-butyl acrylate must be greater than that for methyl methacrylate. The experimental values of this quantity for n-butyl acrylate and methyl methacrylate were found to be 18.6 and 13.3 kcal./mole respectively, lending support to the above theory [79].

At higher acrylate content, new initiation steps involving n-butyl acrylate units become likely, as well as the possibility of transfer reactions and the modification of the termination step. It is the interplay of all these contributions which determines the overall activation energy as found by methods such as T.G.A.

3.4 Differential Thermal Analysis

An atmosphere of nitrogen flowing at a rate of

1.5 litres/min. was employed since the Du Pont 900 Differential Thermal Analyzer cannot operate under high vacuum conditions. The sample size was in the region of 10mg.,being heated at 10°C/min. from ambient to 500°C.

For copolymers rich in methacrylate an endotherm occurs at the same temperature as degradation,Fig.3.20. Pyrolysis is a complex reaction during which various processes both endothermic, such as bond rupture or volatilization, and exothermic, such as cross linking, can happen simultaneously. In such cases the D.T.A. thermogram shows only the net heat effect and may not give complete information on all of the individual reactions.

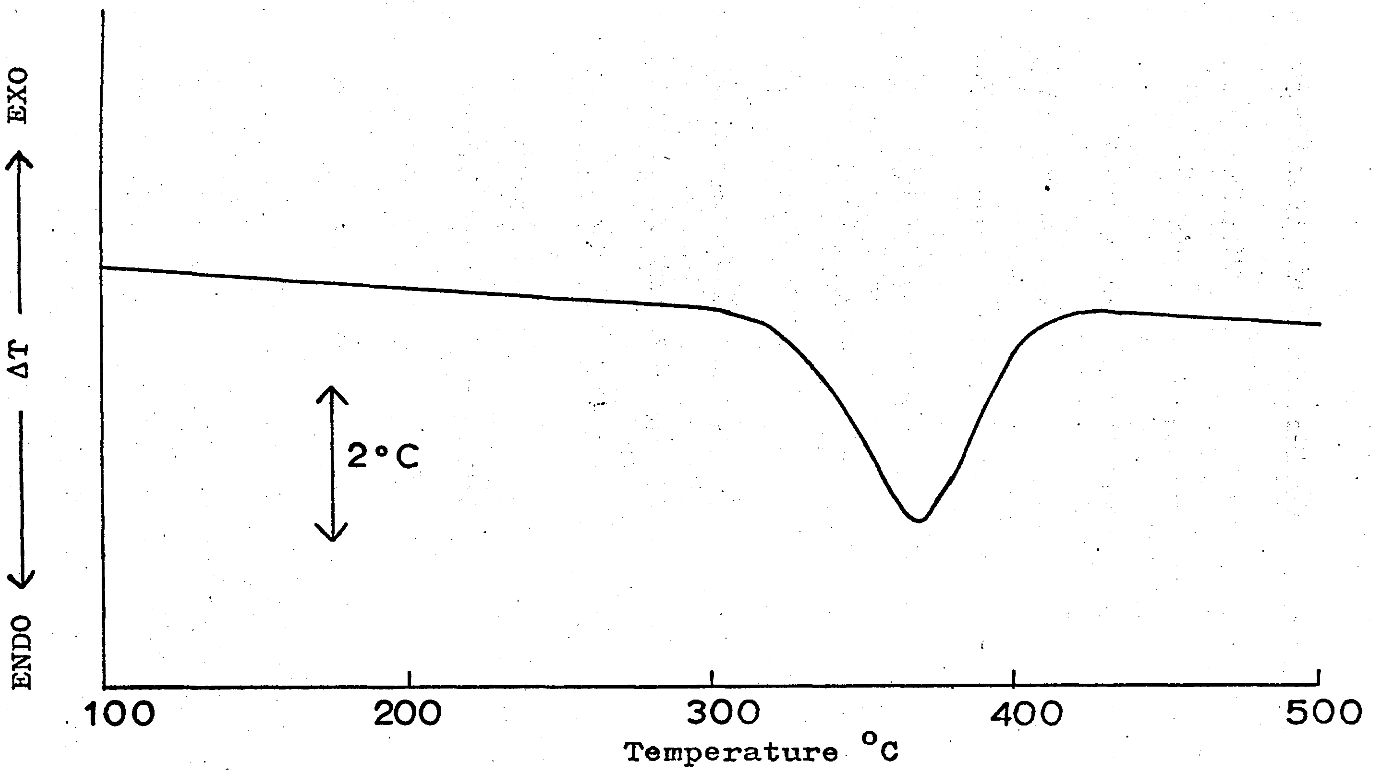


Fig.3.20 D.T.A. of a 0.4 mole percent n-butyl acrylate copolymer.
Sample size 11.8mg.

CHAPTER 4

IDENTIFICATION OF THE PRODUCTS OF DEGRADATION

4.1 Introduction

Before any quantitative measurements can be undertaken, a knowledge of the nature of the degradation products is necessary so that techniques may be devised to estimate these materials. Preliminary degradations were carried out for times up to twenty four hours at 313°C using the sealed tube technique, samples of the product gases and liquid volatiles being obtained as in section 2.2a. Where possible, more than one technique was used to elucidate the structure of these compounds.

4.2 Analysis of Product Gases

(a) Gas Chromatography

Experiments were carried out on these gases as described in section 2.6. The resulting traces, using the columns listed in table 2.3 under the conditions previously specified, are shown in Figs.4.1-4.3. The retention time for each peak was obtained, and standard samples of the pure gases, (Mathieson Inc.), were introduced into the column under the same conditions. A sample of carbon monoxide was made by the action of concentrated sulphuric acid on formic acid. Tables 4.1-4.3 list the gases with the same retention times as those shown in Figs.4.1-4.3.

Table 4.1

Peak no. in Fig.4.1	Gas	Retention Time (minutes)	Temperature (^oC)
1	Methane	2.5	40
2	Ethane	6.5	58
3	Ethylene	10.5	78
4	Propane	12.5	88
5a	Propylene	19.0	120
5b	Butane	19.5	123
6	Butene	24.0	145

Table 4.2

Peak no. in Fig.4.2	Gas	Retention Time (minutes)
1	Trans But-2-ene	9.0
2	But-1-ene	11.5
3	Cis But-2-ene	13.5

Table 4.3

Peak no. in Fig.4.3	Gas	Retention Time (minutes)
1	Hydrogen	8.0
2	Carbon Monoxide	11.5
3	Methane	12.5

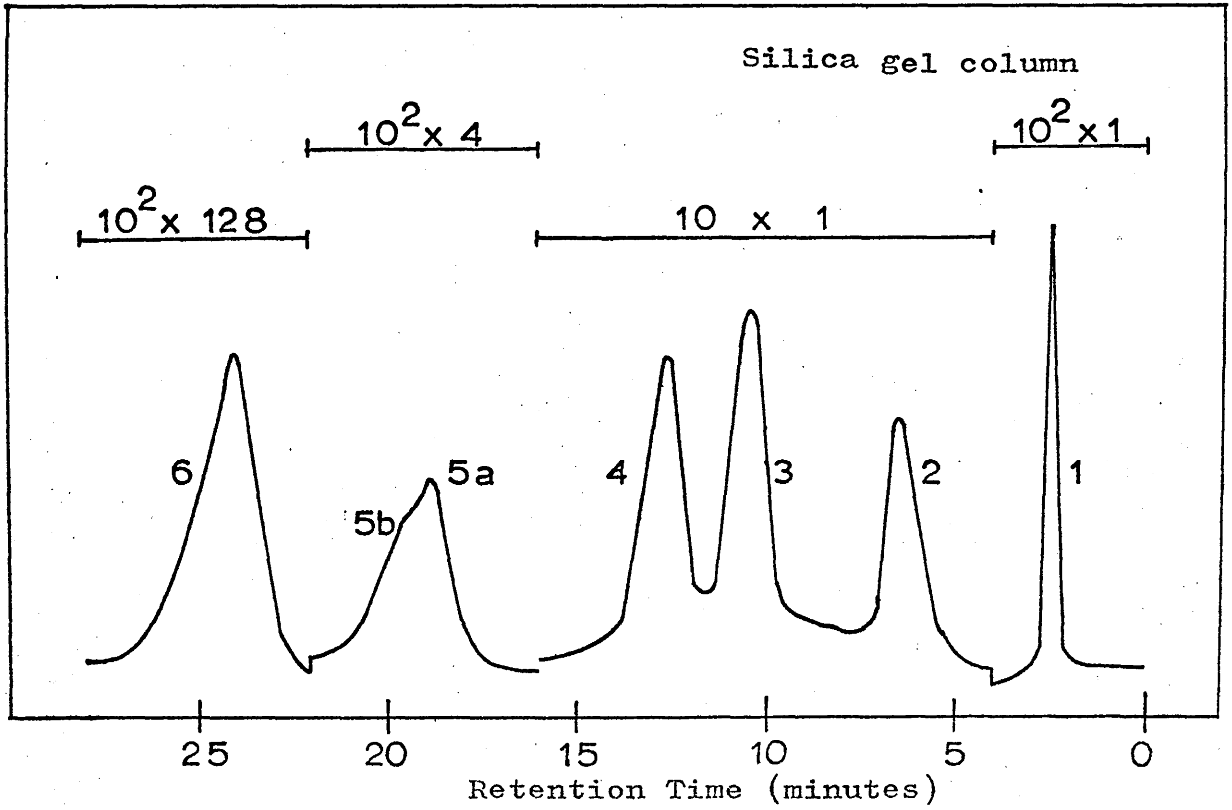


Fig.4.1 G.L.C. trace for a 50.0 mole percent n-butyl acrylate copolymer degraded at 313°C for 11 hours. Column run isothermally at 40°C for 3min. then programmed at 5°C/min.

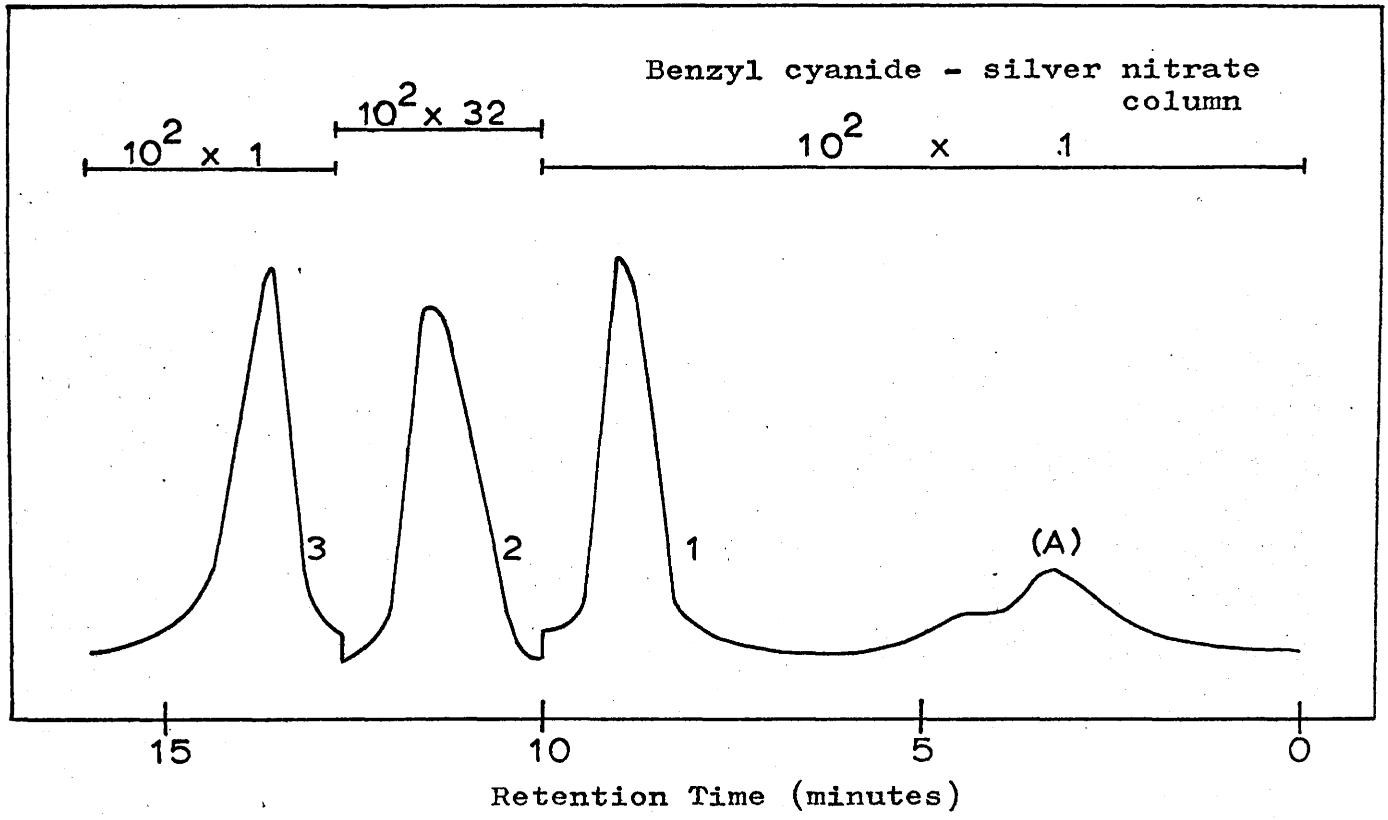


Fig.4.2 Room temperature g.l.c. of a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C for 16 hours.

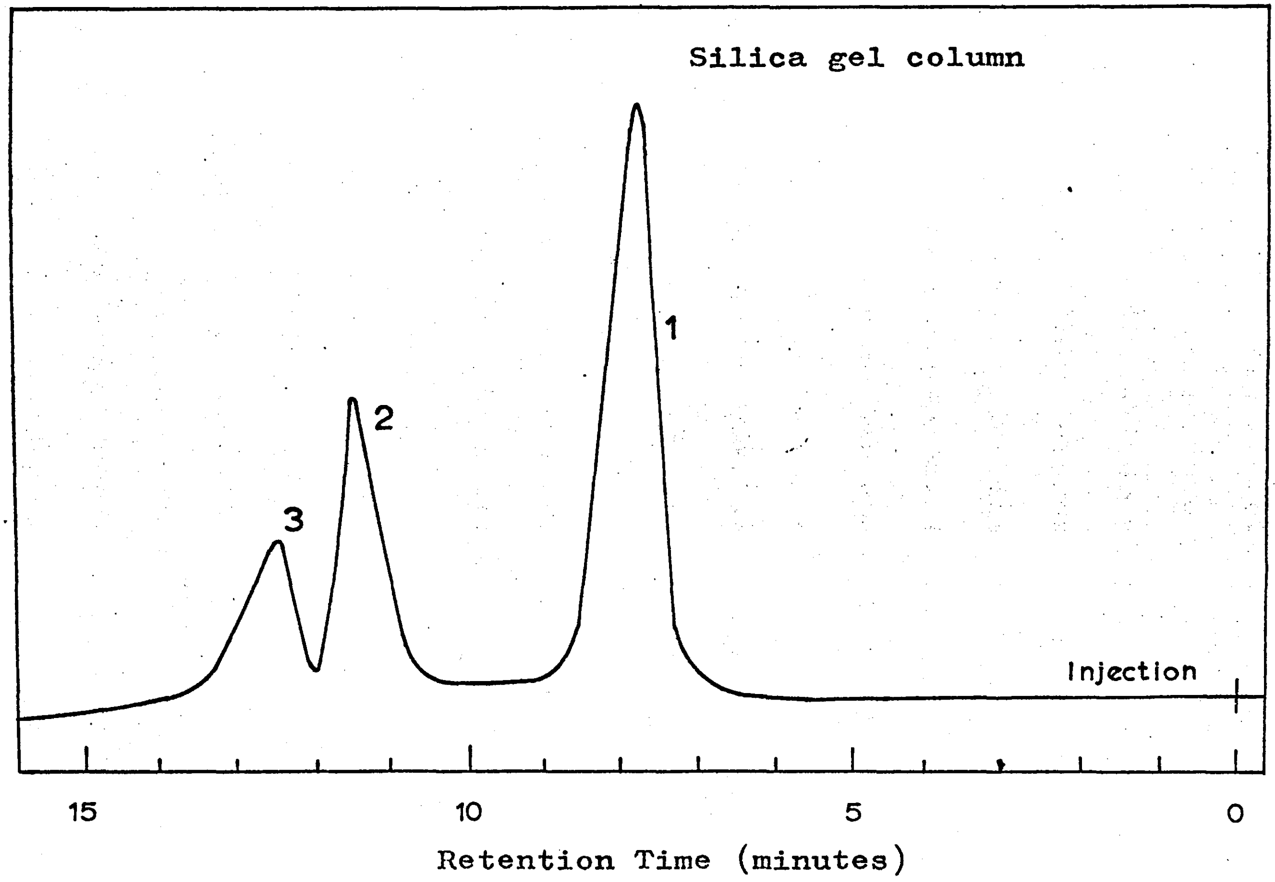


Fig.4.3 Room temperature g.l.c. of the permanent gas fraction from the degradation of a 52.4 mole percent n-butyl acrylate copolymer pyrolyzed at 313°C for 24 hours.

The initial column used for gas analysis was silica gel in conjunction with a flame ionization detector. The results from these experiments did not indicate which of the isomeric butenes were present, so that it was necessary to use the silver nitrate - benzyl cyanide column to obtain this information. The small peak (A) in Fig.4.2 with a retention time somewhat less than that for trans but-2-ene corresponds to peaks 1-5 of Fig.4.1. Care must be taken not to heat this column since decomposition is liable to occur at about 50°C. The sample size required to obtain acceptable chromatograms of the permanent gases, Fig.4.3, increased with decreasing acrylate content, and, as 1.5g. of the 52.4 mole percent n-butyl acrylate copolymer were used, no examination was made of copolymers with lesser amounts of acrylate.

(b) Mass Spectrometry

Mass spectrometric data on the product gases were obtained as in section 2.7 using an electron beam energy of 20ev. Fig4.4 compares the cracking patterns obtained from a standard sample of but-1-ene (Mathieson Inc.) and from the gases evolved when a 16.3 mole percent n-butyl acrylate copolymer was degraded. Table 4.4 lists the fragment masses in order of abundance and gives the possible structures corresponding to each. A significant difference

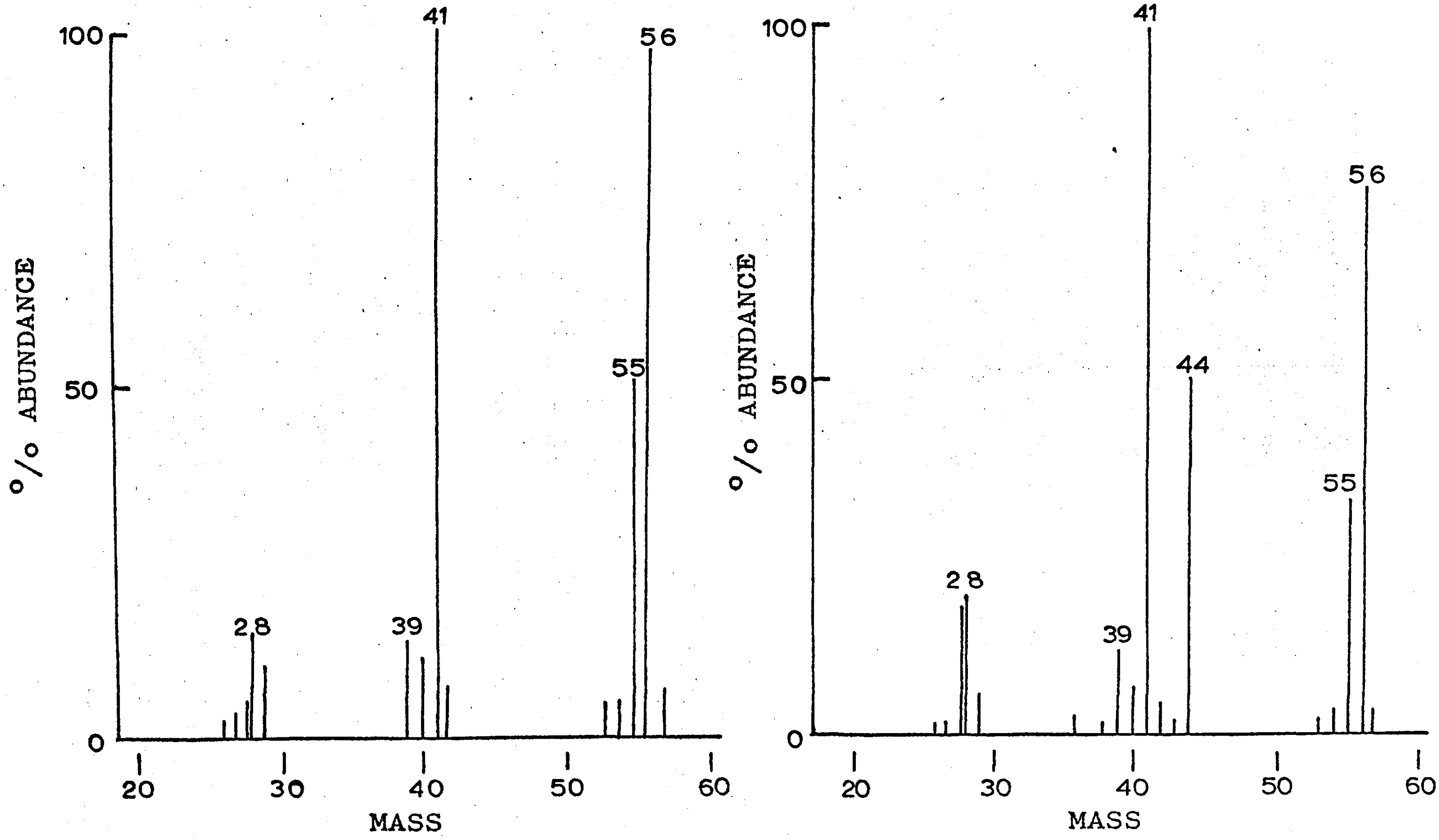


Fig.4.4 (a) But-1-ene standard.

(b) Product gases from a 16.3 mole $^{o}/_{o}$ n-butyl acrylate copolymer degraded for 12 hours at 313^{o}C.

Table 4.4

Mass in Order of Abundance	Structure
41	$CH_2=\overset{+}{C}-CH_3$
56	$[CH_3-CH_2-CH=CH_2]^{+\cdot}$
44	$[O=C=O]^{+\cdot}$
55	$CH_3-\overset{+}{C}H-CH=CH_2$
28	$\dot{C}H_2-\overset{+}{C}H_2$

between Figs.4.4a and 4.4b is that the peak in 4.4b at mass 44, attributed to CO_2, is absent from Fig.4.4a. This shows that the product gases contain carbon dioxide in addition to the gases already listed in tables 4.1-4.3. There are not sufficient differences in the mass spectra of the isomeric butenes to allow them to be readily distinguished, since double bonds appear to be able to migrate easily in the molecular ion. It may also be noted that in Fig.4.4 there is a doublet at mass 28 and that, comparing the spectra of but-1-ene and the evolved gases, the peak of lower mass has increased in size in the latter relative to the peak of higher mass. Mass 28 may be ascribed to carbon monoxide, nitrogen, or ethylene, in order of increasing mass. This makes it likely that the enhancement of the lower mass 28 peak is due to carbon monoxide.

(c) Infra-red

A typical infra-red spectrum for the gaseous degradation products from a 93.4 mole percent n-butyl acrylate copolymer, obtained as in section 2.9a, is shown in Fig.4.5. The assignments of the various absorptions are listed in table 4.5. These are consistent with the presence of a vinyl double bond $RCH{=}CH_2$ which is found in only one of the butenes, but-1-ene. The presence of carbon dioxide is confirmed by the absorptions at 2350cm.$^{-1}$ and 677cm.$^{-1}$, while the characteristic absorption at 2140cm.$^{-1}$ can be attributed to carbon monoxide.

4.3 Analysis of the Liquid Volatiles

(a) Gas-Liquid Chromatography

A typical chromatogram of the liquid products from a 50.0 mole percent n-butyl acrylate copolymer, run on a 1°/o S.E.30 column as specified in table 2.3 is shown in Fig.4.6. The retention times of the various peaks in this trace could be accounted for by the materials given in table 4.6, which are reasonable products of degradation.

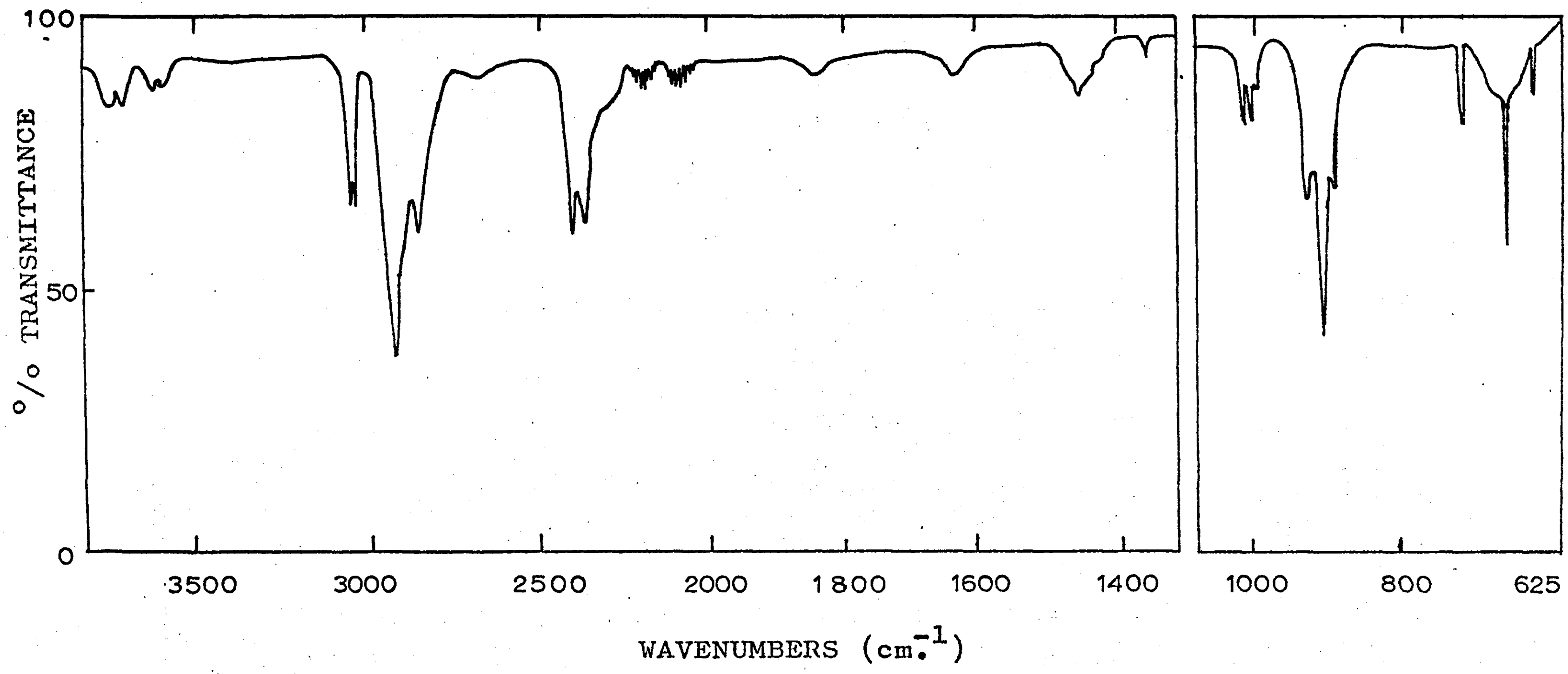


Fig.4.5 Infra-red spectrum of a 93.4 mole percent n-butyl acrylate copolymer degraded for 12.5 hours at 313°C.

Table 4.5

Assignments of the Infra-red Absorptions Shown in Fig.4.5.

Wavenumber, $cm.^{-1}$	Intensity	Assignment
3090	m	C—H stretch in $=C-H$
2970 2940 2898 2878	s	C—H stretch in $-CH_3$ and $-CH_2-$
2350	s	CO_2 antisymmetric stretch
2140	w	$C\equiv O$ stretch
1835	w	overtone of peak at $912 cm.^{-1}$
1650	m	$C=C$ stretch
1470	m	C—H deformation in $-CH_2-$ and $-C-CH_3$
1309	vw	C—H deformation in $-CH=C-$
998	m	C—H deformation in $-CH=C-$
912	s	CH_2 deformation in $=CH_2$
677	s	CO_2 bend

s = strong m = medium w = weak vw = very weak

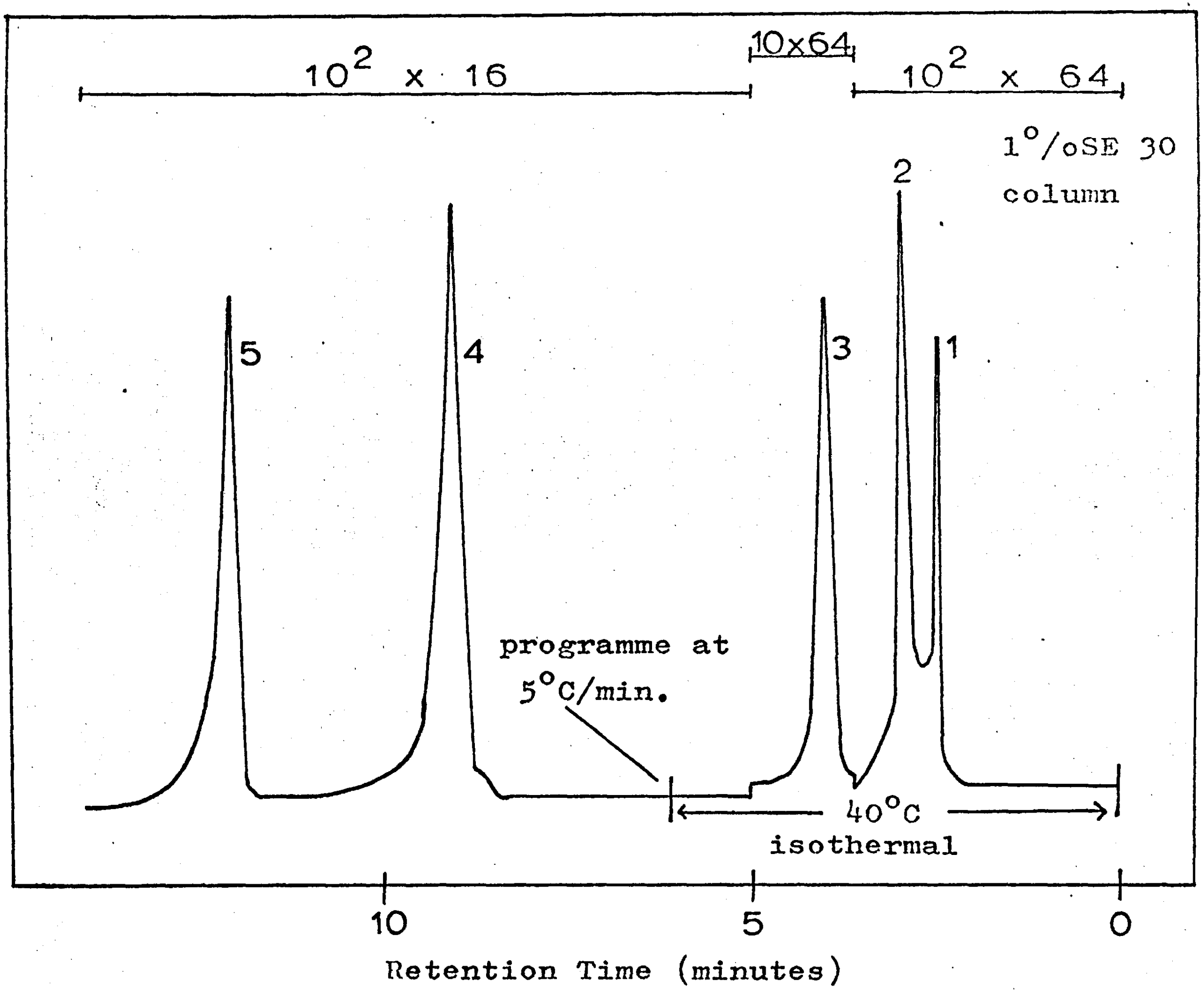


Fig.4.6 G.L.C. trace of the liquid degradation products from the breakdown of a 50.0 mole percent n-butyl acrylate copolymer heated at 313°C for 4 hours.

Table 4.6

Peak no. in Fig.4.6	Component	Retention Time (minutes)	Temperature (^oC)
1	n-Butanol	2.5	40
2	Methyl Methacrylate	3.0	40
3	Toluene (solvent)	4.0	40
4	n-Butyl Acrylate	9.0	54
5	n-Butyl Methacrylate	12.0	70

(b) Combined Gas Chromatography-Mass Spectrometry

(b.1) Experimental

A sample size of 0.1μl. of neat liquid products was found to give acceptable results under the conditions specified in section 2.8, using 70ev. electrons. The g.l.c. trace from a 50.0 mole percent n-butyl acrylate copolymer is shown in Fig.4.7 and the mass spectrum of each of the component peaks given in Figs.4.8-4.12. All the mass spectra presented are in the form of line diagrams corrected for background which show the overall features at a glance. It must now be considered whether these spectra can be accounted for in terms of the proposed structures for each component.

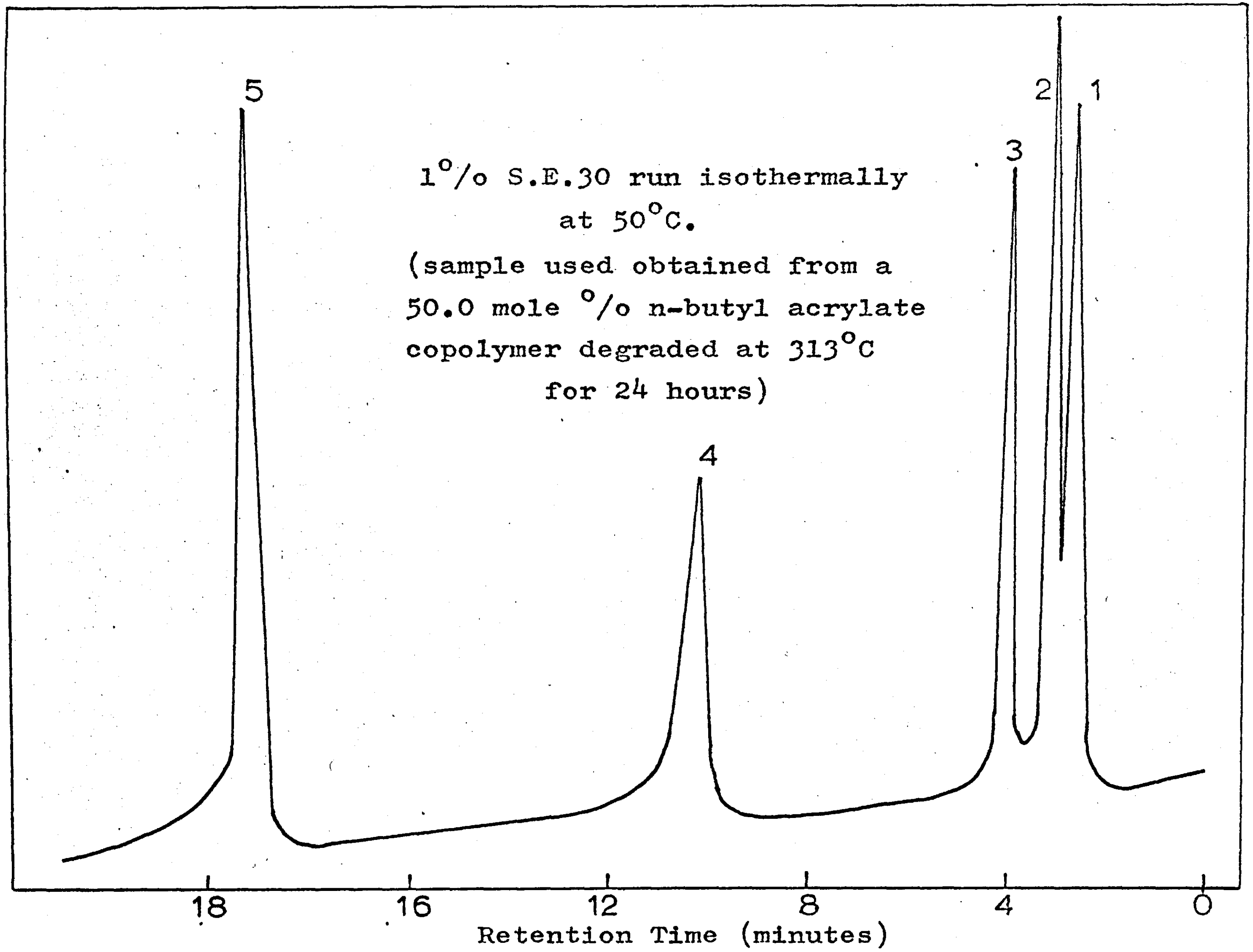


Fig.4.7 G.L.C. trace from G.C.M.S. of liquid degradation products.

