

THE PHOTOTHERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE
AND n-BUTYL ACRYLATE.

A thesis submitted to the University of
Glasgow for the degree of Doctor of
Philosophy, in the Faculty of Science.

by

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August 1971.

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August 1971.

R.H. Jenkins.

CONTENTS.

<u>CHAPTER 1.</u>	- GENERAL INTRODUCTION	1
1.1	Introduction	1
1.2	Theoretical Considerations	2
1.3	Photodegradation of Poly (methyl methacrylate)	6
1.4	" " Poly (methyl acrylate)	9
1.5	" " Poly (ethyl acrylate)	11
1.6	" " Poly (tert. butyl acrylate)	12
1.7	" " Poly (n-butyl methacrylate)	13
1.8	" " Poly (ethyl methacrylate)	17
1.9	" " Gopolymers of methyl methacrylate and methyl acrylate	17
1.10	" " Copolymers of methyl methacrylate and acrylonitrile	19
1.11	" " Non Polymeric Esters	21
1.12	Thermal Degradation of Copolymers of Methyl Methacrylate and n-Butyl Acrylate	23
1.13	Title and Aim	24
<u>CHAPTER 2.</u>	- EXPERIMENTAL TECHNIQUES AND APPARATUS	26
2.1	Preparation of Copolymers	26
(a)	Purification of Monomers	26

(b) Purification of Initiator.	26
(c) Preparation of Dilatometers	27
(d) Polymerisation	27
(e) Copolymer Recovery and Purification	29
2.2 Degradation Apparatus	29
(a) Temperature Control	29
2.3 Polymer Form	32
(a) Preparation of Films	32
2.4 Source of Radiation	33
2.5 Transmission of the Ultraviolet Radiation	33
(a) Introduction	33
(b) Transmission by Fused Silica	35
(c) Transmission by Air	35
(d) Monochromaticity of the Source	37
2.6 Experimental Procedure	37
2.7 Molecular Weight Determination	37
(a) Vapour Pressure Osmometer	38
(b) Membrane Osmometer	39
2.8 Product Analysis	40
(a) Introduction	40
(b) Spectroscopic Measurements	41
1) Infra-red	41
2) U.V. Analysis of the Residue	41

(c) Gas Liquid Chromatography	41
(d) Permanent Gas Sampling Apparatus	44
(e) Quantitative Gas Liquid Chromatography	44
(f) Combined Gas Chromatography - Mass Spectrometry	45
(g) Pressure Measurement	45
2.9 Sol-Gel Analysis	47

CHAPTER 3. -

3.1 Preliminary Observations	48
3.2 Determination of Absolute Numbers of Quanta Produced by the Lamp	51
(a) Experimental Procedure	51

CHAPTER 4. - IDENTIFICATION OF PHOTOLYSIS PRODUCTS

4.1 Introduction	55
4.2 Analysis of the Liquid Condensibles	55
(a) Infra-red	55
(b) Interpretation of Spectra	55
(c) Gas Liquid Chromatography	61
(d) Combined Gas Chromatography - Mass Spectrometry	63
d.1 Experimental	63
d.2 Interpretation of Mass Spectra	74
d.3 Processes of Fragmentation of Positive Ions	75

d. 4 Conclusions	82
4.3 Analysis of Permanent Gases	82
(a) Infra-red	82
(b) Gas Chromatography	83
 <u>CHAPTER 5. - QUANTITATIVE ANALYSIS OF DEGRADATION PRODUCTS</u>	 85
5.1 Introduction	85
5.2 Quantitative Analysis	85
5.3 Analysis of Liquid Degradation Products	85
(a) Analytical Techniques	98
(b) Treatment of Results	99
5.4 Analysis of Gaseous Degradation Products	102
5.5 Discussion of Results	111
 <u>CHAPTER 6 - Chain Scission and the Residue</u>	 113
6.1 Introduction	113
6.2 Molecular Weight of the Residue	113
6.3 Calculation of Chain Scission in the Presence of Volatilisation	118
(a) Relation Between Volatilisation and Chain Scission	118
(b) Chain Scission with Time of Degradation	125
6.4 Sol-Gel Analysis	128

(b) Results	128
(c) Discussion	132
6.5 Crosslinking and Scission	134
(a) Introduction	134
(b) Results	134
(c) Conclusions	137
6.6 Spectroscopic Examination of the Residue	138
(a) Infra-red	138
(b) U.V. Visible	140
(c) N.M.R.	142
6.7 Short Chain Fragments	142
(a) Introduction	142
(b) Analysis	143
(c) Discussion	143
 <u>CHAPTER 7 - GENERAL DISCUSSION</u>	 147
7.1 Introduction	147
7.2 Sequence Distribution Data	147
7.3 Blocking Efficiency	149
(a) Zip Lengths	149
(b) Molar Ratios of Monomers in the Degradation	
Products	151
7.4 Mechanistics	152

(a) Production of Methyl Methacrylate	152
(b) Production of n-Butyl Acrylate	153
(c) Production of n-Butyraldehyde	153
(d) Production of n-Butanol	156
(e) Production of n-Butyl Methacrylate	158
(f) Production of Permanent Gases	159
(g) Reaction Pathway	161
7.5 Summary	162

SUMMARY

164

REFERENCES

259

CHAPTER 1.

GENERAL INTRODUCTION.

1.1. Introduction.

The useful life of a polymeric material will ultimately depend upon the environment in which it is utilised and, in particular, upon the degradation reactions which that environment can induce in the polymer. For this reason, it has been important to obtain a fundamental understanding of the chemical effects of a wide variety of degradation agencies, including high energy irradiation, moisture, ozone, atmospheric pollutants such as the oxides of nitrogen and sulphur, and even intermittent mechanical stress. The three basic agencies, to which all polymers are subjected either during fabrication or during their subsequent useful life, are heat, light and oxygen. At the present time a great deal is known about thermal, photolytic and oxidative reactions in homopolymers, but in the past five to ten years copolymers have found increasing commercial application so that it has become important to extend degradation studies to this class of material.

There are three aspects of photo-degradation which are of particular interest, namely reactions in molten polymer, polymer films at ambient temperatures, and polymer solutions. All are vitally important in their separate ways to a complete understanding of environmental degradation processes in polymers. Reactions in polymer

films are most closely relevant to polymers in their normal applications. However, in such a medium the primary products of photolysis tend to be trapped and to undergo a complex of secondary processes so that the overall reaction often becomes extremely difficult to analyse. By carrying out the reaction in molten polymer at elevated temperatures the primary volatile products can readily escape. This means that they can be more readily analysed and the reactions in which they are formed can be isolated from secondary processes. However, in films and in molten polymer the concentration of polymer cannot be varied so that kinetic analyses, which may help to clarify the nature of the reaction, are impossible. Such studies may be most conveniently carried out in solution. Thus, it is clear that these three aspects of photo-degradation are complementary to one another.

1.2. Theoretical Considerations:

Photochemistry is the science of the chemical effects of light, where light includes the infra-red and ultra-violet, as well as the visible regions of the spectrum, i.e. the range of wavelengths from about 1000 to 10,000 Å. The energies of quanta in this range vary from about 1 to 10 e.v. or 23 to 230 k. cal. per mole. These energies are comparable with the strength of chemical bonds. Thus, if a molecule absorbs a photon of visible light, definite chemical effects may be expected, yet the collision is still a rather gentle one. The theoretical considerations have been discussed by many authors¹⁻⁵.

A photochemical reaction begins with the act of absorption of energy in the form of photons. By the Stark-Einstein Law of photochemical equivalence^b this is a quantum process involving one photon per absorbing molecule. The number of molecules absorbing is therefore equal to the number of photons absorbed. It is essential to distinguish clearly between the primary step of light absorption and the subsequent process of chemical reaction. An activated molecule does not necessarily undergo reaction; on the other hand, in some cases, one activated molecule through a chain mechanism may cause the reaction of many other molecules. Thus the Stark, Einstein principle of quantum activation should never be interpreted to mean that one molecule reacts for each quantum absorbed.

The product of absorption of a photon is an excited state in the absorbing molecule, with energy in excess of the normal state equal to the energy of the photon which it absorbed. When the light absorbed results in an electronic transition, chemical reaction may occur, but light which produces only vibrational or rotational changes in the absorbing molecule is photochemically inactive.

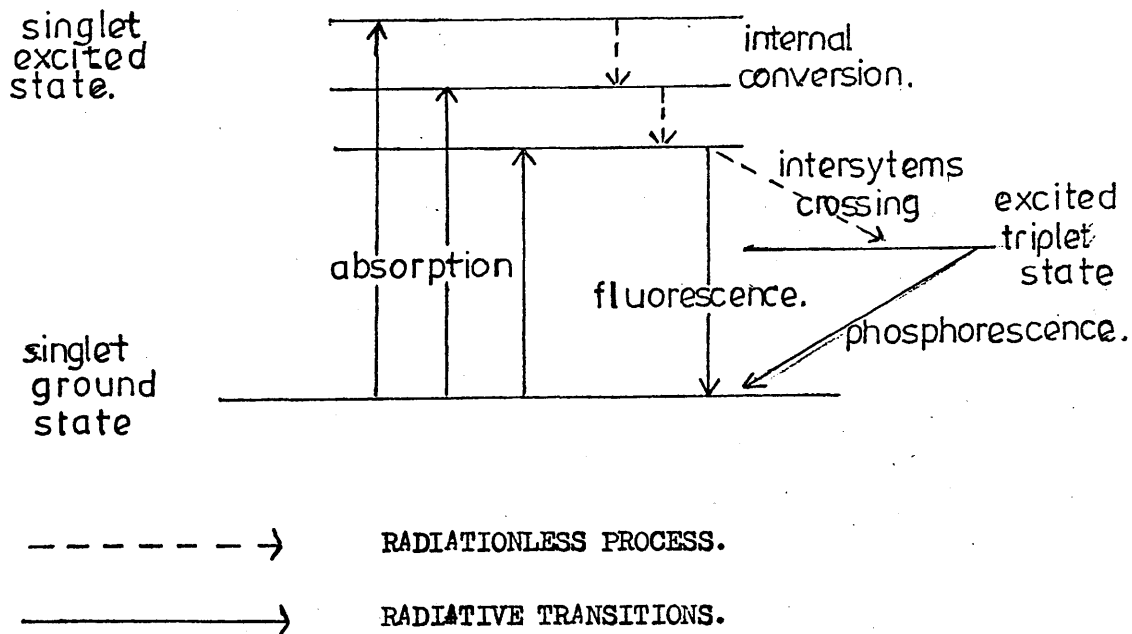
Most organic molecules lie in a singlet ground state. An excited state results from the absorption of a photon. There will usually be an excited triplet state somewhat below the excited singlet. Immediately after the primary quantum jump, a series of extremely rapid events takes place, before any photochemical reaction or emission of luminescent

radiation can occur. A typical situation is shown in Fig. 1.1.

First, there is internal conversion: no matter which upper singlet state has been reached in the primary quantum jump, there is a rapid radiationless transfer of energy to the lowest excited singlet state.

Second, there is intersystem crossing: the molecule may then find itself in an excited triplet level of lower energy. The non-radiative processes are shown and are assumed to involve transfer of energy to the medium in such a way that it appears as thermal energy.

Fig. 1.1. MOLECULAR ENERGY LEVELS CONCERNED IN PHOTOCHEMICAL PROCESSES.



There are two kinds of photolytic processes, primary and secondary. The primary process is the immediate effect of the light on the molecule which absorbs it, whereas the secondary process is the reaction of the molecules, atoms, or radicals produced by the primary process. There are several paths open to the excited molecule formed in the primary step.

(1) It may re-emit a quantum of either the same or a different frequency. This emission is called fluorescence or phosphorescence.

(2) It may collide with other molecules and pass on to them some or all of its excitation energy.

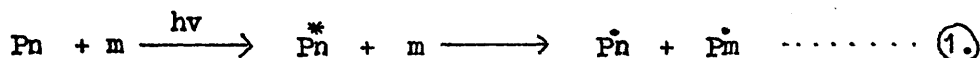
(3) It may collide with another molecule and react with it.

(4) It may spontaneously decompose if the excitation energy reaches a bond that can be broken.

It is important to remember that, because the absorbed energy may be transferred, the site at which the ultra-violet light is absorbed is not necessarily the one at which bond rupture may take place.

In the presence of other molecules, the photolysis of a polymer may occur by any or all of the three processes. The first is the direct absorption of energy followed by homolytic dissociation of some bond.

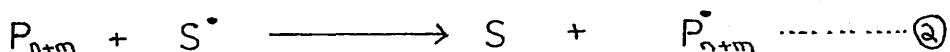
In the case of random scission, the main chain is broken:



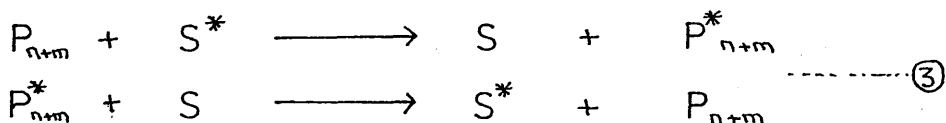
$P_n^* + m$ is an electronically excited state.

Main chain dissociation may be preceded by a 'side bond' dissociation, leading to a polymer free radical P_{n+m}^{\bullet} which could then fragment. These processes could occur in polymer films free from impurities.

In the second and third processes, a molecule S is present or an intramolecular interaction occurs.



This accelerates the degradation process, whereas the reverse of equation (2) would inhibit degradation. Lastly, acceleration or inhibition by a transfer of excitation energy between species may occur.



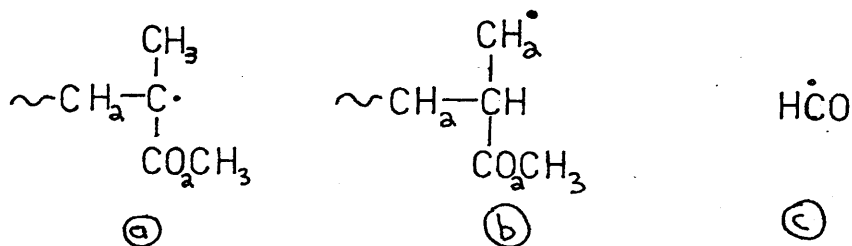
1.3. Photodegradation of Poly (methyl methacrylate)

A thorough investigation of the effects of ultra-violet radiation on poly (methyl methacrylate) was carried out by Melville and Cowley⁷. They irradiated polymer films with light of wavelength 2537 \AA° , in vacuum, at temperatures ranging from 130°C to 200°C ., and observed the monomer evolution using a calibrated Pirani gauge. They found that a temperature of 160°C . was necessary to allow the free diffusion and escape of monomer, whereas below 160°C . the reaction was inhibited by diffusion and an equilibrium between propagation and depropagation was set up. They were concerned primarily with the value of the light intensity exponent and they concluded that the primary process was photo-initiation at the chain ends.

Preliminary investigations by Cowley and Melville⁷ with polymers of methyl and isopropyl esters of methacrylic acid showed degradation at temperatures above 130°C. with light of 2537 Å. This behaviour was in contrast to that exhibited by other common polymers. Great stability was shown by poly methyl acrylate, poly methacrylic acid, poly vinyl acetate, poly isobutene and poly acrylonitrile. In all these cases, the criterion of degradation was taken as the production of volatiles.

Near room temperature in vacuum, films of poly methyl methacrylate undergo random cleavage of the main chain without extensive depolymerisation.⁸⁻¹⁶ The quantum yield for random scission is near 4×10^{-2} scissions per quantum absorbed,⁸ and both oxygen and nitrogen act as inhibitors to photodegradation.⁹ No crosslinking has been observed in the absence of sensitizers and the major photolysis products¹⁶ are methyl formate, methanol, and methyl methacrylate with methane, hydrogen, carbon monoxide and carbon dioxide also being observed. The ultra-violet spectrum,^{8,14} of the degraded polymer exhibits a new bond at 285 mμ, and this has been assigned to either a carbonyl containing chromophore formed in the secondary reactions after the homolysis of the ester C—O bond, or, to conjugated unsaturation in the chain. Longer exposures are required for changes to be observed in the infra-red spectrum.¹⁴ A broadening of the carbonyl band at 1750 cm⁻¹ and new bands at 1615 cm⁻¹ and 1640 cm⁻¹ were noted. These absorptions can be ascribed to olefinic unsaturation. Electron spin resonance

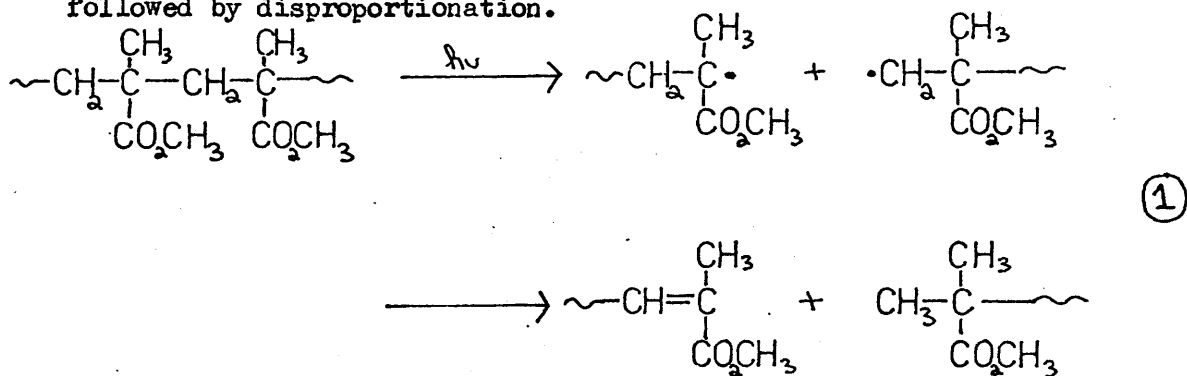
spectra of the ultra-violet irradiated polymer indicate that the free radicals present are (a), (b) and (c)^{9,17}.



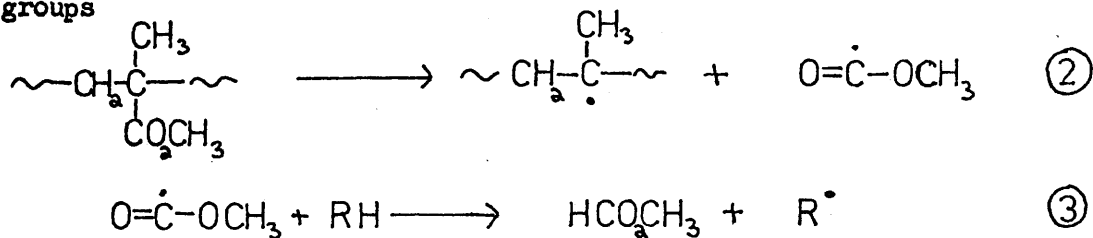
The principle radical is probably (a), although (b) and (c) were observed at 77°K in reversible reactions by the ultra-violet irradiation of a previously gamma irradiated sample.¹⁸

Chain scission may be the result of direct scission of chain bonds

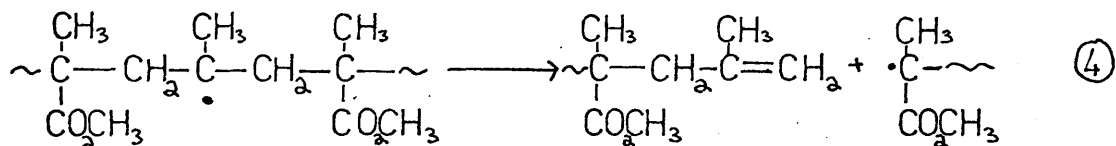
followed by disproportionation.