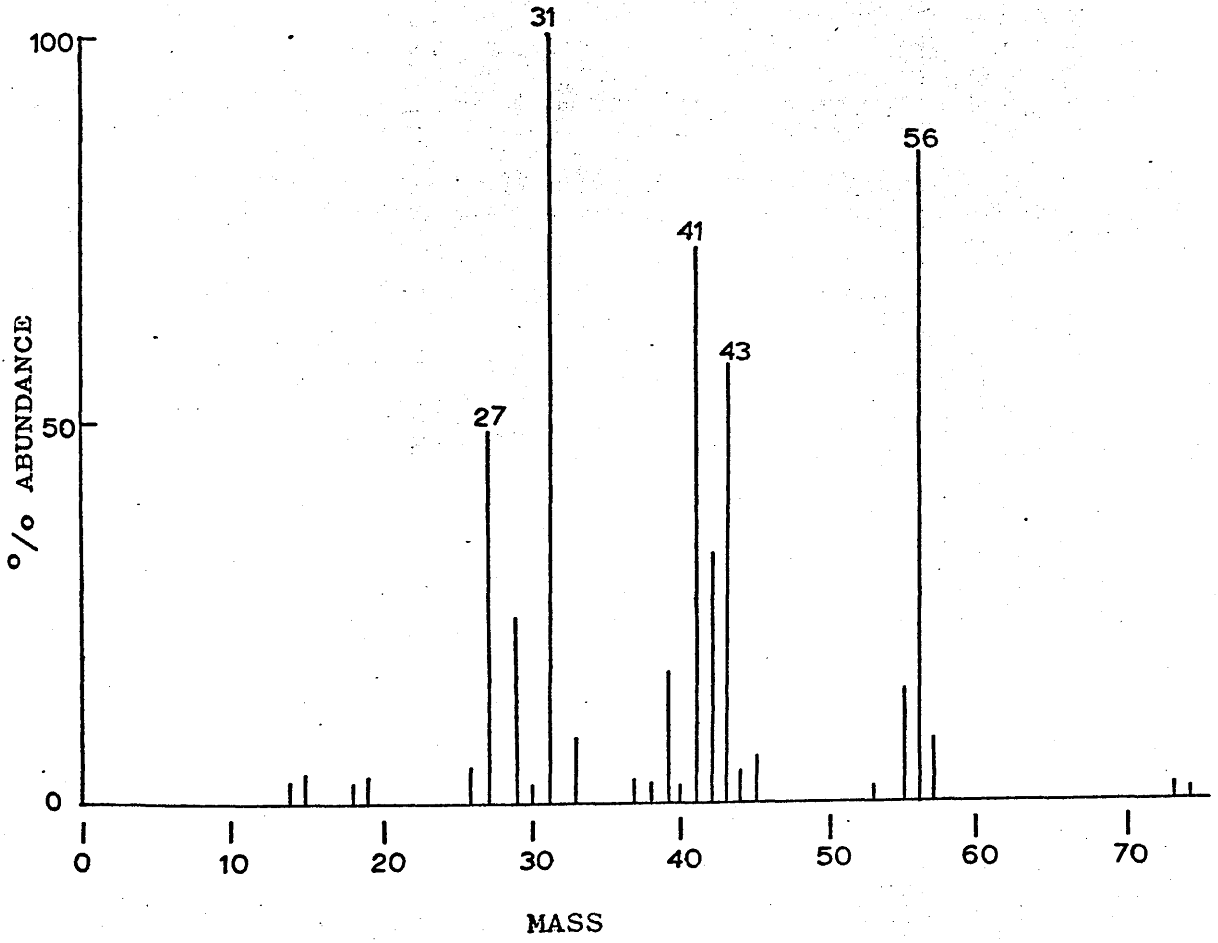


Fig.4.8 Mass spectrum of component 1 in Fig.4.7.(n-butanol)

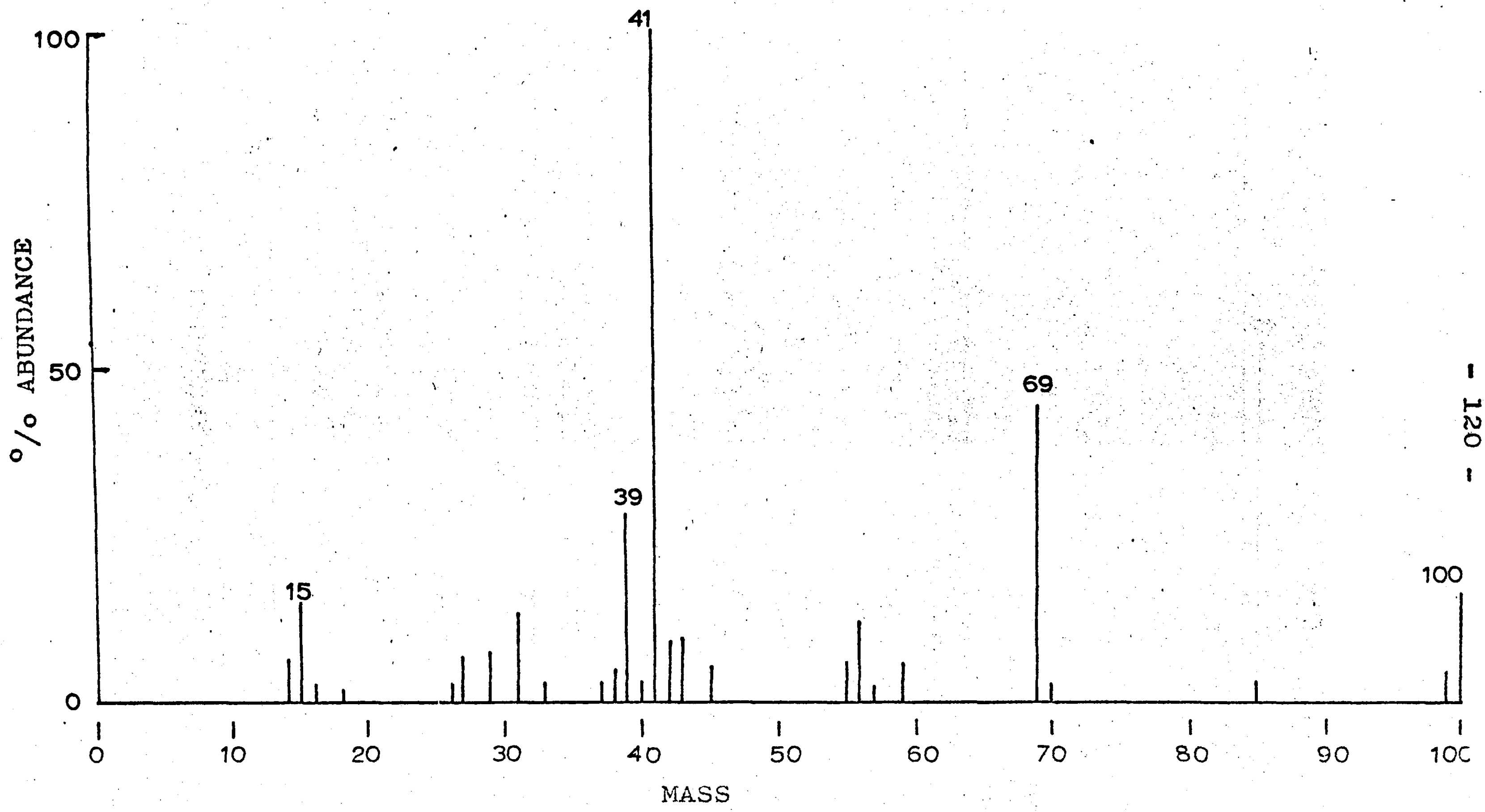


Fig.4.9 Mass spectrum of component 2 in Fig.4.7.(methyl methacrylate)

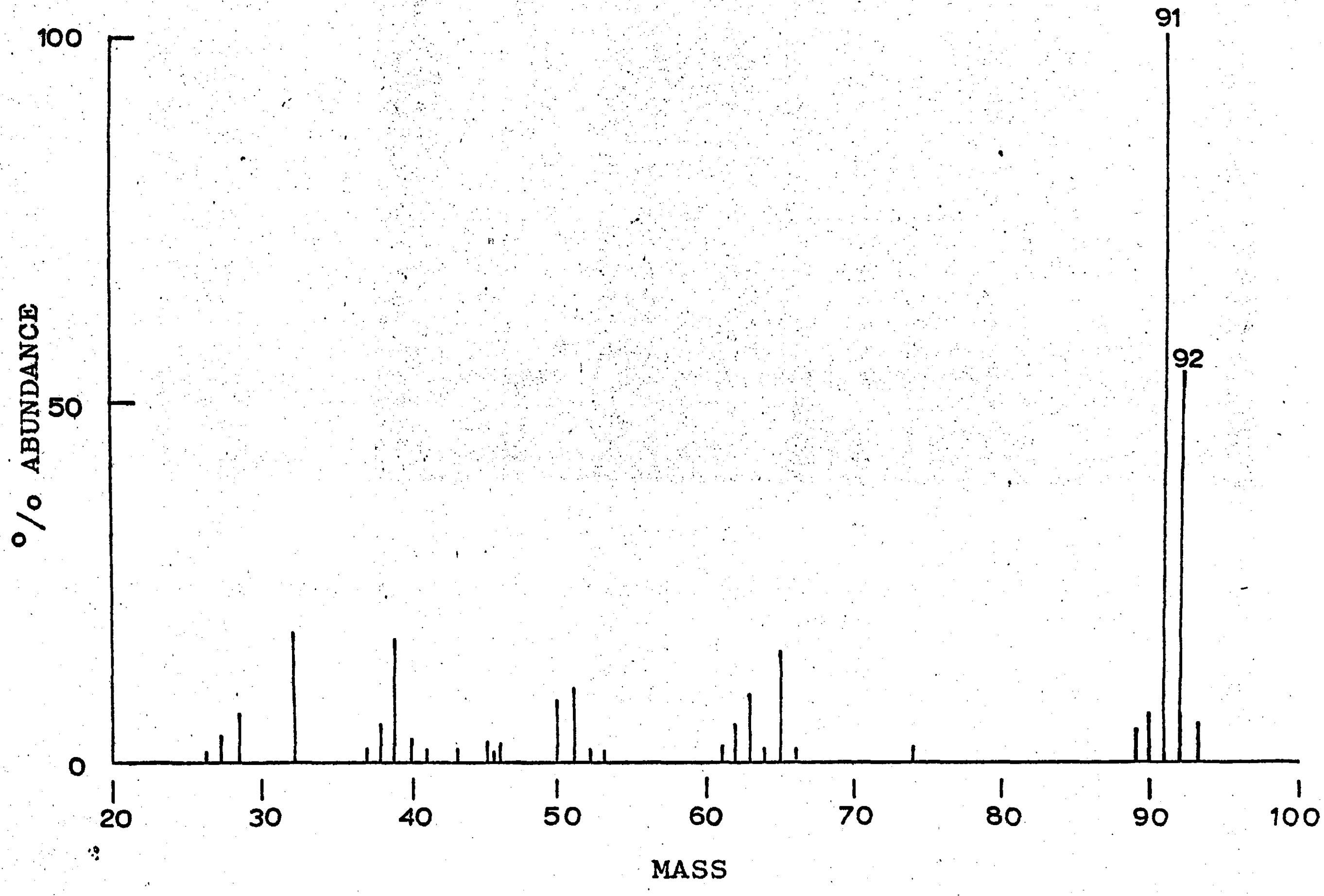


Fig.4.10 Mass spectrum of component 3 in Fig.4.7.(toluene)

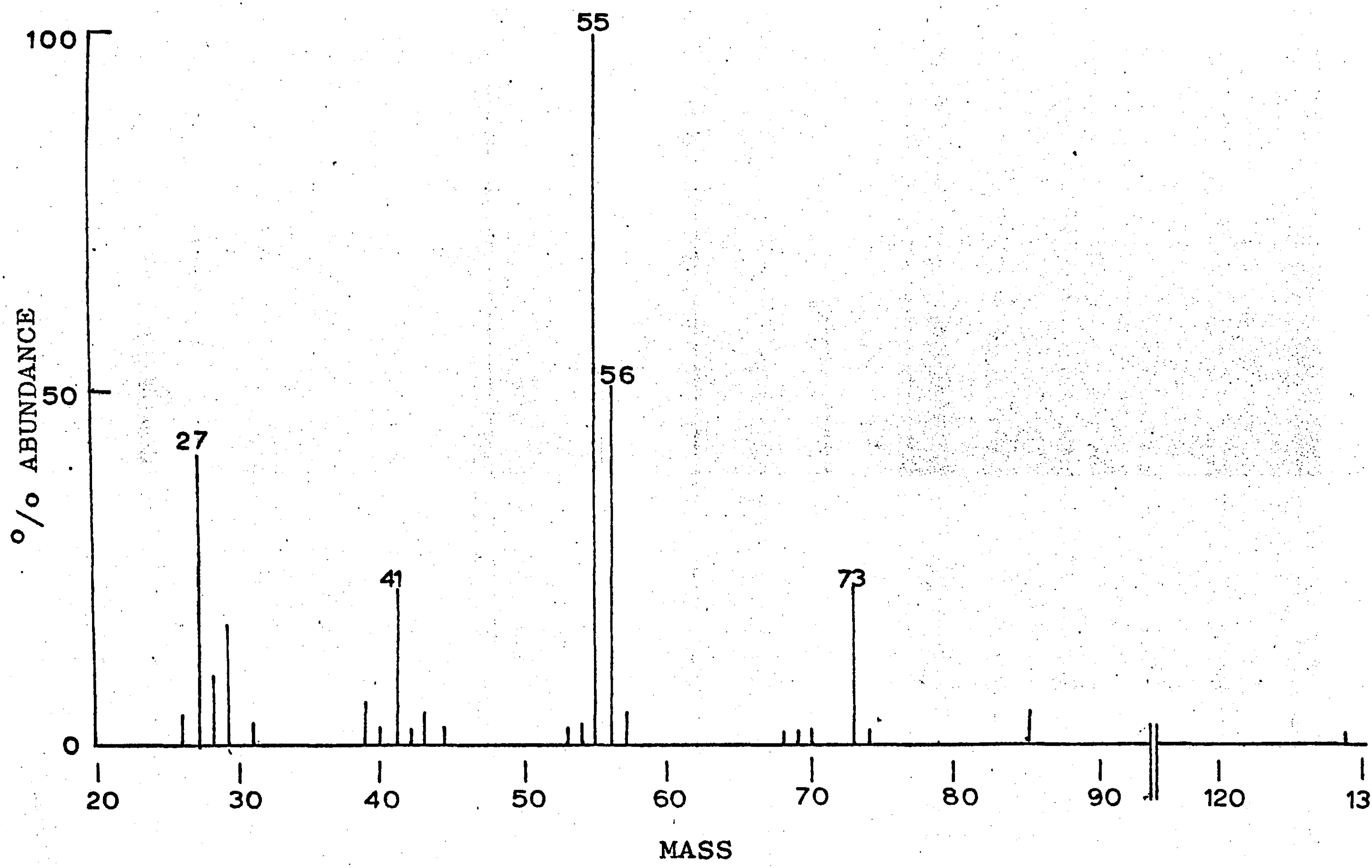


Fig.4.11 Mass spectrum of component 4 in Fig.4.7.(n-butyl acrylate)

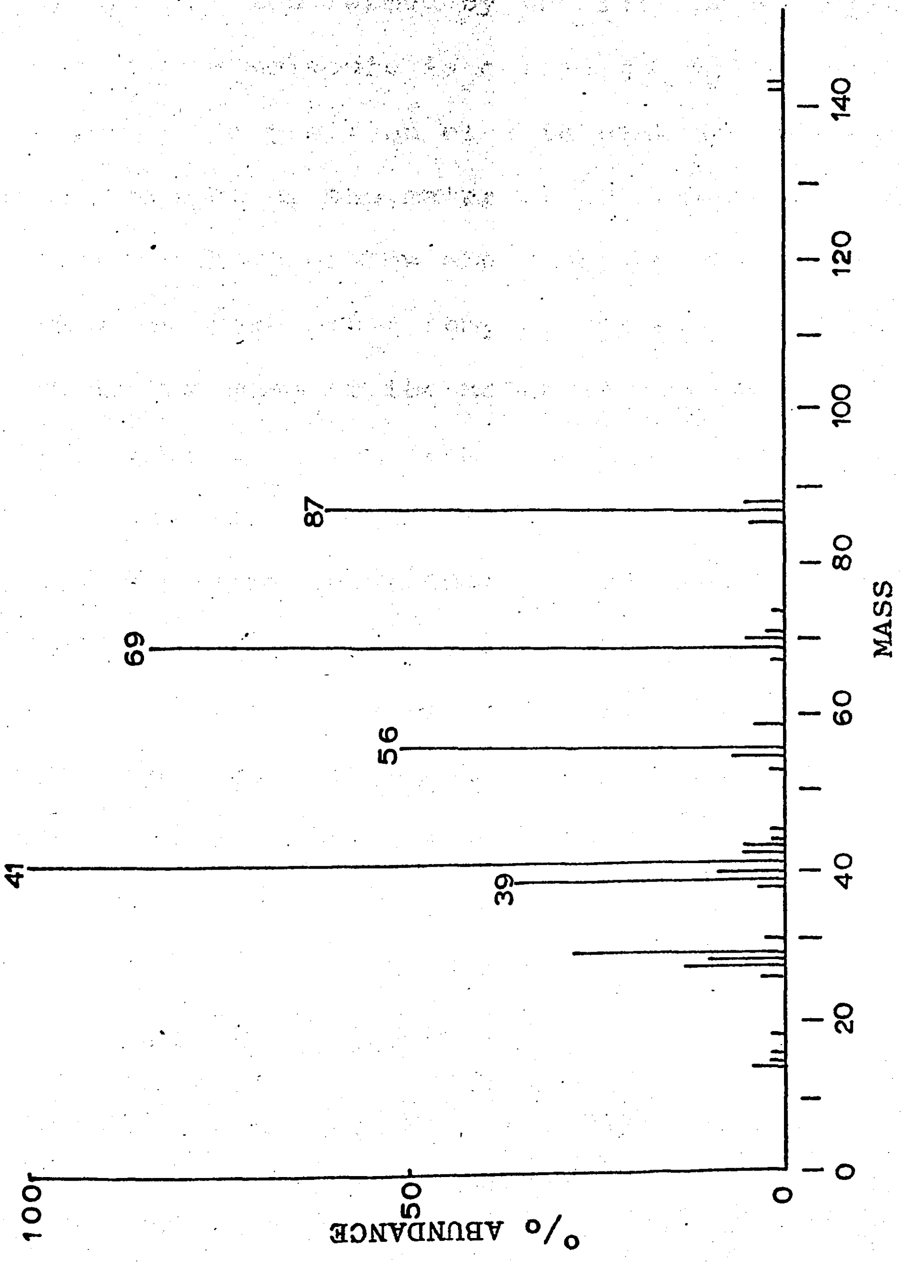


Fig.4.12 Mass spectrum of component 5 in Fig.4.7.(n-butyl methacrylate)

(b.2) Assignment of Mass Spectra

The ion formed by the loss of a single electron from a molecule is called the molecular or parent ion. Yhe position of this peak depends upon the molecular weight of the material present, but in many cases this peak is of low abundance or not present at all. In esters and some other compounds peaks occur at M+1, where M is the mass of the molecular ion due to the abstraction of a proton from a neutral molecule. Since the percentage abundance of the molecular ion depends upon its stability to further decomposition, aromatic compounds give rise to very abundant molecular ion peaks because of the presence of the π electron system, Fig.4.10. The most abundant masses in each spectrum are listed in the order of their relative abundance in table 4.7.

Table 4.7

Suspected Compound	Mass
n-Butanol	31,56,41,43,27.
Methyl Methacrylate	41,69,39,100,15.
Toluene (solvent)	91,92.
n-Butyl Acrylate	55,56,27,73,41.
n-Butyl Methacrylate	41,69,87,56,39.

Assignment of these major fragments is most conveniently done by looking in some detail at one compound, and seeing how similar mechanisms might be extended to other structures. The first compound to be examined was n-butyl methacrylate.

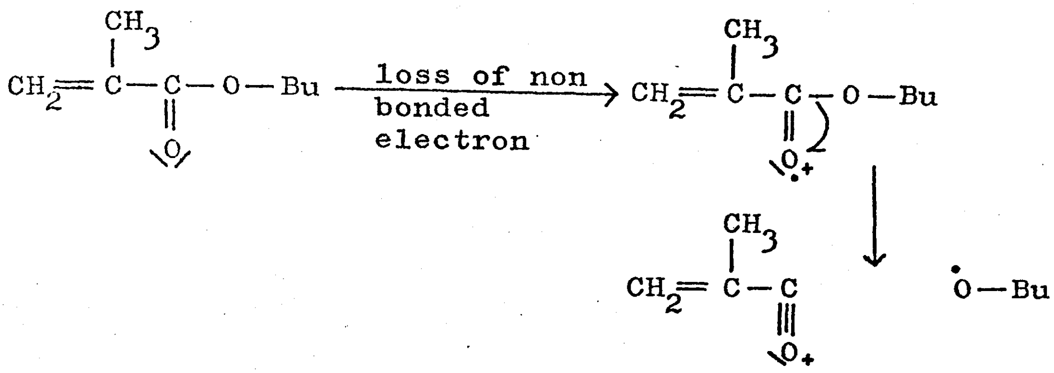
Some common fragmentation processes are [80],

i) Simple fission in which a neutral fragment is lost by the breaking of one bond.

ii) Rearrangement processes in which more than one bond fission occurs accompanied by transfer of one hydrogen atom from one atom to another within the decomposing ion.

iii) Double rearrangement processes in which two hydrogen atoms are transferred simultaneously from the neutral fragment being lost to the fragment ion being formed.

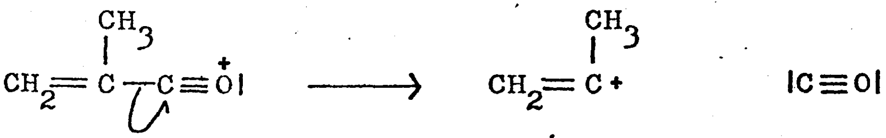
Considering the mass spectrum of n-butyl methacrylate, the fragments of masses 41 and 69 may be accounted for by simple fission. Where such fission occurs a neutral radical is eliminated from the molecular ion. Firstly, a non-bonded electron is lost from the ester carbonyl oxygen atom followed by transfer of an electron to the positively charged site from the α bond. This process is therefore called α fission.



69

(A double headed arrow is used here to mean the transfer of two electrons, while a single headed arrow means the transfer of one electron. The symbol Bu denotes an n-butyl group.)

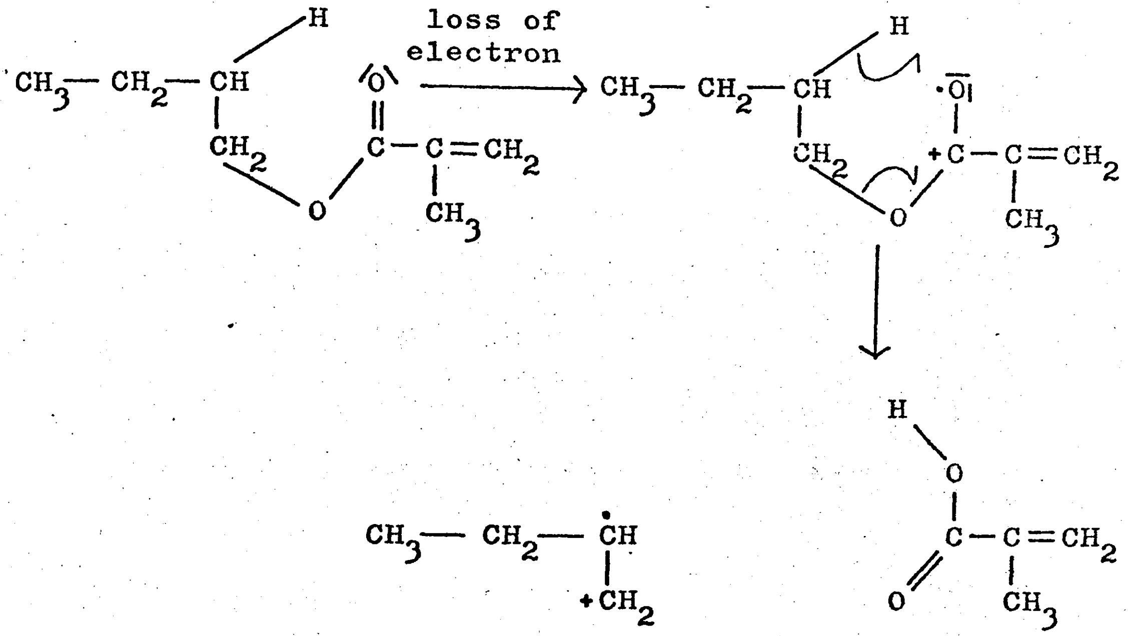
A neutral molecule may then be eliminated from the fragment ion by cleavage of a single bond, the mechanism involving a two electron shift.



41

This process is known as fragment ion fission.

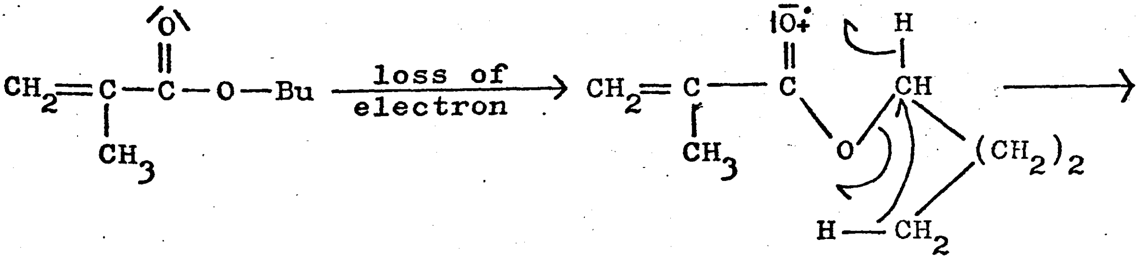
A rearrangement process can be used to explain the fragment of mass 56. The most generally applicable specific rearrangement process is called the McLafferty rearrangement. The essentials are a double bond which has a γ hydrogen available for migration.

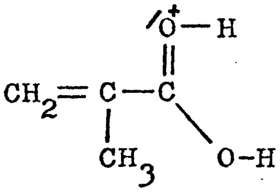


56

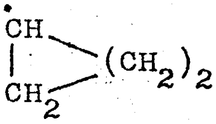
After the loss of an electron from the carbonyl bond the rearrangement proceeds with a proton transfer from the γ carbon and a transfer of two electrons as shown above completes the reaction.

Double rearrangement processes are important in the breakdown of almost every ester greater than methyl. The process, involving the simultaneous rearrangement of two hydrogen atoms, may be represented as follows.





87



In the saturated hydrocarbons fission processes occur as shown below.

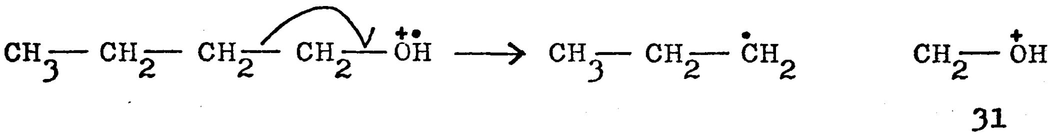
$$(R_3C-CR_3)^{\ddagger} \longrightarrow R_3C^{+} \qquad \dot{C}R_3$$

Such fissions can occur in the n-butyl side chain of the ester. The spectrum will show a series of peaks at odd masses corresponding to the above fission, appearing at masses corresponding to C_nH_{2n+1}. Random processes may also take place whereby a molecule of hydrogen is lost from the fragment ion. Such reactions can explain the peak at mass 39 so far not accounted for in table 4.7 for n-butyl methacrylate.

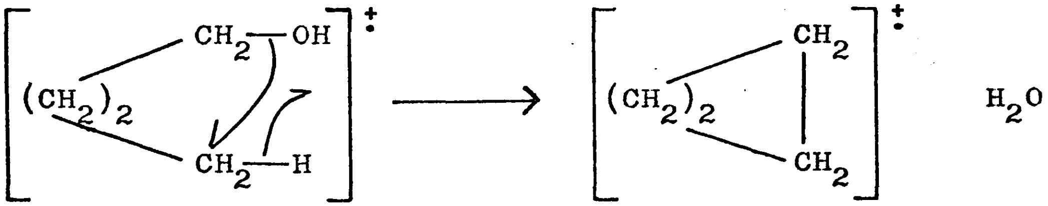
It should be noted that several mechanisms may be invoked to account for a given mass number. Mass 41 for example may be ascribed to the fragment $[CH_2{=}C-CH_3]^+$ from the fission of the fragment ion $R-C\equiv O^+$ or by scission of the n-butyl side chain followed by hydrogen elimination from the fragment $CH_3-CH_2-\overset{+}{C}H_2$

The reaction schemes detailed above may be used to explain the presence of all of the fragments listed for the esters in table 4.7. Only two spectra, those of n-butanol and toluene, require further investigation.

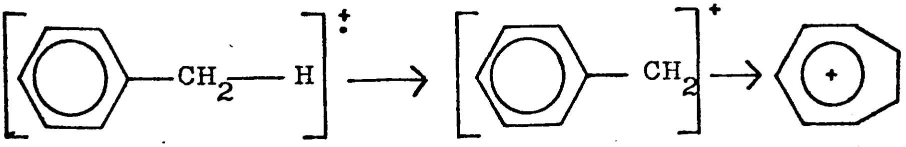
Fission of the bond α to the hydroxyl group of n-butanol leads to a fragment of mass 31.



Random rearrangement of the molecular ion leads to loss of water giving a peak at M-18 = 56.



The solvent, toluene, gives two major peaks. 92 is the mass of the parent ion, while β fission yields a peak at mass 91.



Tropylium Ion, mass 91.

The driving force is the high stability of the resulting aromatic ion. A summary of the mechanisms discussed above applied to all the mass spectra considered is given in table 4.8, while, for each compound, a list of possible structures corresponding to the masses noted in table 4.7 is shown in table 4.9.

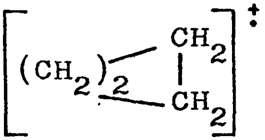
It has been shown that the degradation products suggested on the basis of retention times can be used to give a reasonable account of the main features of the observed mass spectra. Pure samples of each of the compounds listed in table 4.6 were injected separately into the L.K.B. mass spectrometer. The mass spectra obtained were identical to those shown in Figs.4.8-4.12.

Table 4.8

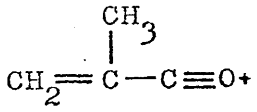
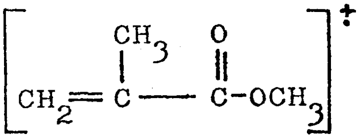
Component	Parent Ion	Fragmentation Process		
		Simple Fission	Rearrangement	Double Rearrangement
n-Butanol	74	43,41,31, 27	56	-
Methyl Methacrylate	100	69,41,39, 15	-	-
Toluene	92	91	-	-
n-Butyl Acrylate	128	55,41,27	56	73
n-Butyl Methacrylate	142	69,41,39	56	87

Table 4.9

n-Butanol

Mass	Structure
31	$CH_2=\overset{+}{O}H$
56	
41	$CH_2=\overset{+}{C}-CH_3$
43	$CH_3-\overset{+}{C}H-CH_3$
27	$CH_2=\overset{+}{C}H$

Methyl Methacrylate

Mass	Structure
41	$CH_2=\overset{+}{C}-CH_3$
69	 $CH_2=\overset{CH_3}{C}-C\equiv O^+$
39	$CH_2=C=\overset{+}{C}H$
100	 $\left[CH_2=\overset{CH_3}{C}-\overset{O}{\overset{\parallel}{C}}-OCH_3\right]^{\ddagger}$
15	CH_3^+

Toluene

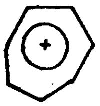
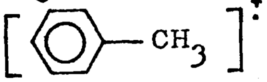
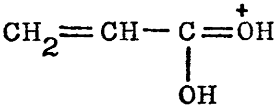
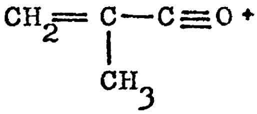
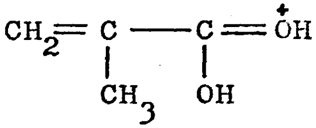
Mass	Structure
91	 Tropylium Ion
92	

Table 4.9 (contd.)

n-Butyl Acrylate

Mass	Structure
55	$CH_2{=}CH{-}C{\equiv}O^{+}$
56	$[CH_3{-}CH_2{-}CH{=}CH_2]^{+\cdot}$
27	$CH_2{=}CH^{+}$
73	 $CH_2{=}CH{-}\underset{OH}{\underset{\vert}{C}}{=}\overset{+}{O}H$
41	$CH_2{=}\overset{+}{C}{-}CH_3$

n-Butyl Methacrylate

Mass	Structure
41	$CH_2{=}\overset{+}{C}{-}CH_3$
69	 $CH_2{=}\underset{CH_3}{\underset{\vert}{C}}{-}C{\equiv}O^{+}$
87	 $CH_2{=}\underset{CH_3}{\underset{\vert}{C}}{-}\underset{OH}{\underset{\vert}{C}}{=}\overset{+}{O}H$
56	$[CH_3{-}CH_2{-}CH{-}CH_2]^{+\cdot}$
39	$CH_2{=}C{=}\overset{+}{C}H$

CHAPTER 5

QUANTITATIVE ANALYSIS OF THE LIQUID AND GASEOUS DEGRADATION PRODUCTS

5.1 Introduction

In the previous chapter the identification of the degradation products was described. It was appropriate to follow this up by quantitative measurements.

The degradations studied were all carried out by the sealed tube technique (2.2a) at two temperatures, 313°C and 332°C, so that the effect of both composition and temperature of degradation on the pattern of breakdown could be observed. A detailed analysis of the gaseous and liquid decomposition products is given, the investigation of the residue being described in a later chapter.

5.2 Analysis of the Gaseous Degradation Products

(a) Analytical Techniques

(a.1) Gas Chromatography

The trace obtained using a silica gel column to analyze the gases evolved on the breakdown of a 50 mole percent n-butyl acrylate copolymer heated for eleven hours at 313°C was shown in Fig.4.1. From the trace it would appear that the major product is butene, provided that the sensitivity of the detector to each of the gases examined is of the same order of magnitude. A determination of these sensitivity factors was made by analyzing mixtures of the pure gases (Mathieson Inc.) containing known amounts of each of the components, made up by using the constant volume manometer, (2.3a). The sensitivity factor for a particular gas, k, relative to some standard, in this case but-1-ene, was defined as the ratio of the areas of the gas and but-1-ene peaks when equal pressures of gas and but-1-ene are considered.

$$k = \left(\frac{\text{area of gas peak}}{\text{area of but-1-ene peak}}\right)\left(\frac{\text{pressure of but-1-ene}}{\text{pressure of gas}}\right)$$

Sensitivity factors are listed in table 5.1 and used in this context to calculate the relative pressures of the various gases present, taking the pressure of butene as 100. Since propylene and n-butane are not separated, an average value of the appropriate sensitivity factors was used. It was not necessary to carry out systematically such a detailed analysis on the other copolymers, as it is sufficient to show that the but-1-ene peak is by far the largest, so that its exact relationship to the other gases determined by this method is of little consequence. The value quoted in table 5.1 for methane is of necessity lower than that actually present in the evolved gases, since distillation under liquid nitrogen was involved in preparing these product gases for g.l.c.

Table 5.1

G.L.C. Data for a 50.0 Mole Percent n-Butyl Acrylate Copolymer Degraded at 313°C for 11 Hours.

Gas	$\frac{\text{Area of Gas Peak}}{\text{Area of Butene Peak}}$	Sensitivity Factor, k, Relative to But-1-ene	Pressure Relative to Butene
Methane	0.23	0.60	0.38
Ethane	0.03	0.96	0.03
Ethylene	0.05	0.70	0.07
Propane	0.04	1.54	0.03
Propylene	1.12	0.98 } 1.39	1.01
n-Butane		1.80	
Butene	100.00	1.00	100.00

Table 5.2

G.L.C. Data for a 16.3 Mole Percent n-Butyl Acrylate Copolymer Degraded at 313°C for 16 Hours.

Gas	$\frac{\text{Area of Gas Peak}}{\text{Area of But-1-ene Peak}}$	Sensitivity Factor, k, Relative to But-1-ene	Pressure Relative to But-1-ene
Trans But-2-ene	4.42	0.91	4.86
But-1-ene	100.00	1.00	100.00
Cis But-2-ene	4.08	1.01	4.04

analysis , (2.6a). Remembering that to examine the permanent gases at all, large sample sizes were required, it may be concluded that methane is a minor degradation product in comparison to butene.

The isomeric butenes were separated using a benzyl cyanide - silver nitrate column, (table 2.3), and the trace obtained for the degradation products from a 16.3 mole percent n-butyl acrylate copolymer at 313°C was shown in Fig.4.2. It is to be expected that the sensitivity of the detector to the butenes would be about the same, and this was confirmed by once again making up standard mixtures of pure gases. The results are quoted in table 5.2 which also lists the relative pressures of gases found from the trace of Fig.4.2, assuming the pressure of but-1-ene to be 100. Once more no detailed experiments were carried out routinely on the other copolymers, it being sufficient to show that but-1-ene is the predominant isomer present.

Although the permanent gases make only a very small contribution to the measured total gas pressure, it was considered of interest to examine in a semi-quantitative fashion the relative amounts of carbon monoxide, methane, and hydrogen present. To this end the sample bulb of the gas sampling apparatus, Fig.2.9, was filled with

Table 5.3

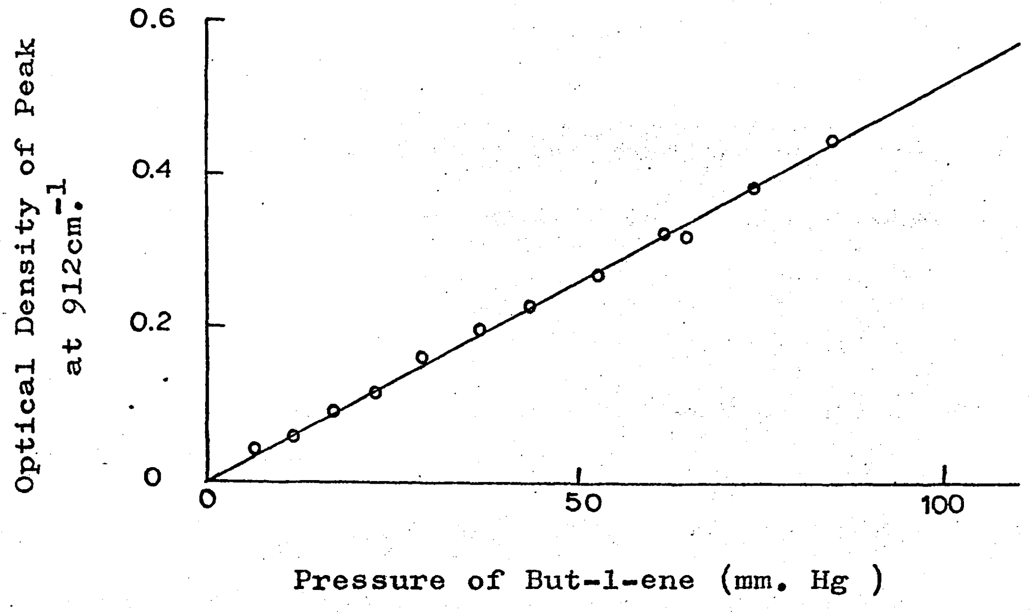
G.L.C. Data for a 52.4 Mole Percent n-Butyl Acrylate Copolymer Degraded at 313°C for 24 Hours.

Gas	Height of Gas Peak / Height of CO Peak	Peak Height for One Atmosphere of Gas Relative to CO	Pressure Relative to CO
Hydrogen	200	10.6	18.9
Carbon Monoxide	100	1.0	100.0
Methane	80	1.3	61.6

approximately one atmosphere of each of these gases in turn and the height of the peaks obtained on the g.l.c. trace measured. The column employed was silica gel used as specified in table 2.3. Taking the height of the peak due to carbon monoxide as unity, these results are shown in table 5.3. This table also lists the relative height of the peaks shown in Fig.4.3, obtained from the degradation of 1.5g. of a 52.4 mole percent n-butyl acrylate copolymer degraded at 313°C for twenty four hours, and gives the pressure of each gas relative to carbon monoxide as 100. No further investigation of the permanent gases was undertaken.

(a.2) Infra-red Spectroscopy

As detailed in (2.9a) plots of optical density versus pressure were made for pure samples of but-1-ene and carbon dioxide and these are shown in Fig.5.1. The use of these plots establishes that these gases constitute the major part of the gaseous degradation products, since such analyses show that the total pressure of evolved gases may be accounted for by carbon dioxide and butene alone. This greatly simplifies the quantitative analysis of the gaseous breakdown products, since routinely infra-red measurements are all that are required.



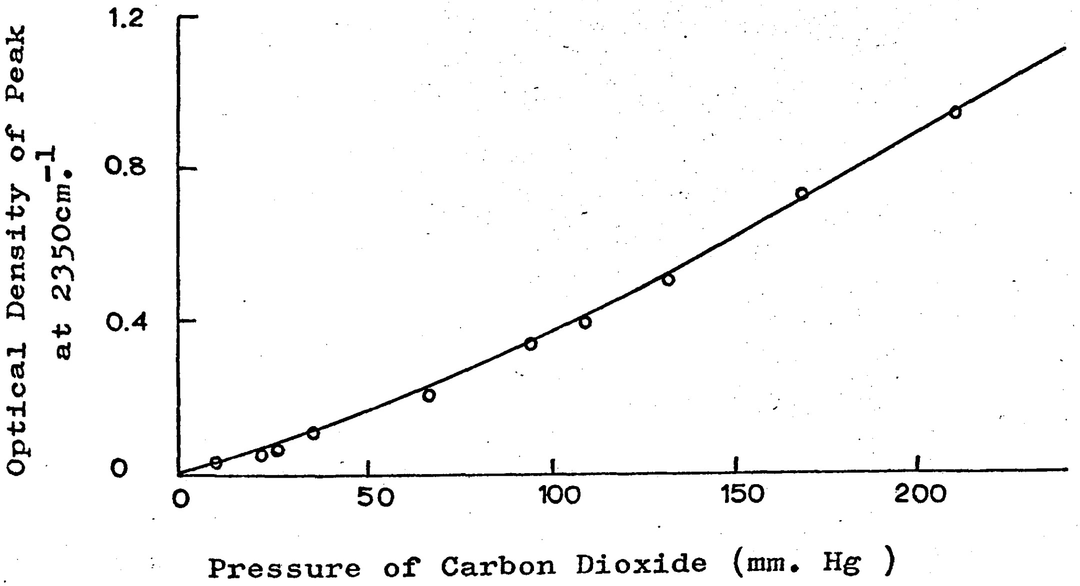


Fig.5.1 Infra-red Calibration Curves for But-1-ene and Carbon Dioxide.

(b) Treatment of Results

The method of examining the gases given in (2.9a) involves a pressure measurement of total gas on the constant volume manometer, P_{total}. The pressures attributed to carbon dioxide and but-1-ene read from the calibration curves of Fig.5.1, were found generally to come to about 5-15°/o more than the total gas pressure as found using the manometer. This same effect has been reported in connection with measurements of the gaseous products of decomposition of polyacrylates [29]. Thus infra-red data were used to find the ratio of the pressures of carbon dioxide, (P_{CO_2}), to but-1-ene, $(P_{but-1-ene})$. Corrected pressures, CP_{CO_2} and $CP_{but-1-ene}$, were found for each of these gases such that,

$$\frac{CP_{CO_2}}{CP_{but-1-ene}} = \frac{P_{CO_2}}{P_{but-1-ene}} \quad \ldots\ldots\ldots(1)$$

and

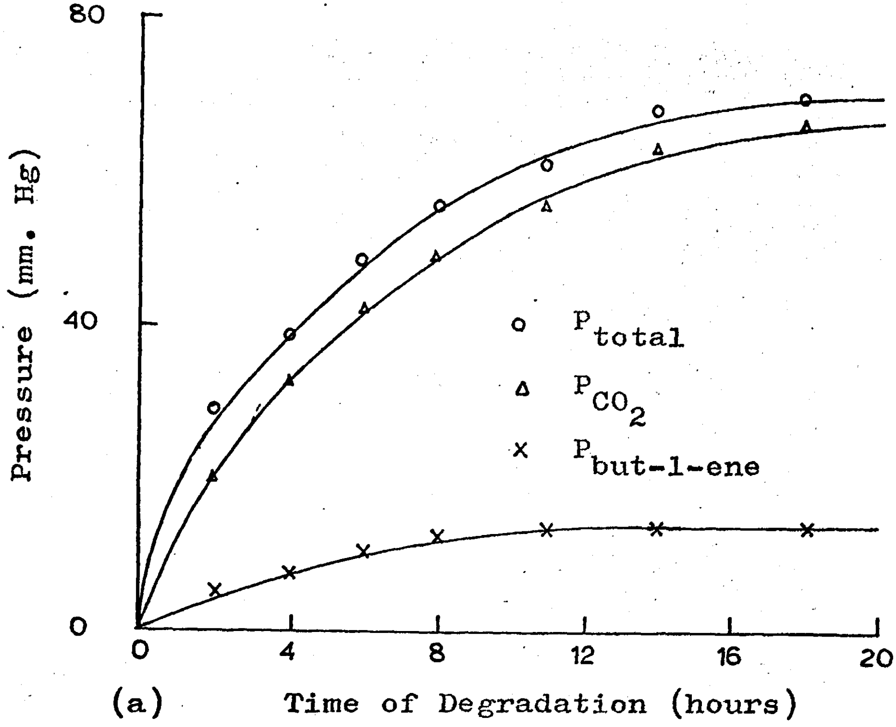
$$P_{total} = CP_{CO_2} + CP_{but-1-ene} \quad \ldots\ldots\ldots(2)$$

A typical calculation for a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C involves plotting total gas pressure, P_{total}, against time of degradation, then reading off values, P'_{total}, from this curve at suitable intervals, in this case two hour periods.

Graphs of P_{co_2} and $P_{but-1-ene}$ are then plotted from the infra-red data, and values, P'_{CO_2} and $P'_{but-1-ene}$,read off from these curves every two hours. From these measurements values of CP_{CO_2} and $CP_{but-1-ene}$ are calculated throughout the degradation from equations (1) and (2). These plots are shown in Fig.5.2 and the data presented in table 5.4. A similar treatment was used for all the other copolymers examined. Plots of total gas pressure, carbon dioxide pressure and but-1-ene pressure are given in Figs.5.3-5.8, and the data shown in tables 5.5-5.10.

Measureable amounts of gases were not evolved from the 0.4 mole percent n-butyl acrylate copolymer examined, while only carbon dioxide was detected from the decomposition of a 3.9 mole percent n-butyl acrylate copolymer at 313°C. In the latter case $P_{total} = CP_{CO_2}$ so that infra-red measurements were not required.

In order that a comparison of the amount of gases evolved from the copolymers examined can be made, plots of the number of millimoles of gas per gram of initial polymer are shown in Figs.5.9-5.13, and the data listed in tables 5.4-5.10. These calculations were made taking the temperature of measurement of gas pressure as 20°C, and using a value of 53.58cc. for the volume of the constant volume manometer, Fig.2.4.



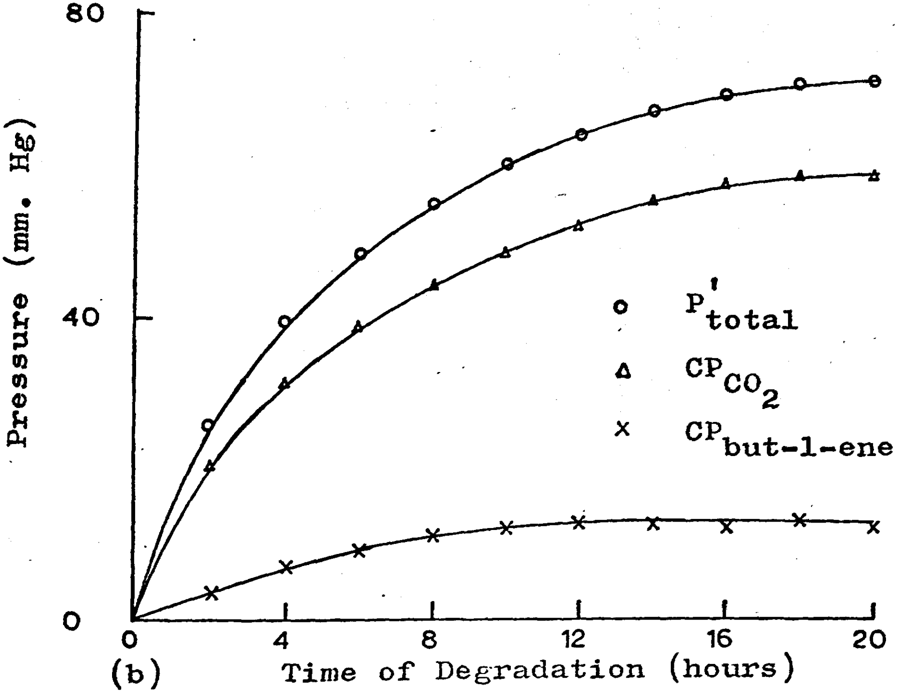


Fig.5.2 Gas pressure plots for a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C.

Table 5.4

Gas Evolution Data for a 16.3 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	4	6	8	11	14	18	
P_{total}	28.8	38.8	48.8	56.0	61.8	69.2	70.5	Initial Polymer Weight = 0.331g.
P_{CO_2}	20.0	32.2	42.6	49.2	56.0	64.0	67.3	
$P_{but\text{-}1\text{-}ene}$	5.1	7.6	10.8	12.9	13.4	13.7	14.2	

Time of Degradation, hours	2	4	6	8	10	12	14	16	18	∞
P'_{total} (Fig.5.2)	25.5	39.0	48.0	55.0	60.0	64.0	67.3	69.8	71.0	71.0
P'_{CO_2} (Fig.5.2)	20.0	33.0	42.0	49.6	55.3	59.5	63.0	65.5	67.0	68.0
$P'_{but\text{-}1\text{-}ene}$ (Fig.5.2)	4.6	8.0	10.4	12.1	13.2	13.8	14.0	14.0	14.0	14.0
CP_{CO_2}	20.7	31.4	38.5	44.2	48.4	52.0	55.1	57.5	58.7	58.9
$CP_{but\text{-}1\text{-}ene}$	4.8	7.6	9.5	10.8	11.6	12.0	12.2	12.3	12.3	12.1
m.moles CO_2 per g. polymer	.184	.278	.341	.393	.429	.459	.486	.511	.520	.523
m.moles but-1-ene per g. polymer	.042	.067	.085	.097	.103	.106	.109	.109	.109	.109
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	1.0	1.6	2.0	2.3	2.5	2.6	2.8	2.9	2.9	2.9

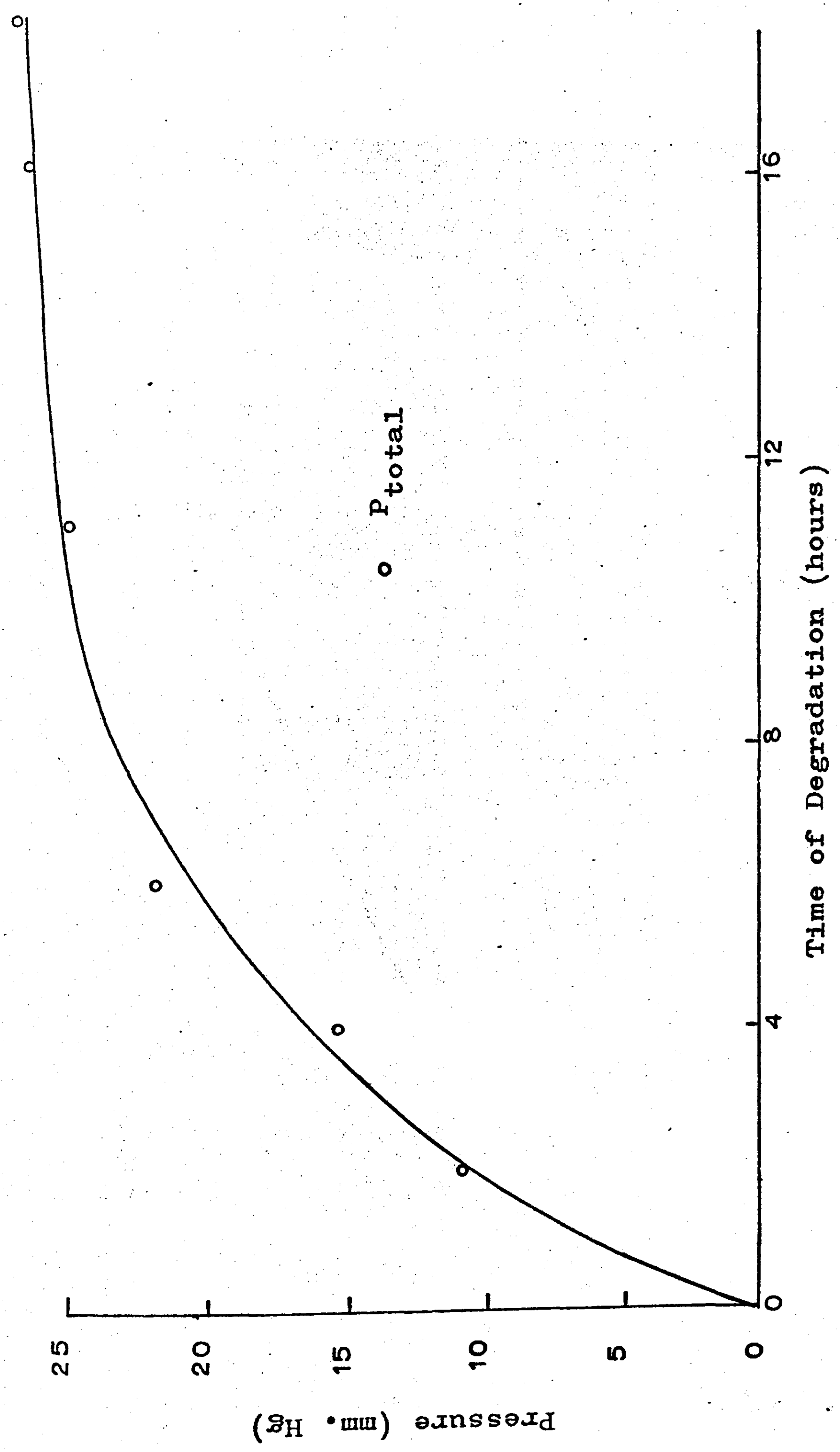


Fig.5.3 Gas pressure plot for a 3.9 mole percent n-butyl acrylate copolymer degraded at 313°C.

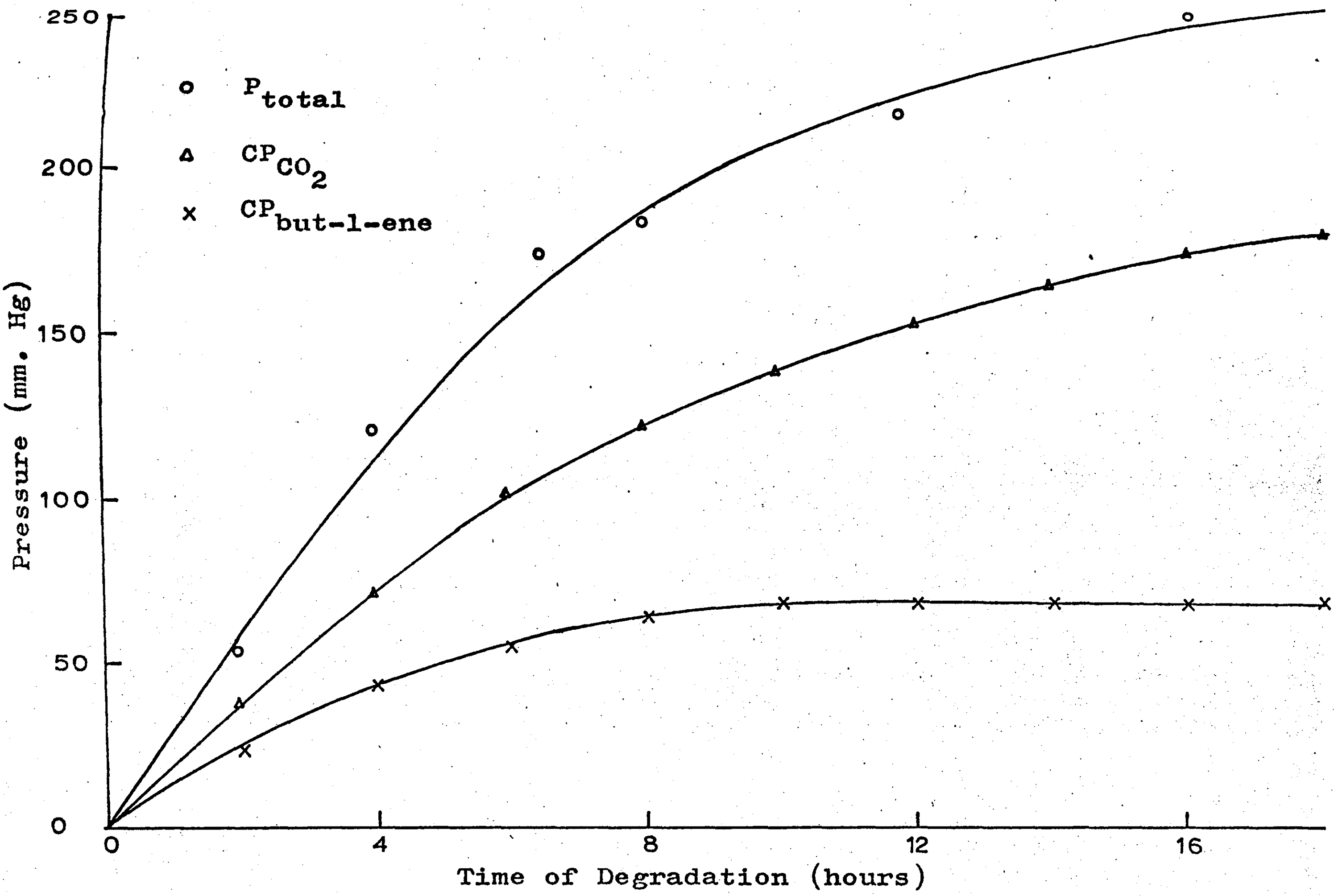


Fig.5.4 Gas pressure plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 313°C.

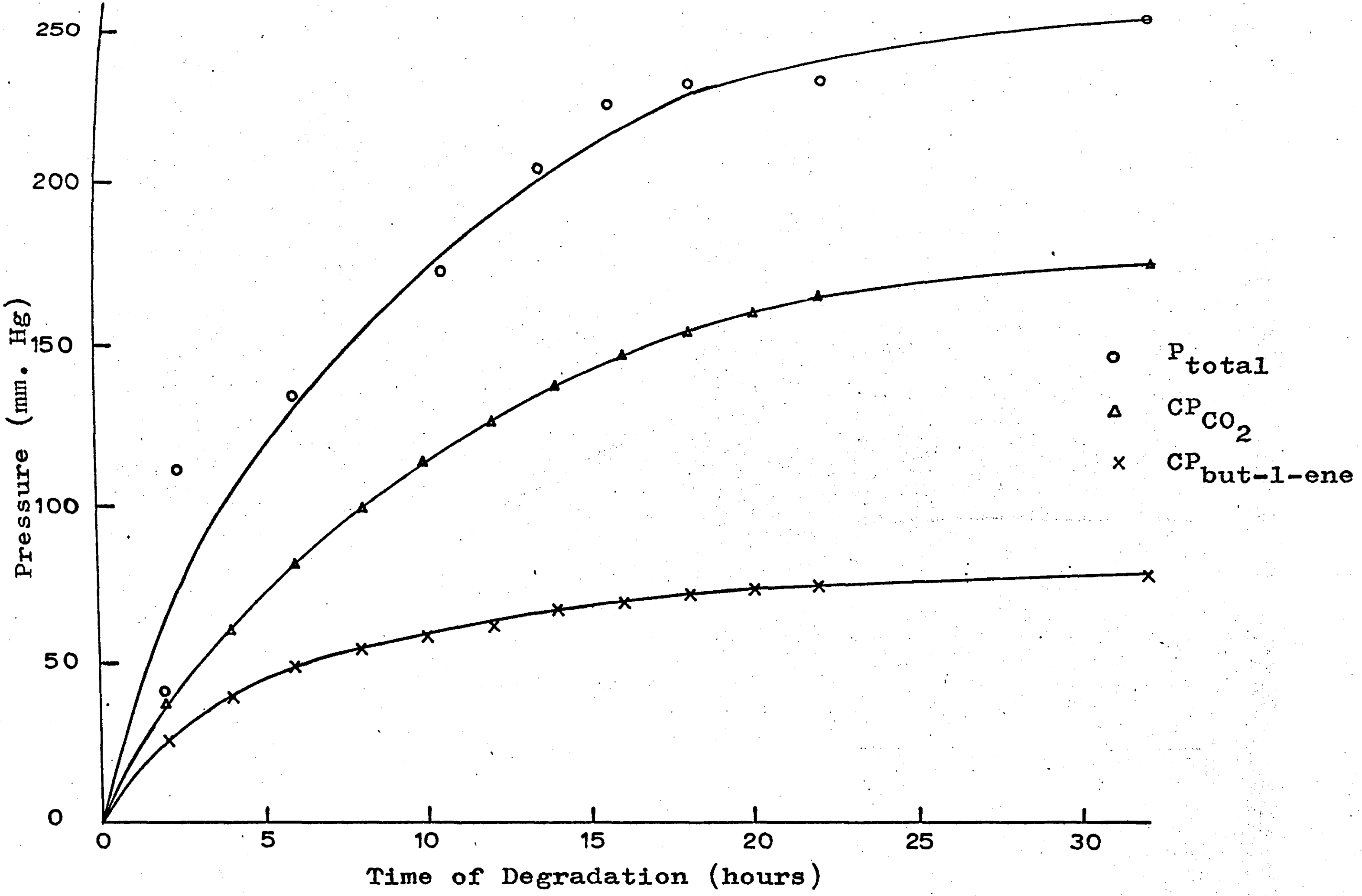


Fig.5.5 Gas pressure plots for an 82.2 mole percent n-butyl acrylate copolymer degraded at 313°C.

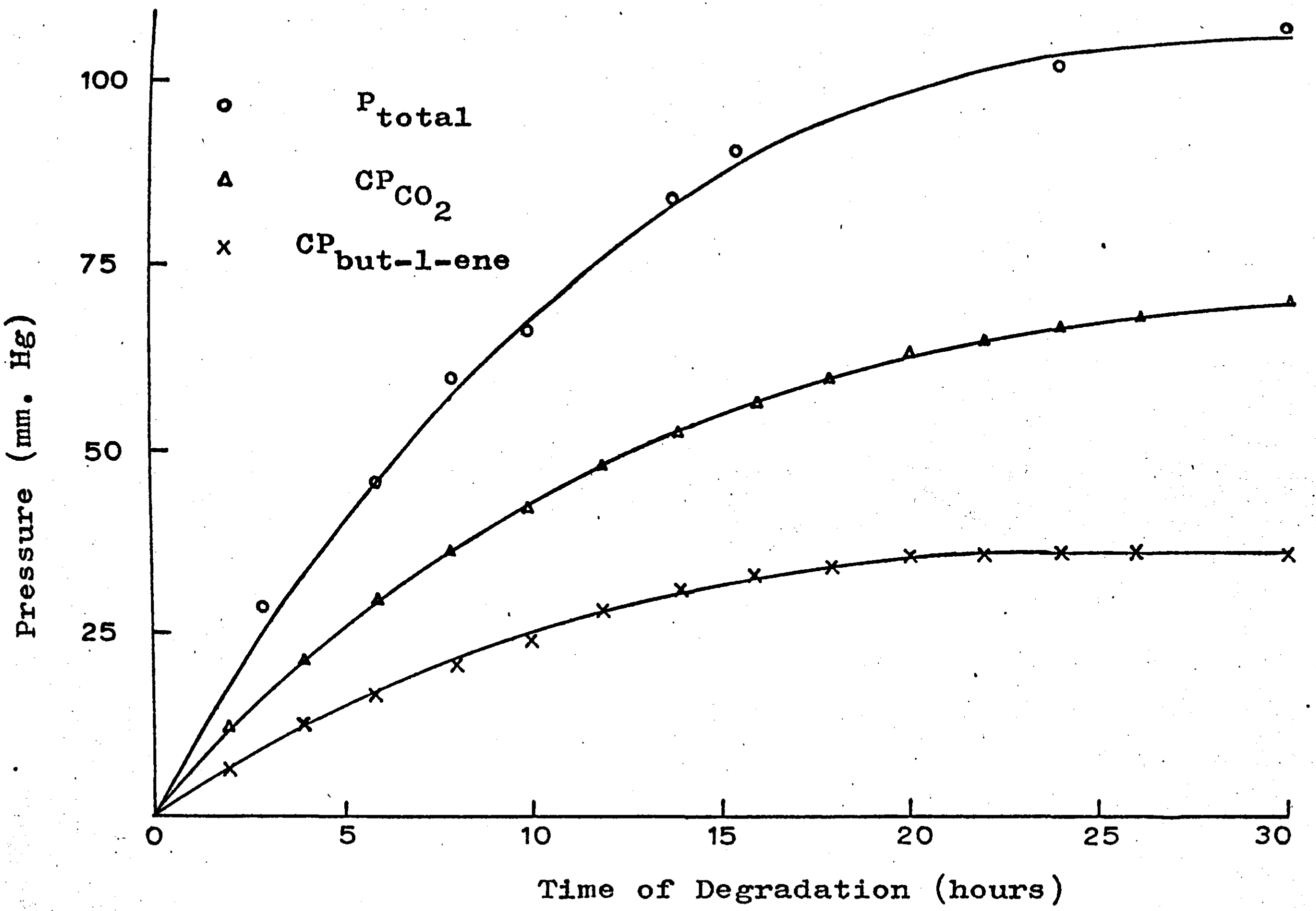


Fig.5.6 Gas pressure plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 313°C.

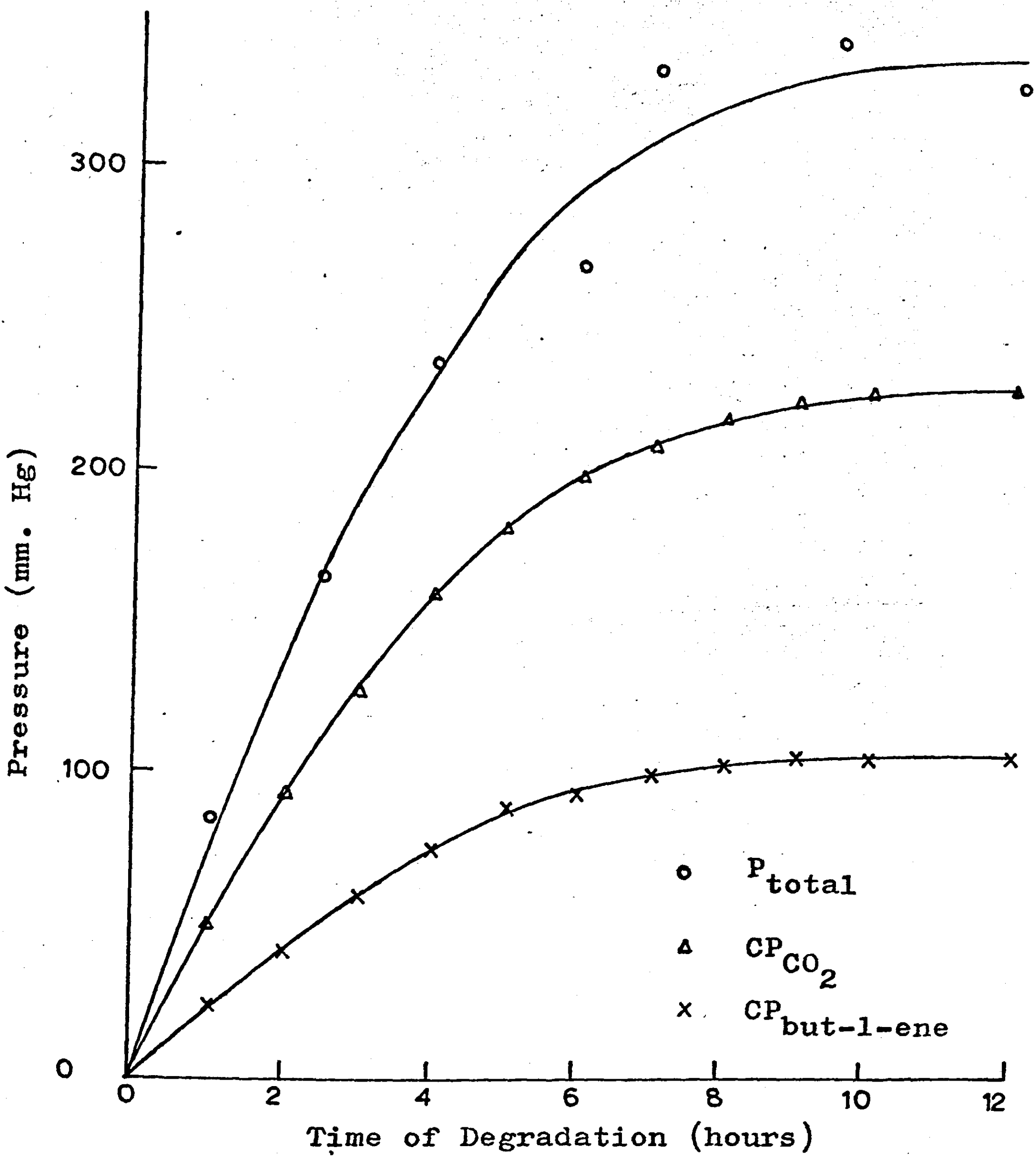


Fig.5.7 Gas pressure plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 332°C.

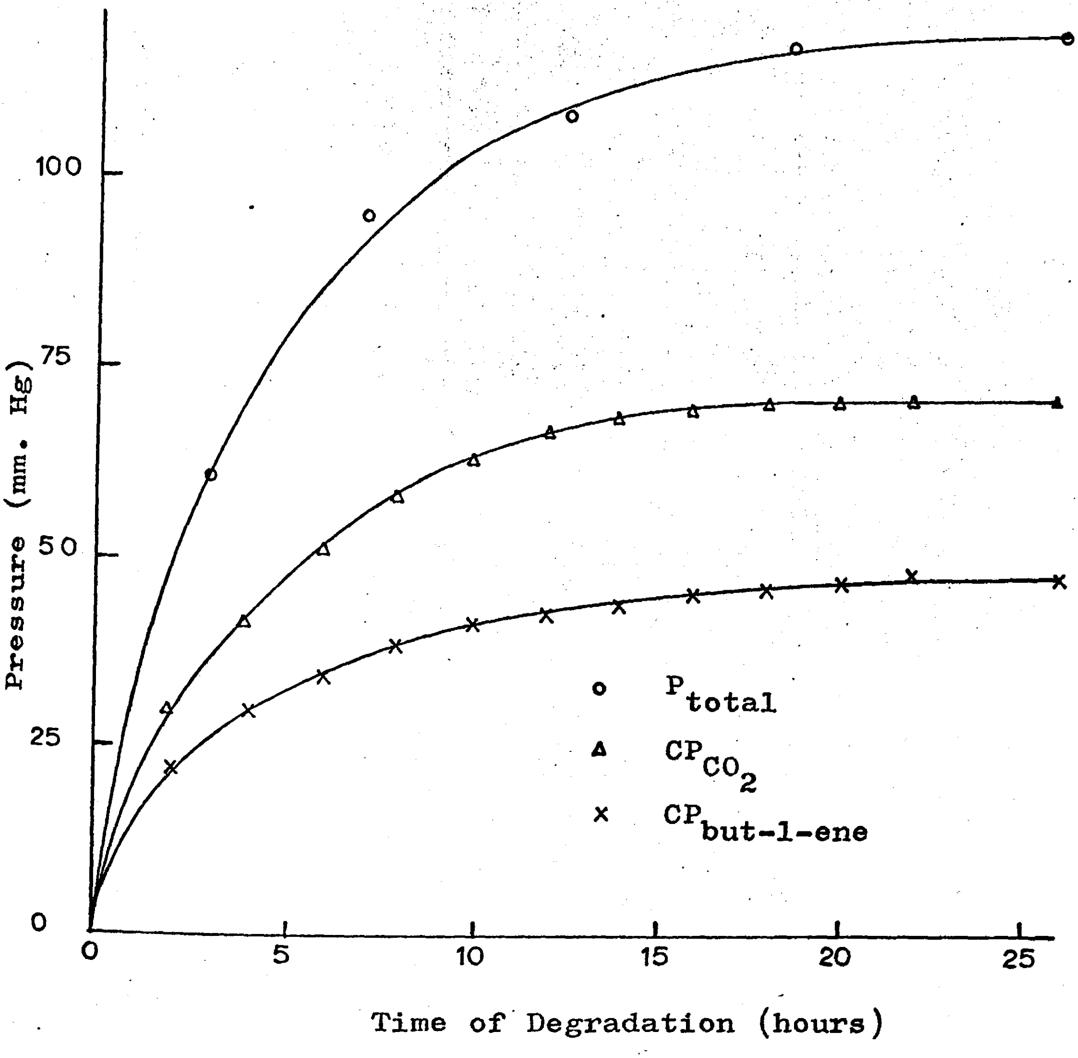


Fig.5.8 Gas pressure plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 332°C.

Table 5.5

Gas Evolution Data for a 3.9 Mole $^{o}/_{o}$ n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	4	6.5	11	16	18	Initial Polymer Weight = 0.345g.
P_{total}	10.6	15.4	21.6	24.6	26.0	26.5	

Time of Degradation, hours	2	4	6	8	10	12	14	16	18	∞
P'_{total} (Fig.5.3)	10.6	16.2	20.2	23.0	24.4	24.9	25.5	26.0	26.5	26.5
m.moles CO_2 per g. polymer	.090	.139	.171	.194	.209	.212	.217	.220	.226	.226
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}}$ x 100	0.4	0.6	0.8	0.9	0.9	0.9	1.0	1.0	1.0	1.0

Table 5.6

Gas Evolution Data for a 50.0 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	4	6.5	8	11.5	16	Initial Polymer Weight = 0.430g.
P_{total}	52.8	120.2	172.5	183.8	216.0	248.2	

Time of Degradation, hours	2	4	6	8	10	12	14	16	∞
P'_{total} (Fig.5.4)	60.0	113.0	156.0	188.0	207.9	222.2	234.0	245.0	250.0
CP_{CO_2}	37.2	71.1	100.5	123.5	139.6	152.7	164.1	175.1	180.1
$CP_{but-1-ene}$	22.8	41.9	55.5	64.5	68.3	69.5	69.9	69.9	69.9
m.moles CO_2 per g. polymer	.253	.486	.686	.842	.951	1.04	1.12	1.19	1.23
m.moles but-1-ene per g. polymer	.156	.286	.379	.440	.465	.474	.477	.477	.477
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	2.0	3.7	5.1	6.2	6.8	7.2	7.6	7.9	8.1

Table 5.7

Gas Evolution Data for an 82.2 Mole $^{o}/_{o}$ n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	3	6	10.5	13.5	15.5	18	22	32
P_{total}	40.0	111.8	133.9	172.0	203.5	223.2	229.9	230.0	253.0

PART A Data Calculated for Degradation Times up to 12 Hours.

Time of Degradation, hours	2	4	6	8	10	12	
P'_{total} (Fig.5.5)	65.0	102.0	129.5	153.0	172.0	189.0	Initial Polymer Weight = 0.270g.
CP_{CO_2}	38.2	62.5	81.1	98.9	113.5	126.3	
$CP_{but-1-ene}$	26.8	39.5	48.4	54.1	58.5	62.7	
m.moles CO_2 per g. polymer	.415	.678	.881	1.07	1.23	1.37	
m. moles but-1-ene per g. polymer	.293	.430	.526	.589	.637	.681	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	3.5	5.4	6.8	8.0	9.0	9.9	

Table 5.7(contd.)

Gas Evolution Data for an 82.2 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

PART B Data Calculated for Degradation Times Greater Than 12 Hours.

Time of Degradation, hours	14	16	18	20	22	∞	
P'_{total} (Fig.5.5)	204.0	216.2	226.0	233.9	239.5	253.0	Initial Polymer Weight = 0.270g.
CP_{CO_2}	137.7	146.4	153.6	159.7	164.9	174.7	
$CP_{but\text{-}1\text{-}ene}$	66.3	69.8	72.4	74.2	74.6	78.3	
m.moles CO_2 per g. polymer	1.50	1.59	1.67	1.73	1.79	1.90	
m.moles but-1-ene per g. polymer	.719	.759	.785	.807	.811	.852	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	10.6	11.3	11.8	12.2	12.4	13.1	

Table 5.8

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	3	6	8	10	13.75	15.5	24	30
P_{total}	29.0	45.9	59.9	66.2	83.8	89.8	101.8	107.0

PART A Data Calculated for Degradation Times up to 14 Hours.