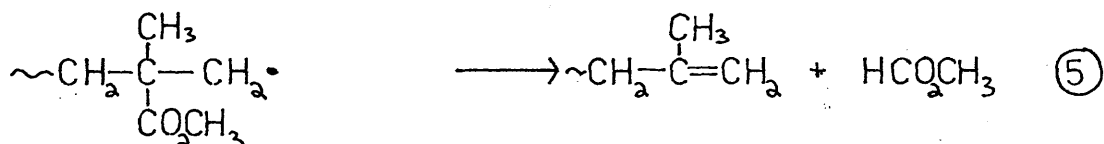
Methyl formate must result from the splitting off of the pendant ester groups



Chain scission could also result from



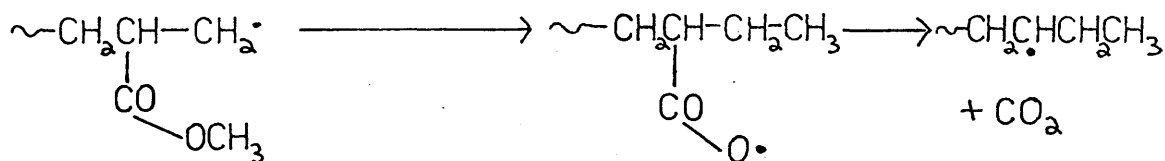
Methyl formate might also be formed in reaction (5) after main chain scission.



1.4. Photodegradation of Poly (methyl acrylate)

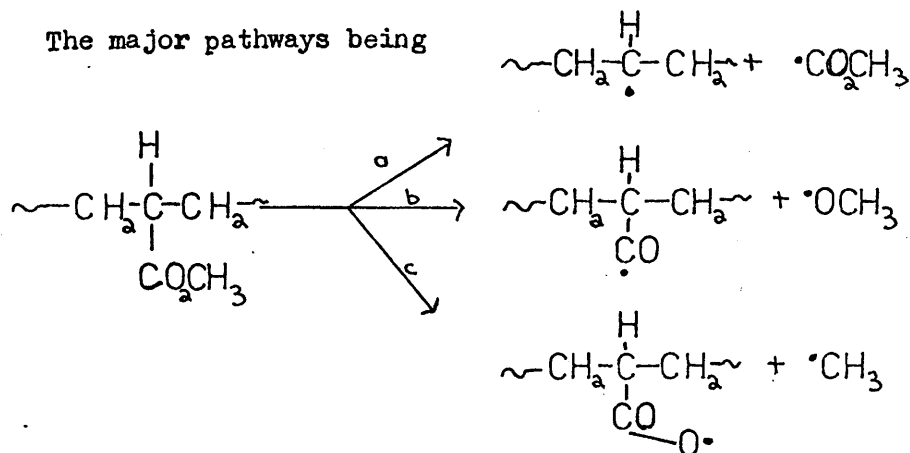
Poly methyl acrylate has been observed to crosslink during both radiolysis¹⁹ and thermolysis,²⁰ whereas in poly methyl methacrylate crosslinking is usually absent during degradations except under special conditions such as photolysis in the presence of specific sensitizers.²¹ Fox, Isaacs, Stokes and Kagarise²² studied the photolysis of thin films of poly methyl acrylate with 2537 Å radiation at 22°C. in vacuum and air. In vacuum, crosslinking was indicated by the formation of benzene insoluble material. In air exposures no visible insoluble material is formed. However, a qualitative comparison of the sedimentation patterns of undegraded and degraded samples of poly methyl acrylate showed that crosslinking occurs in both air and vacuum conditions.

Crosslinking must occur through radicals formed by abstraction of the tertiary hydrogen atom along the polymer chain. From air exposures it appeared that gelation is retarded by oxygen acting as a radical scavenger, and although scission is unaffected, crosslinking is inhibited. Spectral changes are minimal, the only detectable change being the formation of a weak band at about 280 mμ. Formaldehyde, methanol and methyl formate originating from the pendant ester groups were detected, along with carbon monoxide, carbon dioxide, methane and hydrogen. Depolymerisation to monomer is unimportant. Carbon dioxide accumulates in amounts which increase exponentially with dose. It was suggested that carbon dioxide is associated with a decomposition of chain ends, since the total number of chain ends resulting from chain scission also increases with dose. Such a decomposition is represented by the equation

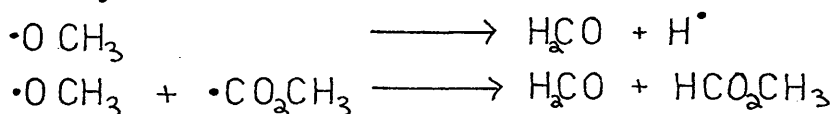


The products can all originate from the ester groups in the polymer.

The major pathways being

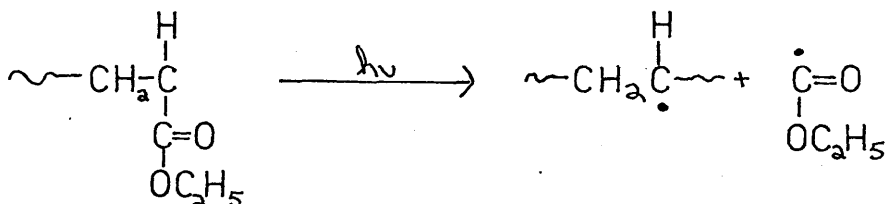


Methyl formate and methanol would result from the combination of hydrogen atoms with $\cdot\text{CO}_2\text{CH}_3$ and $\cdot\text{OCH}_3$ respectively. Formaldehyde could be formed by two routes

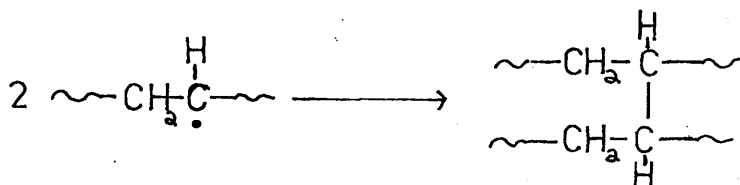


1.5. Photodegradation of Poly(ethyl acrylate)

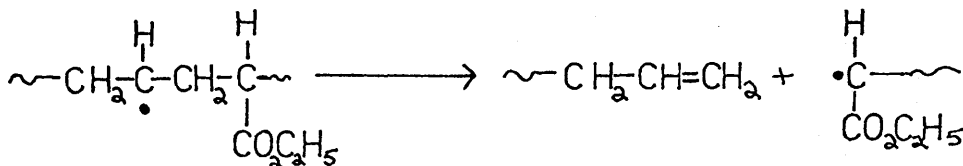
Irradiation of films of poly (ethyl acrylate), with ultra-violet light, at room temperature, in the absence of oxygen results in simultaneous crosslinking and chain rupture^{as}. The volatile products were analysed and found to contain hydrogen, methane, carbon monoxide and carbon dioxide. The following reaction was postulated



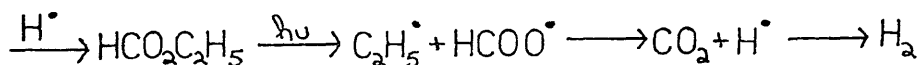
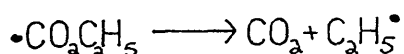
Crosslinking results from the combination of two polymer radicals



Main chain scission can occur as follows



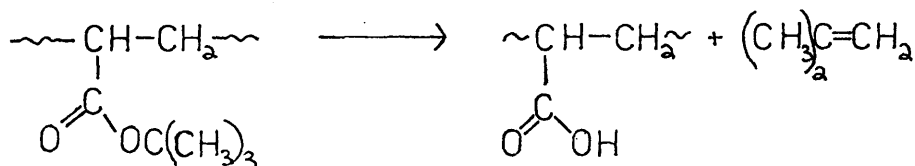
Various products may be formed by reactions of the $\cdot\text{CO}_2\text{C}_2\text{H}_5$ radical.



Below the glass transition temperature (-17°C) the rate of crosslinking is strongly depressed but chain scission exhibits little temperature dependence in this region.

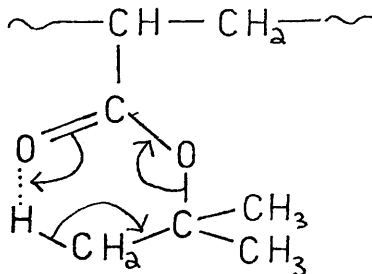
1.6. Photodegradation of Poly (tert-butyl acrylate)

Monahan²⁴ studied the photolysis (2537 \AA) of thin films of poly (tert-butyl acrylate) under 1 atmosphere pressure of helium in the temperature range $20-110^\circ\text{C}$. The major products of photolysis were found to be isobutene and poly (acrylic acid).



[$T_g = 69^\circ\text{C}$, M.P. = 262°C .]

Hydrogen, methane, propylene, isobutane, carbon dioxide, water, tert-butyl acrylate and acrylic acid were also identified in trace quantities. The reaction is initially first order with an intensity exponent of unity. A unimolecular first order decomposition was postulated with a six-membered transition state:



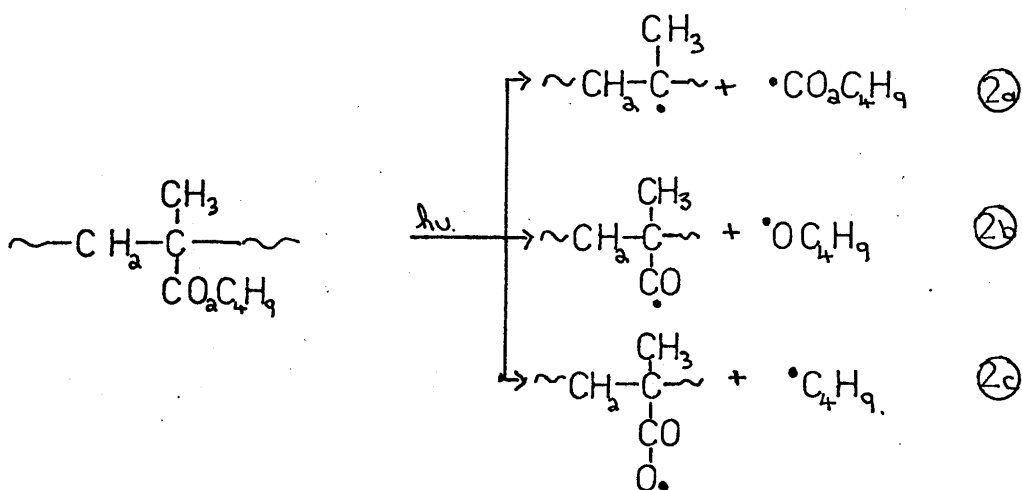
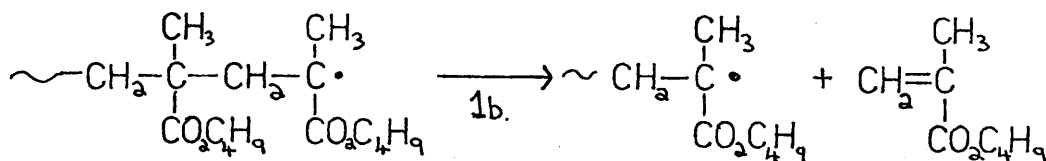
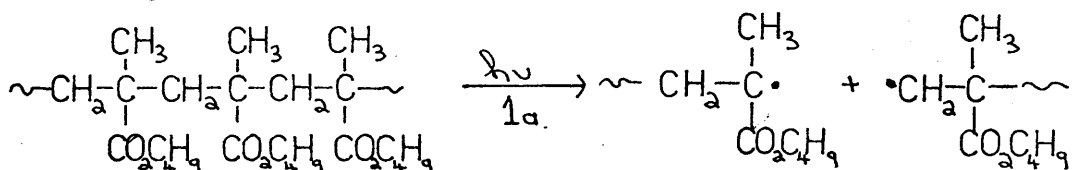
This concerted movement of electrons had previously been proposed by Grassie and Grant.²⁵ This type of molecular decomposition may be general for acrylate ester polymers containing β hydrogen atoms. Disproportionation of the tert-butyl radical to isobutene and isobutane was found to be negligible. This was thought to further support a molecular, rather than a radical mechanism.

1.7. Photodegradation of Poly (n-butyl methacrylate)

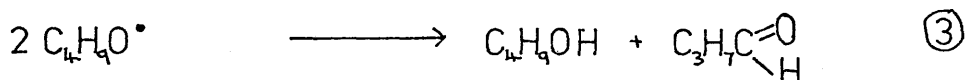
Isaacs and Fox²⁶ studied the photodegradation of poly (n-butyl methacrylate) films at 50°C and 100°C, in vacuum. At 100°C, the polymer loses 90 to 95 % of its original weight after about 30 hours exposure. About 4 % of insoluble polymer was formed during this process. At 50°C only about half as much poly (n-butyl methacrylate) was volatilised. After 60 hours exposure at 50°C, volatilisation had virtually ceased and about 25 % of the original material remained as an insoluble residue. Crosslinking therefore, decreased with increasing temperature since at the higher temperature depolymerisation was a competing process. The products of photolysis, identified by g.l.c., were carbon dioxide, n-butane, but-1-ene, n-butyraldehyde, n-butyl formate,

butanol-1, and n-butyl methacrylate. Thus in addition to monomer, almost every product was produced that could arise from the cleavage of bonds in the ester side chain. Monomer, n-butyl formate and but-1-ene accounted for about three quarters of the total volatile products. Increasing the temperature of degradation resulted in an increase in the in the relative yield of monomer, and except for but-1-ene, decreased the relative yields of the other products.

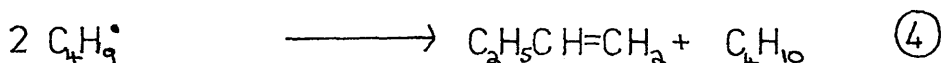
The volatile products of degradation were accounted for by the following reaction sequence.



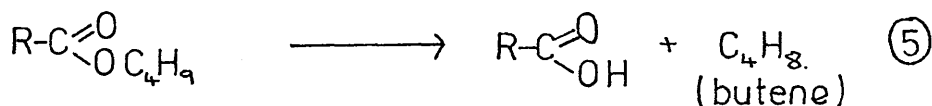
n-butyl formate, butanol-1, and n-butane can be produced by termination of the free radicals, produced by reaction (2), by hydrogen atoms abstracted from the polymer. The butoxy radical produced in reaction (2b) could disproportionate to yield butanol-1 and n-butyraldehyde.



The yields of these two products were approximately equal. The butyl radicals of reaction (2c) could yield but-1-ene and n-butane by disproportionation.

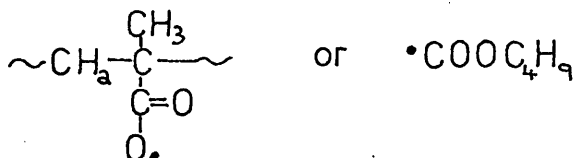


Borkowski and Ausloos²⁷ showed that but-1-ene can be produced by a direct photolytic process from non polymeric butyl esters.



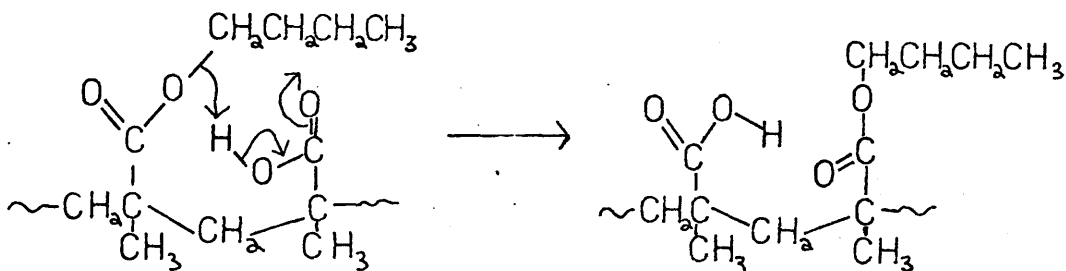
It was suggested that this process (5) of direct photolysis was more likely than reactions (2c) and (4) since much more but-1-ene than n-butane was found.

Carbon dioxide, which was a minor photolysis product, was thought to result from the radicals.



formed in reaction (2), or from the photolysis of acids formed by a reaction analogous to reaction (5).

Grassie and Mac Callum²⁸ made a comparison of the thermal and photo-initiated degradation (2537 Å) of poly n-butyl methacrylate. Both poly (n-butyl) and poly (t-butyl) methacrylate were completely converted to monomer under irradiation at 170°C, in vacuum. In the thermal degradation the n-butyl ester gave only 40% monomer and the tert-butyl ester gave mostly olefin (isobutylene), monomer yields being on the order of only 1 %. Preheating n-butyl methacrylate/methacrylic acid copolymers at 170°C. was found to inhibit the photo-degradation. It was suggested that in the methacrylate ester polymer, once an acid group formed it could migrate along the chain and encounter a second acid group resulting in anhydride formation. The acid migration can be formulated as



In a further study Mac Callum²⁹ showed that the photolysis of poly n-butyl methacrylate at 170°C. was unlike that of poly (methyl methacrylate) in that initiation can occur at random sites along the chain, since the rate of depolymerisation is unaffected by hydrogenation of the unsaturated chain end.

1.8. Photodegradation of Poly (ethyl methacrylate)

Recently MacCallum and Schoff³⁰ studied the photolysis of poly (ethyl methacrylate) and poly (methyl methacrylate) at temperatures above that of the glass transition. Poly (ethyl methacrylate) has a lower glass transition temperature (81°C.) than poly methyl methacrylate (105°C.) so that degradation was expected to be less complicated by diffusion effects. The mechanism was studied through the kinetics of the reaction rather than through the molecular weight changes. With the exception of a very small amount of information in a paper by Maxim and Kuist,³¹ no work other than by MacCallum³⁰ appears to have been undertaken on the photolysis of poly (ethyl methacrylate). Mac Callum and Schoff³⁰ found only monomer as a photolysis product. The order of reaction with respect to weight for both polymers was between 1.5-2.0, and both showed an intensity exponent of 1.0. It was concluded that the initial mechanism for both was random scission of the polymer main chain bonds followed by complete unzipping of the molecules, whereas Cowley and Melville⁷, on the basis of molecular weight data, proposed that the photolysis of poly(methylmethacrylate) occurred by end initiation.

1.9. Photodegradation of Copolymers of Methyl Methacrylate and Methyl Acrylate.

The photolysis of methyl methacrylate/methyl acrylate copolymers was studied at 170°C. in vacuum by Grassie, Torrance and Colford,^{32a} using

2537 Å radiation. Four copolymers with molar ratios, M.M.A./M.A., of 112/1, 26/1, 7.7/1, 2/1, were photodegraded and from molecular weight changes it was concluded that a random scission process occurs. No crosslinking was observed even in the 2/1 copolymer as the residual material was completely soluble. The pattern of volatile products was comparable with that produced in the purely thermal reaction³³, except that approximately one in ten of the methyl acrylate units was liberated as monomer, compared with one in four in the thermal reaction. As in the thermal reaction³³, the copolymers were stabilised, with respect to volatilisation, with increasing methyl acrylate content. The relationship between chain scission and volatilisation was linear, and it was concluded that, as in the thermal reaction, radicals are formed as a direct result of chain scission and that volatilisation occurs by depolymerisation of these radicals. The zip length of the photo reaction was very much greater than in the thermal reaction. Since the zip lengths decreased with increasing methyl acrylate content, it was deduced that the methyl acrylate units must block the depropagation reaction. This blocking action is not complete as small amounts of methyl acrylate monomer appear in the volatile products. The rate of chain scission is not strongly dependent upon the methyl acrylate content showing that chain scission does not occur preferentially at methyl acrylate units, but rather at random. In the thermal reaction a strict 1/1 ratio between carbon dioxide molecules produced and chain

scissions applied, but in the photo reaction a very much higher proportion of CO_2 was found.