Time of Degradation, hours	2	4	6	8	10	12	14	
P'_{total} (Fig.5.6)	19.0	34.0	46.5	57.5	67.0	76.0	83.5	Initial Polymer Weight = 0.085g.
CP_{CO_2}	12.5	21.7	29.8	36.5	42.6	48.3	52.9	
$CP_{but\text{-}1\text{-}ene}$	6.5	12.3	16.7	21.0	24.4	27.7	30.6	
m.moles CO_2 per g. polymer	.435	.753	1.02	1.26	1.47	1.67	1.82	
m.moles but-1-ene per g. polymer	.224	.424	.576	.729	.847	.953	1.06	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	3.1	5.7	7.8	9.6	11.2	12.7	14.0	

Table 5.8(contd.)

Gas Evolution Data for a 93.4 Mole $^{o}/o$ n-Butyl Acrylate Copolymer Degraded at $313^{o}C$.

PART B Data Calculated for Degradation Times Greater Than 14 Hours.

Time of Degradation, hours	16	18	20	22	24	26	∞	
P'_{total} (Fig.5.6)	90.0	94.5	98.5	101.0	103.0	104.5	106.0	Initial Polymer Weight = 0.085g.
CP_{CO_2}	56.9	60.1	63.1	65.1	67.1	68.6	70.1	
$CP_{but-1-ene}$	33.1	34.4	35.4	35.9	35.9	35.9	35.9	
m.moles CO_2 per g. polymer	1.96	2.07	2.18	2.25	2.32	2.36	2.42	
m.moles but-1-ene per g. polymer	1.14	1.19	1.22	1.24	1.24	1.24	1.24	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	15.1	15.8	16.5	16.9	17.2	17.4	17.7	

Table 5.9

Gas Evolution Data for a 50.0 Mole $^{o}/_{o}$ n-Butyl Acrylate Copolymer Degraded at 332^{o}C.

Time of Degradation, hours	1.25	2.5	4	6	7	9.5	12
P_{total}	86.1	167.3	237.0	270.3	331.7	345.8	334.0

<u>PART A</u> Data Calculated for Degradation Times up to 6 Hours.

Time of Degradation, hours	1	2	3	4	5	6	
P'_{total} (Fig.5.7)	77.8	139.2	190.4	237.4	275.2	298.8	Initial Polymer Weight = 0.346g.
CP_{CO_2}	53.5	96.3	129.7	160.9	186.0	202.0	
$CP_{but\text{-}1\text{-}ene}$	24.3	42.9	60.7	76.5	89.2	96.8	
m.moles CO_2 per g. polymer	.454	.815	1.10	1.36	1.58	1.71	
m.moles but-1-ene per g. polymer	.205	.364	.514	.647	.757	.821	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	3.2	5.6	7.7	9.6	11.2	12.1	

Table 5.9(contd.)

Gas Evolution Data for a 50.0 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

<u>PART B</u> Data Calculated for Degradation Times Greater Than 6 Hours.

Time of Degradation, hours	7	8	9	10	∞	
P'_{total} (Fig.5.7)	316.1	327.5	337.5	339.8	340.1	Initial Polymer Weight = 0.346g.
CP_{CO_2}	213.8	221.6	228.6	230.9	231.2	
$CP_{but\text{-}1\text{-}ene}$	102.3	105.9	108.9	108.9	108.9	
m.moles CO_2 per g. polymer	1.81	1.88	1.94	1.96	1.96	
m.moles but-1-ene per g. polymer	.867	.899	.922	.922	.922	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	12.8	13.3	13.7	13.8	13.8	

Table 5.10

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

Time of Degradation, hours	3	7	10.5	18.5	24
P_{total}	60.2	94.2	108.0	117.0	120.0

<u>PART A</u> Data Calculated for Degradation Times up to 12 Hours.

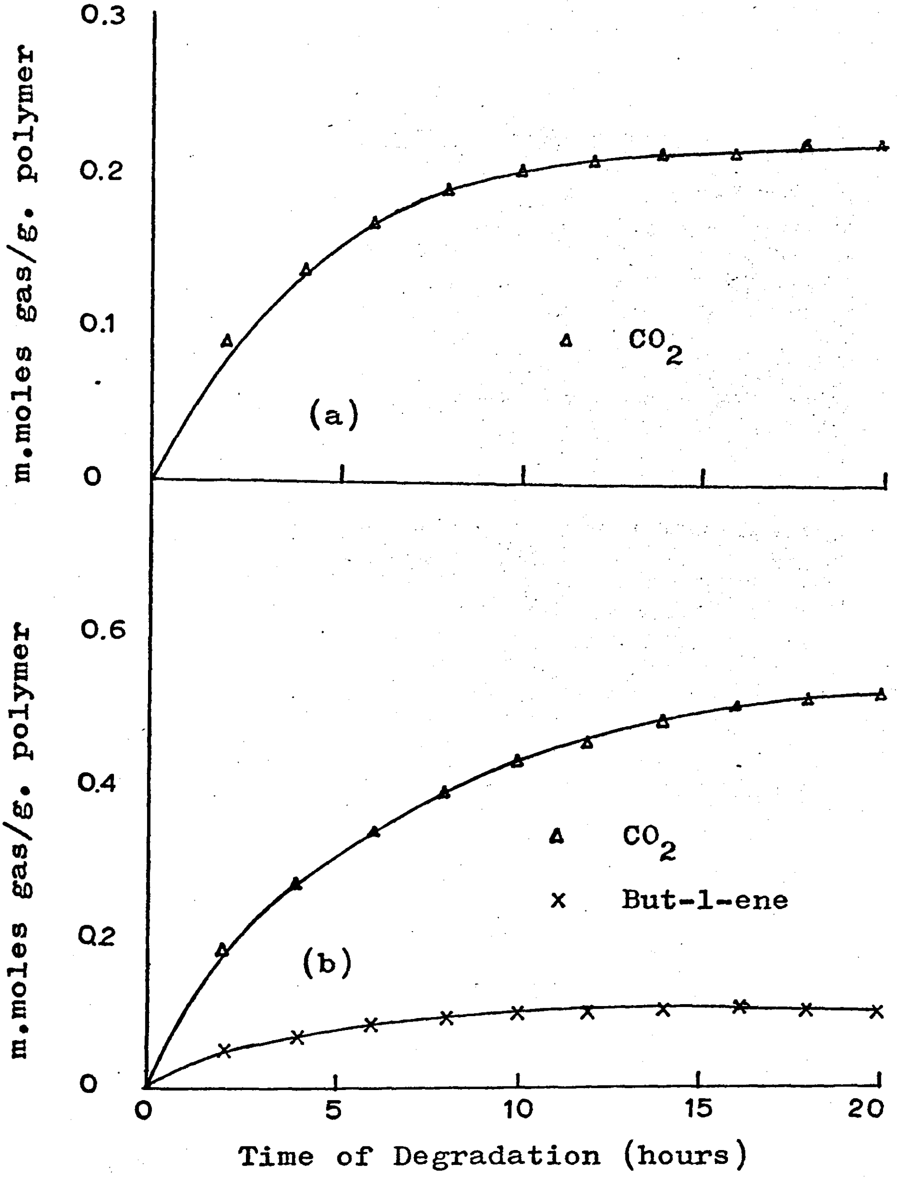
Time of Degradation, hours	2	4	6	8	10	12	
P'_{total} (Fig.5.8)	50.0	70.0	85.0	95.5	103.0	108.0	Initial Polymer Weight = 0.079g.
CP_{CO_2}	29.0	40.7	51.2	57.7	62.7	66.0	
$CP_{but-1-ene}$	21.0	29.3	33.8	37.8	40.3	42.0	
m.moles CO_2 per g. polymer	1.08	1.51	1.90	2.14	2.33	2.46	
m.moles but-1-ene per g. polymer	.785	1.09	1.25	1.41	1.49	1.56	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	9.1	12.7	15.4	17.3	18.6	19.5	

Table 5.10(contd.)

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

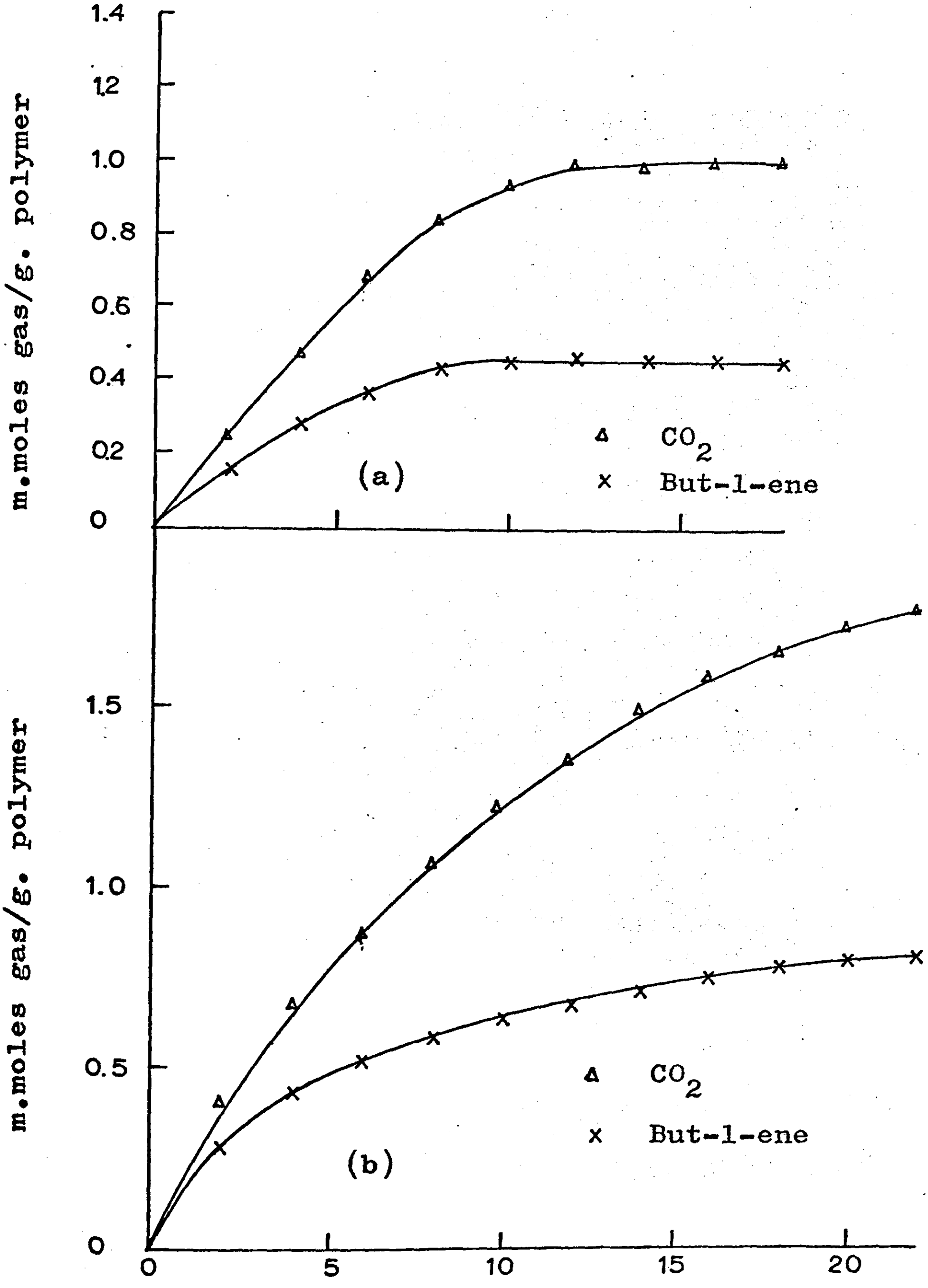
<u>PART B</u> Data Calculated for Degradation Times Greater Than 12 Hours.

Time of Degradation, hours	14	16	18	20	22	∞	
P'_{total} (Fig.5.8)	112.0	115.0	117.0	118.0	119.2	120.0	Initial Polymer Weight = 0.079g.
CP_{CO_2}	68.2	69.7	70.4	70.8	71.3	71.8	
$CP_{but\text{-}1\text{-}ene}$	43.8	45.3	46.6	47.2	47.9	48.2	
m.moles CO_2 per g. polymer	2.53	2.58	2.62	2.63	2.65	2.67	
m.moles but-1-ene per g. polymer	1.62	1.68	1.73	1.75	1.78	1.78	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	20.2	20.8	21.2	21.4	21.6	21.7	



(a) 3.9 mole °/o n-butyl acrylate copolymer.
(b)16.3 mole °/o n-butyl acrylate copolymer.

Fig.5.9 Gas evolution plots for copolymers degraded at 313°C.



(a) 50.0 mole °/o n-butyl acrylate copolymer.
(b) 82.2 mole °/o n-butyl acrylate copolymer.

Fig.5.10 Gas evolution plots for copolymers degraded at 313°C.

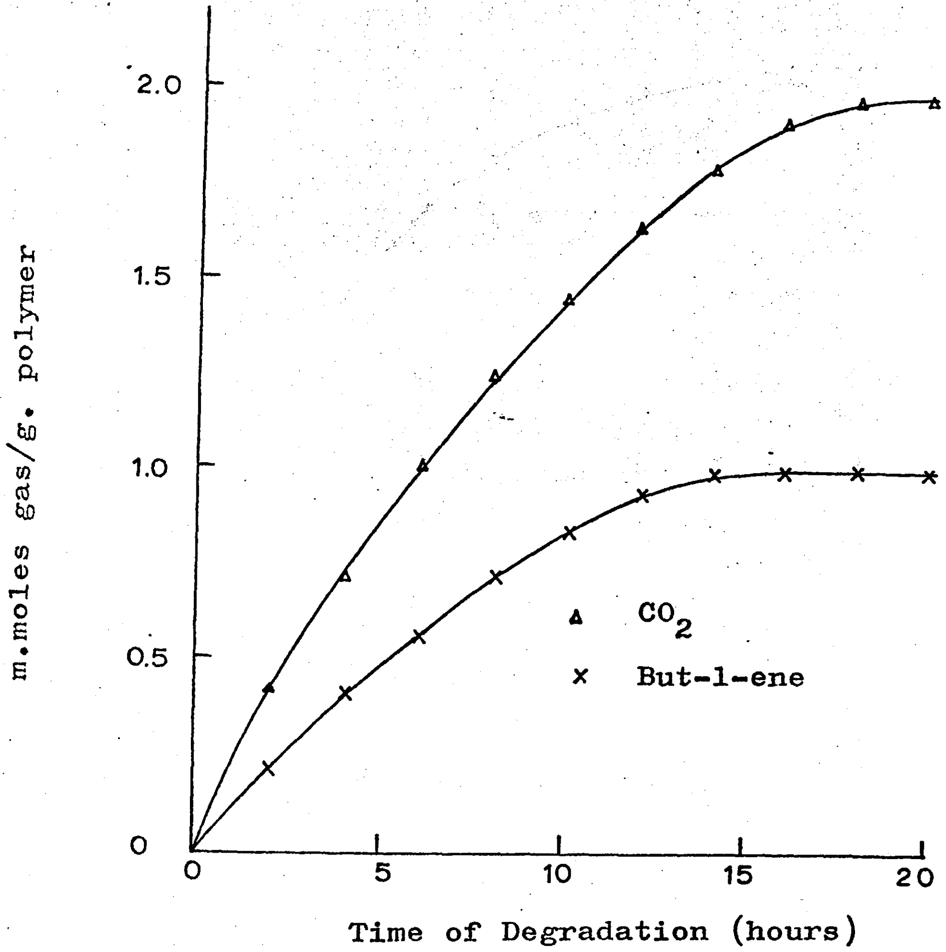


Fig.5.11 Gas evolution plot for a 93.4 mole °/o n-butyl acrylate copolymer degraded at 313°C.

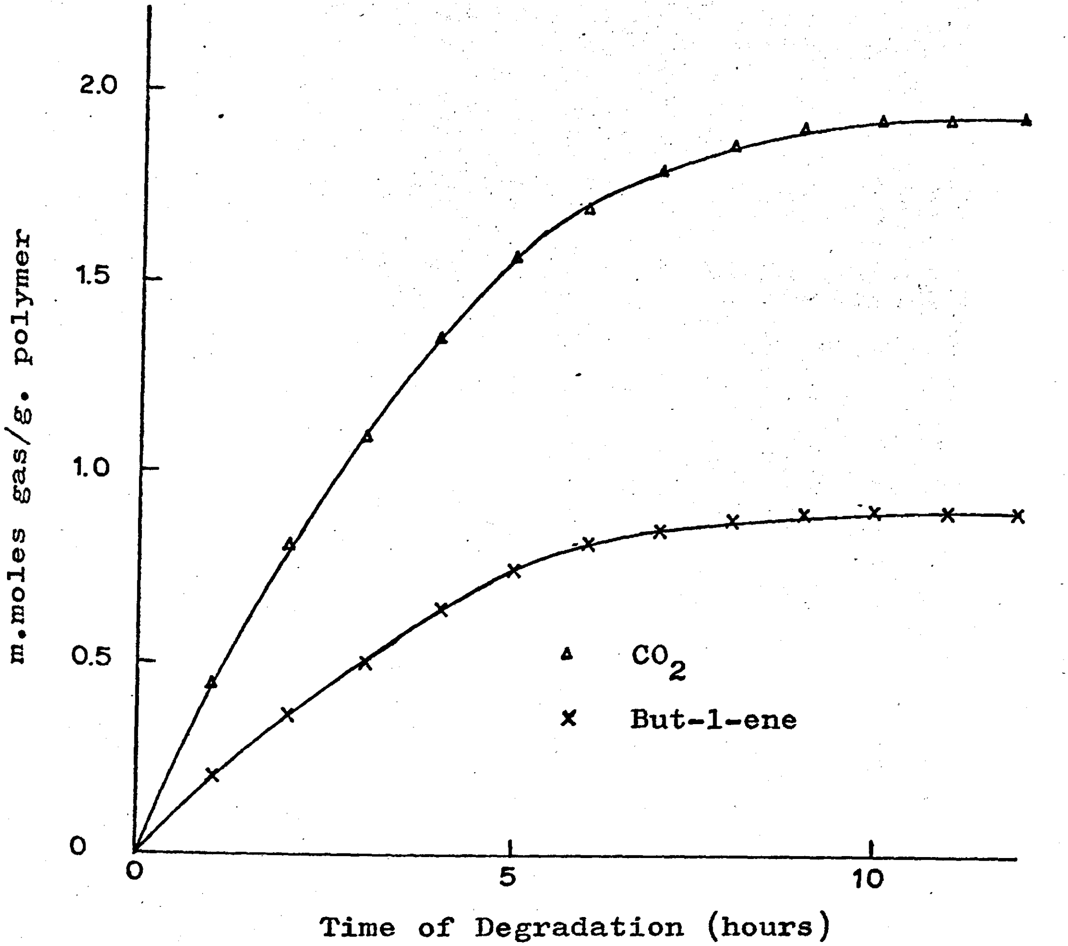


Fig.5.12 Gas evolution plot for a 50.0 mole °/o n-butyl acrylate copolymer degraded at 332°C.

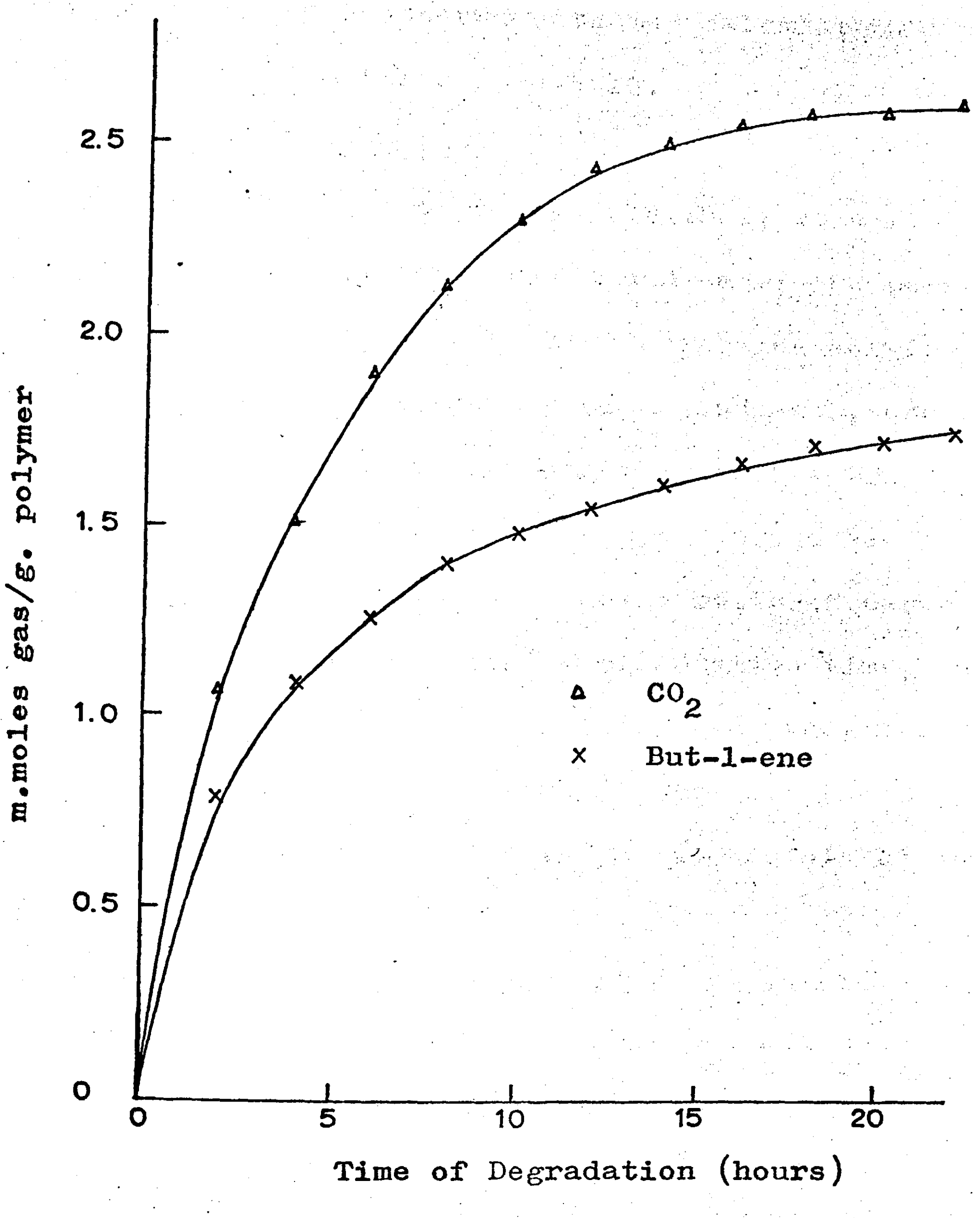


Fig.5.13 Gas evolution plot for a 93.4 mole °/o n-butyl acrylate copolymer degraded at 332°C.

In order to obtain a mass balance, the percentage by weight of the gaseous products was calculated. These values are given in tables 5.4-5.10.

(c) Discussion of Results

It is clear from Figs.5.9-5.13 that, as expected, the amount of both carbon dioxide and but-1-ene per gram of initial polymer increases with increasing acrylate content for a fixed temperature of degradation, and that it also increases with increasing temperature when copolymers of a given composition are considered.

Another trend is that the molar ratio of carbon dioxide to but-1-ene at infinite degradation time, table 5.11, decreases both with increasing acrylate content and with increasing temperature.

An interesting quantity is the amount of but-1-ene produced per gram of n-butyl acrylate in the original copolymer, for if but-1-ene production is associated with single acrylate units, then this quantity would be expected to stay constant over the copolymer composition range examined. In addition but-1-ene production would be expected to occur even when acrylate units are present as isolated entities. The fact that but-1-ene is evolved on the degradation of a 16.3 mole percent n-butyl acrylate copolymer, when more than 75^{o}/o of the acrylate

Table 5.11

Copolymer Composition (mole $^o/o$ acrylate)	Temp. of Degradation	CO_2 Pressure (mm. Hg) at t_∞	But-1-ene Pressure (mm. Hg) at t_∞	Molar Ratio(=pressure ratio) CO_2 :But-1-ene at t_∞
16.3	313	58.9	12.1	4.9
50.0	313	180.1	69.9	2.6
82.2	313	174.7	78.3	2.2
93.4	313	70.1	35.9	2.0
50.0	332	231.2	108.9	2.1
93.4	332	71.8	48.2	1.5

Table 5.12

Copolymer Composition (mole $^o/o$ acrylate)	Temp. of Degradation	(g. But-1-ene/g. polymer) x 10^2	g. n-Butyl Acrylate/g. polymer	(g. But-1-ene/g. n-Butyl Acrylate) x 10^2
16.3	313	0.61	0.20	3.05
50.0	313	2.67	0.56	4.76
82.2	313	4.77	0.86	5.57
93.4	313	6.97	0.95	7.36
50.0	332	5.18	0.56	9.10
93.4	332	21.75	0.95	22.95

units present are flanked by methacrylate units, indicates that sequences of acrylate units are not required for the production of this gas. The data in table 5.12, however, show that the amount of but-1-ene obtained from any given n-butyl acrylate unit depends to some extent upon the acrylate content of the polymer. This apparent anomaly might be explained by noting that a first step in the ester decomposition reaction of polyacrylates to olefin and acid is the abstraction of the tertiary hydrogen atom on the polymer chain, Fig.1.3. This initiating step is more likely to occur the higher the concentration of acrylate units since the acrylate radical is more reactive than the methacrylate radical, which prefers to depolymerize rather than to take part in hydrogen abstraction reactions such as this.

5.3 Calculation of Mass Balance Data

The percentage by weight of gas evolved on degradation of the copolymers has already been calculated, tables 5.4-5.10. Similar data for the liquid products, $^{o}/oL$, and the residue, $^{o}/oR$, are given in tables 5.13-5.19 and plotted in Figs.5.14-5.22 as percentage of initial weight of copolymer versus time of degradation. From both the liquid product and residue curves for each polymer values of the percentage of liquids, $^{o}/oL'$, and percentage

Table 5.13

Data for the Degradation of a 3.9 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	4	6.5	8.5	16	18
Weight of Liquids, g.	.144	.244	.306	.326	.349	.333
Weight of Residue, g.	.175	.115	.051	.035	.013	-
°/o Liquids, °/o L.	41.7	70.7	88.7	94.5	101.2	96.5
°/o Residue, °/o R.	50.7	33.3	14.8	10.1	3.8	-

Initial Polymer Weight = 0.345g.

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18
°/o L' (Fig.5.14)	43.0	67.5	84.0	94.0	98.0	99.0	99.0	99.0	99.0
°/o R' (Fig.5.14)	50.0	31.0	18.0	9.8	6.2	4.8	3.9	3.8	3.8
°/o Gas (table 5.5)	0.4	0.6	0.8	0.9	0.9	0.9	1.0	1.0	1.0
°/o Total Products	93.4	99.1	102.8	104.7	105.1	104.7	103.9	103.8	103.8

Table 5.14

Data for the Degradation of a 16.3 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	4	6	8	11	16	18	
Weight of Liquids, g.	.150	.210	.250	.290	-	.300	.300	Initial Polymer Weight = 0.331g.
Weight of Residue, g.	.232	.141	.079	.046	.033	.017	.017	
°/o Liquids, °/o L.	45.3	63.4	75.5	87.6	-	90.6	90.6	
°/o Residue, °/o R.	70.1	42.6	23.9	13.9	10.0	5.1	5.1	

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18
°/o L' (Fig.5.15)	37.5	63.9	77.9	85.4	88.0	89.8	90.8	91.0	91.0
°/o R' (Fig 5.15)	69.5	43.4	24.5	14.3	10.0	7.2	5.3	5.0	5.0
°/o Gas(table 5.4)	1.0	1.6	2.0	2.3	2.5	2.6	2.8	2.9	2.9
°/o Total Products	108.0	108.9	104.4	102.0	100.5	99.6	98.9	98.9	98.9

Table 5.15

Data for the Degradation of a 50.0 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	4	6.5	8	11.5	15	16	24	Initial Polymer Weight = 0.430g.
Weight of Liquids, g.	.064	.129	.148	.165	.219	-	.250	.279	
Weight of Residue, g.	.327	-	.239	.225	.192	.178	.157	.126	
°/o Liquids, °/o L.	14.9	30.0	34.4	38.4	50.9	-	58.1	64.9	
°/o Residue, °/o R.	76.0	-	55.6	52.3	44.7	41.4	36.5	29.3	

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18	20
°/o L' (Fig.5.16)	18.0	27.7	35.0	40.7	46.0	50.7	54.7	58.7	61.0	63.0
°/o R' (Fig.5.16)	76.4	65.0	57.8	52.0	48.2	44.5	41.2	38.0	35.2	32.8
°/o Gas (table 5.6)	2.0	3.7	5.1	6.2	6.8	7.2	7.6	7.9	8.1	8.1
°/o Total Products	96.4	96.4	97.9	98.9	101.0	102.4	103.5	104.6	104.3	103.9

Table 5.16

Data for the Degradation of an 82.2 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	6	10.5	13.5	15.5	24
Weight of Liquids, g.	.012	.079	.097	.106	.124	.149
Weight of Residue, g.	.225	.173	.122	.125	.112	.080
°/o Liquids, °/o L.	4.4	29.3	35.9	39.3	45.9	55.2
°/o Residue, °/o R.	83.3	64.1	45.2	46.3	41.5	29.6

Initial Polymer
Weight = 0.270g.

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18	20	22
°/o L' (Fig.5.17)	9.3	17.2	24.1	29.8	34.8	39.3	43.2	46.7	49.7	52.3	54.3
°/o R' (Fig.5.17)	80.0	70.5	63.0	57.4	52.0	46.8	42.5	38.5	35.3	33.0	30.9
°/o Gas (table 5.7)	3.5	5.4	6.8	8.0	9.0	9.9	10.6	11.3	11.8	12.2	12.4
°/o Total Products	92.8	93.1	93.9	95.2	95.8	96.0	96.3	96.5	96.8	97.5	97.6

Table 5.17

Data for the Degradation of a 93.4 Mole$^{o}/o$ n-Butyl Acrylate Copolymer at 313^{o}C.

Time of Degdn.,hrs.	3	6	8	10	13.75	15.5	18	24	Initial Polymer Weight = 0.085g.
Wt. of Liquids,g.	.013	.019	.022	.027	.030	.032	.039	.037	
Wt. of Residue,g.	.076	.063	-	.052	.036	.034	.044	.032	
Wt. of Chain Fragments,g.	-	-	-	-	.002	.004	.001	.003	
$^{o}/o$ Liquids, $^{o}/o$L.	15.3	22.4	25.9	31.8	35.3	37.6	45.9	43.5	
$^{o}/o$ Residue, $^{o}/o$R.	89.4	74.1	-	61.2	42.4	40.0	51.8	37.6	
$^{o}/o$ Chain Fragments, $^{o}/o$C.	-	-	-	-	2.4	4.7	1.2	3.5	

Time of Degdn.,hrs.	2	4	6	8	10	12	14	16	18	20	22	24
$^{o}/o$ L' (Fig.5.18)	10.8	17.7	23.8	28.1	32.4	35.5	38.3	40.5	42.6	43.9	44.7	45.5
$^{o}/o$ R' (Fig.5.18)	89.5	81.2	74.0	67.4	61.5	55.0	50.0	45.7	42.3	39.6	37.6	35.7
$^{o}/o$ C' (Fig.5.18)	0.6	1.2	1.7	1.9	2.3	2.5	2.8	3.0	3.1	3.3	3.6	3.6
$^{o}/o$ Gas(table 5.8)	3.2	5.7	7.8	9.6	11.2	12.7	14.0	15.1	15.8	16.5	16.9	17.2
$^{o}/o$ Total Products	104.1	105.8	107.3	107.0	107.4	105.7	105.1	104.3	103.8	103.3	102.8	102.0

Table 5.18

Data for the Degradation of a 50.0 Mole ^{o}/o n-Butyl Acrylate Copolymer at 332^{o}C.

Time of Degdn.,hrs.	1.25	2.5	4	7	9.5	12
Wt. of Liquids,g.	.076	.163	.197	.214	.232	.236
Wt. of Residue,g.	.254	.194	.126	.071	.035	.024
Wt. of Chain Fragments,g.	-	.005	.032	.042	.028	.048
^{o}/o Liquids, ^{o}/oL.	22.0	47.1	56.9	61.8	67.0	68.2
^{o}/o Residue, ^{o}/oR.	73.4	56.1	36.4	20.5	10.1	6.9
^{o}/o Chain Fragments, ^{o}/oC.	-	1.4	9.2	12.1	8.1	13.9

Initial Polymer
Weight = 0.346g.

Time of Degdn.,hrs.	1	2	3	4	5	6	7	8	9	10	11
^{o}/o L$'$ (Fig.5.19)	19.2	39.1	50.3	56.9	59.8	61.9	63.4	64.4	65.4	65.9	66.3
^{o}/o R$'$ (Fig.5.20)	79.9	61.8	48.0	36.4	28.8	23.4	18.2	14.2	11.5	9.3	7.6
^{o}/o C$'$ (Fig.5.19)	2.0	3.1	5.3	6.9	8.2	9.2	9.9	10.8	11.1	11.5	11.6
^{o}/o Gas(table 5.9)	3.2	5.6	7.7	9.6	11.2	12.1	12.8	13.3	13.7	13.8	13.8
^{o}/o Total Products	104.3	109.6	111.3	109.8	108.0	106.6	104.3	102.7	101.7	100.5	99.3

Table 5.19

Data for the Degradation of a 93.4 Mole ^{o}/o n-Butyl Acrylate Copolymer at 332^{o}C.

Time of Degdn.,hrs.	3	7	10.5	12.5	18.5	24
Wt. of Liquids,g.	.026	.036	.036	.037	.040	.039
Wt. of Residue,g.	.047	.030	.028	.022	.014	.012
Wt. of Chain Fragments,g.	.003	.007	-	.009	.009	.013
^{o}/o Liquids,^{o}/oL.	32.9	45.6	45.6	46.8	50.6	49.4
^{o}/o Residue,^{o}/oR.	59.5	38.0	35.4	27.8	17.7	15.2
^{o}/o Chain Fragments,^{o}/oC.	3.8	8.9	-	11.4	11.4	16.5

Initial Polymer
Weight = 0.079g.

Time of Degdn.,hrs.	2	4	6	8	10	12	14	16	18	20	22	24
^{o}/o L' (Fig.5.21)	27.1	35.8	41.0	44.2	46.3	47.6	48.4	48.9	49.4	49.6	49.6	49.6
^{o}/o R' (Fig.5.22)	67.6	54.2	46.2	39.4	33.0	28.1	24.2	21.1	19.0	17.3	16.1	15.8
^{o}/o C' (Fig.5.21)	3.2	5.3	7.2	8.8	10.0	10.9	11.8	12.4	13.1	13.5	13.8	14.1
^{o}/o Gas(table 5.10)	9.1	12.7	15.4	17.3	18.6	19.5	20.2	20.8	21.2	21.4	21.6	21.7
^{o}/o Total Products	107.0	108.0	109.8	109.7	107.9	106.1	104.6	103.2	102.7	101.8	101.1	101.2

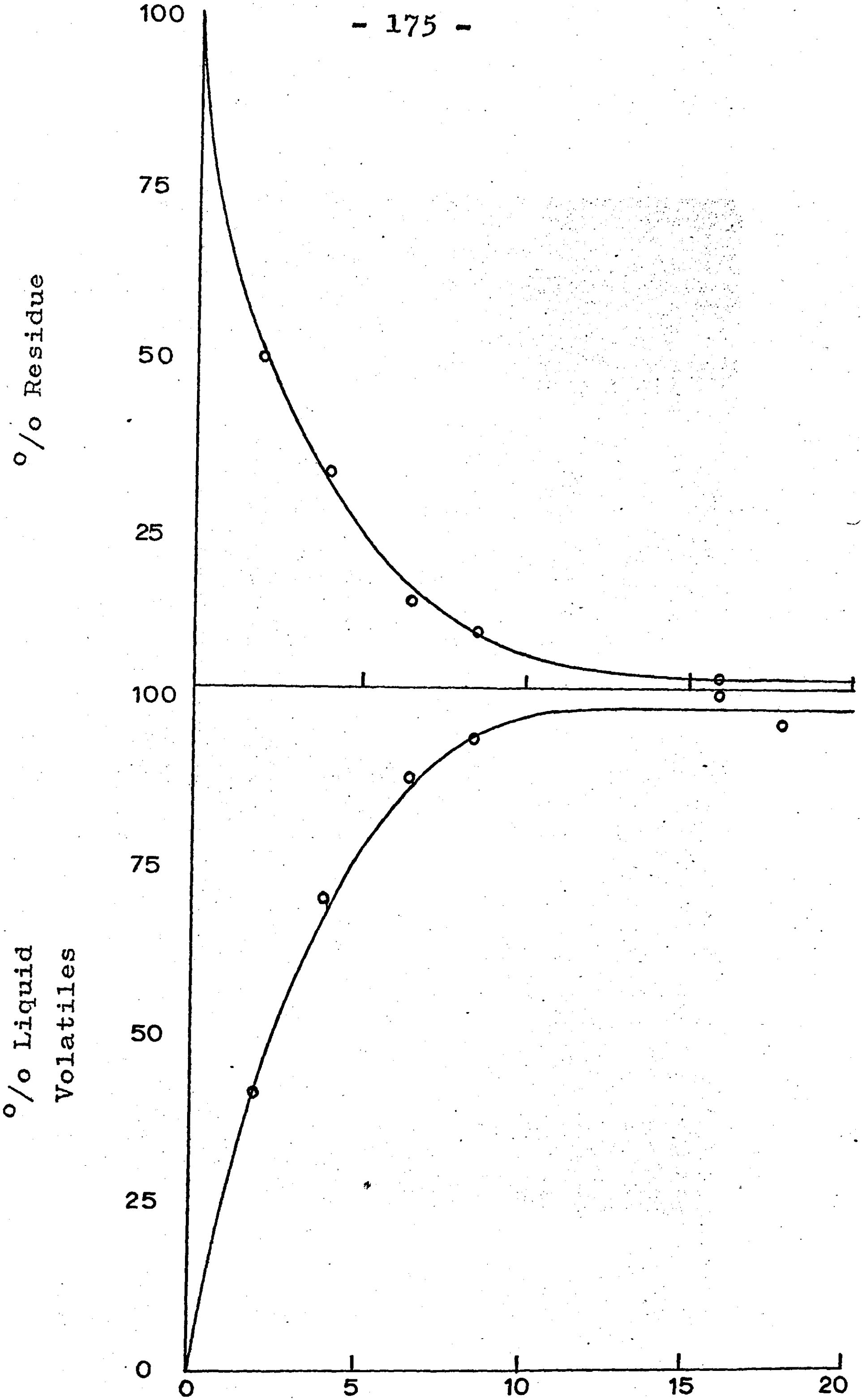


Fig.5.14 Residue and liquid volatile plots for a 3.9 mole percent n-butyl acrylate copolymer degraded at 313°C.

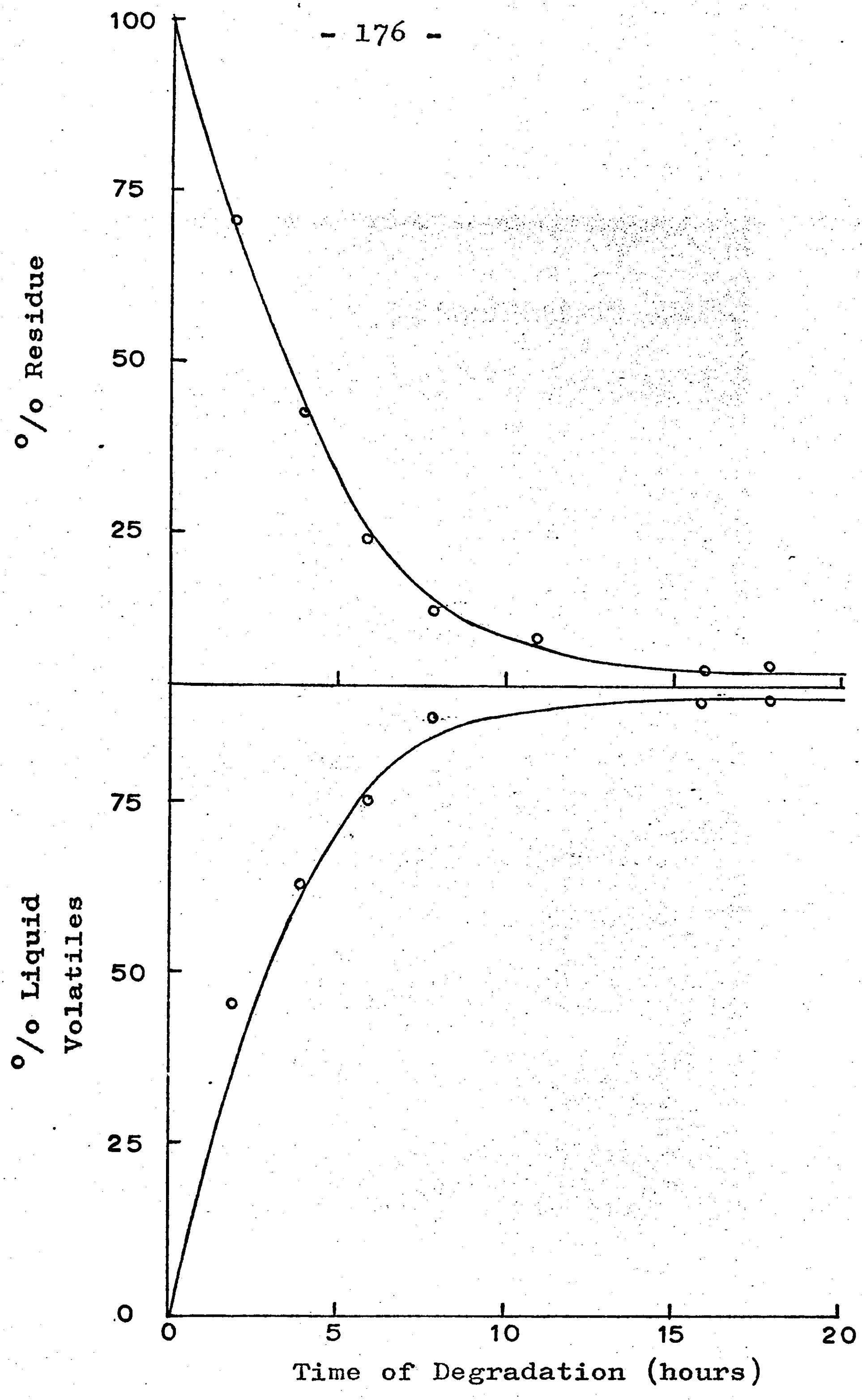


Fig.5.15 Residue and liquid volatile plots for a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C.

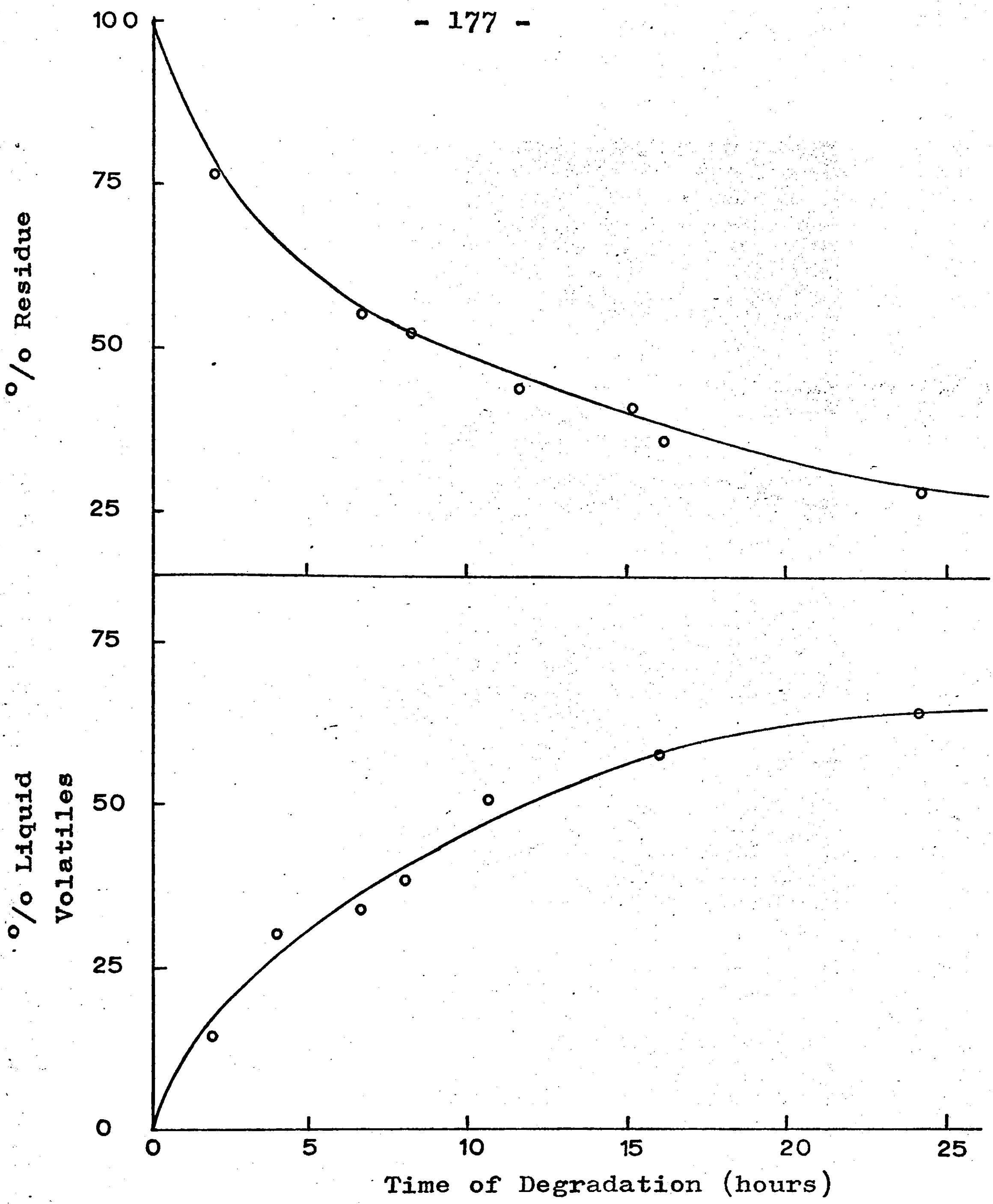


Fig.5.16 Residue and liquid volatile plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 313°C.

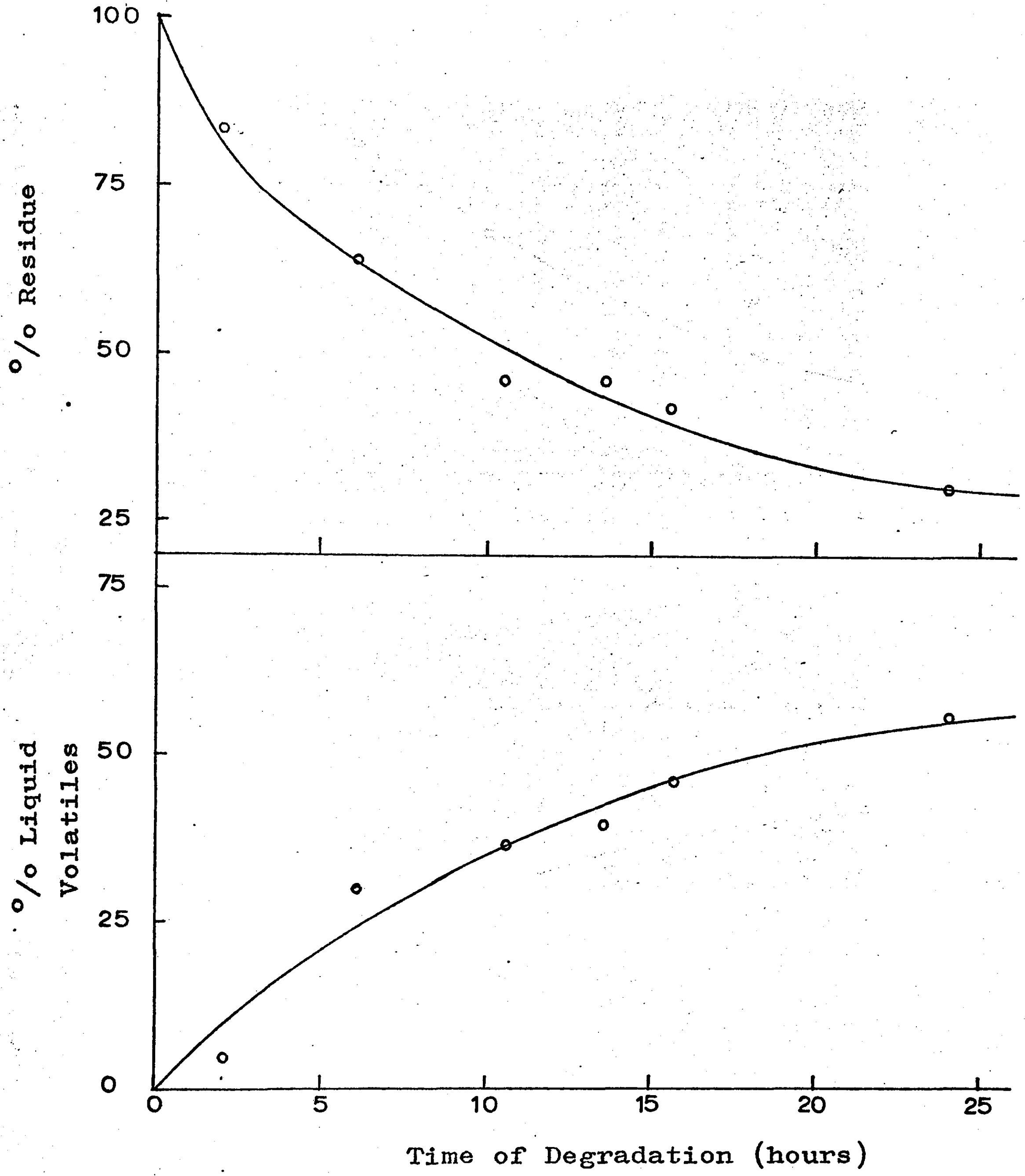


Fig.5.17 Residue and liquid volatile plots for an 82.2 mole percent n-butyl acrylate copolymer degraded at 313°C.

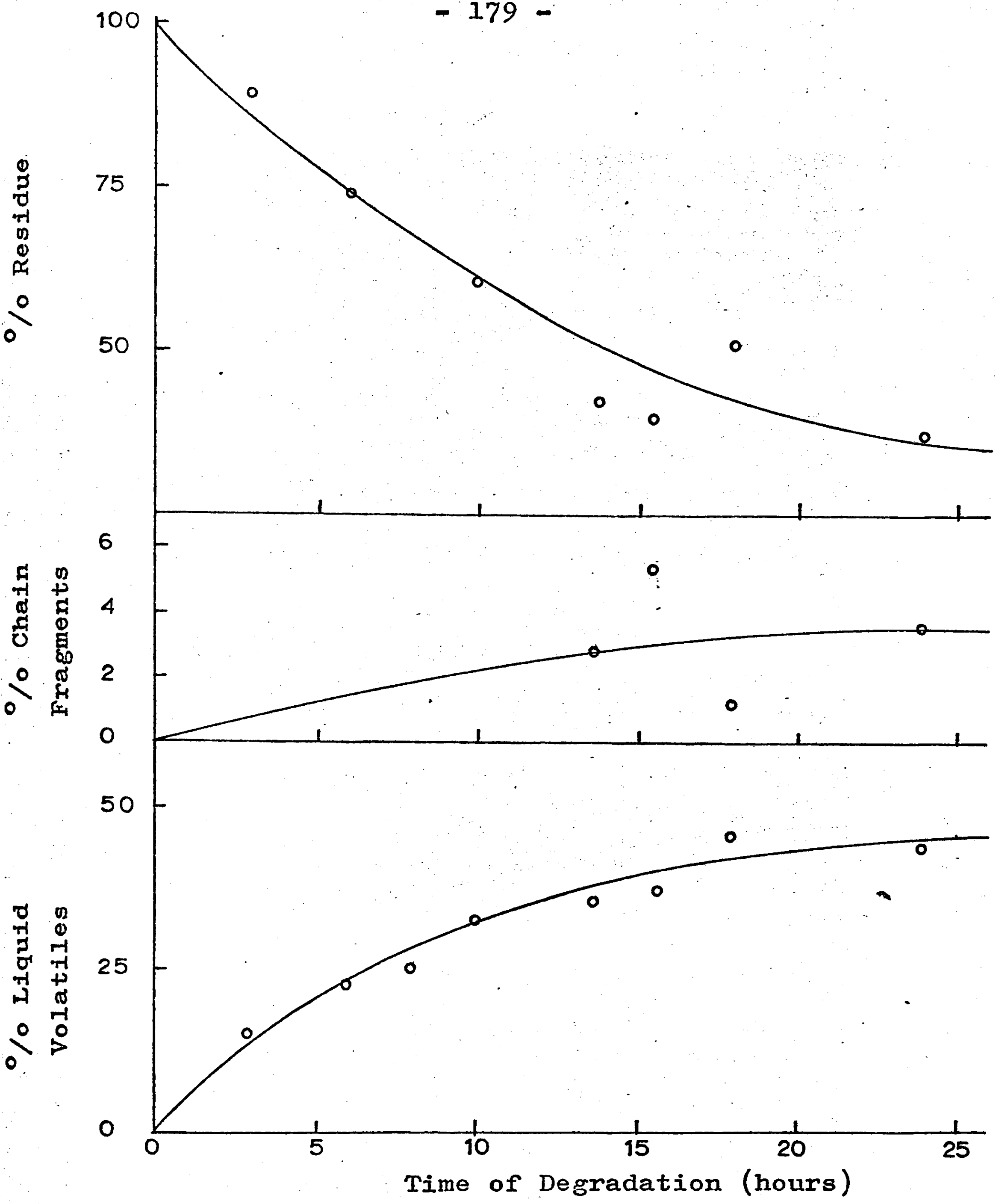


Fig.5.18 Residue, chain fragment, and liquid volatile plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 313°C.

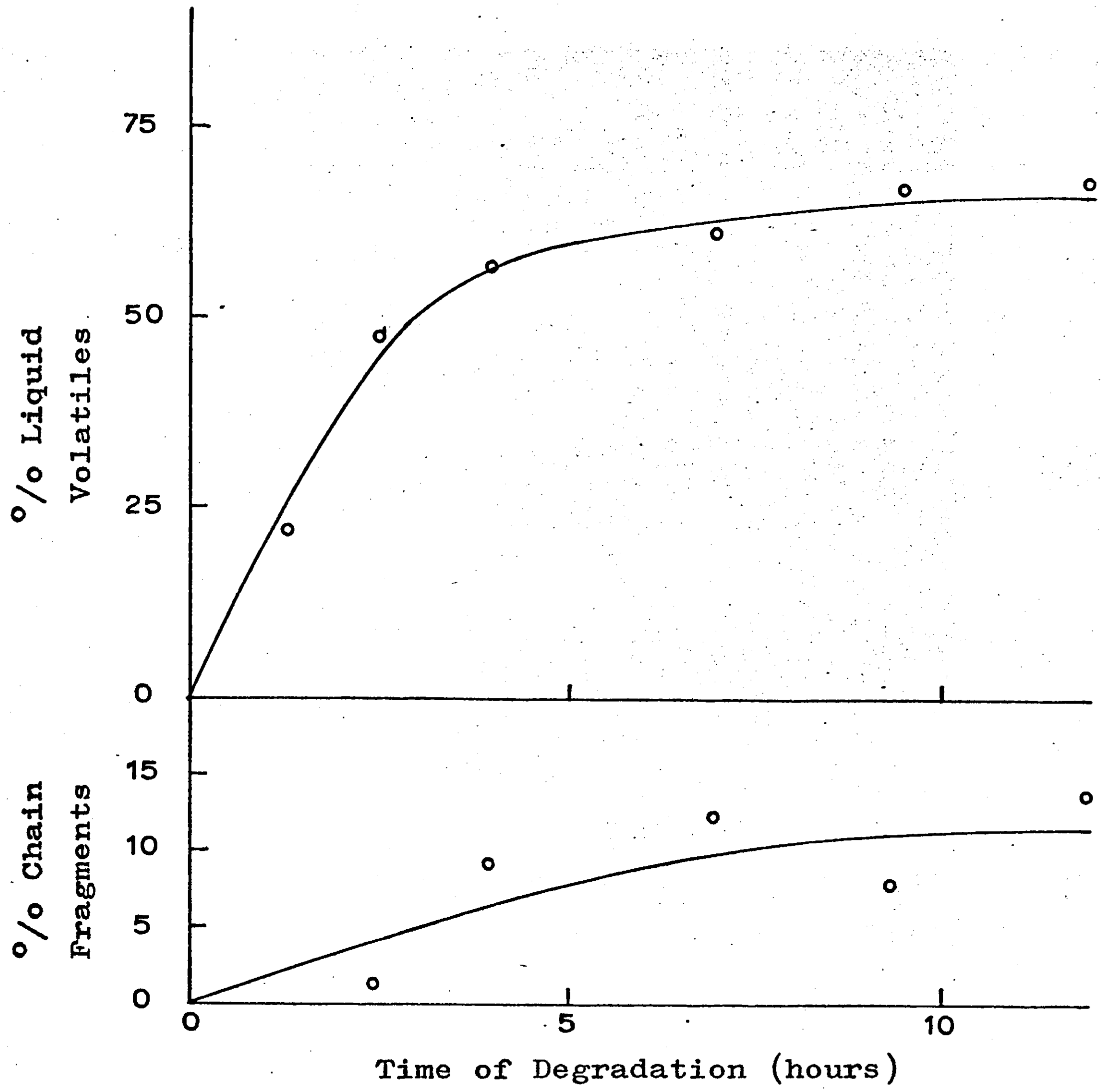


Fig.5.19 Liquid volatile and chain fragment plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 332°C.

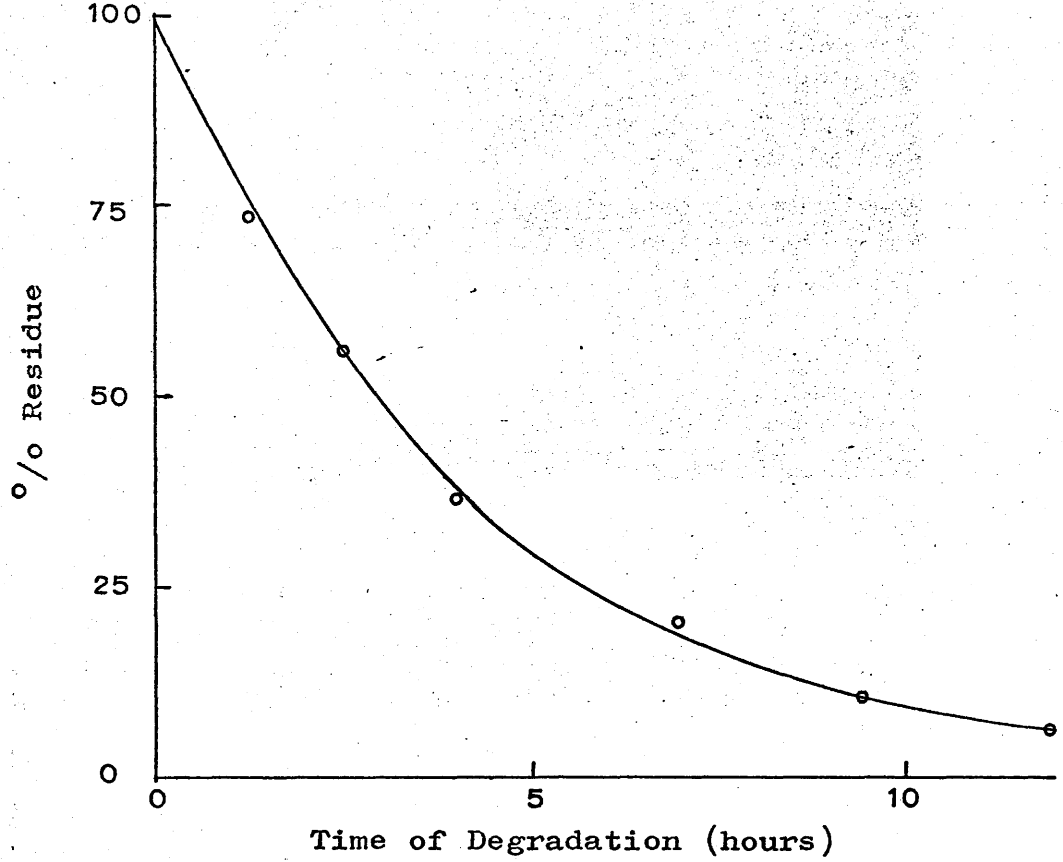


Fig.5.20 Residue plot for a 50.0 mole percent n-butyl acrylate copolymer degraded at 332°C.

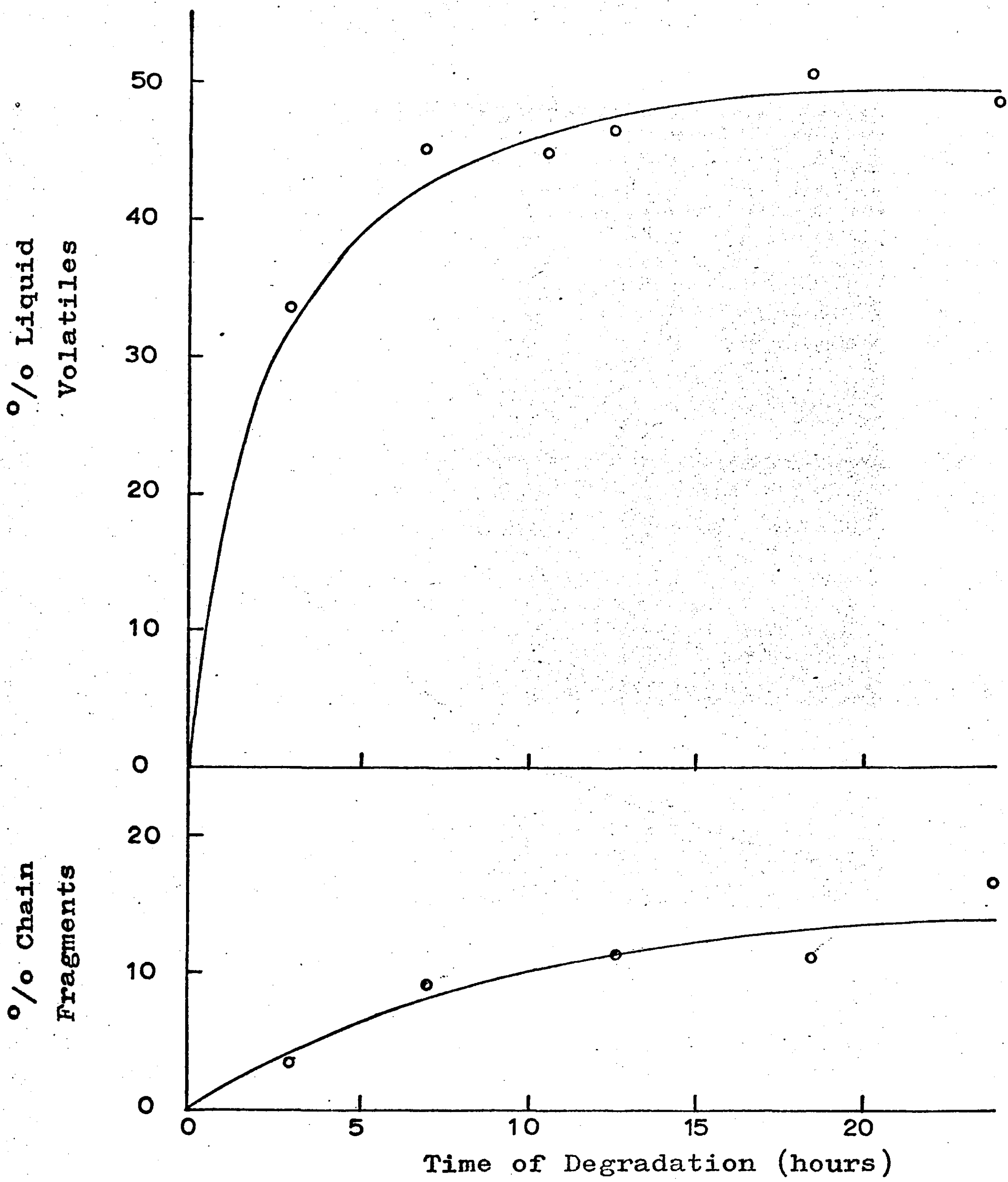


Fig.5.21 Liquid volatile and chain fragment plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 332°C.

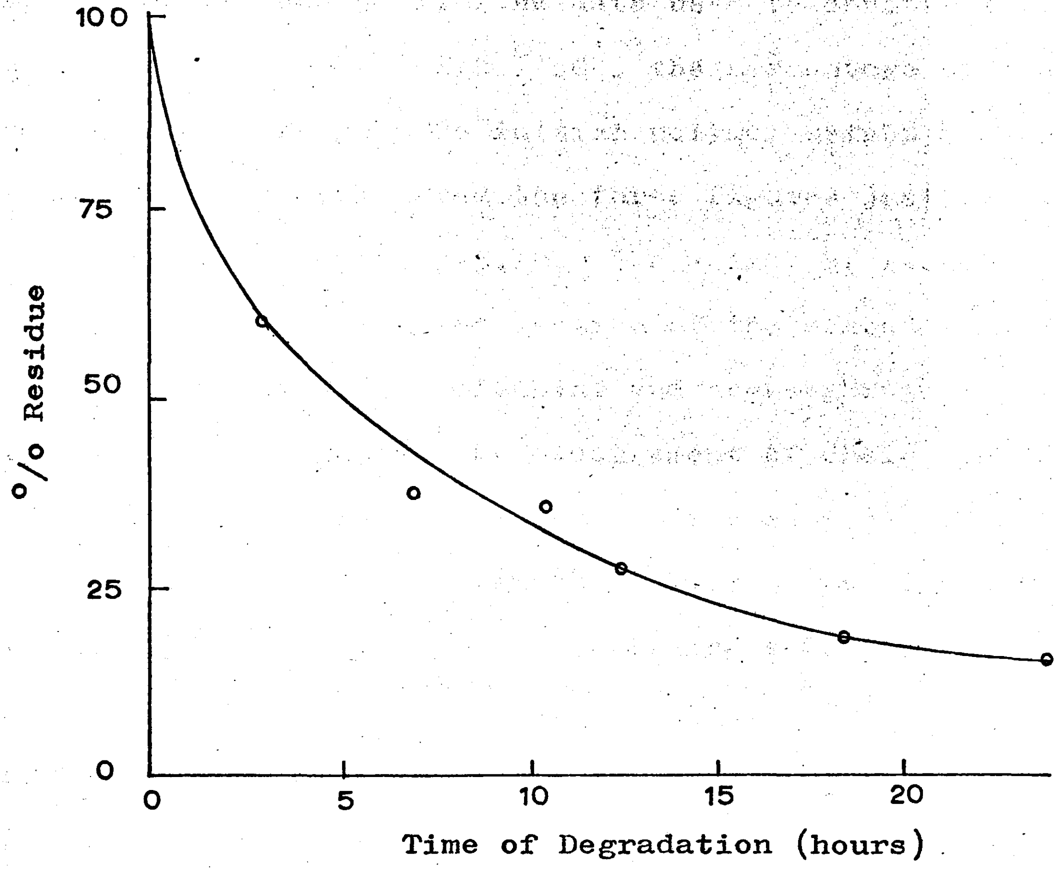


Fig.5.22 Residue plot for a 93.4 mole percent n-butyl acrylate copolymer degraded at 332°C.

residue, $^{o}/oR'$, were read off at suitable intervals and are given in tables 5.13-5.19. In the case of copolymers of high acrylate content curves of chain fragments as a percentage of initial weight, $^{o}/oC$, are plotted in Figs.5.18,5.19 and 5.21. The data used to construct these curves together with $^{o}/oC'$, the percentage of chain fragments with respect to initial polymer weight read off at suitable intervals from the three figures just mentioned, are given in tables 5.17-5.19. The weight of residue was determined by weighing the section of the sealed tube in which it was contained, cleaning and re-weighing, a similar procedure being adopted for measurement of chain fragments and liquid volatiles. As a check for copolymers of high methacrylate content the weight of residue was found by dissolving it in toluene, the resulting solution being made up in a standard flask and the concentration of a known volume determined. This method could not be used on all of the copolymers examined because of the insolubility of some of the residues.

5.4 Analysis of the Liquid Degradation Products

(a) Analytical Techniques

The liquid products of degradation were analyzed by g.l.c. (2.6). Since it was shown in the last chapter that good separation of methyl methacrylate and n-butanol was not obtained on a 1°/o S.E.30 column, it was decided for quantitative measurements to use a 10°/o dinonyl phthalate (D.N.P.) column, table 2.3. A typical chromatogram is shown in Fig.5.23 and table 5.20 gives the retention times of the peaks of interest.

Table 5.20

Peak no. in Fig.5.23	Component	Retention Time (minutes)
1	Methyl Methacrylate	8
2	n-Butanol	10

As detailed in (2.6b) for each determination a known weight of a suitable standard, cyclohexane for the D.N.P. and ethyl benzoate for the S.E.30 column, was added to a weighed amount of sample. The sensitivity of the detector to pure samples of the liquid degradation products was determined by injecting mixtures of known composition into the chromatograph, the results being quoted in table 5.21. Once these factors had been determined the percentage by weight of any of these components could be found as described in (2.6b). In copolymers of high methacrylate content it is very difficult to remove the last traces of toluene from the films deposited in the sealed tubes. These small amounts of solvent can be allowed for by determining the exact amounts present by quantitative g.l.c. measurements.

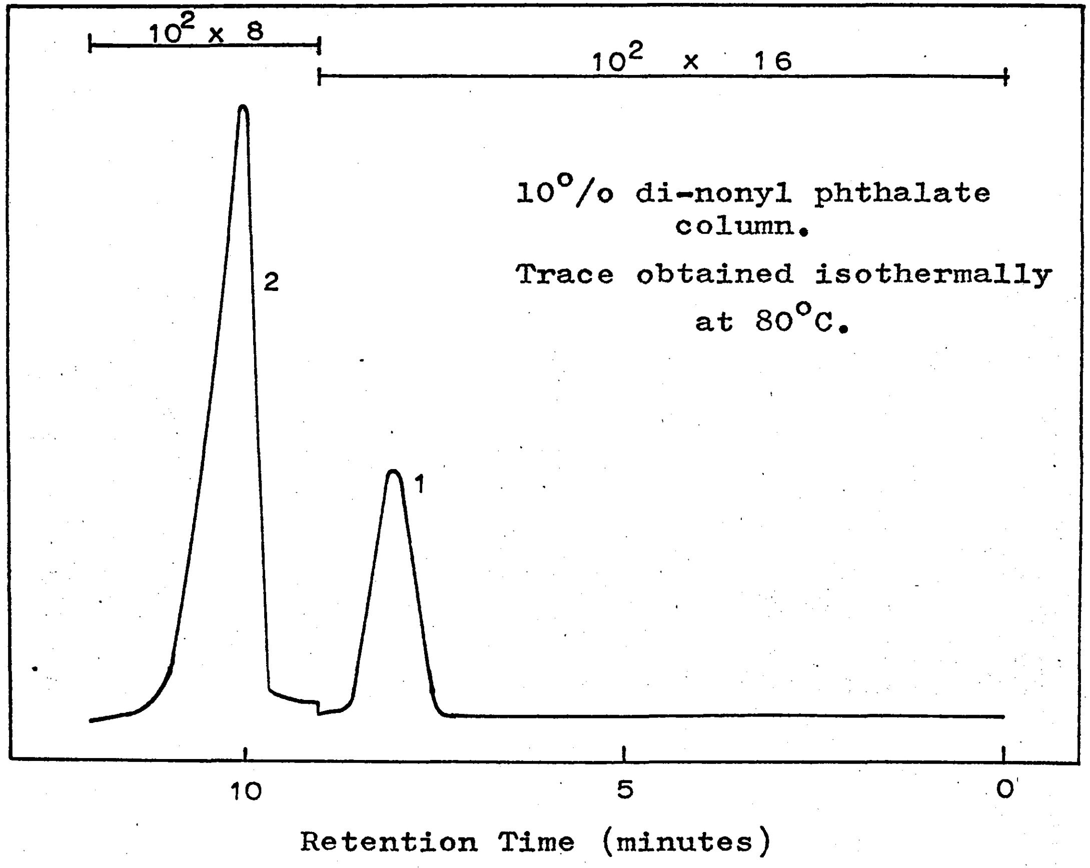


Fig.5.23 G.L.C. trace of the liquid degradation products from a 50.0 mole percent n-butyl acrylate copolymer pyrolyzed at 313°C for 16 hours.

Table 5.21

1°/o S.E.30 Column

Component	Sensitivity Factor Relative to Ethyl Benzoate
n-Butyl Acrylate	0.33
n-Butyl Methacrylate	0.29

10°/o D.N.P. Column

Component	Sensitivity Factor Relative to Cyclohexane
Methyl Methacrylate	0.51
n-Butanol	0.40

Table 5.22 shows the percentages of each of the four liquid components analyzed for, with respect to the total weight of the liquid fraction. The difference between the sum of the percentages in table 5.22 and 100°/o may be accounted for in terms of short chain fragments which have distilled into the capillary portion of the sealed tube during degradation. It was not possible to put a reliable value on the small amounts of n-butyl acrylate found in the breakdown products of the 93.4 mole percent copolymer, so that the term "trace", implying less than one percent, is used in table 5.22. A similar situation is found with both n-butyl acrylate and n-butyl methacrylate in the degradation products of a

Table 5.22

Analysis of the Liquid Degradation Products

Copolymer Composition (mole °/o BuA)	Temp. of Degdn. (°C)	Time of Degdn. (hours)	°/oMMA	°/oBuOH	°/oBuA	°/oBuMA
0.4	313	2	100	nil	nil	nil
	313	4	100	nil	nil	nil
	313	12	100	nil	nil	nil
	313	37	100	nil	nil	nil
3.9	313	2	100	nil	trace	trace
	313	4	95	nil	trace	trace
	313	6.5	99	nil	trace	trace
	313	8.5	97	nil	trace	trace
	313	16	98	nil	trace	trace
	313	18	97	nil	trace	trace
16.3	313	2	70	nil	2	4
	313	4	75	nil	3	2
	313	6	76	nil	5	4
	313	8	65	nil	3	3
	313	11	70	nil	-	-
	313	16	78	nil	-	-
	313	18	74	nil	4	3

MMA = methyl methacrylate
BuOH = n-butanol
BuA = n-butyl acrylate
BuMA = n-butyl methacrylate
"trace" = less than one percent
\- = value not measured

Table 5.22(contd.)

Analysis of the Liquid Degradation Products.

Copolymer Composition (mole $^o/o$ BuA)	Temp. of Degdn. (^oC)	Time of Degdn. (hours)	$^o/o$MMA	$^o/o$BuOH	$^o/o$BuA	$^o/o$BuMA
50.0	313	2	21	11	8	6
	313	4	25	20	5	7
	313	6.5	20	31	7	5
	313	11.5	22	44	-	-
	313	15	26	47	-	-
	313	16	22	34	9	6
	313	24	22	33	9	6
82.2	313	3	1	25	1	1
	313	6	2	34	2	1
	313	13.5	1	48	-	-
	313	15.5	2	46	-	-
	313	18	2	45	2	1
	313	22	1	44	2	1
93.4	313	2	nil	22	trace	nil
	313	3	nil	28	trace	nil
	313	4	nil	32	trace	nil
	313	6	nil	53	trace	nil
	313	8	nil	77	trace	nil
	313	10	nil	71	trace	nil
	313	13.75	nil	72	trace	nil
	313	18	nil	64	trace	nil
	313	24	nil	64	trace	nil

Table 5.22(contd.)

Analysis of the Liquid Degradation Products.

Copolymer Composition (mole °/o BuA)	Temp. of Degdn. (°C)	Time of Degdn. (hours)	°/oMMA	°/oBuOH	°/oBuA	°/oBuMA
93.4	332	3	nil	57	trace	nil
	332	7	nil	58	trace	nil
	332	10.5	nil	72	trace	nil
	332	12.5	nil	70	trace	nil
	332	18.5	nil	79	trace	nil
	332	24	nil	77	trace	nil

3.9 mole percent n-butyl acrylate copolymer.