Recently Grassie and Scotney³⁴ have been studying the photolysis of methyl methacrylate/methyl acrylate copolymer films at room temperature, using 2537 \AA radiation. Copolymers containing more than 50 mole % of methacrylate remain soluble. The rate of cross-linking decreases with decreasing acrylate content of the copolymers, and it was deduced that crosslinking is not associated with single acrylate units but requires sequences of at least two units. The rate of chain scission was found to decrease, as expected, with decreasing methacrylate content at high methacrylate content, and then surprisingly go through a minimum in the vicinity of 40-50 % methacrylate followed by a rapid increase as the methacrylate content decreased further, showing that the rate of scission in pure poly(methyl methacrylate) and pure poly(methyl acrylate) was of the same order. The photolysis products include hydrogen, carbon monoxide and dioxide, methane, methyl formate and methanol.

1.10. The Photodegradation of Copolymers of methyl methacrylate and Acrylonitrile.

Four methyl methacrylate/acrylonitrile copolymers with molar ratios 40/1, 40/1, 16/1 and 8/1 were photodegraded by Grassie and Farish³⁵ at 160°C . using light of wavelength 2537 \AA . Volatilisation resulted almost exclusively in the production of methyl methacrylate and a rapid

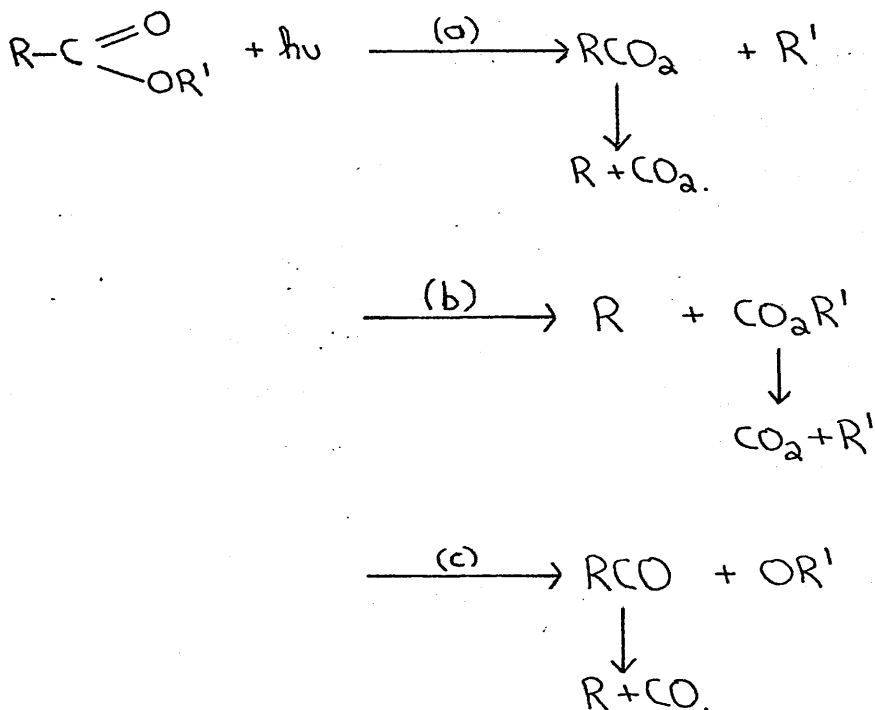
decrease in the molecular weight of the residue. Chain scission was found to be associated with acrylonitrile units, the rate of chain scission increasing with the acrylonitrile content of the copolymer.

It was proposed that radiation was absorbed by the nitrile groups resulting in a scission to radicals in the vicinity of the acrylonitrile units, followed by depolymerisation as far as the next acrylonitrile unit in the chain. Recombination of a proportion of the radicals was possible because of the extremely high viscosity of the medium.

The results of the purely thermally induced degradation of the same copolymer system at 280°C can be compared with the photoreaction at 160°C and the differences in overall characteristics accounted for in terms of three factors. Firstly, initiation in the photoreaction occurs at the acrylonitrile units and at random in the methyl methacrylate chain segments of the copolymer in the thermal process. Secondly, at the higher temperature, acrylonitrile units are more readily liberated in the depolymerisation process. Finally, the photoreaction is occurring in a medium of higher viscosity which restricts diffusion of long chain radicals thus making recombination easier.

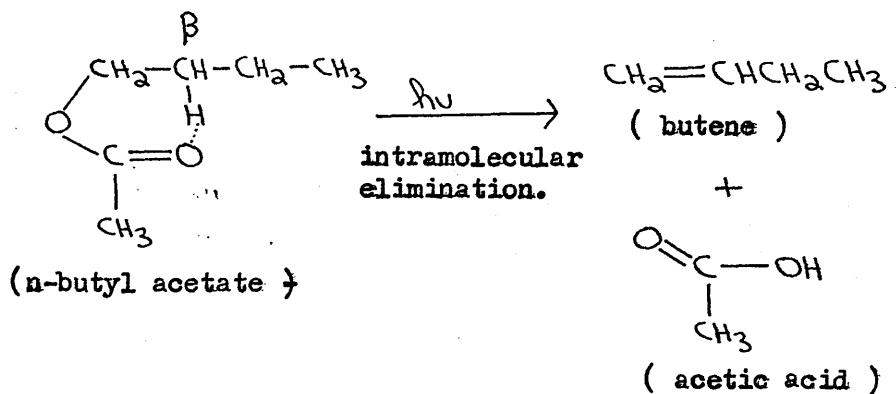
1.10. The Photodegradation of Non Polymeric Esters.

It has been shown that the excitation of the ester molecule results in three possible bond cleavages, involving the ester linkages, producing free radicals.^{3, 37-41.}

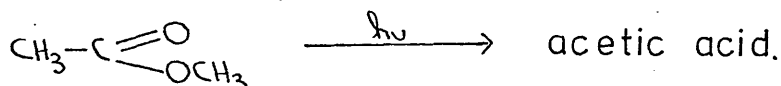


Since the decomposition of the radicals RCO_2 and $\text{CO}_2\text{R}'$ should be fast, processes (a) and (b) would be indistinguishable. The R and RO radicals have a higher activation energy for decomposition³ than the RCO_2 , $\text{CO}_2\text{R}'$ or RCO radicals and can react by routes other than decomposition after the primary act.

It is well established that³⁷⁻⁴⁰ esters containing one or more βH atoms in the alkyl group will decompose photochemically by intramolecular rearrangement into an olefin and the corresponding acid.



Isaacs and Fox²⁶ photolysed both n-butyl acetate and methyl acetate the latter having no βH in the alkyl group,



and found that acetic acid was a principal product of the photolysis.

It was concluded that the study was insufficient to elucidate the mechanism for the production of acid in ester photolysis.

Other minor products from the photolysis of n-butyl acetate were shown to be butyraldehyde, acetaldehyde, acetone, ethanol, butan-2-ol, n-butane, carbon dioxide, ethylene, carbon monoxide, methane, and other unidentified volatile products. Many of these products would result from secondary photolysis of the initial products which were not removed as they were formed.

Ausloos³⁷ studying the photolysis of a few simple alkyl esters in the liquid phase, found that carbon monoxide and dioxide were produced from all.

1.12. Thermal Degradation of Copolymers of Methyl Methacrylate
and n-Butyl Acrylate.

Grassie and Fortune⁴² studied the purely thermal degradation of copolymers of methyl methacrylate and n-butyl acrylate. The copolymers were prepared in bulk and thermal analysis techniques used included thermal volatilisation analysis (T.V.A.), thermogravimetric analysis (T.G.A.) and differential thermal analysis (D.T.A.). The copolymers became more stable to thermal breakdown as the acrylate content was increased. The liquid and gaseous degradation products, the chain fragments and residue were each examined by standard analytical techniques. The liquid degradation products were found to be methyl methacrylate, n-butyl acrylate, n-butanol, n-butyl methacrylate and residual toluene (solvent). The main gaseous products were carbon monoxide and but-1-ene, with traces of methane, ethane, ethylene, propane, propylene, butane and trans and cis but-2-enes. The non-condensable gases were hydrogen, carbon monoxide and methane, but no quantitative measurements were made on the permanent gases since their contribution to the total measured gas pressure was very small.

Using molecular weight data it was shown that as the acrylate content was increased breakdown by random scission became more important relative to breakdown by depolymerisation processes. Mechanisms were postulated to account for the formation of the major products, but the alcohol evolution mechanism was not satisfactorily explained.

1.13. The Title and Aim.

A detailed study of the purely thermal degradation of methyl methacrylate / n-butyl acrylate copolymers⁴² having been carried out it was thought interesting to study the photothermal reaction of this copolymer system as was previously done with the methyl methacrylate-methyl acrylate system.^{32,33} This would add to our knowledge of the degradation processes which occur in polymers and copolymers of methacrylate and acrylate and assist in assembling a more comprehensive and unified picture of the degradation processes which occur in that class of polymers. The term 'photothermal' degradation is used here to imply the photolysis of copolymers in a molten state but below the thermal degradation threshold. Copolymers covering the entire composition range were prepared and degraded photochemically at a temperature of 165°C. Table 1.1. shows the glass transition temperatures (T_g), melting points (M.P.) and thermal degradation threshold for each of the homopolymers.

Table 1.1.

Polymer	T_g °C.	M.P. °C.	Thermal Threshold °C.
poly M.M.A.	105 ⁴³	<160 ⁴³	270 ⁴²
poly n-Bu.A.	-54 ⁴³	47 ⁴³	300 ⁴⁴

This table demonstrates that it is reasonable to expect that if methacrylate - acrylate copolymers are subjected to irradiation at 165°C , they will be in a molten state yet below the thermal degradation threshold temperature. The polymers were degraded in the form of thin films (60-100mgs.) and the source of irradiation was a Hanovia 'Chromatolite' low pressure mercury lamp emitting light of wavelength 2537 \AA .

CHAPTER 2

EXPERIMENTAL TECHNIQUES AND APPARATUS.

2.1. Preparation of Copolymer Samples.

(a) Purification of methyl methacrylate and n-butyl acrylate monomers.

Methyl methacrylate (B.D.H. Limited) and n-butyl acrylate (Koch Light Laboratories) were washed three times with 5M sodium hydroxide to remove the inhibitor, and three times with distilled water to remove traces of alkali. The purified monomer was dried for 24 hours over calcium chloride, followed by 24 hours over freshly dried calcium hydride. Finally, the monomer was filtered into a reservoir containing some calcium hydride and stored, until required, in a refrigerator at -18°C . Before use they were degassed twice in a reservoir, attached to a vacuum system, by the usual freezing and thawing method. The first 5 per cent was distilled off and discarded, after which the required quantity was distilled into a graduated reservoir, and finally into the dilatometer.

(b) Purification of Initiator.

2,2' Azobisisobutyronitrile (Kodak Limited) was purified by recrystallisation from methanol (m.pt. 104°C .). The initiator was introduced into the dilatometer as a freshly prepared solution in Analar toluene, the solvent being removed on the vacuum line. The dilatometer was then pumped for several hours under a high vacuum, light being excluded to prevent the decomposition of the initiator.

(c) Preparation of Dilatometers.

Pyrex glass dilatometers of approximately 100 ml. capacity with a 5 ml. graduated stem, were washed with cleansing solution, distilled water, and finally Analar acetone, and attached to the vacuum line. The dilatometers were then flamed intermittently for several hours, prior to the addition of the initiator solution.

(d) Polymerisation.

After degassing and vacuum distillation, monomer mixtures of known composition were polymerised in bulk in dilatometers at $60^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$.

(Poly n-butyl acrylate homopolymer was polymerised in solution.)

The initiator concentrations are given in Table 2.1. Polymerisation was carried to 8 per cent where possible, but with copolymers of high acrylate content, polymerisation could only be carried to 3 or 4 per cent because of the high viscosity of the medium. For the calculation of the copolymer composition the reactivity ratios used were as follows.⁴⁵

$$r_1 (\text{M.M.A.}) = 1.80$$

$$r_2 (\text{nBu.A.}) = 0.37$$

All polymerisations were carried out in bulk at 60°C ., except for poly n-butyl acrylate homopolymer which was a solution polymerisation using n-butyl acetate (B.D.H. Limited) as solvent. In this case the polymerisation temperature was $40^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$.⁴⁴

TABLE 2.1.

Copolymer Composition and Molecular Weight Data.

Nominal Composition M.M.A./nBu.A.	Actual Composition (Mole %)		Initiator Conc. % Wt./Vol. Azobis isobutyronitrile	Molecular Weight
	M.M.A.	nBu.A.		
P.M.M.A. Homopolymer	100	—	0.17	389,000
100/1	99.01	0.99	0.17	260,000
25/1	96.1	3.9	0.17	347,000
5/1	83.7	16.3	0.042	1,330,000
1/1	50	50	0.084	230,000
1/1	50	50	0.042	1,000,000
1/5	17.8	82.2	0.084	506,000
1/15	6.6	93.4	0.002	1,410,000
P.nBu.A. Homopolymer	—	100.	0.11 ←	2,800,000
			Solution Polymerisation	

(e) Copolymer Recovery and Purification.

Copolymers were dissolved in Analar toluene and precipitated by running the solution slowly into 5 litres of Analar methanol, with constant stirring. This procedure was repeated three times. Those with a high methacrylate content precipitated as a fine powder, while acrylate rich samples were produced as rubbery solids. All the polymers were freeze-dried from solution in benzene.

In addition to the seven copolymers covering the whole composition range, a methyl methacrylate homopolymer was synthesised. A homopolymer of n-butyl acrylate was also available,⁴⁴ prepared by solution polymerisation so that it was possible to examine the degradative behaviour of the entire composition range.

2.2. Degradation Apparatus.

Photochemical degradation must be carried out in a silica vessel which is transparent to the ultraviolet light. The disposition of the photolysis cell is shown in Fig. 2.1. The two halves of the cell are joined by a ground glass joint.

(a) Temperature Control.

The photolysis cell was heated to the required temperature (165°C) by means of a Woods metal bath controlled by a proportional temperature controller and an isolating transformer.⁴⁵

When the reaction vessel was immersed to a depth of half an inch, a temperature control of $\pm 0.5^{\circ}\text{C}$. was attained inside the vessel for

FIG. 21. PHOTOLYSIS CELL AND METHOD OF ANALYSIS.

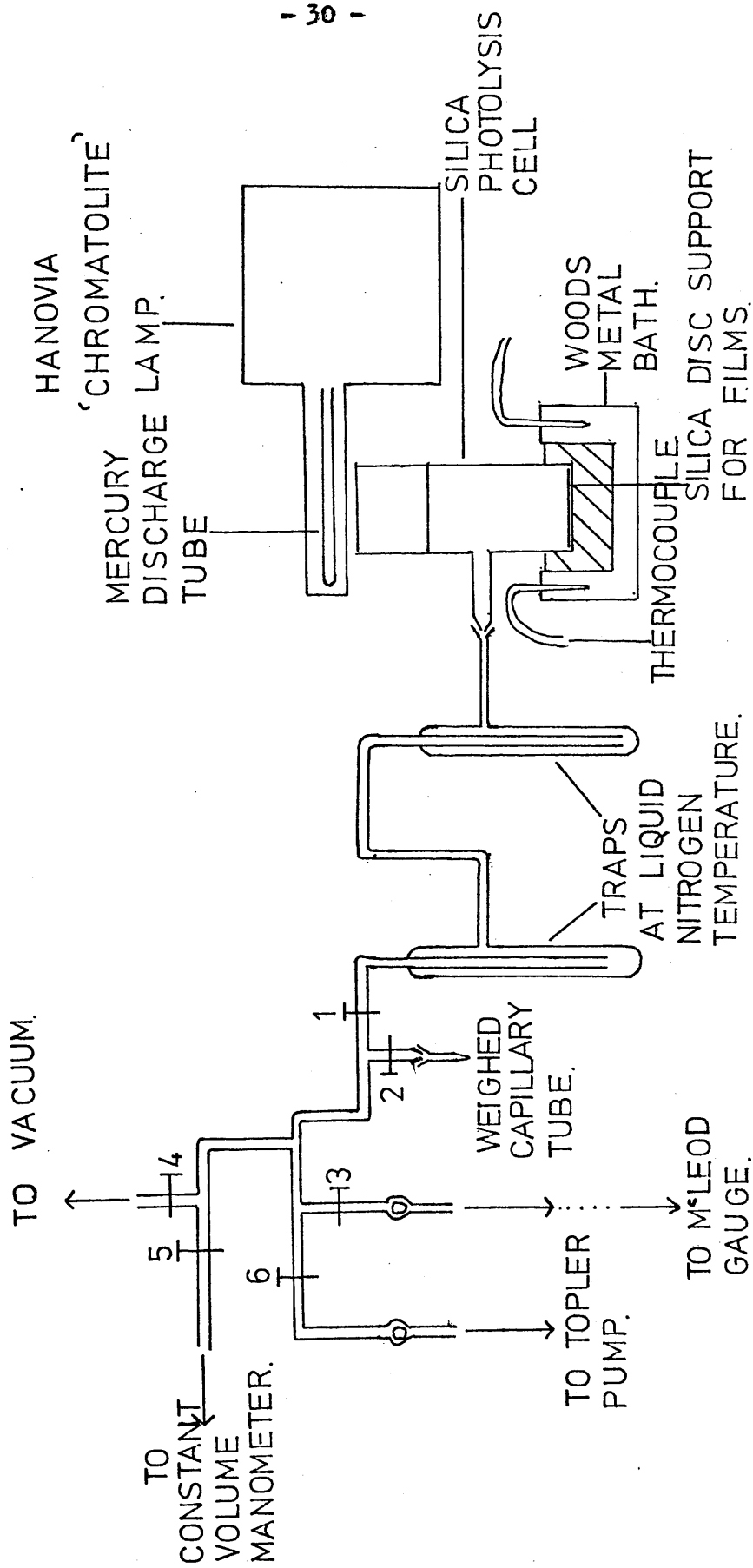
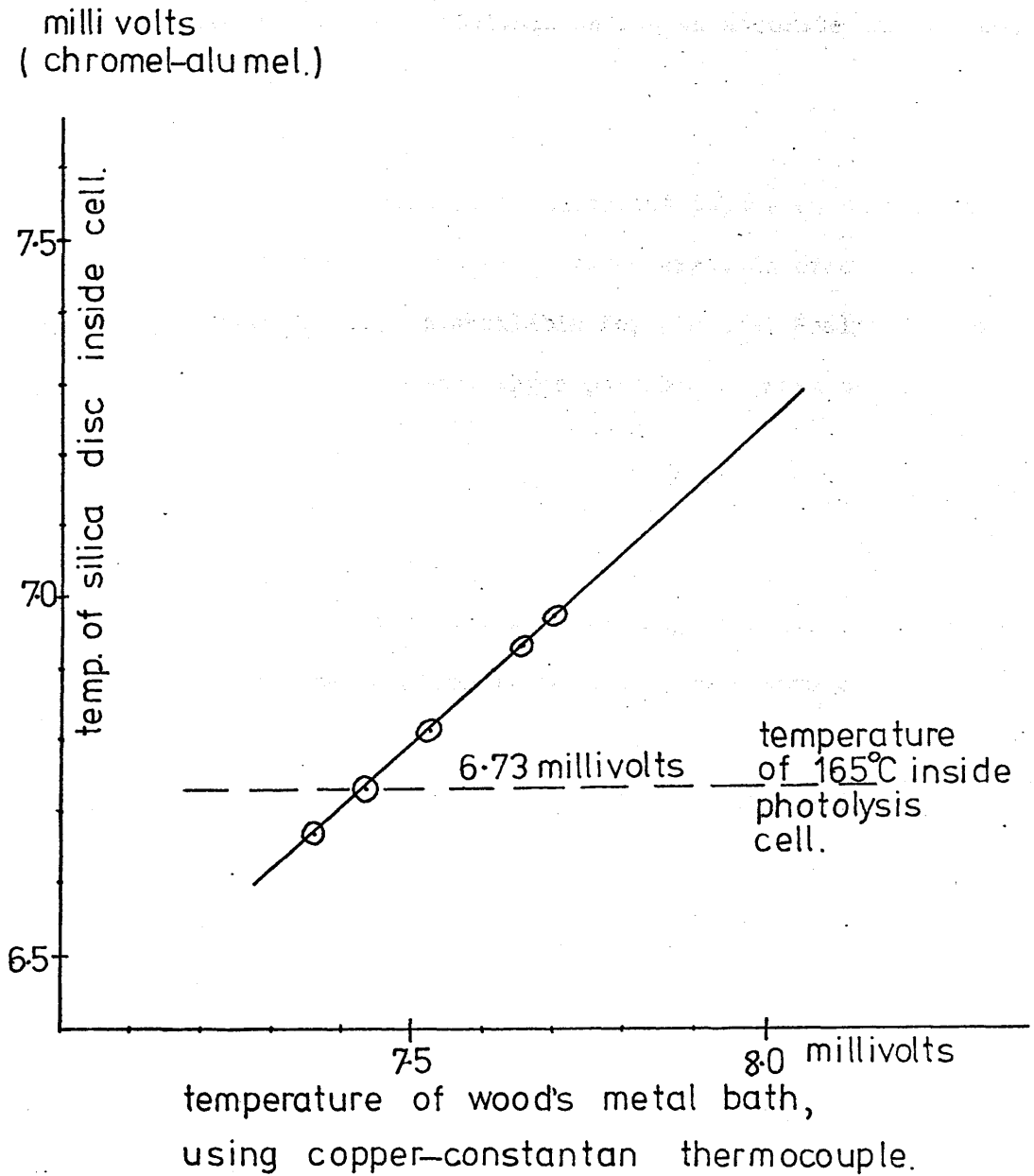


FIG. 2.2. CALIBRATION OF TEMPERATURE.



long operating periods. The inside temperature was calibrated using a copper-constantan thermocouple to record the temperature of the Woods metal bath, and a chromel-alumel thermocouple to record the temperature of the silica disc inside the photolysis cell. An accurate calibration was attained as shown in Fig. 2.2.

2.3. Polymer Form.

In photodegradation studies it is important to use as thin films of polymer as possible but to expose a maximum area, in order that, as much material as possible may be available for chemical analysis. In choosing a suitable film thickness, three possible sources of error must be considered.

- a. Rates of diffusion of volatile products for the degrading polymer.
- b. Temperature gradient in the polymer.
- c. A skin effect such that the radiation is completely absorbed in the surface layers so that the reaction is not homogenous throughout the polymer.

It is to be expected that the use of powdered polymer would result in conflicting and erratic results on account of the large number of uncontrollable variables associated with such a system, for example surface area of the powder, particle size, layer thickness and so on.

(a) Preparation of Films

Several standard methods are available for preparing polymer films, for example, melting, moulding, pressing, etc., but each suffers from

the disadvantage that the polymer may become partially degraded, or oxidised during the formation of the film.

Alternatively, the homopolymers and copolymers were dissolved in Analar benzene and an aliquot (calculated to produce a film thickness of 100μ) was allowed to evaporate on an optically flat silica disc. The disc and film were then placed in a vacuum oven at 40°C . for 16 hours to remove residual solvent. The silica disc which supported the film was then placed inside the photolysis reaction cell. The average weight of the polymer films was 0.085 - 0.100 gms.

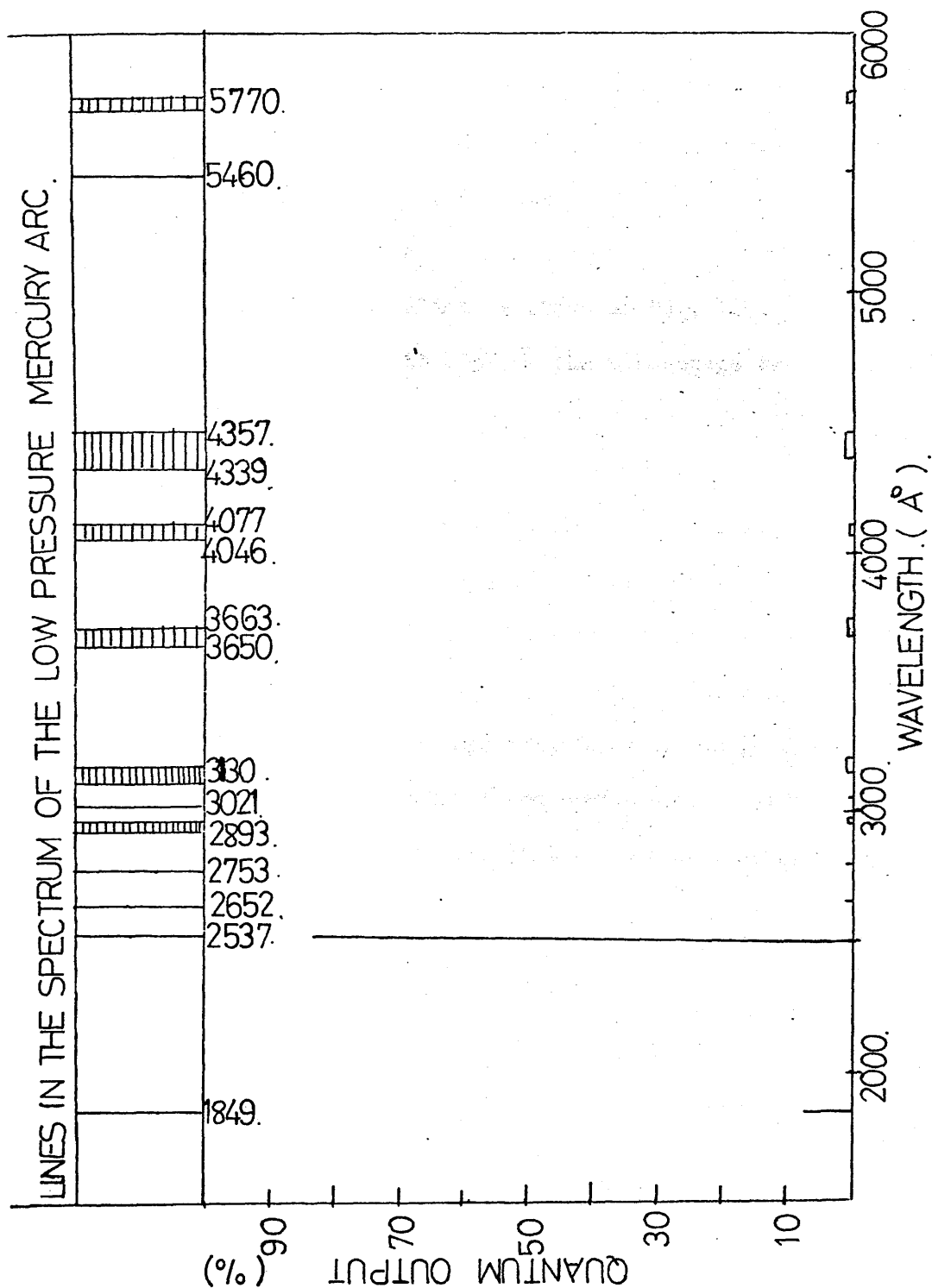
2.4. Source of Radiation.

A Hanovia 'Chromatolite' low pressure mercury resonance lamp was used as shown in Fig. 2.1. This produces a typical mercury emission spectrum, the intensities of the two resonance lines at 184.9 \AA and 2537 \AA being very much greater than those of all the other wavelengths present. The output of this lamp is shown in Fig. 2.3. The mercury discharge tube was placed directly above the cell, at a distance of 18 cm. from the polymer film. The lamp was connected to a LTH Transistorised 1kVA Voltage Regulator which ensured that any variations in the mains output did not affect the lamp emission.

2.5. Transmission of the Ultraviolet Radiation.

(a) Introduction.

The output of the lamp transversed 3 cm. of air, 2 mm. of fused silica and 15 cm. of vacuum inside the photolysis cell before finally



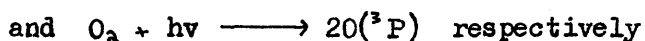
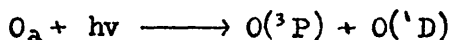
impinging on the films. The nature of the radiation eventually reaching the film was modified to some extent by the absorbing characteristics of silica and air media, and it is therefore worthwhile to examine these characteristics.

(b) Transmission By Fused Silica.

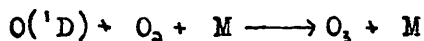
The transmission of fused silica is shown in Fig. 2.4. This shows that for light of wavelength 2537 \AA , the percentage transmission is 86 per cent.

(c) Transmission by Air.

The only component in air which is capable of absorbing the ultraviolet radiation produced is oxygen, the other constituents being completely transparent in this region of spectrum. The oxygen absorption spectrum consists of two sets of bands, the one system converging at 2400 \AA , and the more important Schumann-Runge system having a threshold wavelength at 2000 \AA and converging towards 1761 \AA .⁴⁷ These two absorptions correspond to two photo-dissociations of oxygen molecules,



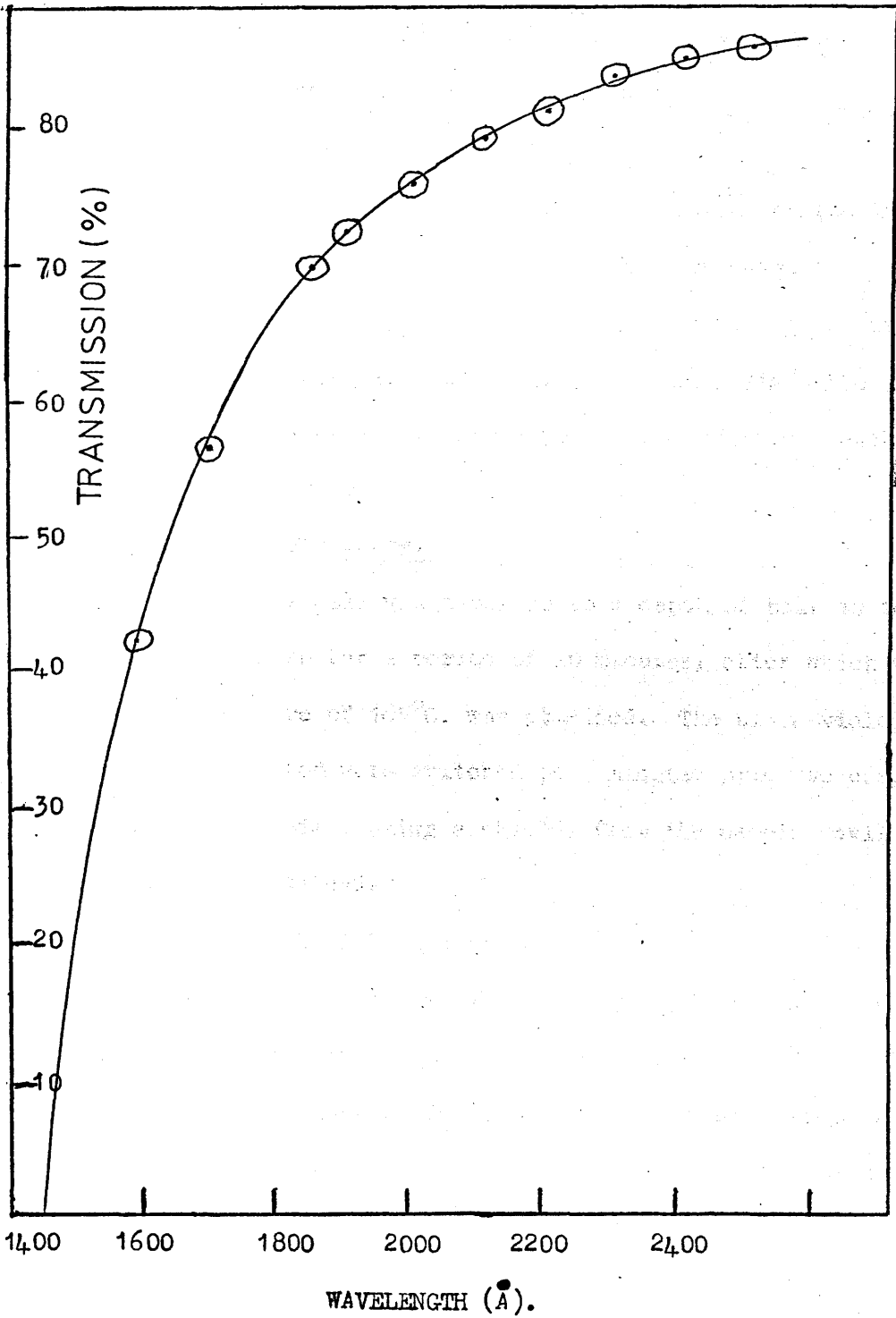
Ozone is produced concurrently according to the equations,



M is the necessary third body.

FIG. 2.4.

ABSORPTION SPECTRUM OF FUSED SILICA(2mm.).



It is obvious then that only the 1849 \AA line has an energy associated with it which exceeds the threshold energy for the photo-dissociation of oxygen. This line is thus absorbed by the air, and only 1 cm. of air is sufficient to absorb it completely.⁴⁸

(d) Monochromaticity of the Source.

Fig. 2.3. shows that 93 per cent of the output of the lamp is composed of the mercury resonance radiation with wavelengths of 1849 \AA and 2537 \AA . The intensity of the former is reduced to an extremely low value in traversing the arc to polymer path. Since the intensities of the longer wavelengths are negligible, the radiation reaching the polymer is virtually monochromatic (2537 \AA)

2.6. Experimental Procedure.

The photolysis cell was immersed to a depth of half an inch in the Woods metal bath for a period of 20 minutes, after which time the required temperature of 165°C . was attained. The ultra-violet lamp and voltage regulator were switched on 5 minutes prior to use, and the radiation was excluded, using a shield, from the sample until the temperature was attained.

2.7. Molecular Weight Determination.

An important part of any polymer investigation must be the study of the molecular weight changes with period of degradation. The osmotic pressure method, leading directly to number average molecular weights has been particularly valuable in degradation experiments and

two types of osmometers were used covering different molecular weight ranges.

(a) Vapour Pressure Osmometer. (Hewlett-Packard Inc.)

Operation of this instrument depends upon the difference in resistance (ΔR) between two thermistor beads when one is coated with solvent and the other with polymer solution in an atmosphere saturated with solvent vapour. The thermistor probe, extending into the sample chamber, carries the two small thermistor beads. The sample chamber is saturated with the solvent by filling the solvent cup. A drop of solution is applied to one of the beads, and the corresponding change in resistance, ΔR , is measured as a function of time. After several minutes a stationary state is reached. Four of the six syringes can be used to apply the solution so that measurements at four concentrations can be made successively and the results extrapolated to zero concentration.^{49,50.}

Provided that the temperature is kept constant, the resistance depends on the vapour pressure round the bead, which in turn, depends on the number of solute molecules per unit weight of solvent (n).

$$\Delta R \propto n$$

But, $n \propto \frac{C}{\overline{M}_n}$ where C is concentration in gm./100 gm. solvent

and \overline{M}_n is the number average molecular weight.

$$\therefore \overline{M}_n = \frac{Kc}{\Delta R} \text{ where } K \text{ is a constant.}$$

The value of $\frac{\Delta R}{C}$ used is that at infinite dilution, obtained by extrapolation, since interactions between polymer molecules is significant even at low concentrations.

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

(b) Membrane Osmometer.

The instrument used was a Hewlett-Packard High Speed Membrane Osmometer, Model 501 using Membranes Cellophane 300. The basic equation relating osmotic pressure to number average molecular weight, \overline{M}_n , is the expression of van't Hoff,

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

where R and T have the usual significance.

The molecular weight was obtained by measuring the osmotic pressure of solutions of the polymers of different concentrations, and by plotting $\left(\frac{\pi}{c}\right)$ versus c

c = conc. of polymer, gm./100 gm.

π = osmotic pressure.

This leads to a straight line from which $\left(\frac{\pi}{c}\right)_0$ may be obtained by extrapolation to infinite dilution. A simple conversion factor⁵¹ 2.53×10^5

$\left(\frac{\pi}{c}\right)_0$ gave the molecular weight directly from $\left(\frac{\pi}{c}\right)_0$.

A typical plot of osmometer data is shown in Fig. 2.5.

2.8. PRODUCT ANALYSIS

(a) Introduction.

In this work the terms 'liquid condensibles', 'permanent gases', and 'cold ring' (short chain fragments) are used to distinguish between the different classes of products. The permanent gases were found to be present in only very small quantities.

For the analysis of the degradation products the silica degradation cell was linked to two small traps at liquid nitrogen temperature, and the copolymer film (100 mgs.) was irradiated at 165°C. for the required time, in vacuum. The liquid products retained in the traps at liquid nitrogen temperature were either distilled into an infra-red cell or condensed into a previously weighed capillary and stored at -18°C. until required. The cold ring formed on the sides and window of the photolysis cell. This was dissolved in Analar chloroform and after evaporation of the solvent on a salt plate, an infra-red spectrum was obtained.

To obtain samples of the permanent gases, the traps were maintained at liquid nitrogen temperature, and the products remaining gaseous, were collected in a sample bulb using a Topley pump. By weighing the silica supporting disc alone and the disc plus the film before and after irradiation, it was possible to calculate the percentage weight loss. The residue remaining on the silica disc was dissolved in toluene and the molecular weight obtained.

(b) SPECTROSCOPIC MEASUREMENTS.

(1) Infra-red.

Infra-red spectra of the condensibles were obtained on a Perkin Elmer 257 Grating Infra-red Spectrophotometer. I.R. spectra of the copolymers and residue were obtained using the Perkin Elmer 225 and 257 spectrometers. The residue was run as a film deposited on a sodium chloride disc from chloroform solution, or by grinding the residue with dry KBr and pressing out a disc.

(2) U.V. Analysis of the Residue.

A Unicam S.P.800 Spectrophotometer was used with the polymer supported by the optically flat silica disc.

(c) GAS LIQUID CHROMATOGRAPHY

G.L.C. data was obtained using a Microtek G.C. 2000R Research Gas Chromatograph equipped with dual columns, flame ionisation detector with isothermal and linear temperature programming. A modified Gallenkamp chromatograph, with a thermal conductivity detector, was used for the analysis of the permanent gases. A list of the columns employed is given in Table 2.2. The 5% D.N.P., 5% B34. column proved to be most effective in separating the liquid products.

TABLE 2.2.

COLUMN	PROGRAMME	USE	DETECTOR
10 ft. $\frac{1}{4}$ inch diameter, 5% D.N.P. 5% B.34. on 100-120 mesh embacel.	Isothermal at 60°C, then Isothermal at 80°C.	Separation of all the liquid products.	Flame ionization
10 ft. $\frac{1}{4}$ inch diameter. 1% S.E.30. on 100-120 mesh embacel. (S.E.30 is a silicone gum.)	Isothermal at 40°C., then programme at 10°C/min. to 250°C.	Liquid volatiles	Flame ionization
10 ft. $\frac{1}{4}$ inch diameter 10% D.N.P. on 100-120 mesh embacel.	Isothermal at 80°C.	Liquid volatiles	Flame ionization
20 ft. $\frac{1}{4}$ inch diameter 30-60 mesh silica gel.	Isothermal at room temperature	Permanent gases.	Thermal conductivity

typical plot of osmometer
data.