(b) Treatment of Results

As the percentages of methyl methacrylate, n-butyl acrylate and n-butyl methacrylate noted in table 5.22 do not change in a systematic fashion with degradation time, an average value for these quantities, V_a, was used. V_a represents the percentage by weight of a compound with respect to the weight of the total liquid products. Since the percentage of liquid products with respect to initial polymer weight, $^o/oL'$, is listed in tables 5.13-5.19, the percentage of a component with respect to initial polymer weight can be calculated throughout the degradation. It is most convenient here to express the concentration of product in terms of millimoles of product per gram of initial polymer, and table 5.23 lists the concentrations of methyl methacrylate, n-butyl acrylate and n-butyl methacrylate in these units. For any given copolymer the percentage of n-butanol in table 5.22 changes in a regular fashion as the degradation proceeds, and is plotted in Figs.5.24 and 5.25 for 50,82.2 and 93.4 mole percent n-butyl acrylate copolymers. Values from these curves taken every two hours were used to calculate the number of millimoles of n-butanol produced per gram of initial polymer as degradation

Table 5.23

Analysis of the Liquid Degradation Products.

(Data given in terms of millimoles of product per gram initial polymer)

3.9 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time (hours)	2	4	6	8	10	12	14	16	18
Methyl Methacrylate	4.21	6.62	8.23	9.21	9.60	9.70	9.70	9.70	9.70

Traces of n-butyl acrylate and n-butyl methacrylate.

16.3 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time (hours)	2	4	6	8	10	12	14	16	18
Methyl Methacrylate	2.74	4.66	5.69	6.23	6.42	6.56	6.63	6.64	6.64
n-Butyl Acrylate	.12	.20	.24	.27	.28	.28	.28	.28	.28
n-Butyl Methacrylate	.08	.14	.17	.18	.19	.19	.19	.19	.19

Table 5.23(contd.)

Analysis of the Liquid Degradation Products.

50.0 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20
Methyl Methacrylate	.41	.64	.81	.94	1.06	1.17	1.26	1.35	1.40	1.45
n-Butanol	.27	.77	1.40	2.11	2.73	3.01	3.10	3.21	3.20	3.14
n-Butyl Acrylate	.11	.17	.22	.25	.29	.32	.34	.37	.38	.39
n-Butyl Methacrylate	.08	.12	.15	.17	.19	.21	.23	.25	.26	.27

82.2 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22
Methyl Methacrylate	.02	.03	.05	.06	.07	.08	.09	.09	.10	.10	.11
n-Butanol	.29	.65	1.07	1.53	1.98	2.35	2.64	2.85	2.97	3.10	3.08
n-Butyl Acrylate	.01	.03	.04	.05	.05	.06	.07	.07	.08	.08	.08
n-Butyl Methacrylate	.01	.01	.02	.02	.02	.03	.03	.03	.04	.04	.04

Table 5.23(contd.)

Analysis of the Liquid Degradation Products.

93.4 Mole Percent n-Butyl Acrylate Copolymer at 313°C

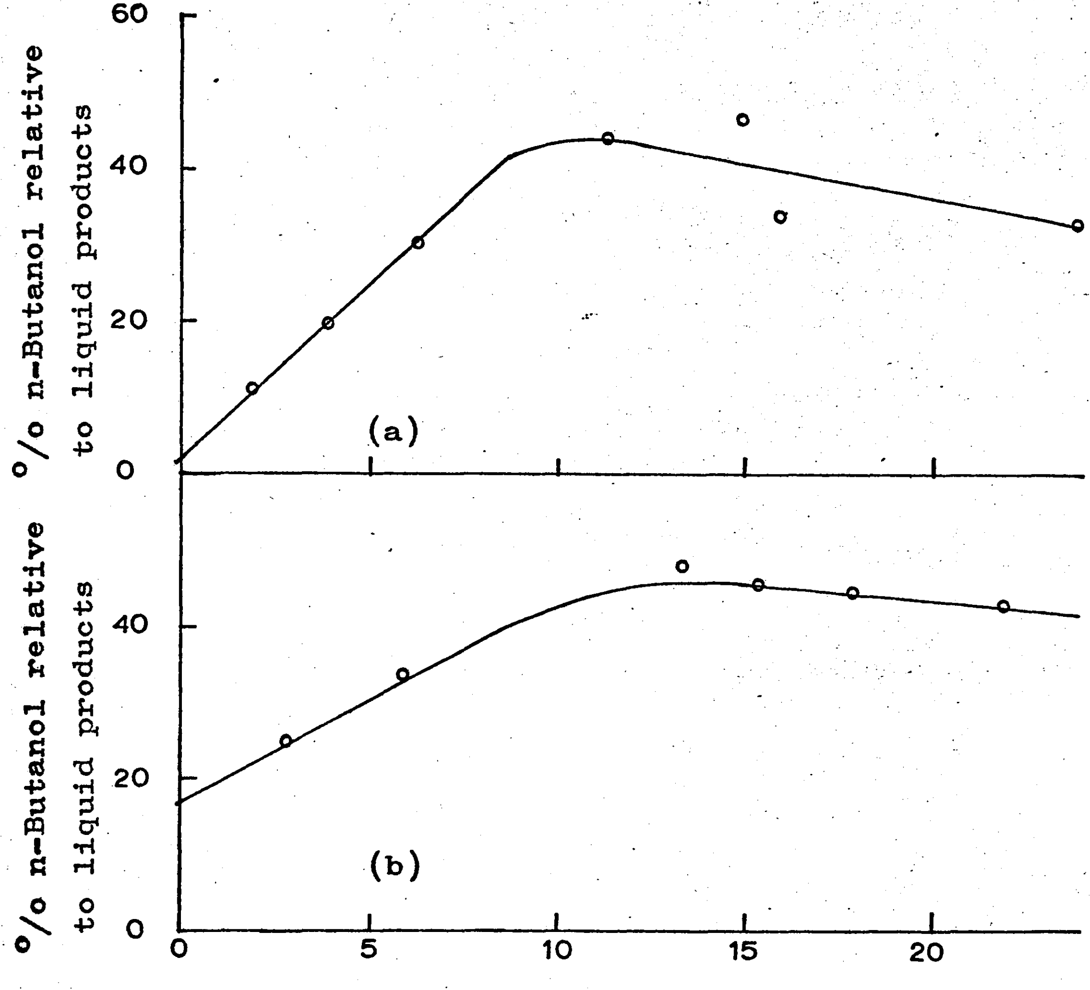
Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22	24
n-Butanol	.32	.82	1.68	2.70	3.24	3.53	3.70	3.79	3.87	3.87	3.81	3.75

Trace of n-Butyl Acrylate.

93.4 Mole Percent n-Butyl Acrylate Copolymer at 332°C

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22	24
n-Butanol	1.91	2.72	3.35	3.84	4.28	4.66	5.03	5.23	5.29	5.28	5.23	5.16

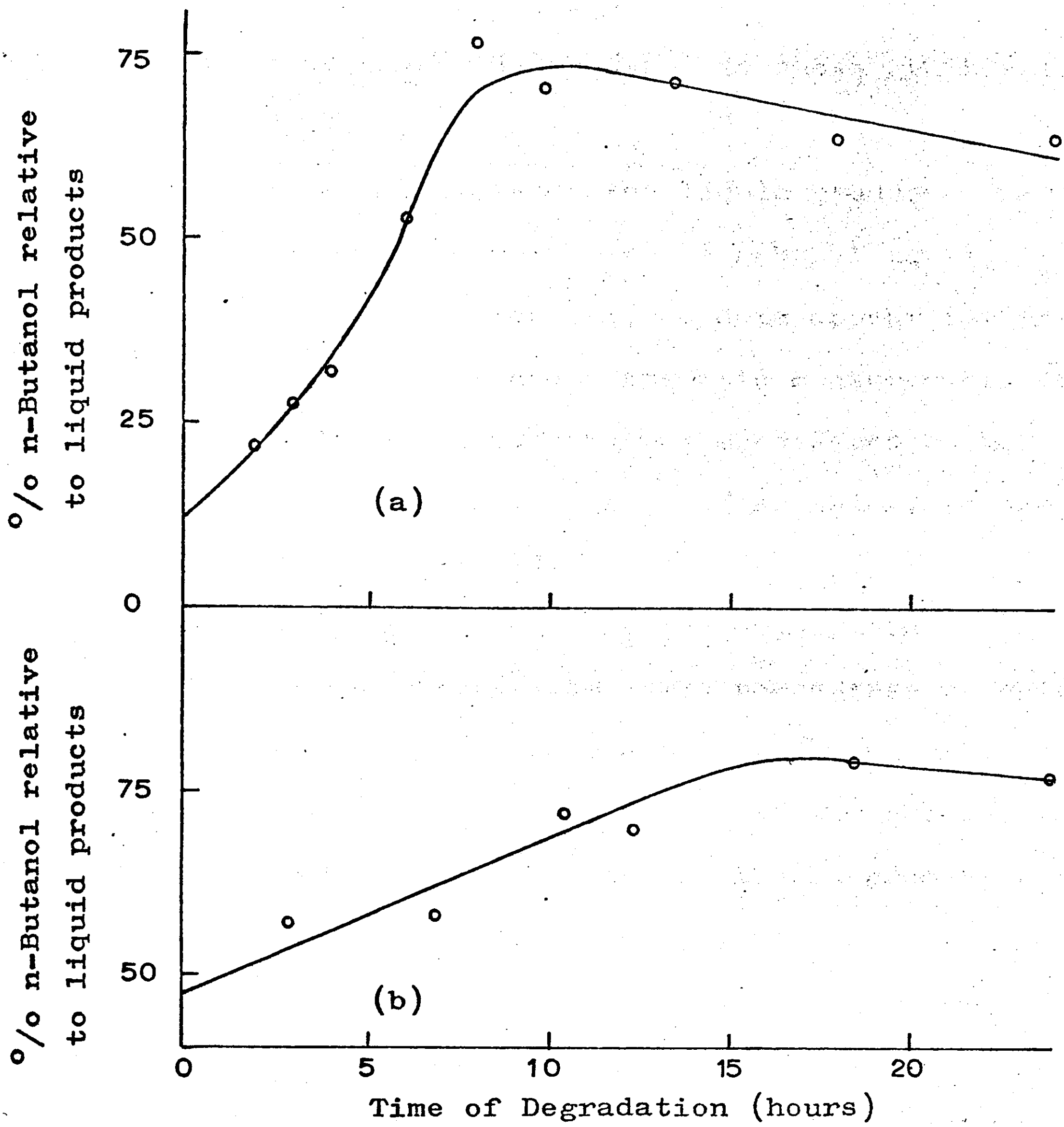
Trace of n-Butyl Acrylate.



(a) 50.0 mole °/o n-butyl acrylate copolymer.

(b) 82.2 mole °/o n-butyl acrylate copolymer.

Fig.5.24 n-Butanol production as a percentage of the total liquid products at 313°C.



(a) Degradation temperature 313°C.
(b) Degradation temperature 332°C.

Fig.5.25 n-Butanol production as a percentage of the total liquid products for a 93.4 mole percent n-butyl acrylate copolymer.

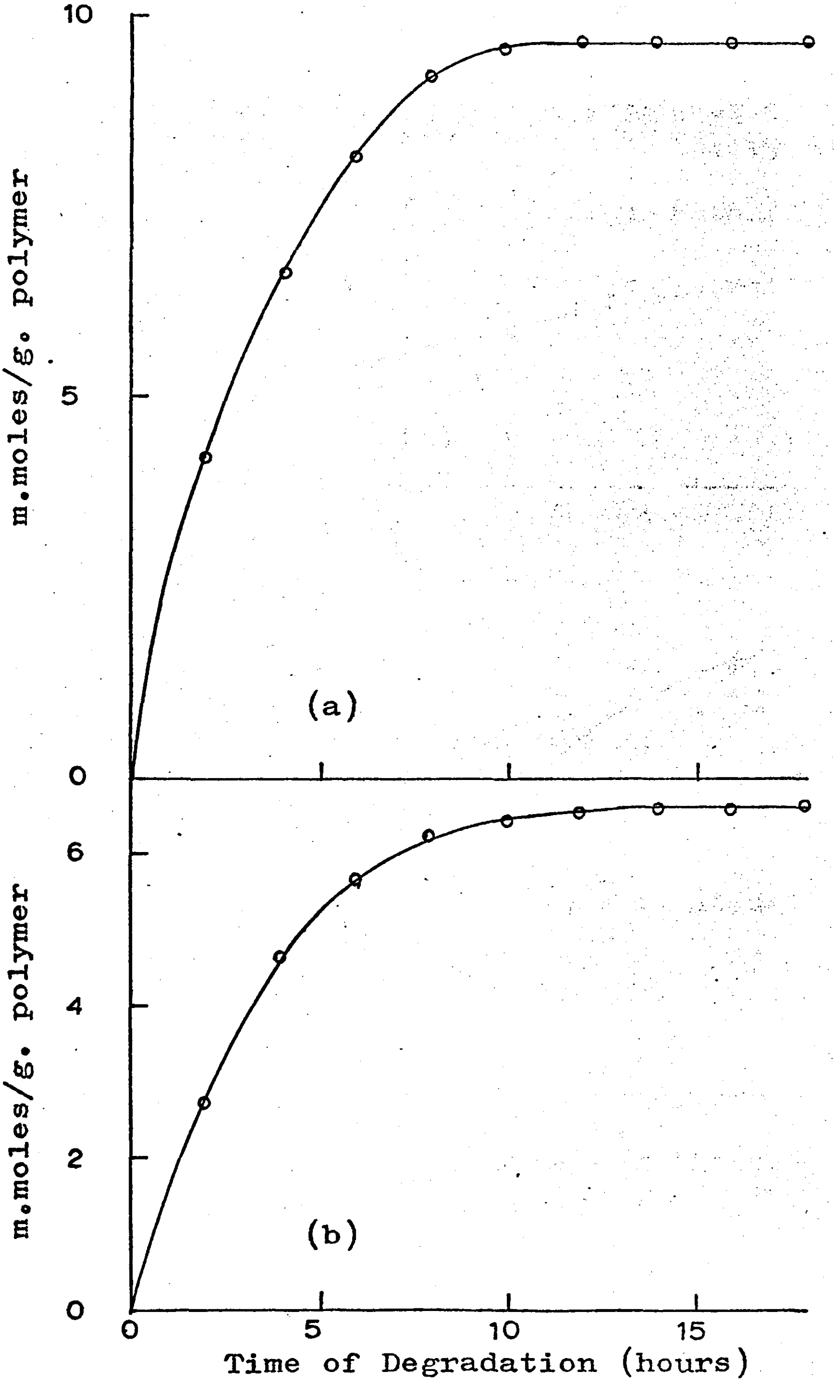
proceeds, which is listed in table 5.23. The production of methyl methacrylate and n-butanol is shown graphically in Figs.5.26-5.28.

Although the analysis of the liquid products from the degradation of a 0.4 mole percent n-butyl acrylate copolymer is given in table 5.22, no data appear for this copolymer in table 5.23 since systematic measurements of the production of volatiles were not considered to be necessary as they would add little, if anything, to the information already obtained.

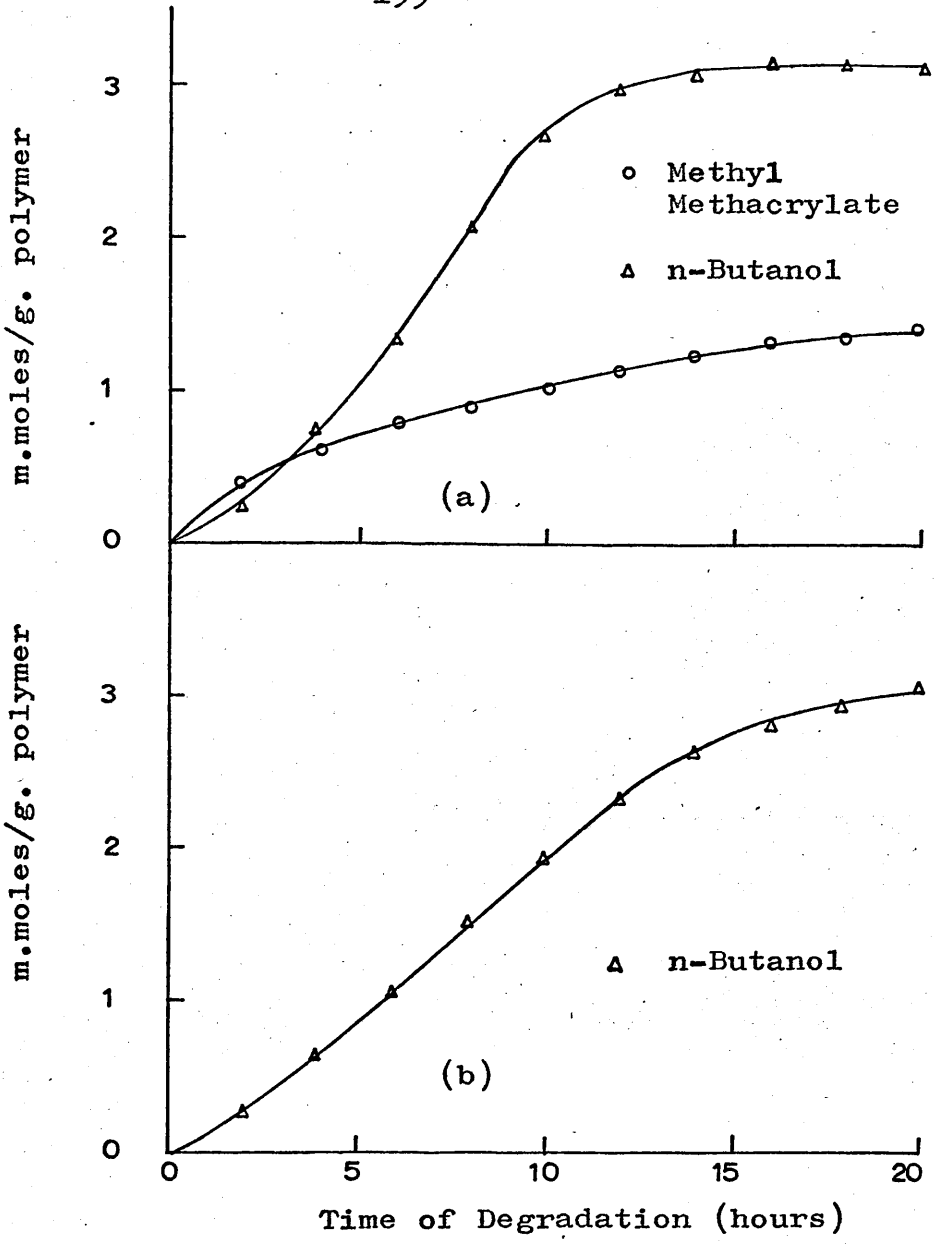
A detailed mass balance for the copolymers degraded is given in table 5.24. The percentage by weight of total chain fragments was obtained by adding the percentage of chain fragments, if any, to the percentage of short chain fragments found in the liquid products. This latter quantity was determined, as previously mentioned, by subtracting the sum of the percentages of alcohol, n-butyl acrylate, n-butyl methacrylate and methyl methacrylate from the total percentage of liquid volatiles, and since it was determined by difference and not directly, is subject to quite large errors.

(c) Discussion of Results

As expected the amount of methyl methacrylate found in the degradation products decreases while the amount of

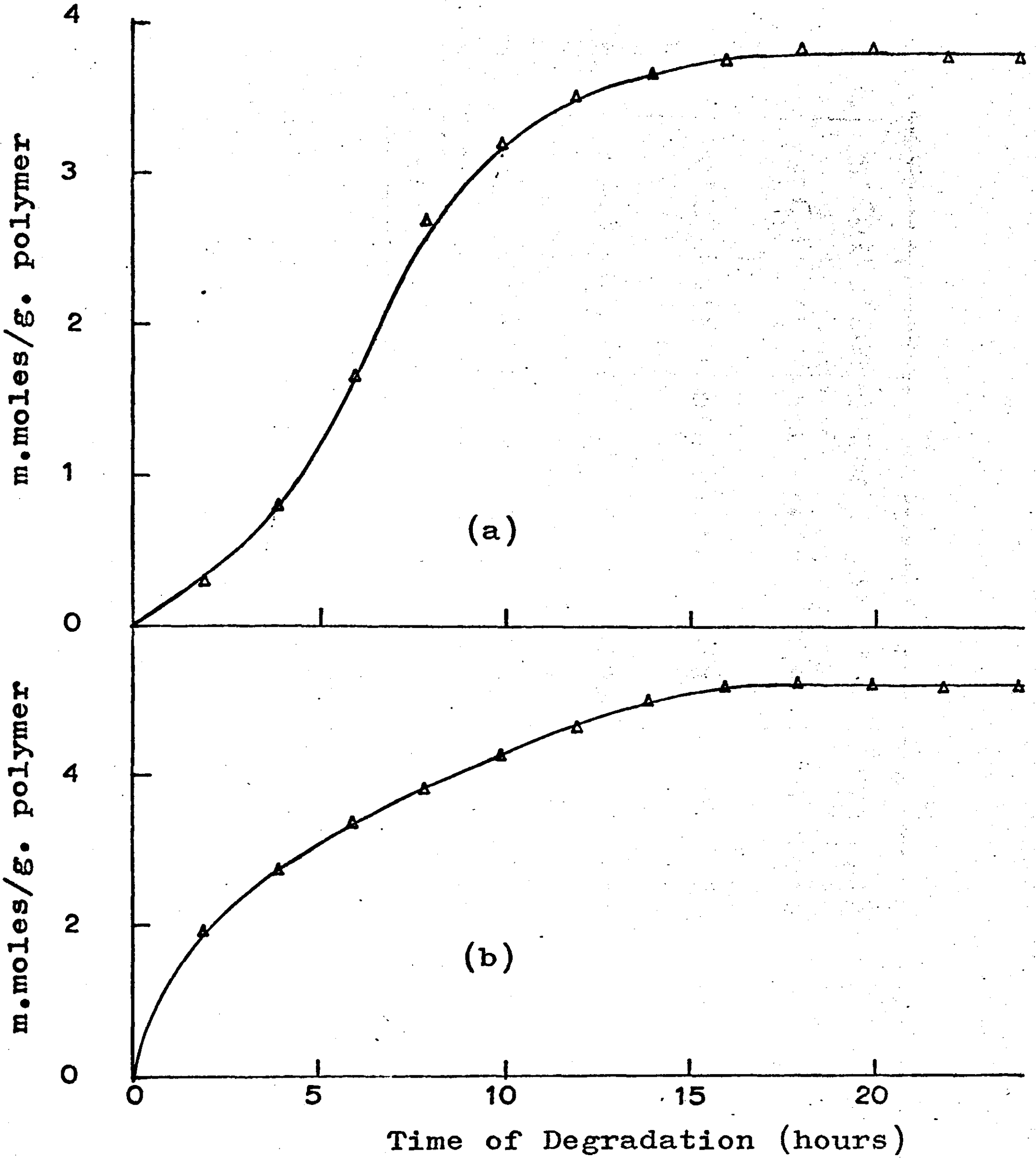


(a) 3.9 mole °/o n-butyl acrylate copolymer.
(b) 16.3 mole °/o n-butyl acrylate copolymer.
Fig.5.26 Plots of methyl methacrylate production at 313°C.



(a) 50.0 mole °/o n-butyl acrylate copolymer.
(b) 82.2 mole °/o n-butyl acrylate copolymer.

Fig.5.27 Plots of methyl methacrylate and n-butanol production at 313°C.



(a) Degradation temperature 313°C.

(b) Degradation temperature 332°C.

Fig.5.28 Plots of n-butanol production for a 93.4 mole °/o n-butyl acrylate copolymer.

Table 5.24

Mass Balance Data

(Data given in terms of percentage of the initial polymer weight.)

<u>3.9 Mole Percent n-Butyl Acrylate Copolymer at 313°C.</u>

Degradation Time (hours)	2	4	6	8	10	12	14	16	18
Carbon Dioxide	.4	.6	.8	.9	.9	.9	1.0	1.0	1.0
Methyl Methacrylate	42.1	66.2	82.3	92.1	96.0	97.0	97.0	97.0	97.0
Total Chain Fragments	.9	1.3	1.7	1.9	2.0	2.0	2.0	2.0	2.0
Residue	50.0	31.0	18.0	9.8	6.2	4.8	3.9	3.8	3.8
Total Products	93.4	99.1	102.8	104.7	105.1	104.7	103.9	103.8	103.8

Table 5.24(contd.)

16.3 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time(hours)	2	4	6	8	10	12	16	18	20
Carbon Dioxide	.8	1.2	1.5	1.7	1.9	2.0	2.2	2.3	2.3
But-1-ene	.2	.4	.5	.6	.6	.6	.6	.6	.6
Methyl Methacrylate	27.4	46.6	56.9	62.3	64.2	65.6	66.3	66.4	66.4
n-Butyl Acrylate	1.5	2.5	3.1	3.4	3.5	3.6	3.6	3.6	3.6
n-Butyl Methacrylate	1.1	2.0	2.3	2.6	2.6	2.7	2.7	2.7	2.7
Total Chain Fragments	7.5	12.8	15.6	17.1	17.7	17.9	18.2	18.3	18.3
Residue	69.5	43.4	24.5	14.3	10.0	7.2	5.3	5.0	5.0
Total Products	108.0	108.9	104.4	102.0	100.5	99.6	98.9	98.9	98.9

Table 5.24(contd.)

50.0 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20
Carbon Dioxide	1.1	2.1	3.0	3.7	4.2	4.6	5.0	5.3	5.5	5.5
But-1-ene	.9	1.6	2.1	2.5	2.6	2.6	2.6	2.6	2.6	2.6
Methyl Methacrylate	4.1	6.4	8.1	9.4	10.6	11.7	12.6	13.5	14.0	14.5
n-Butyl Acrylate	1.4	2.2	2.8	3.3	3.7	4.1	4.4	4.7	4.9	5.0
n-Butyl Methacrylate	1.1	1.7	2.1	2.4	2.8	3.0	3.3	3.5	3.7	3.8
n-Butanol	2.0	5.7	10.3	15.6	20.2	22.3	23.0	23.8	23.7	23.3
Total Chain Fragments	9.4	11.7	11.7	10.0	8.7	9.6	11.4	13.2	14.7	16.4
Residue	76.4	65.0	57.8	52.0	48.2	44.5	41.2	38.0	35.2	32.8
Total Products	96.4	96.4	97.9	98.9	101.0	102.4	103.5	104.6	104.3	103.9

Table 5.24(contd.)

82.2 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22
Carbon Dioxide	1.9	3.0	3.9	4.7	5.4	6.1	6.6	7.2	7.4	7.8	7.9
But-1-ene	1.6	2.4	2.9	3.3	3.6	3.3	4.0	4.1	4.4	4.4	4.5
Methyl Methacrylate	.2	.3	.5	.6	.7	.8	.9	.9	1.0	1.0	1.1
n-Butyl Acrylate	.2	.3	.5	.6	.7	.8	.9	.9	1.0	1.0	1.1
n-Butyl Methacrylate	.1	.2	.2	.3	.3	.4	.4	.5	.5	.5	.5
n-Butanol	2.1	4.8	8.0	11.3	14.6	17.4	19.6	21.1	22.0	22.6	22.8
Total Chain Fragments	6.7	11.6	14.9	17.0	18.5	19.9	21.4	23.3	25.2	27.2	28.8
Residue	80.0	70.5	63.0	57.4	52.0	46.8	42.5	38.5	35.3	33.0	30.9
Total Products	92.8	93.1	93.9	95.2	95.8	96.0	96.3	96.5	96.8	97.5	97.6

Table 5.24(contd.)

93.4 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22	24
Carbon Dioxide	1.9	3.3	4.6	5.6	6.5	7.4	8.1	8.7	9.2	9.6	9.9	10.2
But-1-ene	1.3	2.4	3.2	4.0	4.7	5.3	5.9	6.4	6.6	6.9	7.0	7.0
n-Butanol	2.4	6.1	12.4	20.0	24.0	26.1	27.4	28.1	28.6	28.6	28.2	27.8
Total Chain Fragments	9.0	12.8	13.1	10.0	10.7	11.9	13.7	15.4	17.1	18.6	20.1	21.3
Residue	89.5	81.2	74.0	67.4	61.5	55.0	50.0	45.7	42.3	39.6	37.6	35.7
Total Products	104.1	105.8	107.3	107.0	107.4	105.7	105.1	104.3	103.8	103.3	102.8	102.0

Table 5.24(contd.)

93.4 Mole Percent n-Butyl Acrylate Copolymer at 332°C.

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22	24
Carbon Dioxide	4.7	6.6	8.4	9.4	10.2	10.8	11.1	11.4	11.5	11.6	11.7	11.7
But-1-ene	4.4	6.1	7.0	7.9	8.4	8.7	9.1	9.4	9.7	9.8	9.9	10.0
n-Butanol	14.2	20.0	24.8	28.4	31.7	34.5	37.2	38.7	39.1	39.1	38.7	38.2
Total Chain Fragments	16.1	20.9	23.4	24.6	24.6	24.0	23.0	22.6	23.4	24.0	24.7	25.5
Residue	67.6	54.2	46.2	39.4	33.0	28.1	24.2	21.1	19.0	17.3	16.1	15.8
Total Products	107.0	108.0	109.8	109.7	107.9	106.1	104.6	103.2	102.7	101.8	101.1	101.2

alcohol increases with increasing acrylate content. n-Butanol is not produced until the acrylate content reaches 50 mole percent, table 5.22, that is until acrylate units are present in sequences. From the curves for the production of n-butanol at 313°C, Figs.5.27 and 5.28, it may be seen that the rate of alcohol evolution reaches a maximum after about seven hours degradation, which could imply that the formation of alcohol is autocatalytic in nature. Although Cameron and Kane [27] made no mention of a similar effect for methanol evolution in the degradation of poly(methyl acrylate), this kind of behaviour has been noted in other investigations of alcohol production from polyacrylates [29]. It has been suggested that this effect is a result of the increasing rigidity of the polymer molecule as degradation proceeds[29]. If this is correct, then as the temperature of degradation is raised, it would be reasonable to suppose that the occurrence of such a rate maximum would be less pronounced. At 332°C, Fig.5.28 shows that, for the degradation of a 93.4 mole percent n-butyl acrylate copolymer, no rate maximum is evident. This will be discussed more fully in a later chapter.

In table 5.25 the concentrations of n-butyl acrylate and n-butyl methacrylate at infinite degradation time are listed, the data applying to a pyrolysis temperature of 313°C.

Table 5.25

Copolymer Composition (mole °/o n-butyl acrylate)	n-Butyl Acrylate (m.moles per g. polymer)	n-Butyl Methacrylate (m.moles per g. polymer)
3.9	trace	trace
16.3	0.28	0.19
50.0	0.39	0.27
82.2	0.08	0.04
93.4	trace	nil

At first sight it appears anomalous that while a 50.0 mole percent n-butyl acrylate copolymer produces on degradation 0.39 m.moles/g. polymer of n-butyl acrylate monomer, a copolymer containing 93.4 mole percent acrylate only evolves trace amounts of this compound. This kind of effect, however, has also been reported by McCormick[58] who found that the amount of ethyl acrylate evolved from a 25 mole percent ethyl acrylate - methyl methacrylate copolymer was more than twice that evolved by the acrylate homopolymer, although the copolymer contained only one quarter the amount of acrylate. One explanation is that the acrylate monomer is produced in a depolymerization reaction initiated at methacrylate chain units, capable of unzipping through some of the acrylate units, before termination occurs. In the acrylate homopolymer no methacrylate units are available to initiate such depolymerizations, and since acrylate radicals prefer to take part in transfer reactions rather than to depolymerize, very little monomer is produced.

n-Butyl methacrylate is obtained in highest yield from the 50.0 mole percent n-butyl acrylate copolymer, which is consistent with the idea that its production depends upon the number of acrylate - methacrylate linkages in the chain.

With increasing acrylate content the percentage of chain fragments increases reflecting the increasing number of transfer reactions taking place during breakdown. The stability of the copolymers is shown by the greater percentage of residue found for any given time of degradation the greater the percentage of n-butyl acrylate in the original copolymer.

Use of a higher degradation temperature favours the production of gases, liquids and chain fragments at the expense of the residue.

CHAPTER 6

INVESTIGATION OF THE RESIDUE AND CHAIN FRAGMENTS

6.1 Introduction

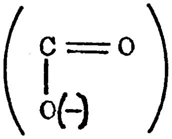
In the last chapter a thorough examination of the gaseous and liquid degradation products was made. It is now appropriate to investigate the other products of decomposition, namely the residue and chain fragments.

6.2 Investigation of the Residue

(a) Spectroscopic Techniques

(a.1) Infra-red

For copolymers of high methacrylate content the entire residue was found to be soluble in carbon tetrachloride, so that spectra of both the degraded and undegraded material could be run in solution. As the acrylate content of the copolymer is increased, the residue becomes increasingly insoluble in organic solvents so that some other technique must be used to obtain spectra. Grinding the residue with potassium bromide and pressing the mixture to form discs was not very successful because of the difficulties of grinding a rubbery material. The best method found for such copolymers consisted of applying a solution of the undegraded polymer in toluene to two salt plates and removing the solvent in a vacuum oven at 80°C. The plates were then placed together, the polymer film being sandwiched between them, and the whole assembly degraded in a sealed tube. Fig.6.1 shows a typical spectrum of an undegraded copolymer together with a spectrum of the same material after degradation between salt plates at 313°C. These differ in that the spectrum of the pyrolyzed copolymer has a shoulder at 1760cm.$^{-1}$ on the carbonyl peak, and a new peak at 1560cm.$^{-1}$, while the other absorptions have broadened. Only degradations carried out on salt plates showed the new absorption. The shoulder at 1760cm.$^{-1}$ becomes better defined when both the acrylate content of the starting material and the time of degradation are increased. In addition to these absorptions, the 93.4 mole percent n-butyl acrylate copolymer exhibits a small peak at 1605cm.$^{-1}$, which has also been reported for the degradation of pure poly(n-butyl acrylate) [29].

Dealing firstly with the absorption at 1560cm.$^{-1}$, the possibilities are strictly limited, the only likely assignment being that of a carboxylate ion  $\left(\begin{array}{l}\mathrm{C{=}O}\\ |\\ \mathrm{O}^{(-)}\end{array}\right)$. The most reasonable explanation is that ester decomposition reactions, Fig.1.3, leave carboxylic acid residues pendant to the main chain. Under the experimental conditions these may react with the salt plates to form the appropriate sodium salt. If this explanation is correct, a polymer

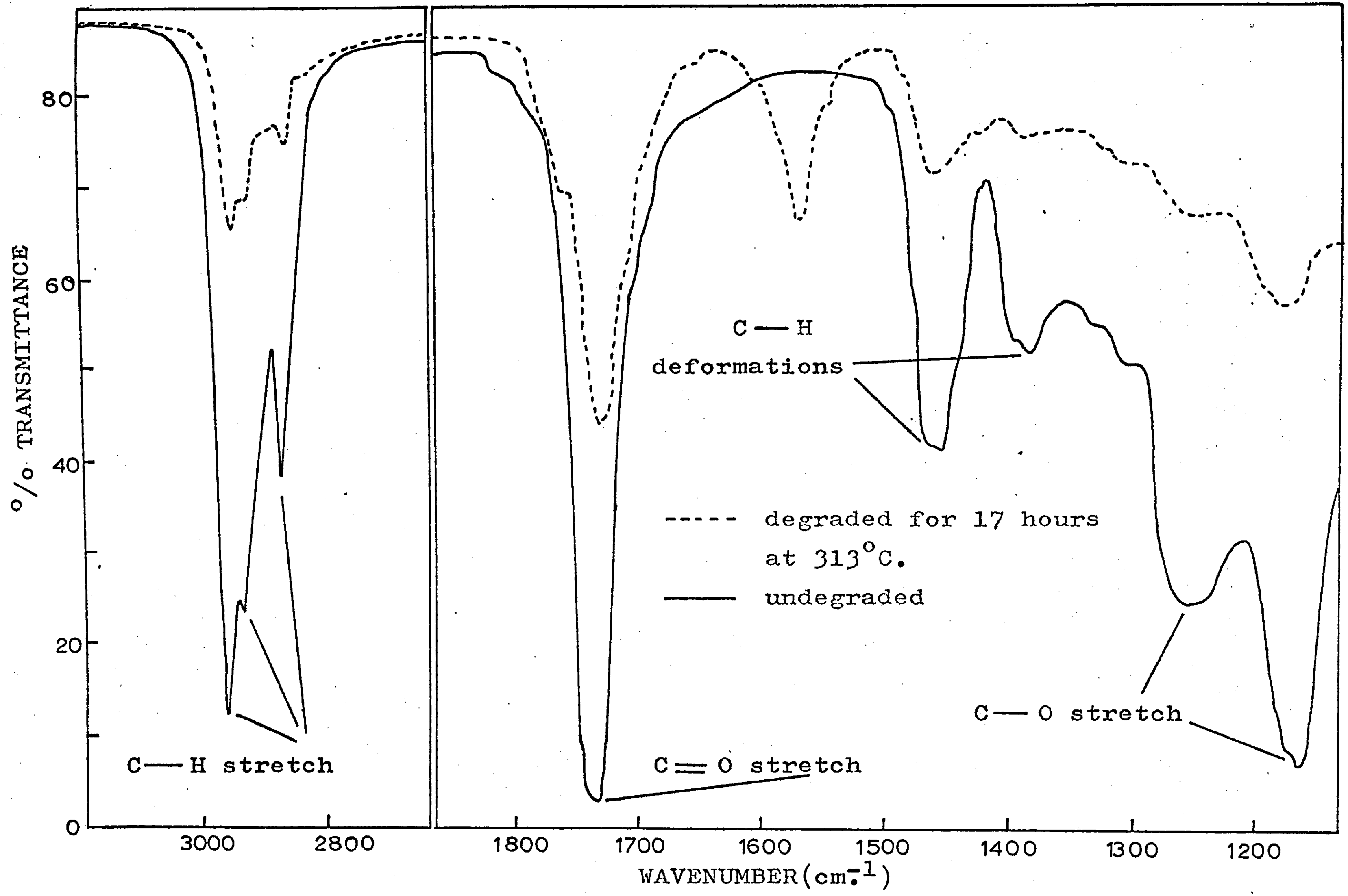


Fig.6.1 Infra-red spectra of an 82.2 mole °/o n-butyl acrylate copolymer.

such as poly(methacrylic acid) should, under similar conditions of degradation, show a similar absorption at 1560cm.$^{-1}$ Because of the insolubility of this polymer in solvents suitable for coating on salt plates it was ground up with sodium chloride and degraded in a sealed tube at 313°C for seven hours. A sample of pure poly(methacrylic acid) was similarly degraded under identical conditions as a control. The sample heated with sodium chloride had an absorption at 1560cm.$^{-1}$, while the control sample had not. Neither does undegraded poly(methacrylic acid) absorb in this region. To check that copolymers of high acrylate content showed this absorption when degraded as a mixture with sodium chloride, a sample of the 82.2 mole percent n-butyl acrylate copolymer was degraded in this way, the new absorption appearing as expected. These experiments confirm the general nature of this absorption.