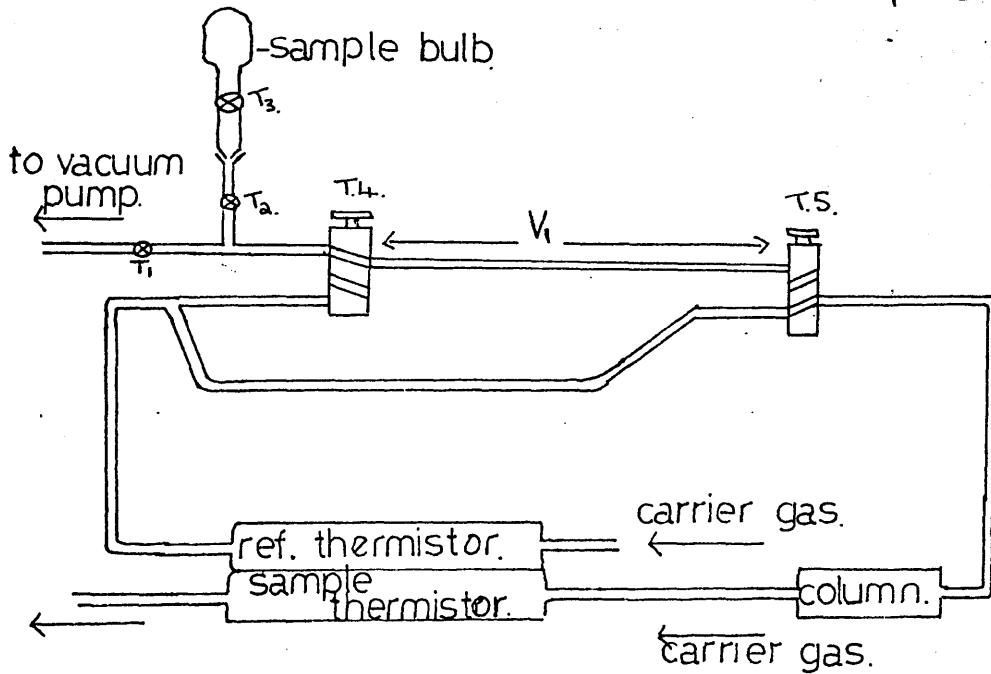
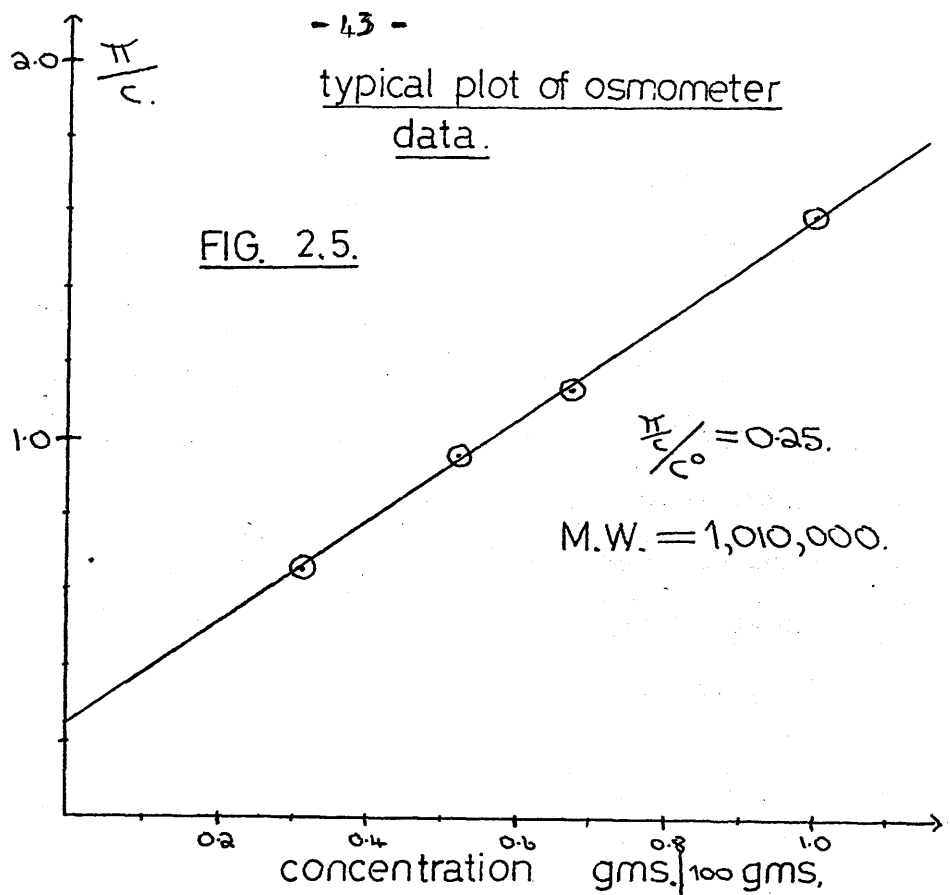


FIG.2.6. Inlet system and schematic diagram
of thermal conductivity G.L.C.

(d.) PERMANENT GAS SAMPLING APPARATUS

The gases were first introduced into the sample bulb using a Topley pump with the traps at liquid nitrogen temperature. The sampling system shown in Fig. 2.6. was constructed so that air could be excluded. The sample bulb was attached to the socket with taps T_1 and T_2 open and taps T_4 and T_5 set as shown. The argon carrier gas thus by-passes the volume V_1 . This volume was filled with gas by closing tap T_1 and opening tap T_2 and T_3 . By shutting T_2 and reversing the positions of T_4 and T_5 the sample was carried to the detector.

(e.) QUANTITATIVE GAS-LIQUID CHROMATOGRAPHY.

An internal standard (cyclohexane) was chosen which did not coincide with the retention time of any constituent. A known weight of this standard was added to a weighed quantity of liquid degradation product, and a g.l.c. trace was obtained. Pure samples of each product and the standard were mixed in known amounts and run on the chromatograph indicating the sensitivity of each product relative to the internal standard. Since the peak area of a product is proportional to its weight, the peak areas of each component were measured by planimetry. 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 Y by weight is given by

$$\%Y = \frac{\text{peak area of } Y}{\text{peak area of standard}} \left(\frac{100}{\frac{\text{wt. of sample}}{\text{wt. of standard}}} \right) \left(\frac{1}{k} \right)$$

(f) COMBINED GAS CHROMATOGRAPHY - MASS SPECTROMETRY.

Until recently, the standard method of analysing complex organic mixtures has been to separate the components by chromatography, to collect each product and analyse it by the normal techniques of I.R., U.V., and N.M.R. to supplement the retention time data from the gas chromatograph. The small samples obtained from degradation experiments very often made it necessary for products from several runs to be combined to give enough of a single component for analysis. The combination of gas chromatography with mass spectrometry has eliminated much of the tedious separation and collection of components.

The instrument used was an L.K.B. 9000 (L.K.B. - Produkter, Stockholm). A block diagram is shown in Fig. 2.7. The chromatographic system consists of a heated inlet and a coiled glass column in an oven which can be operated isothermally or temperature programmed from 1°C to 15°C. per minute up to a temperature of 300°C.

Provided that suitable columns are available to separate the degradation products, this instrument has great potential in polymer degradation.

(g) PRESSURE MEASUREMENT.

Two pressure measuring devices, a constant volume manometer and a McLeod gauge for use in different pressure ranges were attached to the vacuum line. Since the actual pressure of gases found after degradation were negligible no detailed pressure measurements were undertaken.

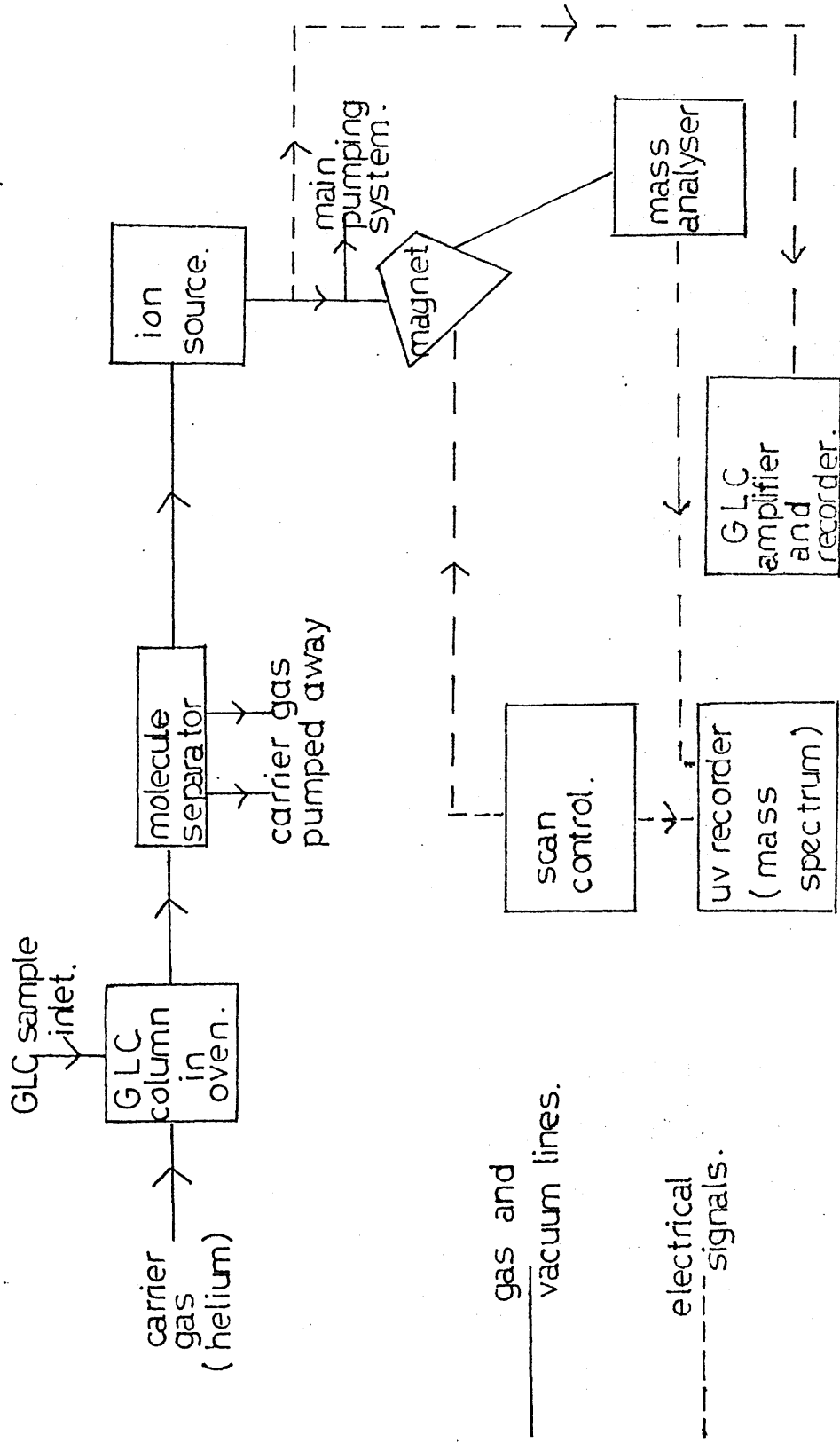


FIG. 27. LKB 9000 GAS CHROMATOGRAPH—MASS SPECTROMETER.

(block diagram of main components.)

2.9. SOL-GEL ANALYSIS.

The residue obtained from copolymers of high acrylate content was found to be partially insoluble in organic solvents such as benzene or toluene. This meant that molecular weight measurements of the residue by osmometry were meaningless. Sol-gel analysis was carried out on this residue using a Soxhlet extractor. Degradations were carried out, as usual, with the film supported on the silica disc. The residue on the disc was weighed and placed in a weighed glass sinter. The whole assembly was then positioned in a Soxhlet extractor such that the solvent could wash, and drain easily from, the disc and residue. Analar benzene (b.pt. $80^{\circ}\text{C}.$) was used as the solvent and the extraction time was twenty four hours. After extracting the soluble portion of the residue, the glass sinter, residue and disc was dried in a vacuum oven at $60^{\circ}\text{C}.$ for four hours, and after cooling was accurately reweighed. The difference in the total weight of sinter, disc and residue, before and after extraction gives the weight of the soluble residue. This weight could also be determined by distilling off benzene from the solvent reservoir after extraction, and determining the concentration of a known volume of this solution. Knowing the weight of the soluble residue extracted, and the initial weight of the residue on the disc, the weight of insoluble material was obtained.

CHAPTER 3.

3.1. PRELIMINARY OBSERVATIONS.

It is proposed to study the degradation initiated by 2537 Å. radiation, of copolymers covering the whole composition range. In order to facilitate the removal of volatile products and to minimise complicating secondary processes the reactions were carried out under vacuum at 165°C. This temperature was chosen because it was well above the melting point of the copolymers, yet, as shown by the thermogravimetric analysis traces, well below the onset of thermal degradation.

Before finally settling upon this temperature it was important to discover if diffusion effects were present. Fig. 3.1. shows the percentage volatilisation, for a given period of time, as the weight (and thickness) of the copolymer was varied between 45 mgs. and 127 mgs. This demonstrates that the diffusion of low molecular weight products must be rapid from all parts of the film, and thus that the rate of volatilisation is independent of polymer thickness.

In the purely thermal degradation, ^{4a}n-butyl acrylate has a strong inhibiting effect on the unzipping reaction in poly (methyl methacrylate). Fig. 3.2. shows the change in percentage volatilisation per hour, upon photolysis, as the methacrylate content of the copolymer is increased. This figure demonstrates that the rate of volatilisation in photodegradation only becomes appreciable when the methacrylate content of the copolymer is greater than 50 per cent.

FIG. 3.1. ⁻⁴⁹⁻ %VOLATILISATION versus WEIGHT.

(for a 50 mole% n butyl acrylate copolymer
degraded $4\frac{1}{2}$ hours, at 165°C .)

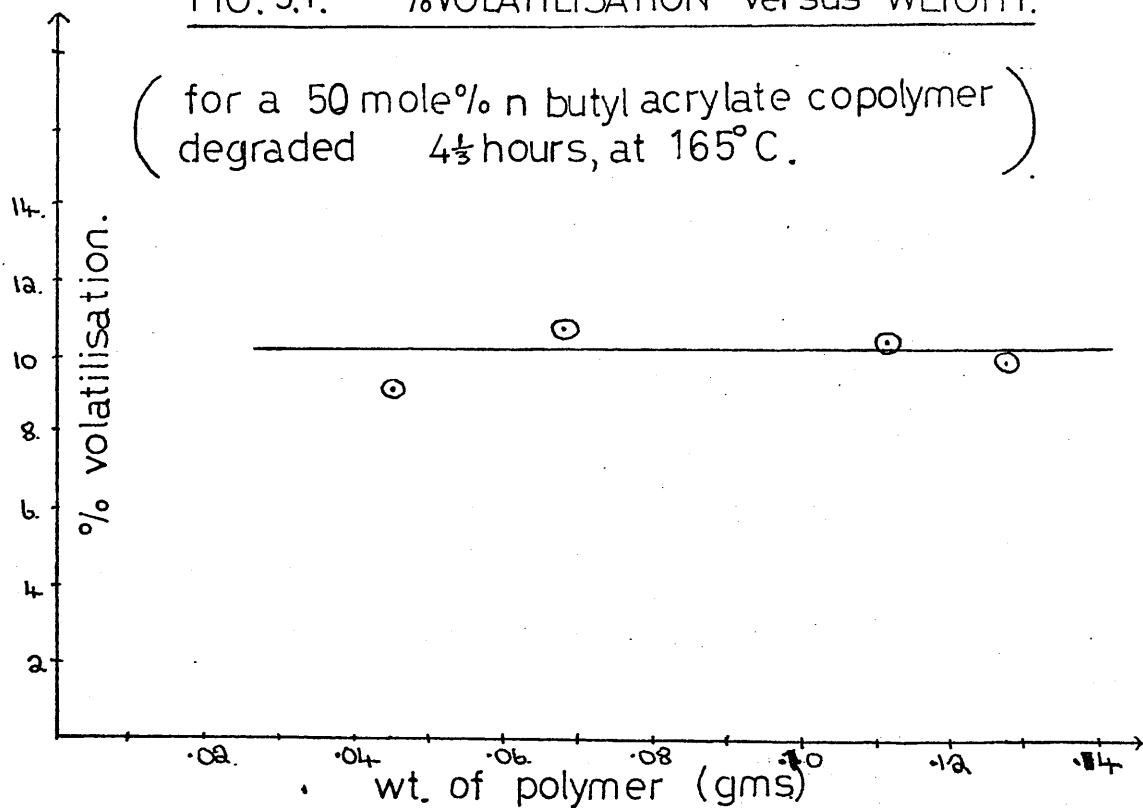


FIG. 3.2.

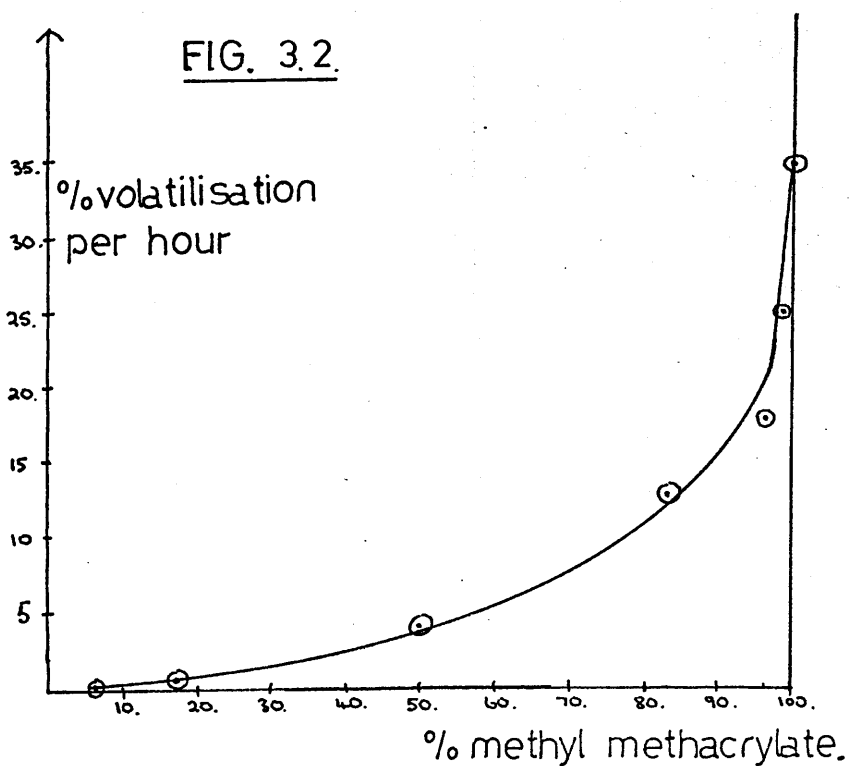


TABLE 3.1. (Results for Fig. 3.1.)

% Volatilisation after $4\frac{1}{3}$ hrs.	1/1 Copolymer Weight.
9.27	.0453
10.90	.0680
10.61	.1112
10.02	.1278

TABLE 3.2. (Results for Fig. 3.2.)

% M.M.A.	% Volatilisation per hour.
100.0	35
99.01	25
96.1	18
83.7	13
50.0	4
17.8	1
6.6	0.4.