The shoulder on the carbonyl peak at 1760cm.$^{-1}$ may be ascribed to a γ lactone, an $\alpha\beta$ unsaturated γ lactone, or a $\beta\gamma$ unsaturated δ lactone. It has been postulated that anhydride groups may be formed in the residue. These functional groups have a doublet absorption at about 1800cm.$^{-1}$ and 1760cm.$^{-1}$ No peak at 1800cm.$^{-1}$ was observed in the decomposition of the copolymers, but it should be pointed out that the reaction of the acid residue with the salt plates may take place in preference to anhydride formation so that production of anhydride units cannot definitely be ruled out by this result. Recently, however, an RM-100 Rotomill (Research and Industrial Instr. Co.) has become available, and can be used to prepare acceptable potassium bromide discs from the residue resulting from decomposition of copolymers of high acrylate content. An examination of the 82.2 mole percent n-butyl acrylate copolymer by this technique showed no absorption at 1800cm.$^{-1}$ so that production of anhydride in the residue can be dismissed.

The absorption at 1605cm.$^{-1}$ can be attributed to conjugated carbon-carbon double bonds.

(a.2) U.V.-Visible

As degradation proceeds the colour of the residual polymer goes through yellow to brown and for similar extents of decomposition the copolymers of greater acrylate content exhibit more pronounced coloration. U.V.-Visible spectra were run of polymeric films deposited on the base of a silica flange, a procedure which was found to be necessary since suitable solvents for the copolymers did not have sufficient transmittance in the U.V. The copolymers examined were the 3.9 mole percent and 82.2

mole percent n-butyl acrylate copolymers. 2ml. of a 50mg./ml. solution of the sample in toluene was pipetted on to the flat base of a silica flange and the solvent removed in a vacuum oven at 80°C. The samples were degraded at 313°C using the glass still, (2.2b), spectra being run by placing the whole flange in the beam of the spectrometer. Scans were run from 880mμ to 200mμ, the undegraded copolymers showing an absorption maximum at about 227mμ corresponding to absorption by the ester group. As the 82.2 mole percent copolymer was degraded there was a general increase in absorption in the region from 420mμ down to 227mμ, while in the case of the 3.9 mole percent copolymer, increasing absorption in this region did not become important till long degradation times, and was still much less than that exhibited by the material richer in acrylate. This new absorption, Fig.6.2, has no characteristic maximum, and may be attributed to the presence of varying lengths of ethylenic unsaturation, the maximum length of such conjugation being about eight double bonds which corresponds to a μ_{max} of 415mμ.

(a.3) N.M.R.

The soluble residue from breakdown of the 50.0 mole percent n-butyl acrylate copolymer at 313°C was examined by N.M.R. A spectrum of degraded material is

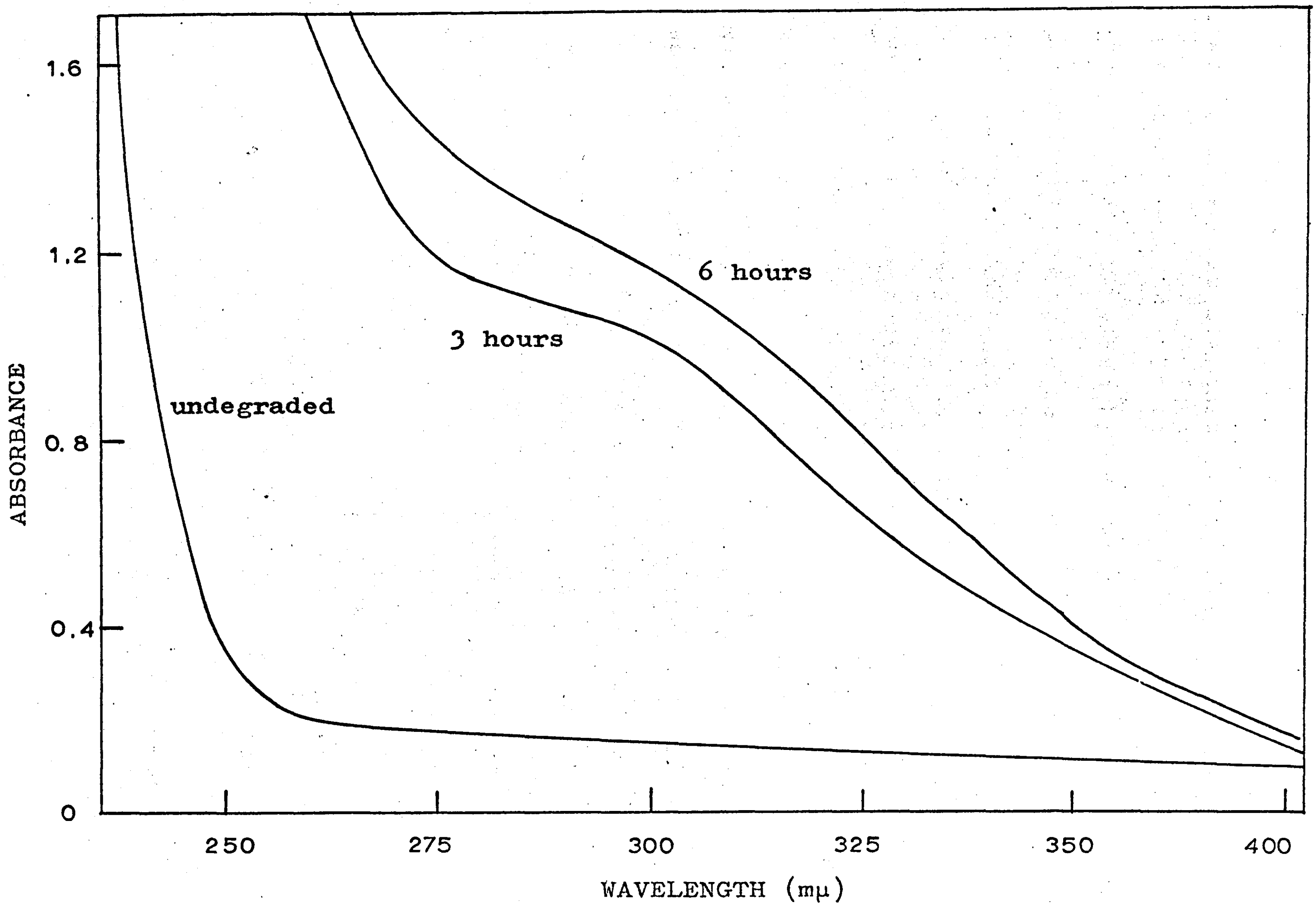


Fig.6.2 U.V. spectra of an 82.2 mole °/o n-butyl acrylate copolymer degraded for the times shown.

shown in Fig.6.3 run in carbon tetrachloride with tetramethyl silane as standard. No new absorptions appeared on decomposition, and the ratio of the two kinds of ester group present as given by the ratio of $-OCH_2-$ to $-OCH_3$ protons also remained constant.

(b) Elemental Analysis

Micro analysis was carried out on the residue obtained by the degradation of a 50.0 mole percent n-butyl acrylate copolymer at 332°C. Because of the tendency of the residue to adhere to the walls of the glass pyrolysis tube, it was quite difficult to obtain a sample for combustion. Table 6.1 lists the relative weights of carbon, hydrogen and oxygen in the sample, the oxygen figure being found by difference.

Table 6.1

Time of Degradation (hours)	°/oC	°/oH	°/oO
0 (calculated data)	63.13	8.83	28.04
14.5	78.98	6.73	14.29
24.0	77.80	6.53	15.63

These results show that on degradation the carbon content rises while the hydrogen and oxygen content falls. A similar result has been reported for decomposition of the homopolymer, poly(n-butyl acrylate) [29]. The complexity of the degradation of the copolymers as

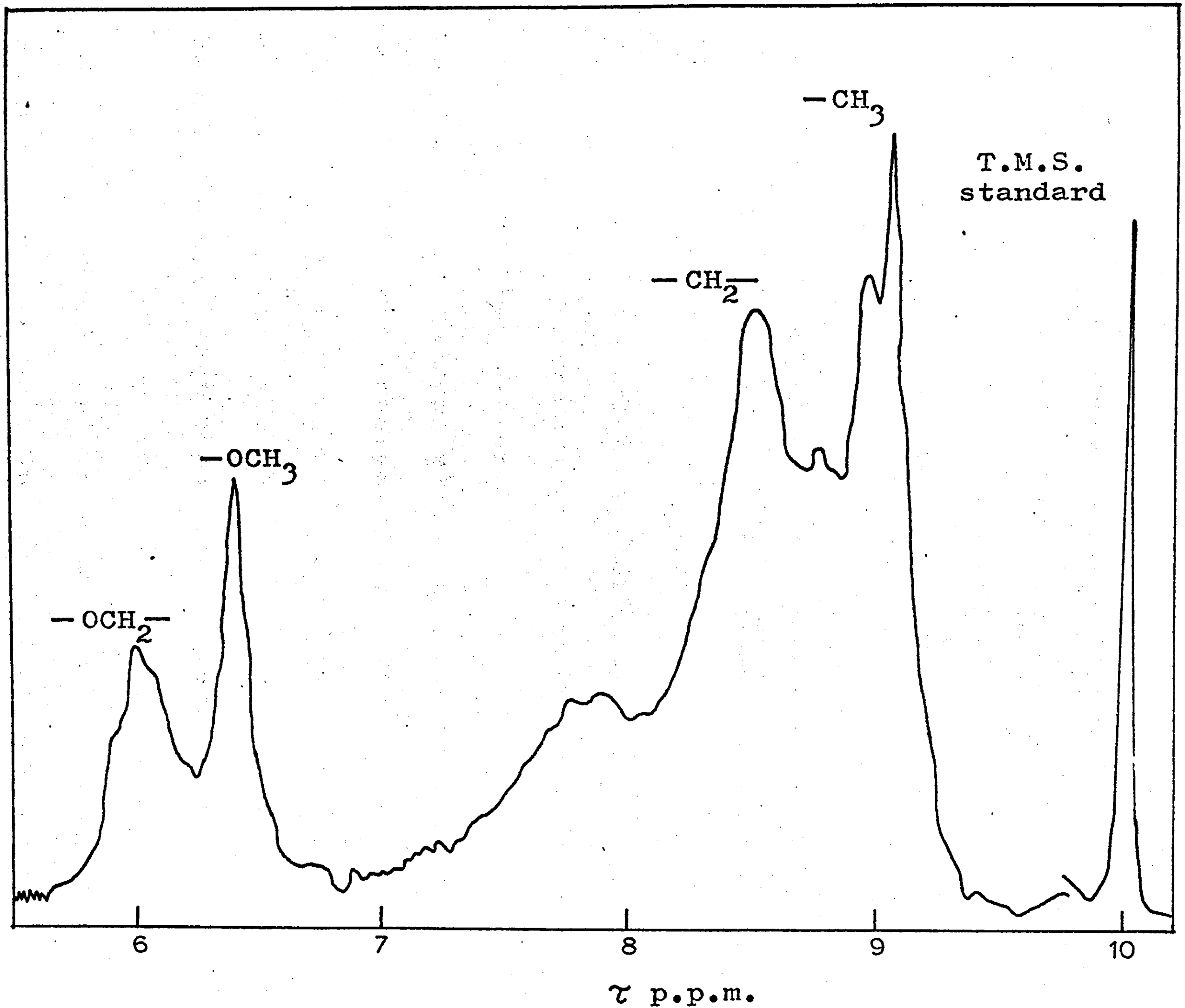


Fig.6.3 N.M.R. of a 50.0 mole °/o n-butyl acrylate copolymer degraded at 313°C for 16 hours.(Run in carbon tetrachloride solution.)

reflected by the variety of products obtained makes interpretation of data such as this extremely difficult, so that extensive examination of copolymer residues by this technique was not undertaken.

(c) Molecular Weight Measurements

The molecular weight changes which occur on degradation at 313°C of the 0.4 mole percent and 50.0 mole percent n-butyl acrylate copolymers are plotted in Fig.6.4. On this type of plot polymers breaking down by depolymerization processes give curves lying above the diagonal AC while those degrading by random scission lie along ABC [6]. The behaviour of the 0.4 mole percent copolymer is much nearer to that displayed by pure poly(methyl methacrylate) than is the behaviour of the 50.0 mole percent copolymer. This is to be expected, but it is interesting to note the disproportionate effect of a small amount of acrylate. A similar type of result has been found for other copolymer systems. In an earlier section, 3.3, copolymers with acrylate contents of up to 50.0 mole percent were treated from a thermogravimetric point of view as degrading by a first order type of process whereas Fig.6.4 would seem to indicate that even with as little as 0.4 mole percent n-butyl acrylate, the copolymers should be treated as randomly degrading

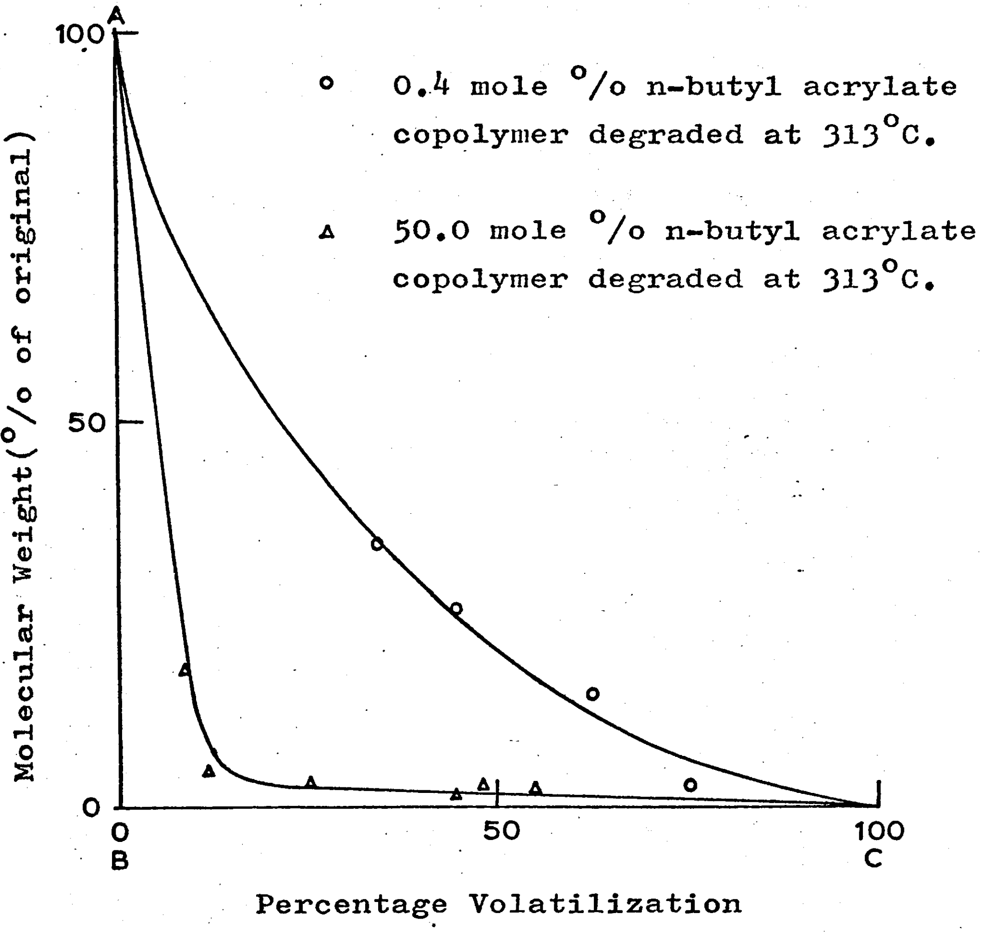


Fig.6.4 Molecular weight versus percentage volatilization plots.

entities. The reason for this apparent contradiction is that a few scissions occurring at random in a polymer molecule will make a great difference to the molecular weight of the sample, but will not lead to any weight loss, unless some scissions occur close together. If a copolymer can degrade both by random scission and by depropagation simultaneously, it is clear that molecular weight measurements will be more sensitive to the random reaction, while weight loss methods will tend to follow the depropagation reaction. It is therefore the relative sensitivity of these two differing methods of following thermal breakdown which leads to an apparently anomalous situation.

(d) Sol-Gel Analysis

(d.1) Introduction

The Soxhlet extraction technique (2.10) was used to investigate the relative amounts of soluble and insoluble material in the polymeric residues. This method ensures a constant supply of fresh solvent with which to perform efficient extraction. Benzene was used since it is desirable to use a fairly low boiling solvent in order to prevent further decomposition of the polymer during extraction. This investigation was extended to include measurements on homopolymers of n-butyl acrylate.

The polymers examined and the degradation conditions employed are listed in table 6.2.

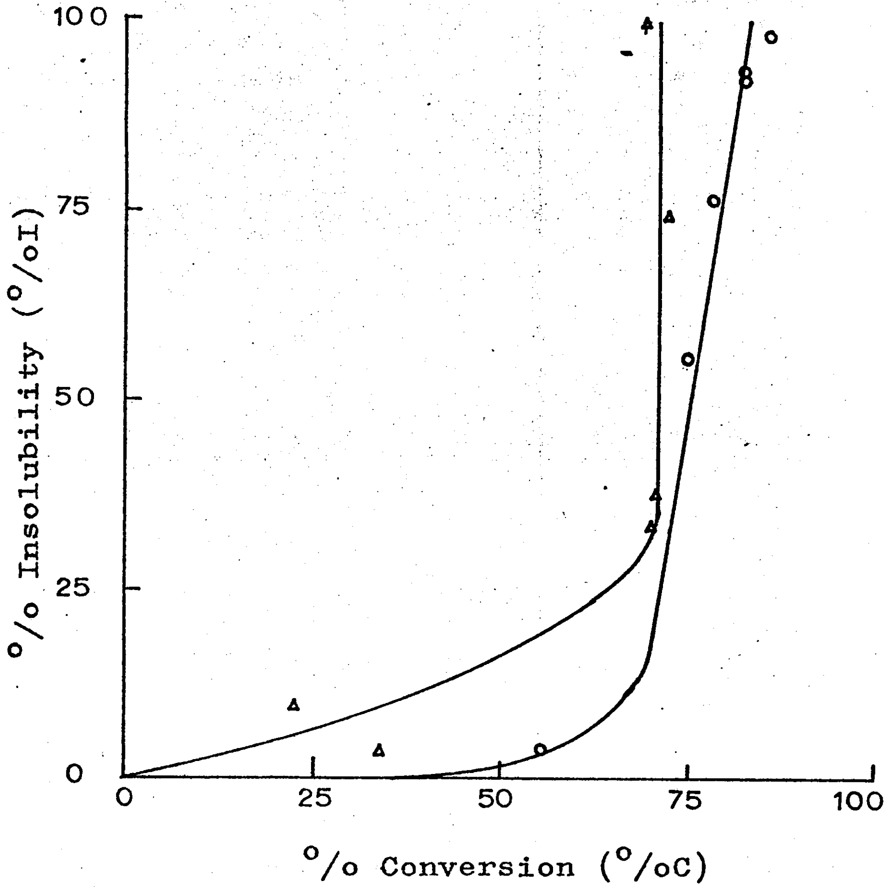
Table 6.2

Polymer Composition (mole $^{o}/o$ n-butyl acrylate)	Molecular Weight, $\overline{M}_n$	Temperature of Degradation, ^{o}C
100	870,000[81]	313 and 329
93.4	76,500	329
93.4	3,160,000[82]	329
52.4	1,330,000	313

As detailed in section 2.10, for each run the weight of gel, $(\Delta Q+\Delta S)$, weight of sol, $(\Delta P-\Delta S)$, and total weight of residue, $(\Delta P+\Delta Q)$, were determined. Knowing in addition the initial weight of polymer degraded, W, the percentage insolubility, $^{o}/oI = [(\Delta Q+\Delta S)/(\Delta P+\Delta Q)] \times 100$, and percentage conversion, $^{o}/oC = [1 - (\Delta P+\Delta Q)/W] \times 100$, were found. The effect of composition, Fig.6.5, molecular weight, Fig.6.6, and temperature of degradation, Fig.6.7, are shown by appropriate plots of $^{o}/oI$ versus $^{o}/oC$ in the figures mentioned, using the values listed in tables 6.3-6.6.

(d.2) Discussion of Results

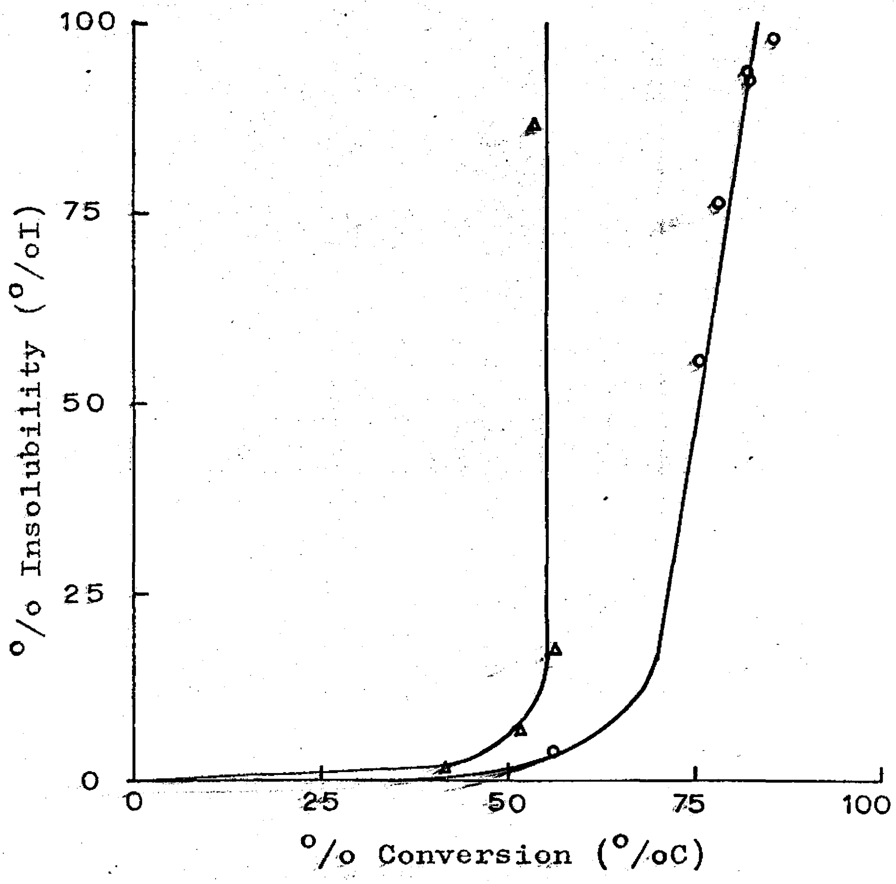
Solubility depends upon the flexibility of the polymer chain and on its ability to adopt any orientation with respect to solvent molecules. Factors



▲ n-butyl acrylate homopolymer, $\overline{M}_n$ 870,000.

○ 93.4 mole °/o n-butyl acrylate copolymer, $\overline{M}_n$ 76,500.

Fig.6.5 Effect of composition on gel formation at 329°C.



▲ 93.4 mole °/o n-butyl acrylate copolymer $\overline{M}_n$ 3,160,000.

o 93.4 mole °/o n-butyl acrylate copolymer $\overline{M}_n$ 76,500.

Fig.6.6 Effect of molecular weight on gel formation at 329°C.

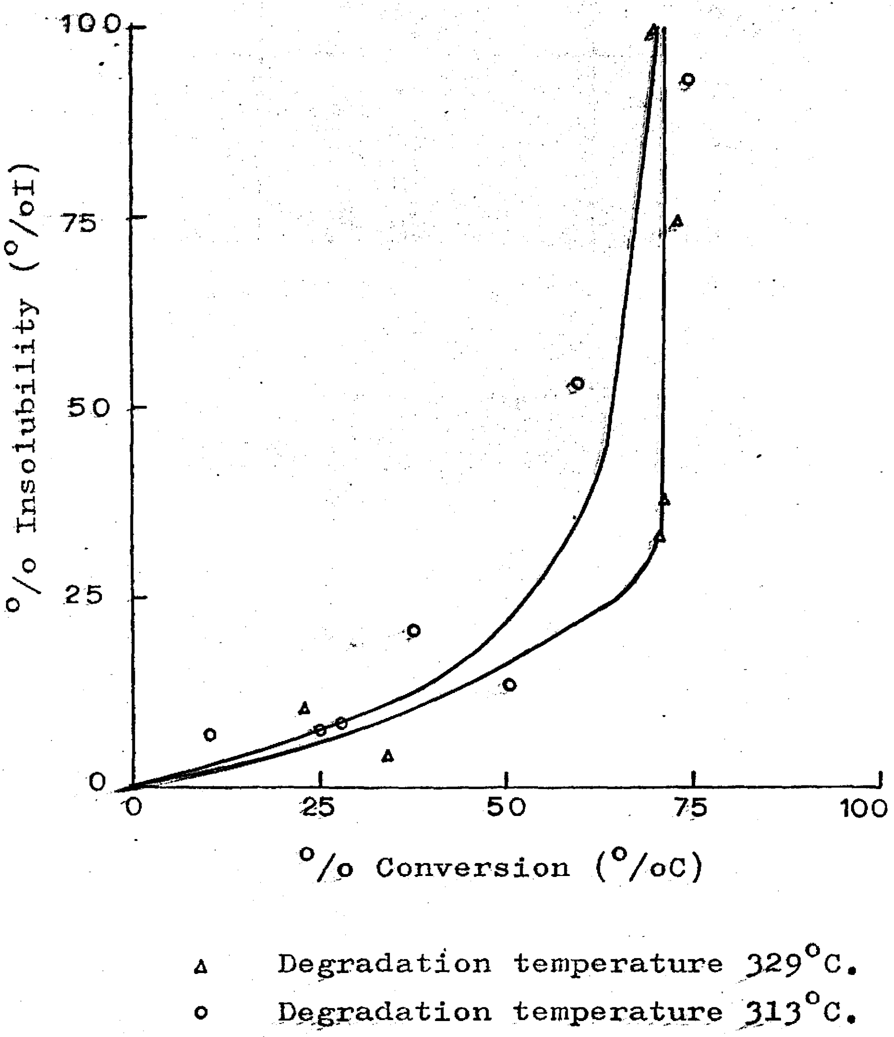


Fig.6.7 Effect of temperature of degradation on gel formation in poly(n-butyl acrylate) $\overline{M}_n$ 870,000.

Table 6.3

Sol-gel Analysis Data for Poly(n-butyl acrylate)

$\bar{M}_n$ 870,000 Degraded at 313°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
1	10	7
2	25	8
4	28	8
10	38	20
16	51	14
20	60	53
24	75	94

Table 6.4

Sol-gel Analysis Data for Poly(n-butyl acrylate)

$\bar{M}_n$ 870,000 Degraded at 329°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
2	23	11
5	34	4
10	71	38
19	72	75
24	69	100

Table 6.5

Sol-gel Analysis Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer, $\overline{M}_n$ 76,500, Degraded at 329°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
4	56	4
10	76	56
21	82	94
24	86	98

Table 6.6

Sol-gel Analysis Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer, $\overline{M}_n$ 3,160,000, Degraded at 329°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
1	43	2
8	52	7
12	57	18
24	55	87

Table 6.7

Sol-gel Analysis Data for a 52.4 Mole °/o n-Butyl Acrylate Copolymer, $\overline{M}_n$ 1,330,000, Degraded at 313°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
4	34	.4
6	38	.3
17	27	.6

which tend to reduce the possibility of attaining such orientations will therefore tend to reduce solubility. The development of insolubility in a polymer as degradation proceeds can be associated with cross linking reactions or the formation of rigid structures by intramolecular processes. The occurrence in the n-butyl acrylate - methyl methacrylate copolymer system of such cross links or rigid structures due to inter- and intramolecular anhydride formation respectively may be discounted as there is no evidence for the existence of such functional groups in the residue, so that it seems likely that insolubility is caused by cross linking of n-butyl acrylate units through their tertiary carbon atoms as in Fig.1.8a, a contribution also being made by the formation of ring systems such as that shown in Fig.1.7 which increase the rigidity of the polymer chain.

(d.2.1) The Effect of Polymer Composition on Gel Formation

Fig.6.5 shows that for a fixed degree of conversion the amount of gel formation in the acrylate homopolymer is always greater than that in the copolymer containing 93.4 mole percent acrylate, when both are degraded at 329°C. Comparison of the data given in tables 6.3 and 6.7 for degradations carried out at 313°C confirm the observation that increasing the acrylate content of the system increases gelation at any given conversion. These results reflect the different modes of breakdown of acrylates and methacrylates.

(d.2.2) The Effect of Molecular Weight on Gel Formation

From the introductory discussion it would appear that gel formation should be a function of both cross link density and the length of the chains being cross linked. Fig.6.6 shows the effect of molecular weight on the formation of gel for 93.4 mole percent n-butyl acrylate copolymers. As predicted, for a given degree of conversion the higher molecular weight material contains a greater proportion of insoluble residue than does the lower molecular weight sample.

(d.2.3) The Effect of Degradation Temperature on Gel Formation

In the case of poly(n-butyl acrylate) degraded at 313°C and at 329°C Fig.6.7 shows that there is greater insolubility at the lower temperature of decomposition than at the higher when the same degree of conversion is considered. This result reflects the effect of temperature on the competing processes of depolymerization, random scission, and cross linking.

(e) Degradation at a Lower Temperature

(e.1) Introduction

An investigation of the relationship between chain scission and carbon dioxide production in the methyl acrylate - methyl methacrylate copolymer system established that there is a one to one correspondence between these processes [36]. It was thus considered to be of interest to investigate what relationship, if any, these reactions bear to one another in the n-butyl acrylate - methyl methacrylate system. In order to study this aspect of the degradation reaction, a lower pyrolysis temperature was chosen than those previously used so that this relationship might be investigated unaccompanied by large scale volatilization reactions.

(e.2) Carbon Dioxide Production and Chain Scission

(e.2.1) Experimental

It has been shown [6] that the number of chain scissions, N, which have occurred per molecule of copolymer is given by,

$$N = (M_o / M_t - 1)$$

in which M_o and M_t are the initial molecular weight and the molecular weight after degradation for time t respectively. This equation only applies strictly if there is neither cross linking nor loss of polymer molecules from the system. Consequently degradation conditions were chosen such that a large fall in molecular weight could be observed without accompanying detectable weight loss.

All degradations were carried out in the glass still at 237°C, (2.2b). The sample size used was approximately 130mg., the polymer being degraded as a film cast on the base of a flange from toluene solution. Measurements of the pressure of carbon dioxide evolved were made using a McLeod gauge,(2.3b), and the number of moles of this gas produced calculated as previously described, (2.3b). After degradation the residue was dissolved in toluene, its molecular weight found as in (2.4), and the number of chain scissions per molecule of original polymer, N, calculated. Knowing the exact weight of sample used and the molecular weight of the undegraded copolymer, the number of moles of carbon dioxide evolved per mole of initial sample may be found.

(e.2.2) Discussion of Results

The results of these measurements are given in table 6.8. The plot of carbon dioxide evolved per molecule versus the number of chain scissions per molecule is given, for a 52.4 mole percent n-butyl acrylate copolymer, in Fig.6.8 which shows that the amount of this

Table 6.8

Data for the Degradation of a 52.4 Mole Percent n-Butyl Acrylate Copolymer at 237°C.

Time of Degradation (hours)	Molecular Weight, M_t	No. of Chain Scissions, N, per Molecule of Polymer	Moles CO_2 per Mole Polymer	Molecules of CO_2 per Chain Scission
0	1,330,000	0	0	0
1	342,000	2.89	1.74	0.60
2	236,000	4.64	3.66	0.79
3	186,000	6.15	4.23	0.69
4	170,000	6.83	6.28	0.92
6	145,000	8.17	8.76	1.07
7	127,000	9.47	10.62	1.12

Sample size 0.133g.

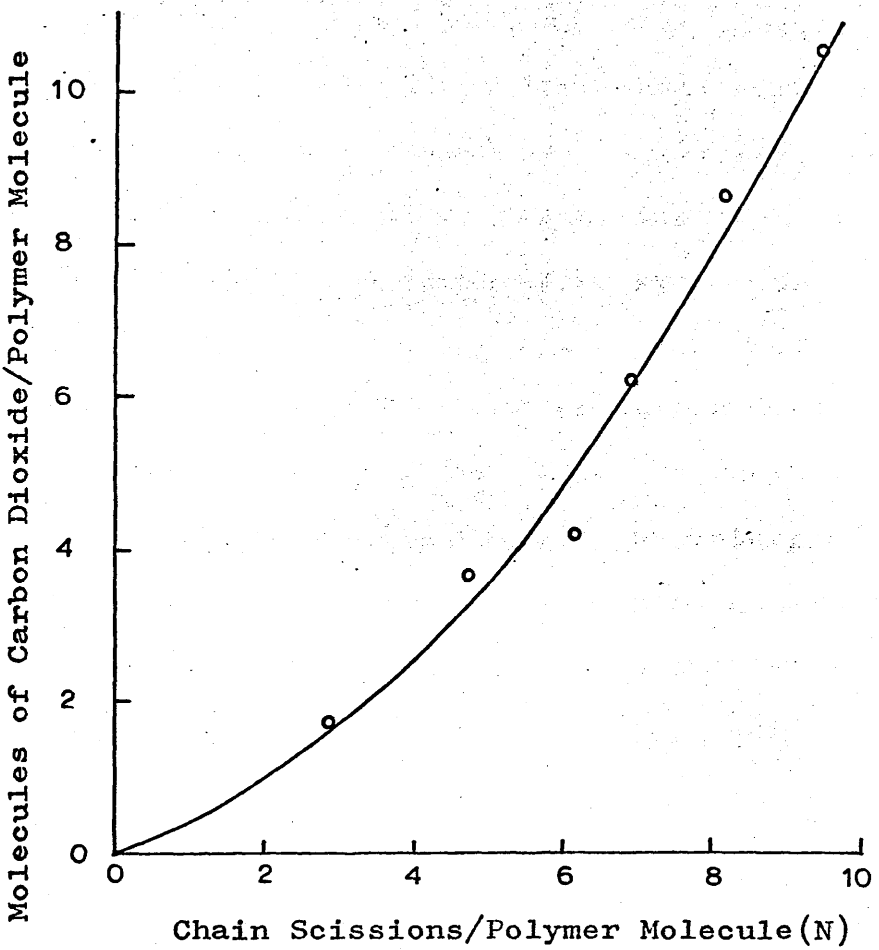


Fig.6.8 Carbon dioxide evolution versus chain scission plot for a 52.4 mole °/o n-butyl acrylate copolymer degraded at 237°C.

gas produced per chain scission is not constant as degradation proceeds, but increases with time of pyrolysis. This straightforward interpretation of Fig.6.8 applies providing that it is assumed that no cross linking occurs. If cross linking does take place to a small extent, however, and this would not seem to be unlikely, then the molecular weight measured after degradation for time t, M_t, would be greater than that found if no cross linking had occurred, so that the value of N calculated would be smaller, and the calculated amount of carbon dioxide per chain scission greater, than the correct value. Thus the data in table 6.8 and Fig.6.8 can also be interpreted in terms of a fixed relationship between chain scission and carbon dioxide production as degradation proceeds, in conjunction with a cross linking reaction. Whichever interpretation is correct, it is clear that simple measurement of carbon dioxide production cannot be used, as it was in the methyl acrylate - methyl methacrylate copolymer system, to determine the extent of chain scission.