3.2. DETERMINATION OF ABSOLUTE NUMBERS OF QUANTA PRODUCED BY THE LAMP.

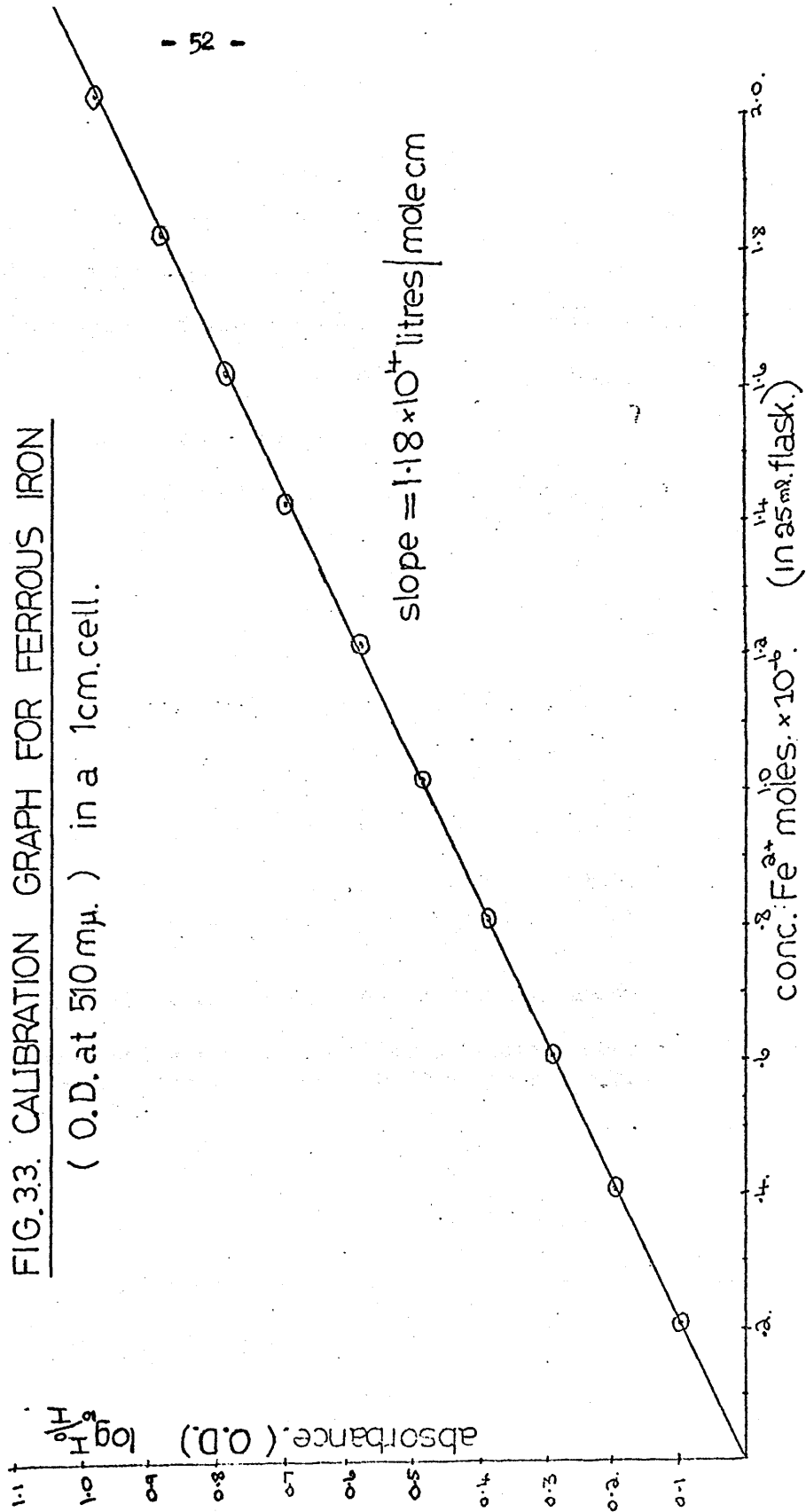
In order to calculate the quantum yields of products the absolute numbers of quanta produced by the lamp must be known. This can be done using the potassium ferrioxalate solution-phase chemical actinometer developed by Parker and Hatchard^{5a} which is simple to use and very sensitive over a wide range of wavelengths.

It is based on the fact that when sulphuric acid solutions of $K_3Fe(C_2O_4)_3$ are irradiated with light of wavelength 2500-5770 Å, the iron is reduced to the ferrous state and the oxalate ion is oxidised. After irradiation, the ferrous ion can be converted into the red-coloured 1,10 phenanthroline - Fe^{2+} complex which is highly absorbing and easily analyzable.

d) EXPERIMENTAL PROCEDURE.

Solid green crystals of $K_3Fe(C_2O_4)_3$ were prepared as described by Parker and Hatchard^{5a}, and Calvert and Pitts³, the latter gives a fully detailed summary of the procedure. A 0.006 M solution, acidified with H_2SO_4 , was prepared. The manipulations and preparation of the ferrioxalate solutions were carried out in a dark room. A standard calibration graph for the analysis of the Fe^{2+} complex was prepared, as shown in Fig. 3.3., using a Hitachi Perkin Elmer 139 U.V. -Vis. Spectrophotometer.

The light intensity in the photolysis cell was determined by irradiating 15 mls. of the ferrioxalate solution (V_1), in a current of



oxygen free nitrogen gas, for a time of 60 secs. After mixing the solution, 10 mls. (V_a) was pipetted into a 25 ml. volumetric flask (V_3), and the phenanthroline complex prepared, along with an identical blank solution using unirradiated actinometer solution. The transmission of the complex solution was measured at $5100 \text{ \AA}.$ in a 1 cm. cell using the blank solution in the reference beam.

The number of Fe^{2+} ions formed during the photolysis ($n_{\text{Fe}^{2+}}$) was calculated using the formula,

$$n_{\text{Fe}^{2+}} = \frac{6.023 \times 10^{20} V_1 V_3 \log\left(\frac{I_0}{I}\right)}{V_a \epsilon} \dots\dots\dots (1)$$

where V_1 = Volume of actinometer solution irradiated (mls.)

V_a = Volume of aliquot taken for analysis (mls.)

V_3 = Final volume to which the aliquot V_a is diluted (mls.)

$\log_{10} \frac{I_0}{I}$ = the measured optical density of the solution at $5100 \text{ \AA}.$
(the 'difference' O.D. between unexposed and irradiated solutions)

l = the path length of the spectrophotometer cell used (cm.)

ϵ = the experimental value of the molar extinction coefficient of the Fe^{2+} complex as determined from the slope of the calibration plot.

The average 'difference' optical density = 0.167.

\therefore the number of Fe^{2+} ions formed = 3.196×10^{17}

The intensity of the light beam incident, I_0^i was calculated from³

$$I_0^i = \frac{n_{\text{Fe}^{2+}}}{\Phi_{\text{Fe}^{2+}} (1 - 10^{-\epsilon l c})} \text{ quanta/sec.} \dots\dots\dots (2)$$

where $\Phi_{Fe^{2+}}$ is the quantum yield of product Fe^{2+} (this was accurately known for 2537 Å. $\Phi_{Fe^{2+}} = 1.25$)

t = time of exposure (sec.)

$$\left(1 - \frac{I}{I_0}\right) = [1 - 10^{-\epsilon[A]t}] = \text{fraction of incident light absorbed.}$$

Using equation (2), $I_0 = 4.26 \times 10^{15}$ quanta/sec.

\therefore Intensity of light beam = 4.26×10^{15} quanta/sec.

CHAPTER 4.

IDENTIFICATION OF PHOTOLYSIS PRODUCTS.

4.1. INTRODUCTION

Before a quantitative study of the photolysis products can be undertaken it is necessary to identify each component using more than one technique if possible. The degradations were carried out in the photolysis cell at 165°C. as described.

4.2. ANALYSIS OF THE LIQUID CONDENSIBLES.

(a) Infra-red

The liquid condensibles were passed into the I.R. cell as described in section 2.8.a. Four copolymers were degraded in the form of films (100 mgs.) cast from a benzene solution and Figs. 4.1. - 4.4. show the relevant details of the spectra obtained

(b) Interpretation of spectra.

Fig. 4.1. (0.99 mole % n-butyl acrylate copolymer) shows the total degradation products after 22 hours irradiated at 165°C.

FREQUENCY	COMMENT
Absorptions between 700 cm^{-1} -650 cm^{-1}	These sharp, well defined, triplet peaks are easily identified as being the C-H out of plane bonding vibrations of benzene.
1750 cm^{-1}	C=O stretching mode.
1644 cm^{-1}	C=C " "
Peaks 3000 cm^{-1} -2900 cm^{-1}	C-H stretch of -CH ₃ or CH
2855 cm^{-1}	C-H stretch of -O-CH ₃
Peaks 3150 cm^{-1} -3000 cm^{-1}	=C-H
2135 cm^{-1}	Ketene.

Fig. 4.2. (16.3 mole % n-butyl acrylate copolymer) shows the total products after 23 hours.

This infra-red spectrum is identical to Fig.4.1.

Fig. 4.3. (50 mole % n-butyl acrylate copolymer) shows the total products after 23 hours. This spectrum is similar to Figs.4.1. and4.2., except that the C-H bonding and C-O stretching modes in the region 1500 cm^{-1} — 1000 cm^{-1} are shown. These were also present in the original spectra from which Figs.4.1. and4.2. were reproduced.

Fig. 4.4. (82.2 mole % n-butyl acrylate copolymer) shows the total products after 48 hours irradiation. The spectrum shows similar features to the others, and the obvious reduction in quantity of volatiles is evident.

The results indicate that the films, although preheated in a vacuum oven at 40°C . for 16 hours prior to irradiation, must contain residual solvent (benzene). The spectra suggest that the major fraction of the products is monomer, either methyl methacrylate or n-butyl acrylate. Infra-red spectra were obtained of the two monomers and they showed absorptions identical to those in Figs. 4.1. - 4.4.

The absorption at 2138 cm^{-1} was interesting. The presence of $\text{C}\equiv\text{C}$ stretch would give rise to an absorption around 2140 cm^{-1} — 2100 cm^{-1} . If the structure were $\text{H}-\text{C}\equiv\text{C}-$, a peak at $3,300\text{ cm}^{-1}$ due to C-H stretching would appear. No such absorption was evident. Hence, if this absorption at 2138 cm^{-1} is an alkyne it can only arise from $\text{R}-\text{C}\equiv\text{C}-\text{R}$,

FIG 4.1. I.R. OF LIQUID VOLATILES FROM A 0.99 MOLE % N-BUTYL ACRYLATE
COPOLYMER DEGRADED FOR 22 HOURS.