(e.3) Mass Spectrometry

The mass spectrum of the volatile materials evolved from a 52.4 mole percent n-butyl acrylate copolymer heated at 237°C for seven hours is shown in Fig.6.9. This spectrum may be interpreted largely in terms of that

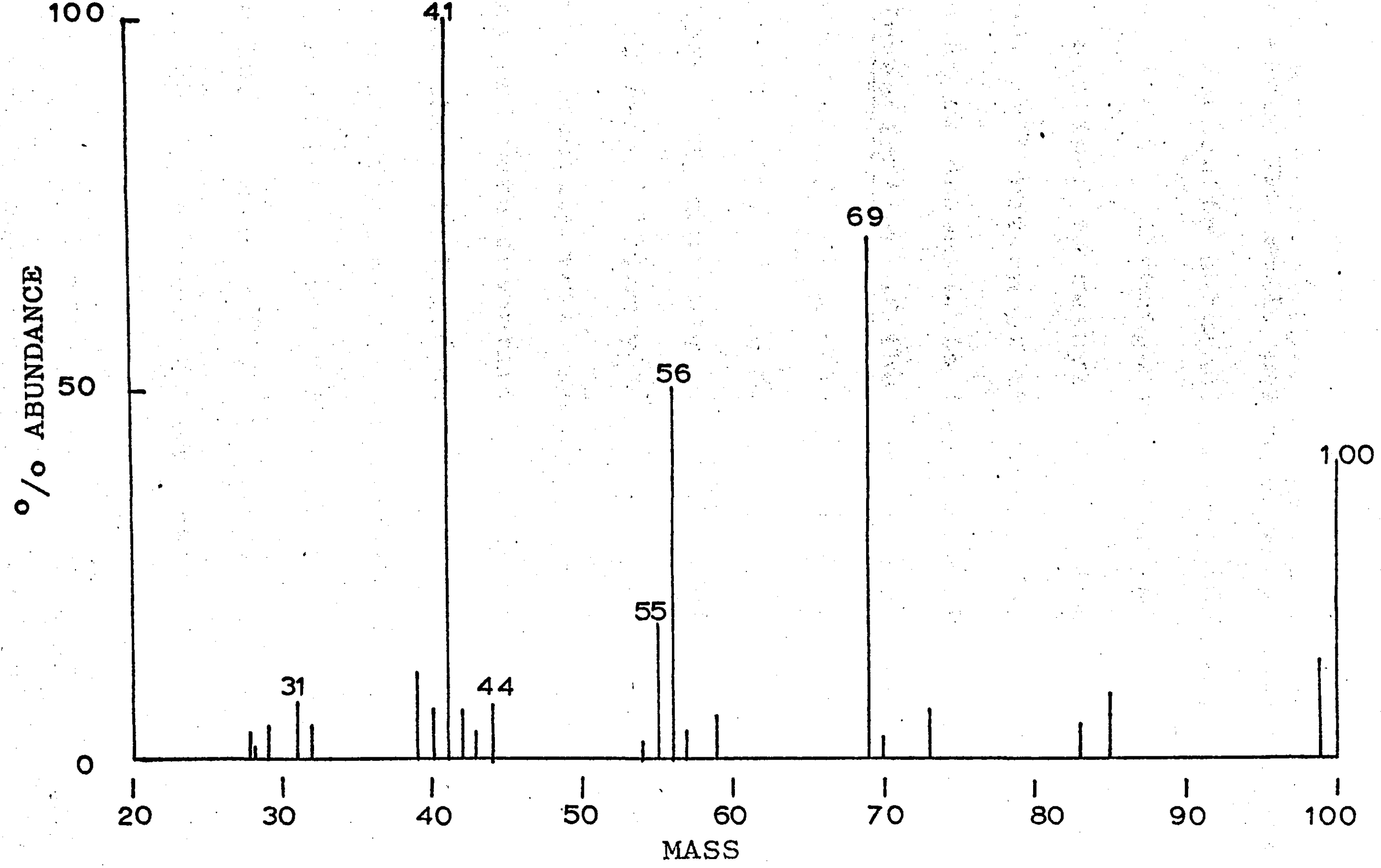


Fig.6.9 Mass spectrum (20ev) of products from the degradation of a 52.4 mole percent n-butyl acrylate copolymer for seven hours at 237°C.

expected from a mixture of methyl methacrylate and but-1-ene. The small peaks at mass 31 and at mass 44 may be attributed to n-butanol and carbon dioxide respectively. Although these peaks are much smaller than those ascribed to methyl methacrylate and but-1-ene, without calibration of the mass spectrometer no conclusions can be drawn as to their relative importance.

6.4 Investigation of the Chain Fragments

No detailed investigation of the chain fragments was undertaken. As in the case of the residue, the colour of these fragments becomes deeper with increasing acrylate content ranging from yellow to brown. Infra-red spectra of this fraction were run as liquid films between salt plates and were essentially similar to that of the residue shown in Fig.6.1. A typical g.l.c. trace of the short chain fragments which distilled into the capillary section of the sealed tube during degradation is shown in Fig.6.10. A $1^{o}/o$ S.E.30 column was used in this work, the retention times for some n-alkanes being shown for comparison.

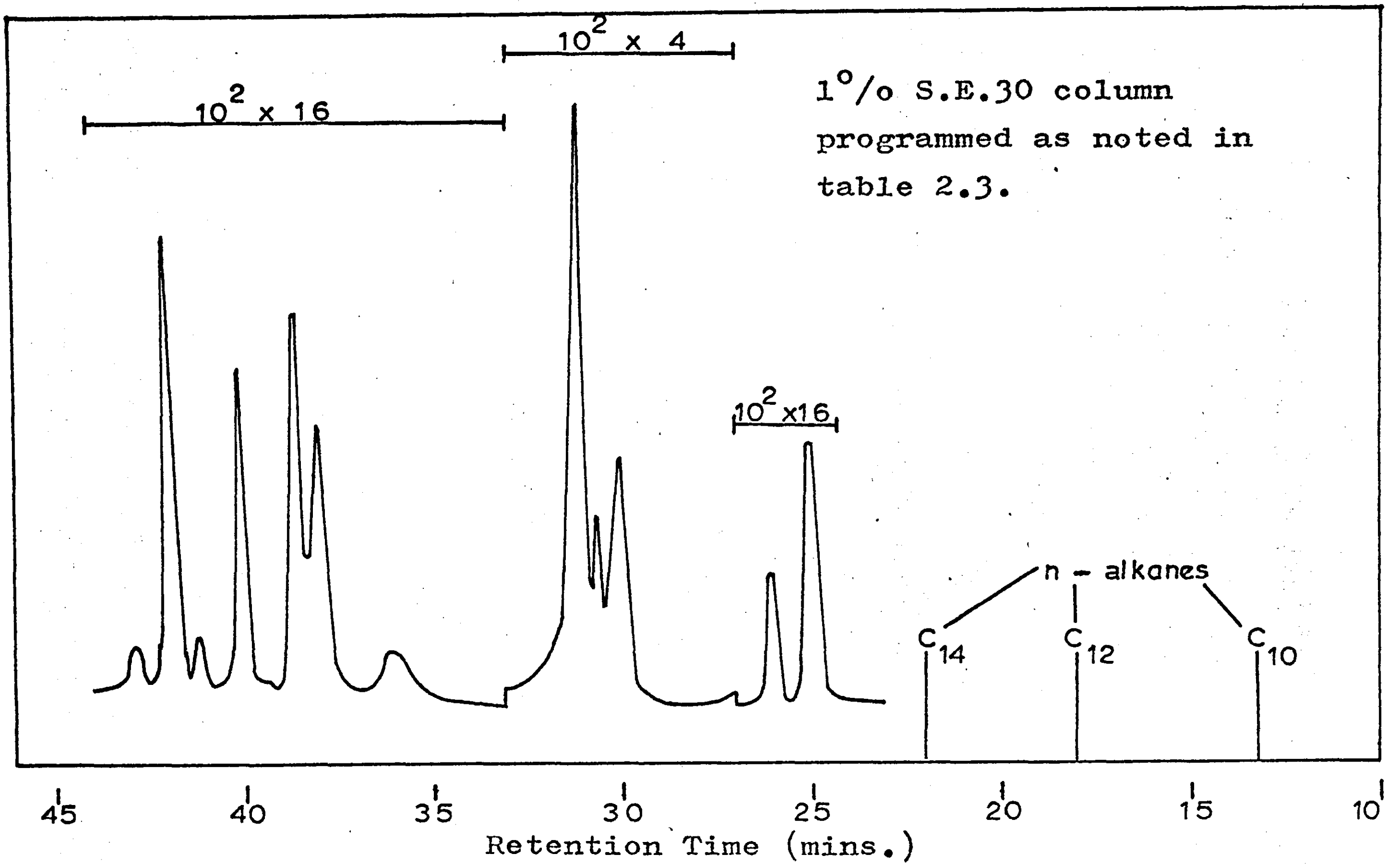


Fig.6.10 G.L.C. trace of short chain fragments from the degradation of a 50.0 mole percent n-butyl acrylate copolymer at 313°C for 11.5 hours.

CHAPTER 7

GENERAL DISCUSSION

7.1 Introduction

In this chapter a critical review is given of the overall degradation characteristics of the copolymer system studied. More detailed discussions on the results obtained and their interpretation have been presented in the appropriate sections throughout. For convenience some of the more important mechanisms are repeated here, the original figure number being given in square brackets.

7.2 Sequence Distribution Data

Copolymerization of two monomers can lead to a variety of copolymers differing in composition and arrangement of monomer units. The two kinds of monomer unit may be randomly distributed, may tend to alternate, or may tend to group themselves in blocks of like units. For the investigation of the degradation of copolymers a knowledge of sequence distribution as well as composition is necessary. Methods of calculating sequence distribution have been devised by Harwood[83,84] using the concept of run numbers. The run number, R, of a copolymer is defined as the average number of uninterrupted monomer sequences which occur in a copolymer chain per hundred monomer units, and may be calculated for the n-butyl acrylate - methyl methacrylate system from a knowledge of the monomer reactivity ratios and the molar percentages of acrylate and methacrylate in the ploymerization mixture. Denoting acrylate units by A and methacrylate units by M it is possible, having found R, to calculate the percentage of A-A, M-M and A-M linkages in the copolymers. Looking at longer sequences, the percentage of A in the centre of the three possible triads, AAA, MAM and MAA, which is equivalent to AAM, may be found. It is also of interest to look at the number average length of acrylate sequences, and this quantity $\bar{A}_n$ is listed with other sequence distribution data in table 7.1. The percentage of acrylate in the middle of AAA triads, relative to all possible triads in the copolymer including those centred on methacrylate units is also a useful quantity and is given in table 7.1 as the relative total percentage acrylate in AAA triads, A_{tp}.

7.3 Mechanistics of Degradation

(a) Production of Alcohol

The importance of n-butanol among the products of degradation of the copolymers increases as the proportion of acrylate in the initial polymer rises. It is

Table 7.1

Sequence Distribution Data for Copolymers of n-Butyl Acrylate and Methyl Methacrylate.

Copolymer Composition (mole °/o n-butyl acrylate)	Diads			°/o Acrylate in centre of triads			Number av. run length $\bar{A}_n$	Relative total °/o acrylate in AAA triads, A_{tp}
	°/o A-A linkages	°/o M-M linkages	°/o A-M linkages	MAA AAM	MAM	AAA		
93.4	87.1	0.3	12.6	12.6	0.5	86.9	14.9	81.3
82.2	66.7	2.4	30.9	30.5	3.5	66.0	5.3	54.2
50.0	22.5	22.5	55.0	49.5	30.3	20.2	1.8	10.1
16.3	2.0	69.4	28.6	21.3	77.2	1.5	1.1	0.2
3.9	0.1	92.4	7.5	7.0	92.9	0.1	1.0	0
0.4	0	99.3	0.7	0	100.0	0	0.7	0

interesting to note that the 50.0 mole percent n-butyl acrylate copolymer is the material of lowest acrylate content which is found to produce alcohol on pyrolysis. It is clear then from table 7.1 that n-butanol is only evolved when non-isolated acrylate units occur, but it is not certain from this data whether the sequence length required is three or only two acrylate units, since the threshold of alcohol formation at the 50.0 mole percent copolymer corresponds to a marked increase in both the number of A-A linkages, from 2.0 to 22.5, and in the relative total percentage acrylate in AAA triads, A_{tp}, from 0.2 to 10.1.

In view of the dependence of alcohol formation on the presence of sequences of acrylate units it would be interesting to test the hypothesis of Grassie and Torrance [36] that a similar situation occurs in the methyl acrylate - methyl methacrylate copolymer system. These workers found that no methanol at all is produced from copolymers containing up to 33.3 mole percent acrylate, but this was the highest acrylate content copolymer they examined. They concluded that this value of 33.3 mole percent methyl acrylate was near the threshold for methanol production. Consequently a methyl methacrylate - methyl acrylate copolymer containing 66.7 mole percent acrylate was synthesised and purified by dissolving in acetone and precipitating from water, care being taken to use no methanol in the purification process, so that if this alcohol were detected on degradation there could be no ambiguity as to its source. On degradation at 313 °C this copolymer gave liquid products which contained 11°/o by weight of methanol. The relevant sequence distribution data are given in table 7.2.

In addition to the mechanism for the production of alcohol from acrylates shown in Fig.7.1[Fig.1.7] Cameron and Kane [27] have proposed an alternative route which again takes into account the need for sequences of acrylate units.

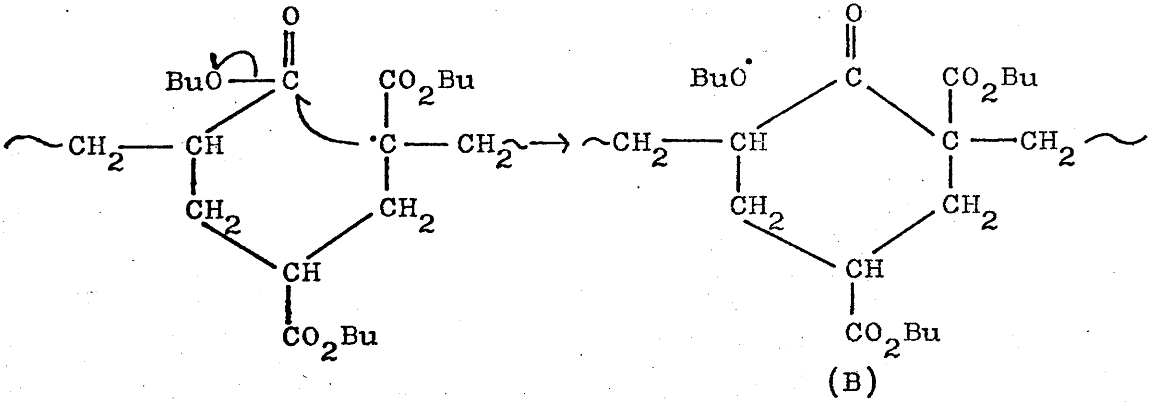


Fig.7.1 **Elimination of n-butanol.**

Bu = $-CH_2-CH_2-CH_2-CH_3$

Table 7.2

Sequence Distribution Data for Copolymers of Methyl Acrylate and Methyl Methacrylate.

Copolymer Composition (mole °/o methyl acrylate)	Methanol Occurrence	Diads	°/o Acrylate in centre of triads			Number av. run length, $\bar{A}_n$	Relative total °/o acrylate in AAA triads, A_{tp}
		°/o A-A linkages	MAA AAM	MAM	AAA		
33.3	No	8.9	39.2	53.6	7.2	1.4	2.4
66.7	Yes	42.3	46.4	13.4	40.2	2.7	26.8

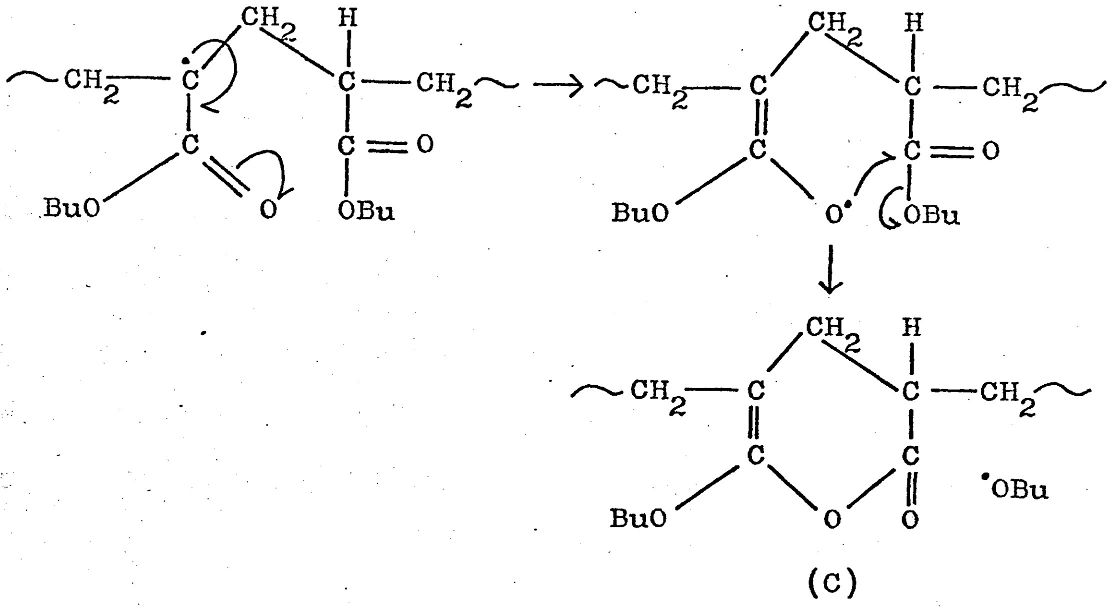


Fig.7.2 Elimination of n-butanol.

Bu = $-CH_2-CH_2-CH_2-CH_3$

The route proposed in Fig.7.1[Fig.1.7] leads to the formation of structure (B), a β keto ester. Since this particular β keto ester cannot exist in the enol form it will exhibit the characteristic absorptions due to the ketone (1700-1720cm.$^{-1}$) and ester carbonyl group (1735-1750cm.$^{-1}$) separately. Any new absorptions in these regions could well be masked by the strong carbonyl absorption due to ester groups already present. The mechanism of Fig.7.2 results in formation of a γδ unsaturated δ lactone (C) which would absorb at around 1764cm.$^{-1}$, and would thus account for the shoulder noted at 1760cm.$^{-1}$ Although this shoulder increases in importance with both time of degradation and the acrylate content of the initial polymer, it could well be unconnected with butanol formation. Fig.7.3 indicates a route by which such an absorption could be accounted for, involving a radical coupling reaction between two adjacent acrylate groups, one of which has undergone ester decomposition as in Fig.7.5[Fig.1.3b.].

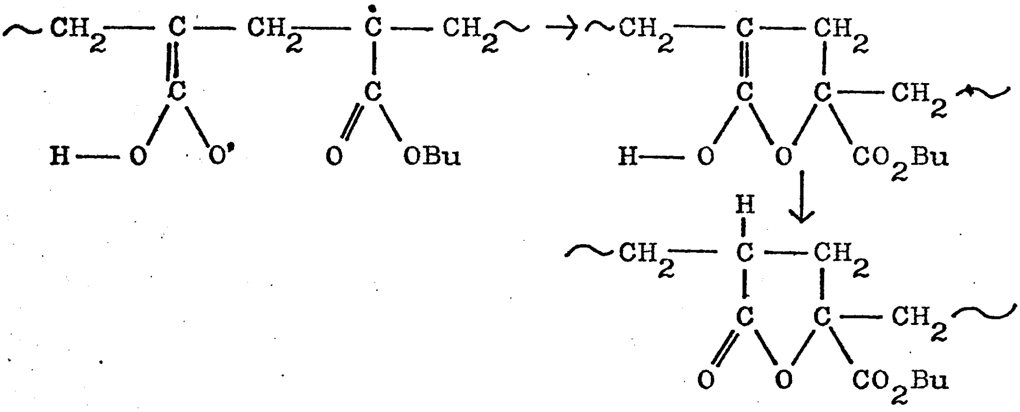


Fig.7.3 Radical coupling reaction. (D)

Bu = $-CH_2-CH_2-CH_2-CH_3$

(D) is a δ lactone absorbing in the region (1760-1780cm.$^{-1}$). U.V. spectra showing as they do no characteristic absorptions, do not make any real contribution to deciding the route by which alcohol is formed.

Both of the mechanisms shown in Figs.7.1 and 7.2 involve attack on an ester group by an acrylate radical. In homopolymers of acrylates there is only one kind of ester group which can be attacked, but when copolymers of acrylates and methacrylates are considered two types of ester are present. If both the methyl and butyl ester groups in the n-butyl acrylate - methyl methacrylate copolymers studied were attacked by an acrylate radical then both methanol and butanol should be evolved. This means that any route proposed for alcohol production must be able to explain the non-appearance of methanol in the degradation products. Molecular models for the structure (B) of Fig.7.1 suggest that in triads such as AMA, AAM and AMM sterically unfavourable 1-3 diaxial interactions involving the α methyl substituent of methacrylate units and the butyl ester of the attacking n-butyl acrylate group occur. Such interactions could explain the absence of methanol among the degradation products. Similar considerations for the lactone (C) of Fig.7.2 tend to suggest that both A-A and A-M sequences could react by this route, implying that some methanol at least would be produced.

The mechanisms of Figs.7.2 and 7.1 suggest that only one acrylate unit in 2 or 3 respectively can degrade to n-butanol. For the pyrolysis of a 93.4 mole percent n-butyl acrylate copolymer in which it is supposed that acrylate units break down to n-butanol exclusively by the routes shown in Figs.7.2 and 7.1 the concentration of butanol expected would be 3.5 and 2.5 millimoles per gram initial polymer. The value actually found for degradation at 313°C for an infinite time is 3.8 (table 5.23). Similar results have been obtained for other acrylate polymers [29]. In order to attempt to reconcile the requirement of sequences of acrylate with these results, the mechanism in Fig.7.4 is tentatively suggested, and is an extension of the route of Fig.7.2.

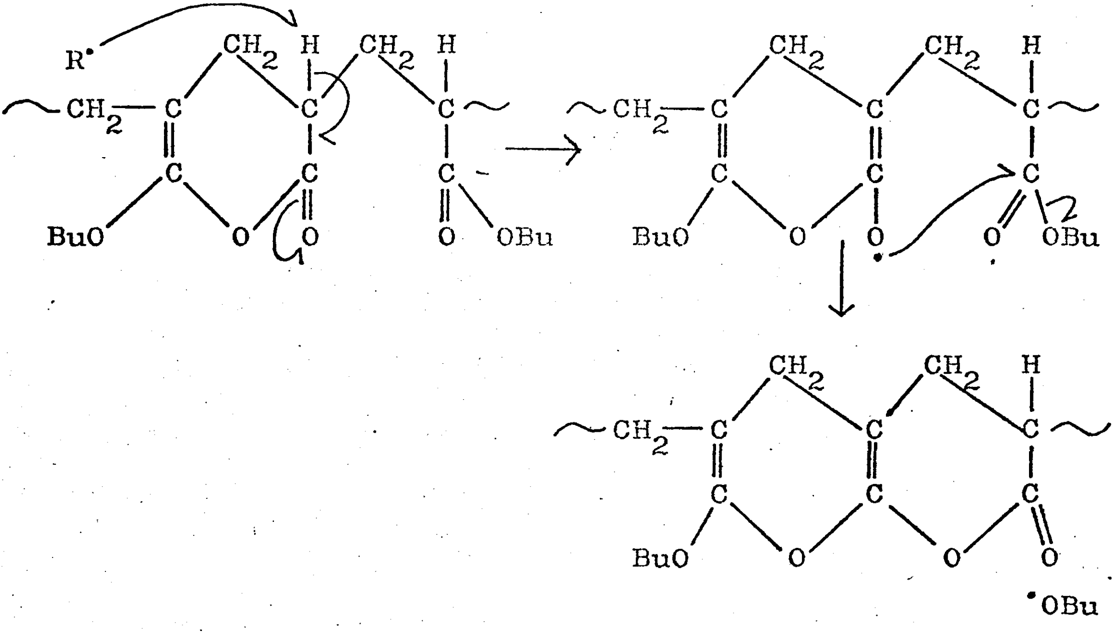


Fig.7.4 Elimination of n-butanol.

$\text{Bu} = -CH_2-CH_2-CH_2-CH_3$

Repetition of this scheme would carry the alcohol elimination reaction on along the polymer chain. Such a reaction could be stopped by the first methacrylate unit encountered after one molecule of methanol has been formed, because there is no suitable tertiary hydrogen to continue this process. Since each sequence of acrylate units produces at most one methanol molecule it is possible that such a low concentration of this alcohol could escape detection in copolymers rich in acrylate. It is difficult to see however why methanol should not be produced in significant amounts from copolymers such as the 50.0 mole percent n-butyl acrylate copolymer which contains 55°/o of A-M bonds. Again, if the scheme shown in Fig.7.4 is an important process a strong band in the infra-red at 1580-1600cm.$^{-1}$ should be present, but was not found.

The autocatalytic nature of alcohol production at 313°C ,Figs.5.27 and 5.28, has been explained in terms of changes in the physical nature of the polymer molecule brought about by this reaction [29]. All the mechanisms so far advocated involve the formation of cyclic structures which decrease flexibility of the polymer chain thus increasing the possibility of reactions involving six membered cyclic structures, such as the reactions considered in this section, at the expense of intermolecular processes such as cross linking.

None of the proposed mechanisms can satisfactorily account for all of the experimental data. Other schemes have been suggested such as an intermolecular version of the route shown in Fig.7.1 but this explains neither the requirement of sequences of acrylate units for alcohol elimination nor the absence of methanol. Thus the picture presented for this reaction is not very satisfactory and further study of this aspect of acrylate-methacrylate degradation is required.

(b) Production of But-1-ene

The fact that but-1-ene is evolved on the degradation of a 16.3 mole percent n-butyl acrylate copolymer when only 2 percent A-A linkages are present and the number average run length is 1.1(table 7.1), indicates that in contrast to alcohol production elimination of this gas does not depend upon acrylate sequences. This view is supported by the data given in (5.2c). Thus the mechanism proposed in Fig.7.5[Fig.1.3b] appears to account adequately for the elimination of but-1-ene from the copolymers.

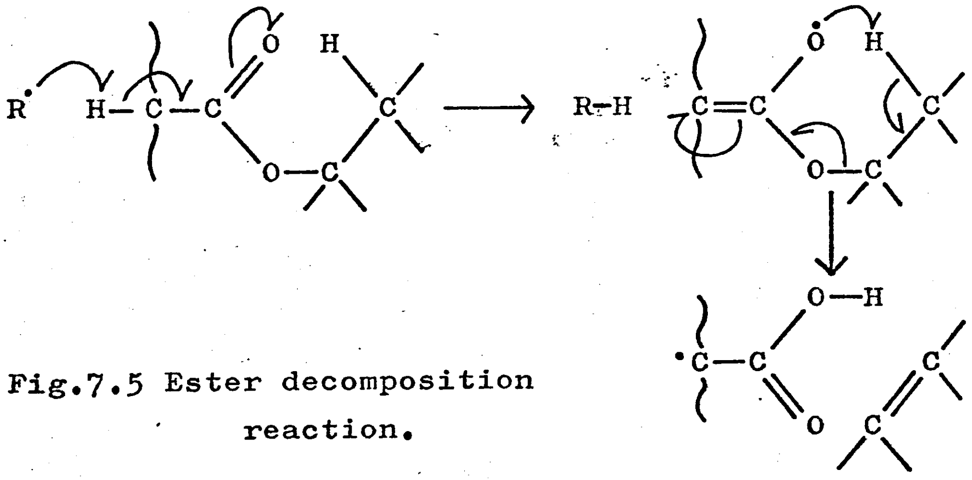


Fig.7.5 Ester decomposition reaction.

(c) Production of Carbon Dioxide

Carbon dioxide may be produced by decarboxylation of acid groups pendant to the main polymer chain after ester decomposition has occurred, Fig.7.5[Fig.1.3b]. Such a mechanism would mean that the highest possible value for the molar ratio of carbon dioxide to but-1-ene would be unity.

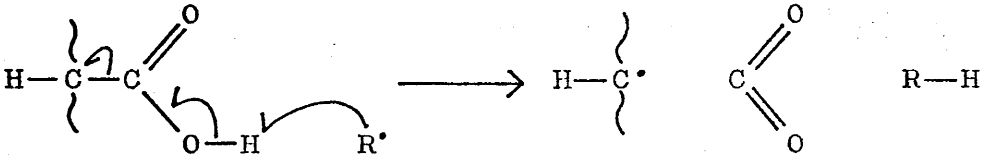
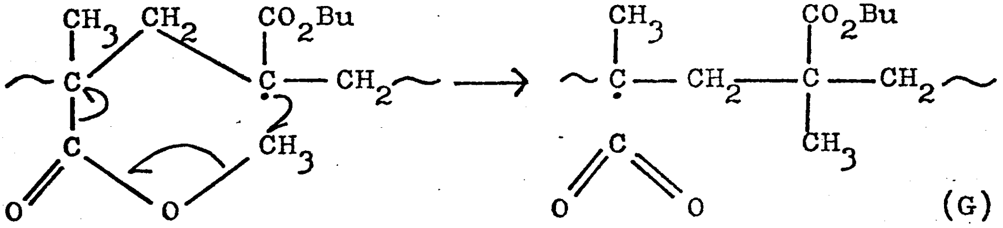


Fig.7.6 Decarboxylation of a carboxylic acid residue.

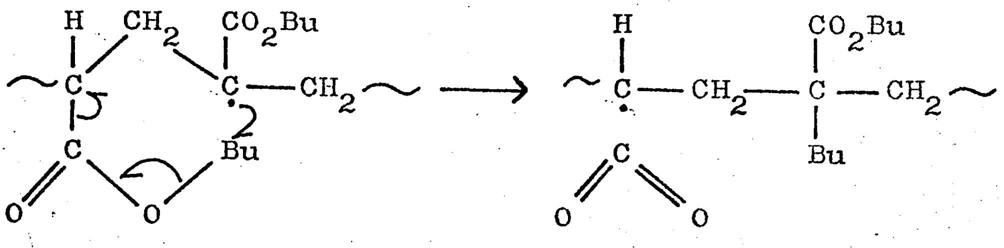
Experimentally it is found (5.2c) that the above ratio for degradations carried out at 313°C ranges from 4.9 for the 16.3 mole percent n-butyl acrylate copolymer to 2.0 for the 93.4 mole percent copolymer. These results must mean that the route shown in Fig.7.6 is not the only one operating.

The reaction scheme shown in Fig.7.7[Fig.1.4] has also been suggested.



(G)

Fig.7.7a Elimination of carbon dioxide.



(H)

Fig.7.7b Elimination of carbon dioxide.

Bu = $-CH_2-CH_2-CH_2-CH_3$

This elimination reaction can occur between an acrylate and a methacrylate unit, Fig.7.7a, or between two acrylate units, Fig.7.7b. If the scheme shown in Fig.7.7b is followed it requires the shift of the rather bulky n-butyl group. However, this type of reaction scheme has been proposed for the degradation of poly(benzyl acrylate) [28] in which the shift of the large benzyl group is involved. The routes shown in Fig.7.7 allow elimination of carbon dioxide without simultaneous production of but-1-ene and do not require that a sequence of two acrylate units is present, it being sufficient for one acrylate unit to be present which can attack a neighbouring methacrylate unit. These points are important since the evolution of carbon dioxide is found to take place when the acrylate content is only 3.9 mole percent, there being only 0.1 percent A-A links in the polymer, and no but-1-ene is evolved.

The relationship between evolution of carbon dioxide and chain scission was reported in (6.2e). These results show that at 237°C there is no definite connection between these two processes.

(d) Production of n-Butyl Methacrylate

The reaction shown in Fig.7.7a results in the formation of the chain radical (G) which can then break down as shown in Fig.7.8a.

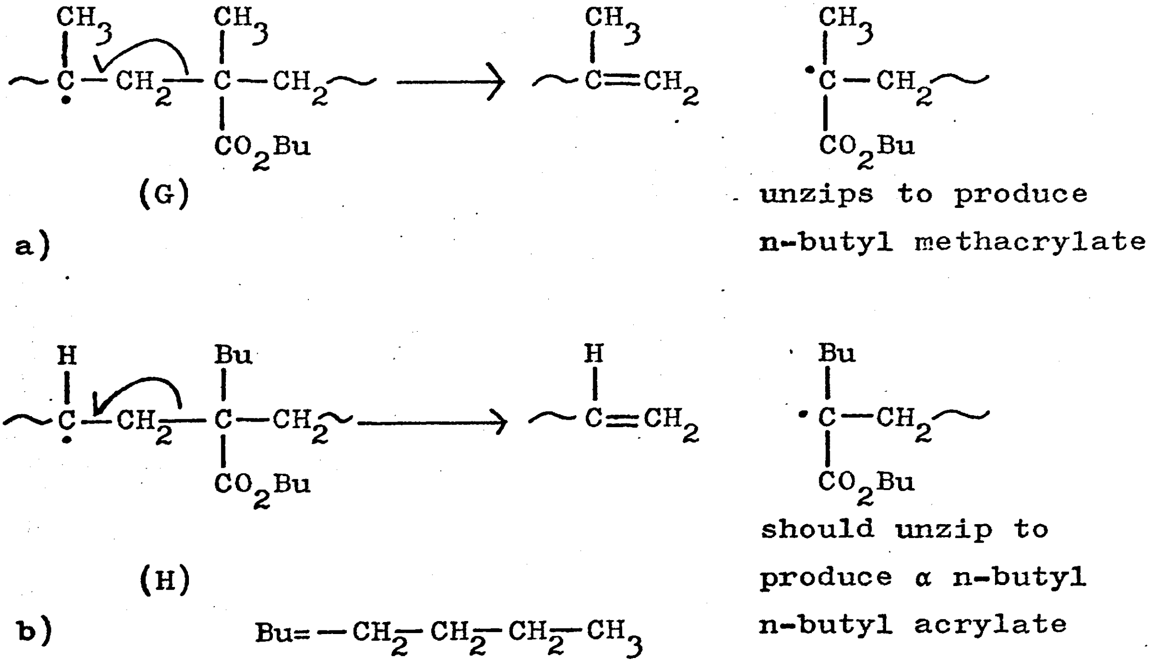
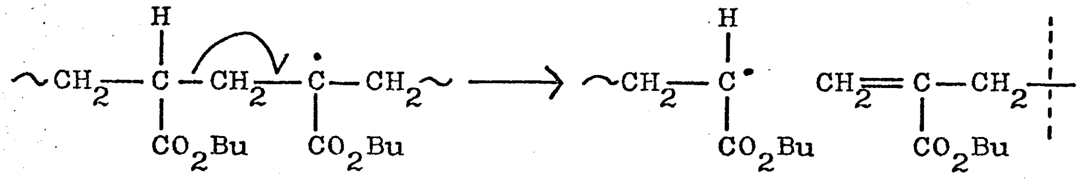


Fig.7.8 Possible reactions of the radicals (G) and (H).

If, however, a similar reaction between two acrylate units takes place the radical which results, (H), Fig.7.7b, could on unzipping produce a molecule of n-butyl acrylate substituted at the α position by an n-butyl group. None of this compound was available so that its retention time on the g.l.c. columns used is not known, but it is feasible that such a compound would appear on the g.l.c. trace among the short chain fragments.

n-Butyl methacrylate can also be formed in a reaction of the type shown in Fig.7.9.



n-butyl methacrylate
produced by scission
of the bond indicated

Fig.7.9 Production of n-butyl methacrylate.
$Bu = -CH_2-CH_2-CH_2-CH_3$

This mechanism would lead, for degradation of acrylate homopolymers in general, to the evolution of the corresponding monomeric acrylate substituted in the α position by a methyl group. These compounds have been reported for all of the primary acrylates so far studied [29].

(e) Production of n-Butyl Acrylate

The amount of this product evolved on degradation of the copolymers initially increases with acrylate content as expected but then falls off again (5.4c).

This was explained in terms of acrylate units being evolved in depolymerizations initiated at methacrylate linkages, so that increasing the acrylate content decreases the possibility of such depolymerizations since homopolymers of acrylates take part in transfer reactions rather than unzipping.

(f) Other Products

The production of chain fragments has already been dealt with as has the cross linking reaction in sections 1.3a and 6.2d respectively.

Both carbon monoxide and hydrogen are evolved in small amounts on copolymer breakdown. Their formation has already been discussed and mechanisms proposed (1.3f).

Methane evolution probably corresponds mechanistically to hydrogen elimination, Fig.1.9, involving the α methyl group of methyl methacrylate units. It could also be formed from the methyl ester group of methyl methacrylate or by breakdown of the n-butyl group in the ester part of the n-butyl acrylate molecule.

The other minor products may be considered as deriving from the breakdown of the n-butyl side chain of the acrylate units.

Methyl methacrylate formation can be adequately accounted for in terms of unzipping of methacrylate units along the polymer backbone.

7.3 Summary

The initiation step in the degradation of the copolymer system studied can be described in terms of random chain scission, as confirmed by molecular weight measurements (6.2c), to produce terminal chain radicals. The increasing difficulty of breaking the linkages in the series methacrylate-methacrylate, acrylate-methacrylate and acrylate-acrylate is reflected by the greater stability of acrylate rich copolymers. If any of the terminal chain radicals involve a methyl methacrylate unit, depolymerization will take place until the unzipping process is blocked by the first n-butyl acrylate unit encountered. Thus two n-butyl acrylate terminated chain radicals have been produced, with or without monomeric methyl methacrylate, depending upon the site of the initial break. These terminal radicals can then depropagate to produce n-butyl acrylate monomer or take part in transfer reactions involving hydrogen abstraction to produce a chain radical. This chain radical may then undergo scission to produce chain fragments or react according to any of the schemes discussed in this chapter resulting in formation of the appropriate product. As the acrylate content of the copolymer increases, transfer reactions producing chain fragments and reactions depending upon sequences of acrylate units, such as alcohol evolution, become important. Termination may take place by mutual destruction of pairs of radicals in processes such as cross linking (6.2d). During the course of the reaction coloration develops in the residue and in the chain fragments, the colour going through yellow to brown with both increasing time of degradation and rising acrylate content. This has been associated with the formation of conjugated carbon-carbon double bonds along the polymer backbone, Fig.1.9.

SUMMARY

This study of the thermal breakdown of copolymers of n-butyl acrylate and methyl methacrylate represents a further contribution to the establishment of a comprehensive picture of the degradation of acrylate - methacrylate copolymer systems.

A series of copolymers covering the whole composition range was synthesised. Degradations were carried out under vacuum either in a dynamic molecular still or using a new technique developed in these laboratories. Thermal methods of analysis such as thermogravimetric analysis (T.G.A.) and thermal volatilization analysis (T.V.A.) showed that the copolymers became more stable to thermal breakdown as the acrylate content was increased. These techniques allowed a suitable temperature range to be chosen in which to study the decomposition isothermally. The gaseous degradation products, liquid products, chain fragments and residue were each examined separately, using, among other techniques, infra-red spectroscopy, gas-liquid chromatography, mass spectrometry and combined gas chromatography - mass spectrometry. The complex nature of the pyrolysis of this copolymer system is reflected

by the great variety of products obtained. The main gaseous products were found to be carbon dioxide and but-1-ene, while the most important liquid products are methyl methacrylate and n-butanol. Quantitative measurements enabled the build up of these products to be followed as degradation proceeds, and mass balance tables were drawn up for each copolymer studied. Pyrolysis was carried out mainly at 313°C but in order to investigate the relationship between carbon dioxide formation and chain scission, a lower temperature, 237°C, was chosen so that this study would not be complicated by large scale volatilization processes. The chain fragments were only briefly examined. Molecular weight measurements on the residue indicated that breakdown by random scission processes becomes more important relative to breakdown by depolymerization processes as the acrylate content was increased. An overall degradation scheme is presented and mechanisms are postulated to account for the formation of all of the important products, although no really satisfactory route for alcohol evolution has been found.

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