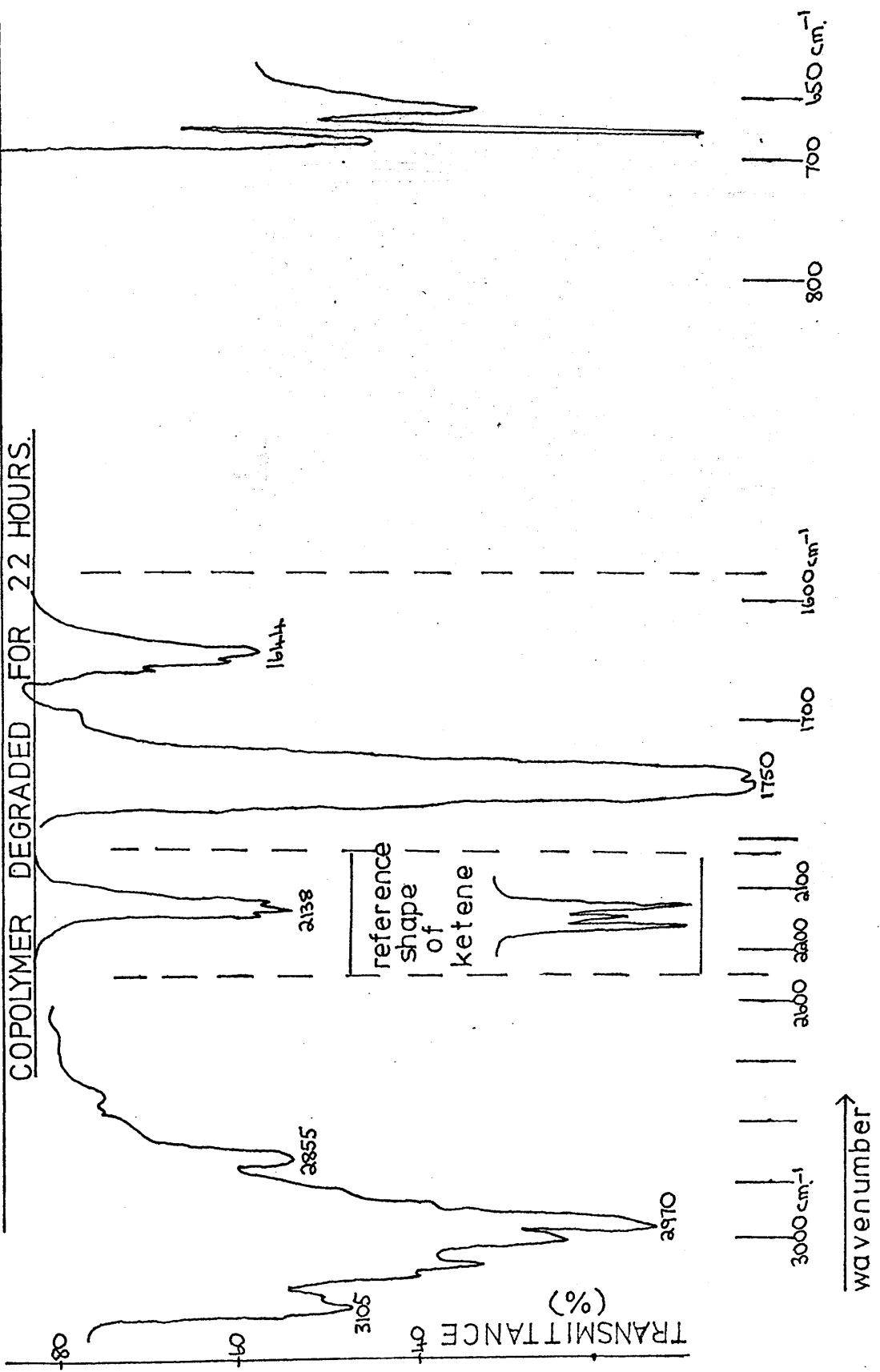


FIG. 4.2. IR. OF LIQUID VOLATILES FROM A 16.3 MOLE % N-BUTYL ACRYLATE
COPOLYMER DEGRADED FOR 23 HOURS

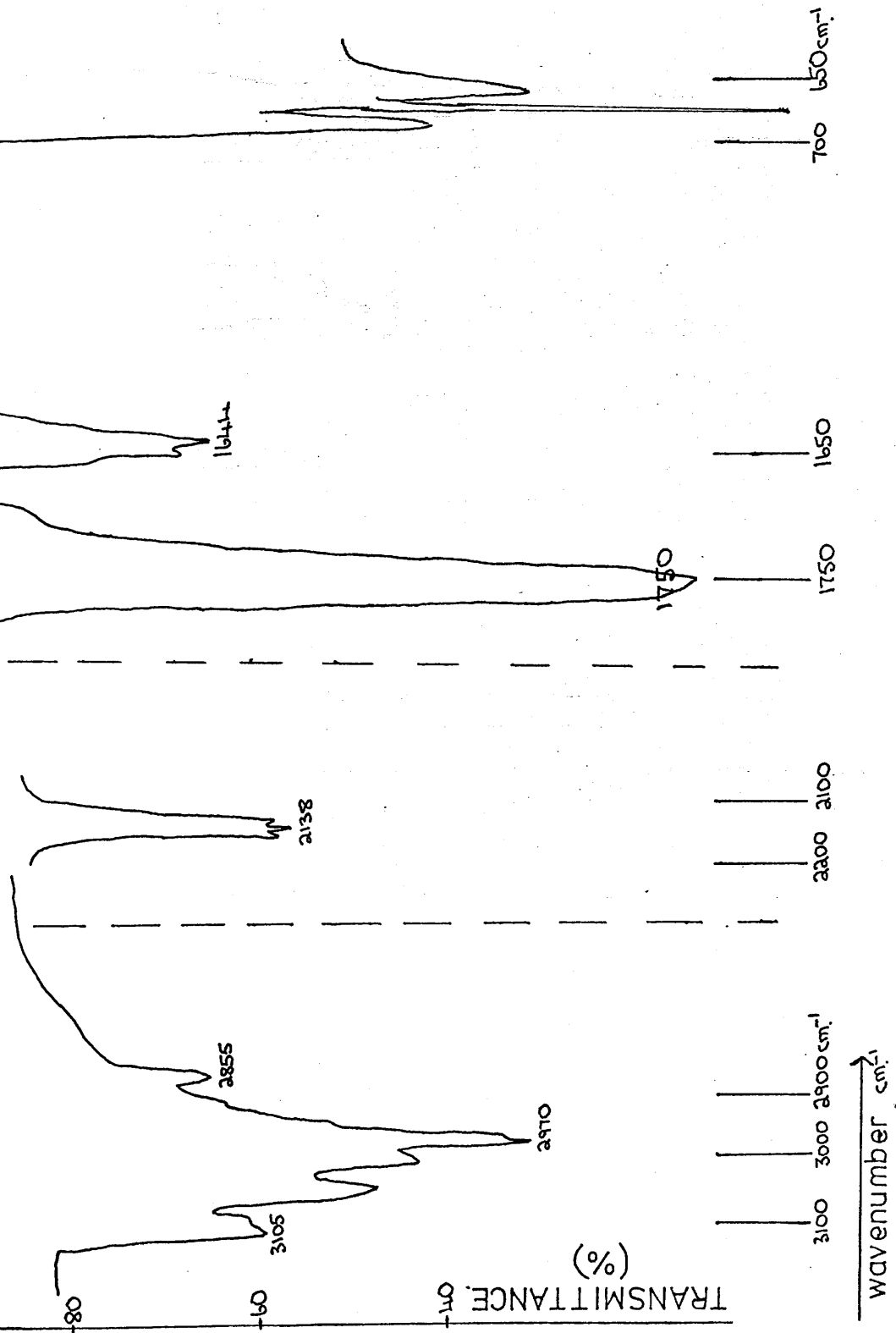


FIG. 4.3. I.R. OF LIQUID VOLATILES FROM A 50 MOLE % N-BUTYL ACRYLATE
 COPOLYMER DEGRADED FOR 23 HOURS

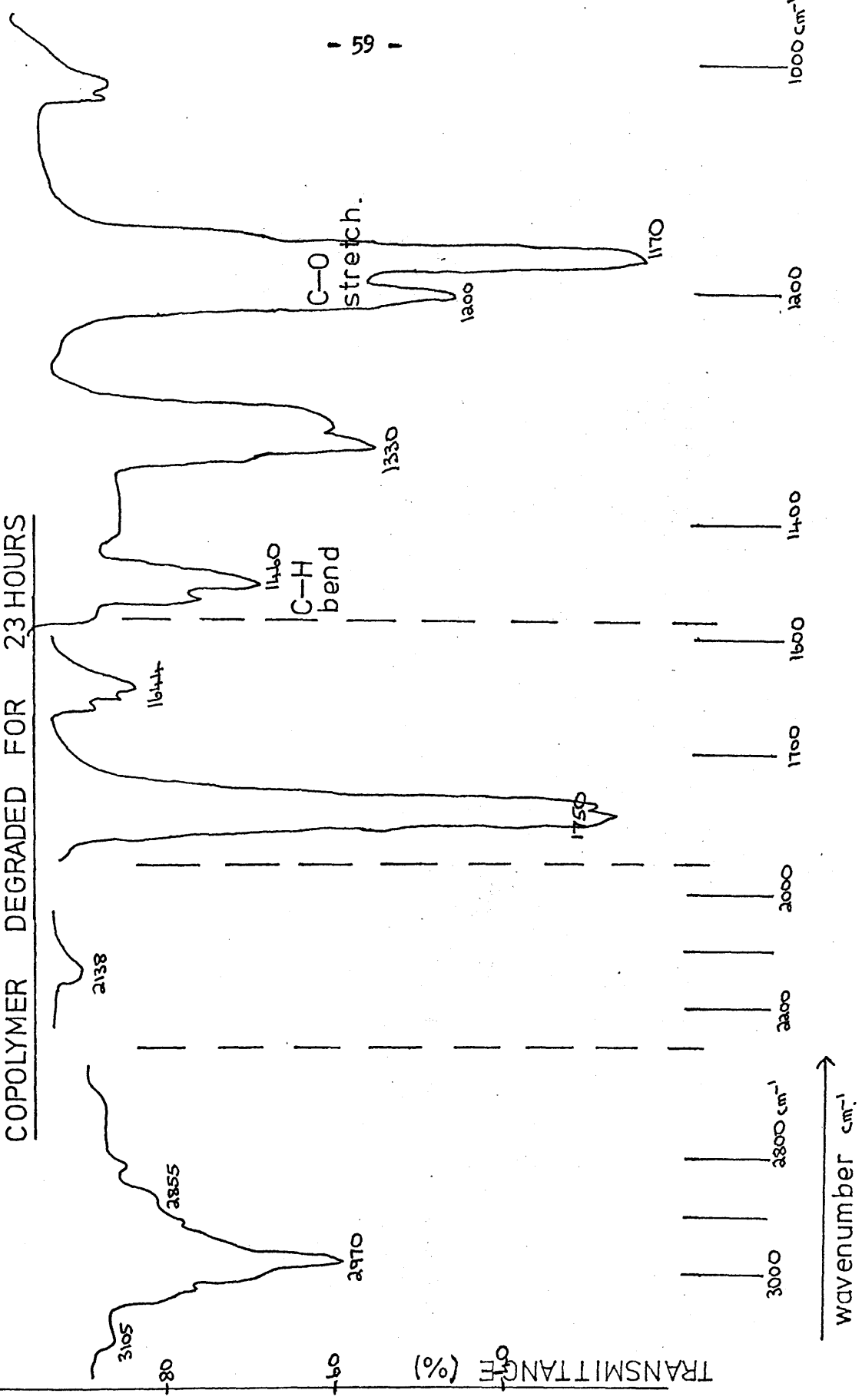
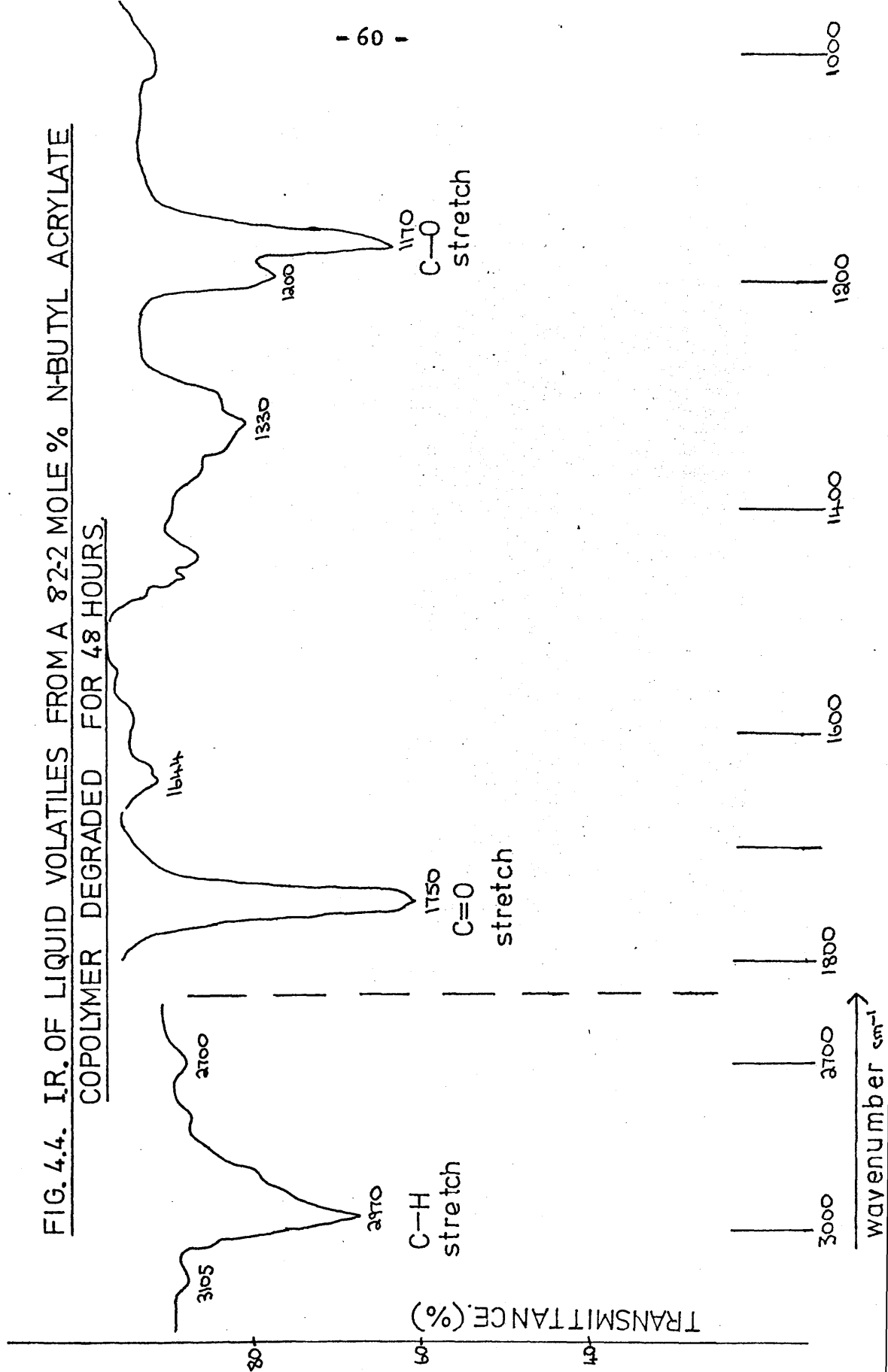


FIG. 4.4. IR. OF LIQUID VOLATILES FROM A 82.2 MOLE % N-BUTYL ACRYLATE
COPOLYMER DEGRADED FOR 48 HOURS.



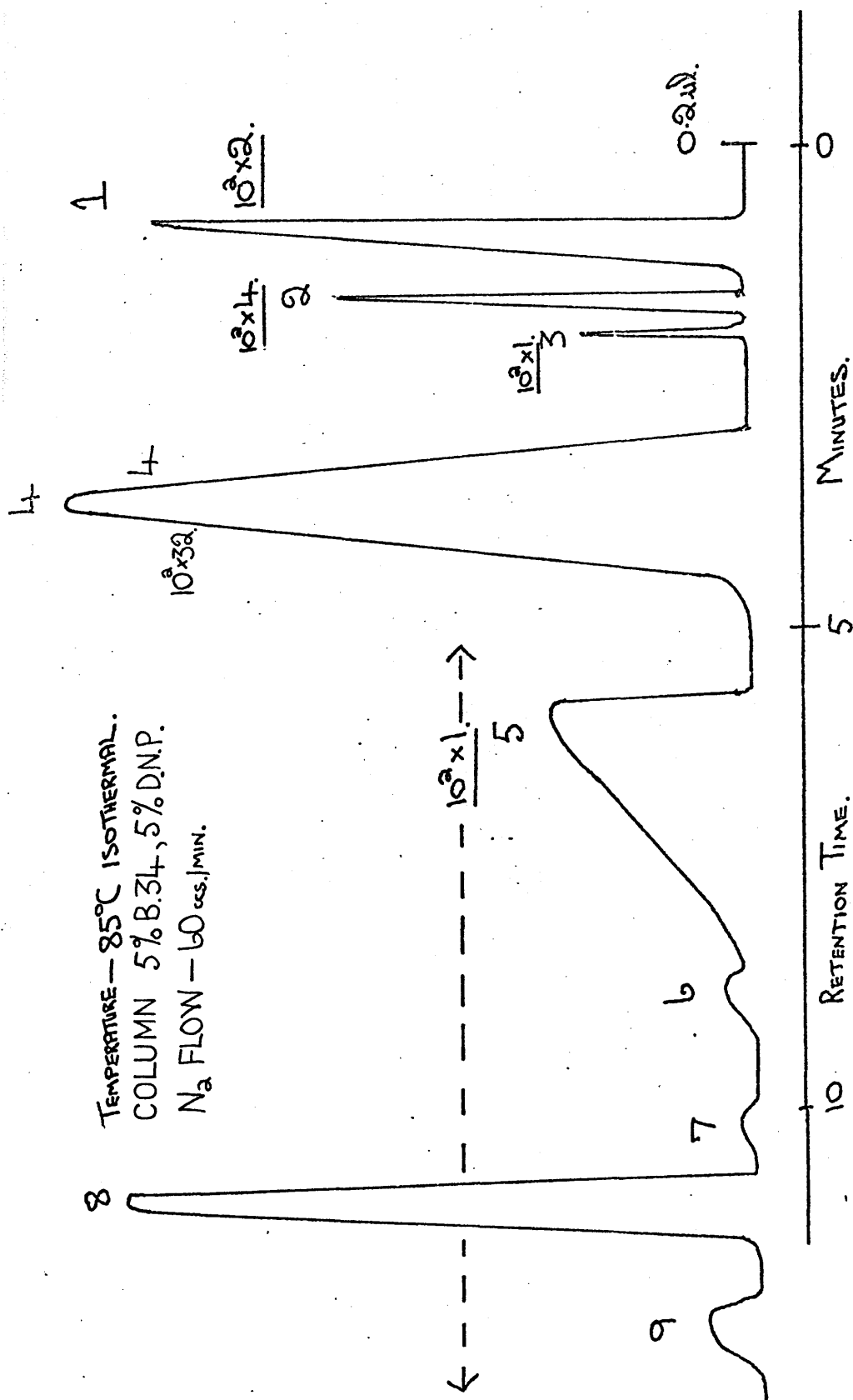
where R is not a hydrogen atom. A reference spectrum of $\text{CH}_3\text{-C}\equiv\text{C-CH}_3$ showed an absorption at 2135 cm^{-1} but this was not the strongest absorption. Hence, it is unlikely that 2135 cm^{-1} is due to an alkyne. A reference spectrum of ketene ($\text{H}_2\text{C=C=O}$) is shown in Fig. 4.1. This has the same absorption, although the shape of the absorption is different. It is therefore likely that the 2138 cm^{-1} absorption is due to a substituted ketene (RCH=C=O).

Obviously large quantities of monomer are present which will obscure the absorptions of other trace materials. The 82.2 mole % n-butyl acrylate copolymer appears to give rise to very few volatiles.

The thermal degradation^{4a} of poly (methyl methacrylate/n-butyl acrylate) copolymers resulted in the formation of carbon dioxide and but-1-ene. It is apparent from the infra-red analysis of the photolysis products that neither of these two components is present, throughout the entire copolymer composition range.

(c) GAS-LIQUID CHROMATOGRAPHY.

The liquid condensible products were condensed into weighed capillary tubes and stored at -18°C . as described in section 2.8a. Samples of $0.1\mu\text{l}$ of neat liquid products were injected into a 5 % D.N.P., 5 % B.34 column as specified in Table 2.2. Fig. 4.5. shows a typical g.l.c. trace of the liquid degradation products from the photolysis of a 50.0 mole % n-butyl acrylate copolymer. There are nine well defined degradation products. By injection of suitable standards and by



G.L.C. TRACE OF THE LIQUID DEGRADATION PRODUCTS FROM THE PHOTOLYSIS OF A
 50.0 MOLE PERCENT N-BUTYL ACRYLATE COPOLYMER.

FIG. 4.5.

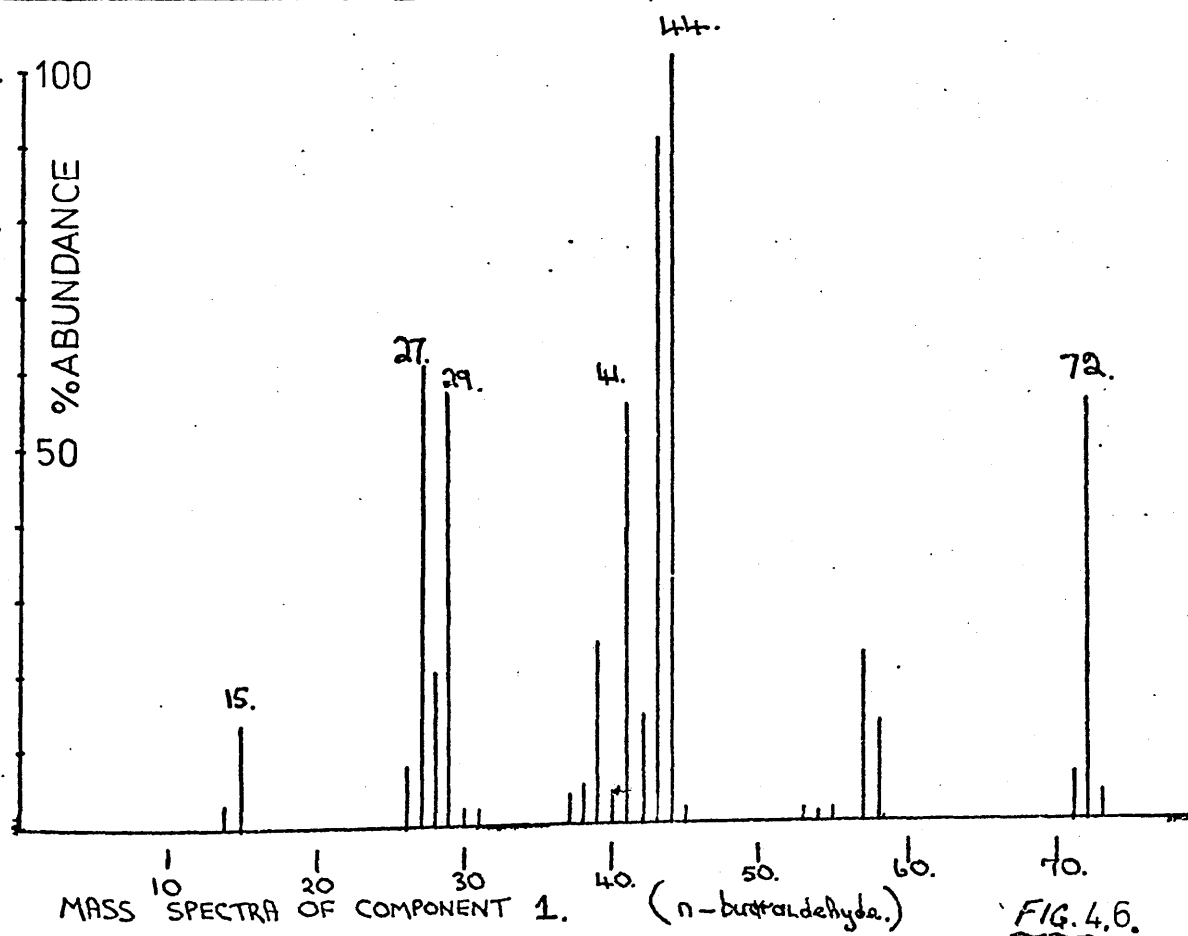
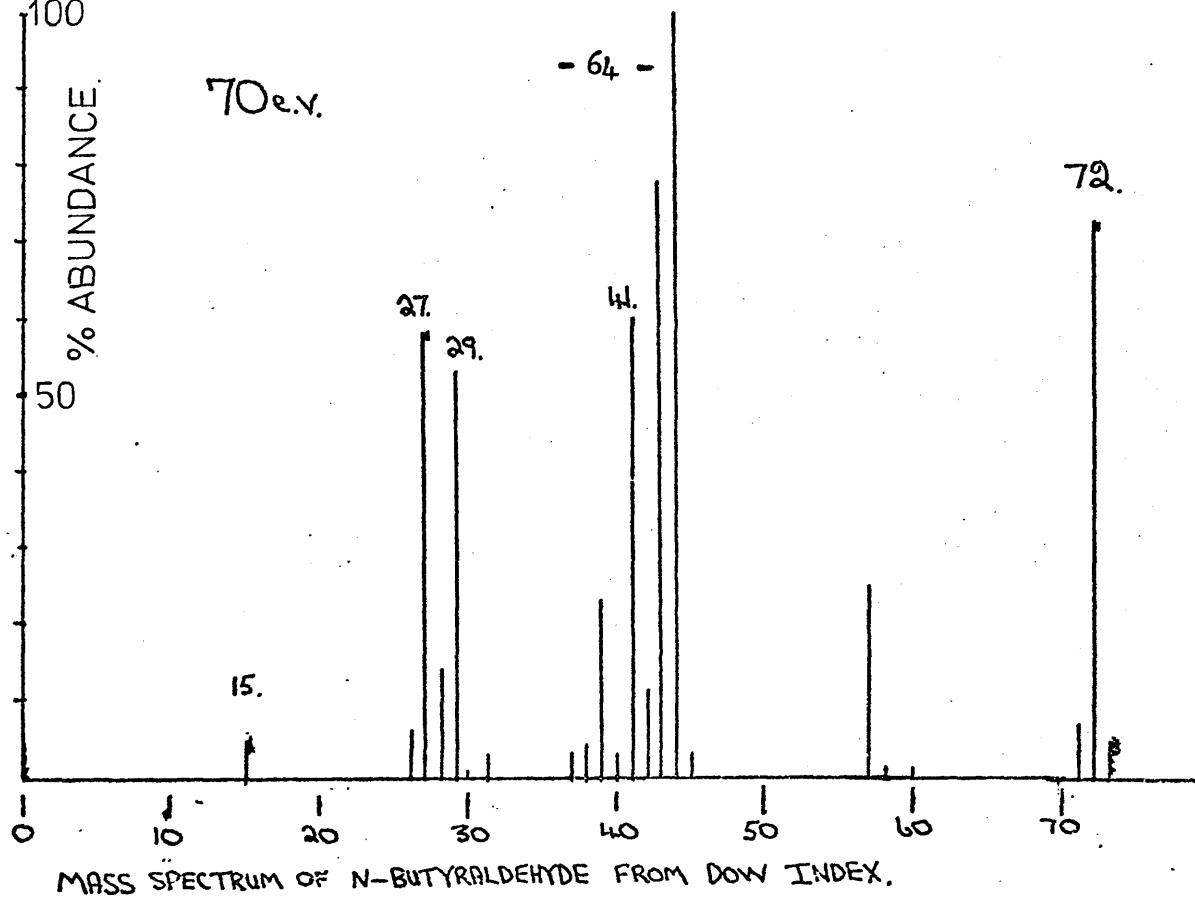
comparison of retention times, various peaks in this trace could be accounted for by the materials given in Table 4.1., which are reasonable degradation products.

TABLE 4.1.

Peak no. in Fig. 4.5.	Component
4	methyl methacrylate.
5	n-butanol.
8	n-butyl acrylate
9	n-butyl methacrylate.

(d) COMBINED GAS CHROMATOGRAPHY - MASS SPECTROMETRY.

d.1. Experimental. Under the conditions specified in section 2.8 e., using 70 e.v. electrons, and a sample of 0.1 μ l of neat liquid, the mass spectrum of each component was obtained. Fig. 4.6. - 4.15. show the mass spectra in the form of line diagrams, corrected for background, where it was present. The overall features are thus shown clearly. A reference mass spectrum is shown where possible for each component. These reference spectra were compiled from Cornu-Massot⁵³ and Dow Indices.⁵⁴



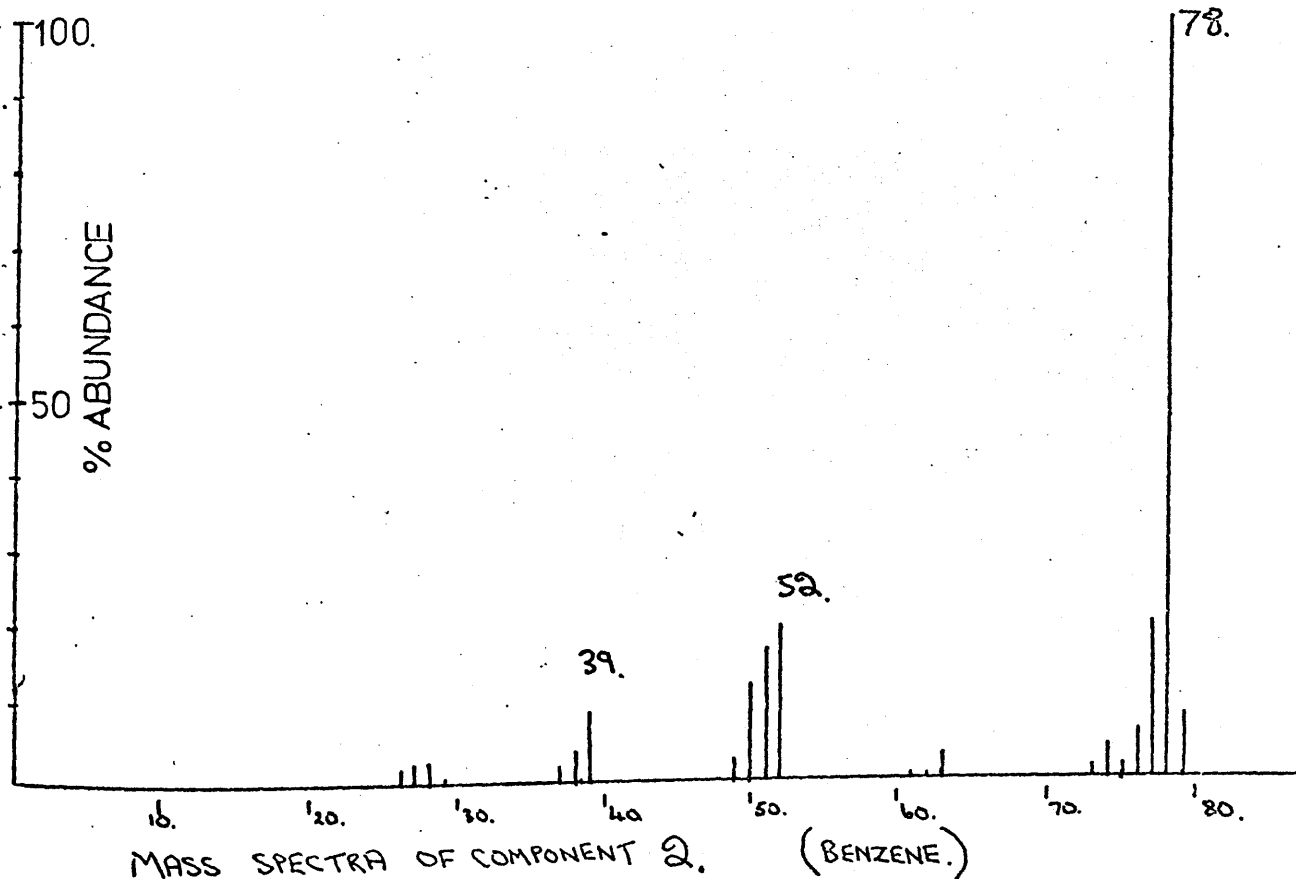
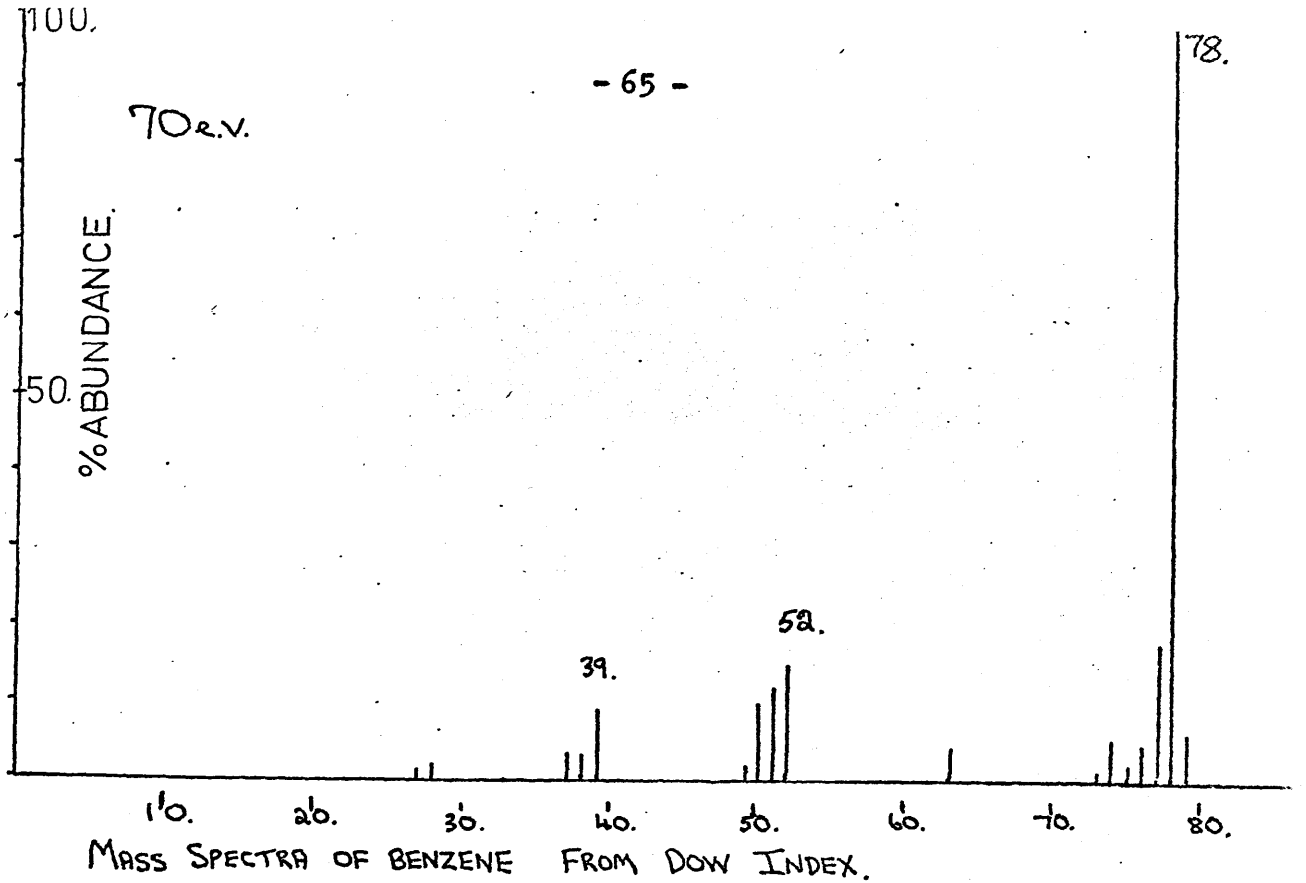


FIG. 4.7.

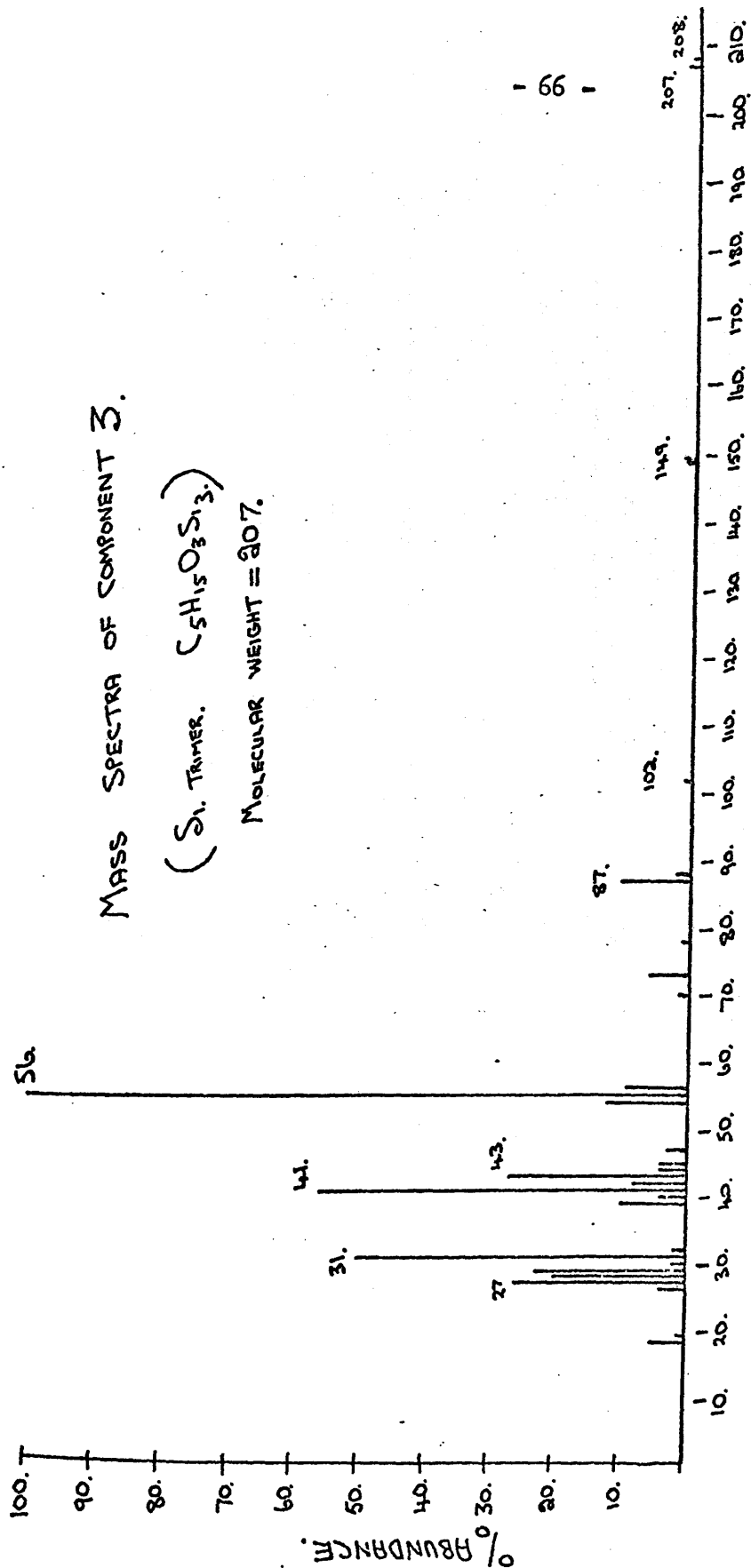


FIG 4.8

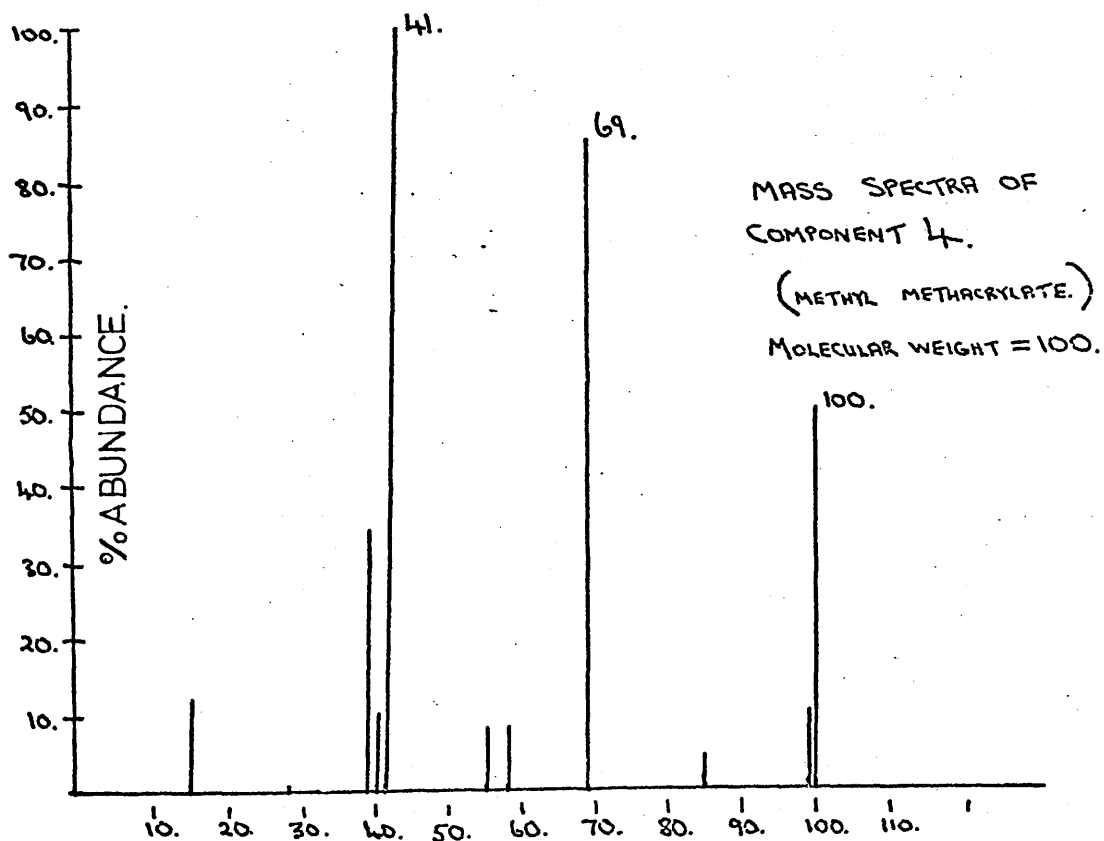
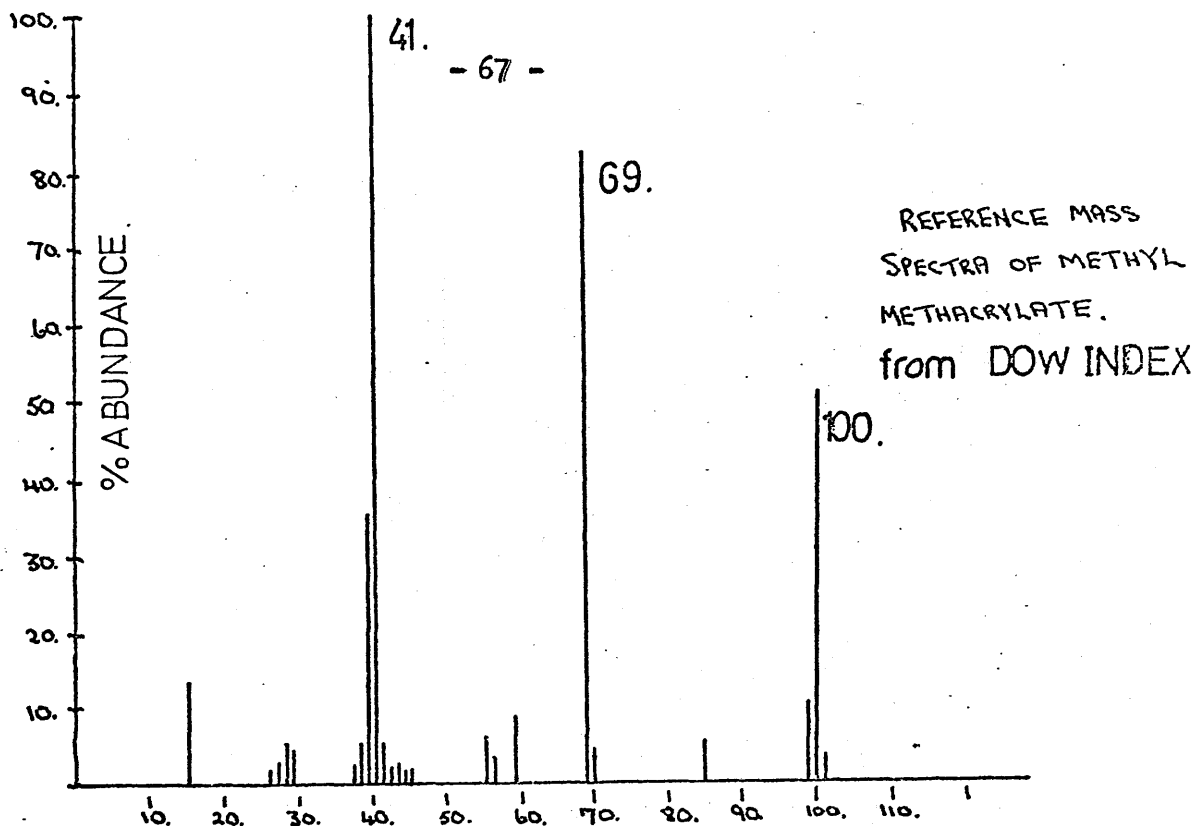
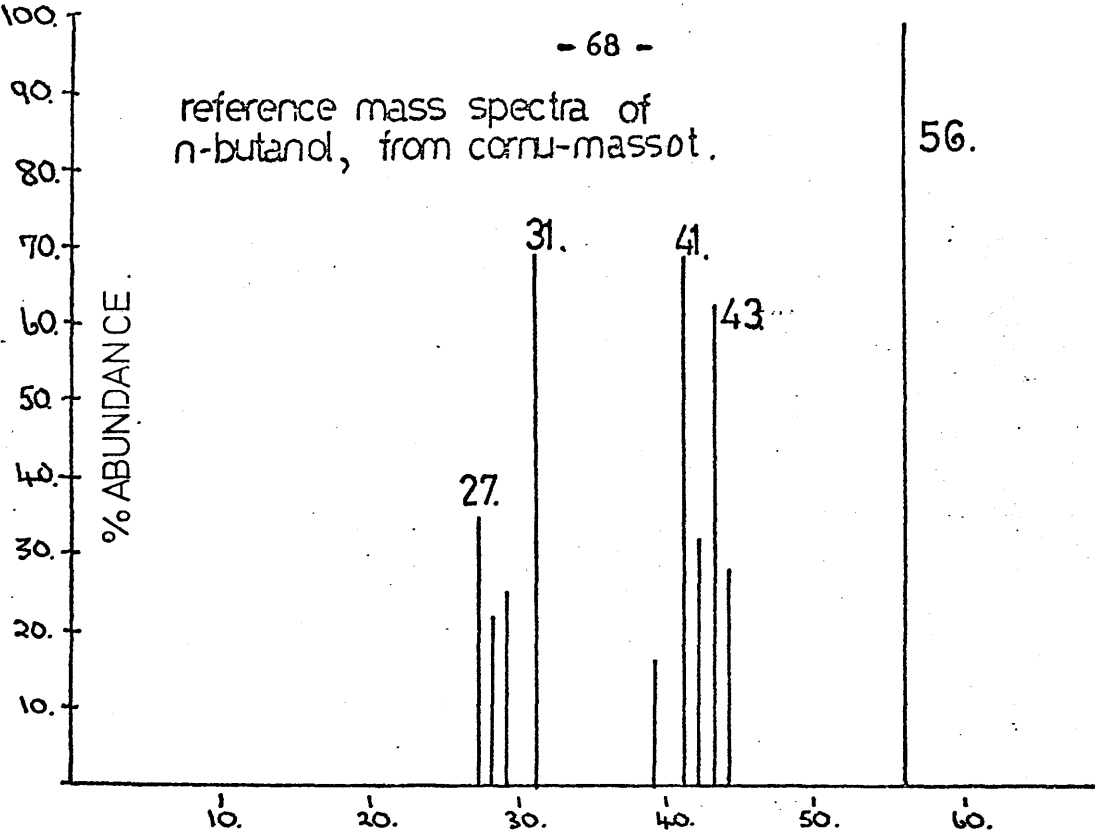


FIG. 4.9.

reference mass spectra of
n-butanol, from cornu-massot.



mass spectra of copolymer
degradation component 5.

(n-butanol)

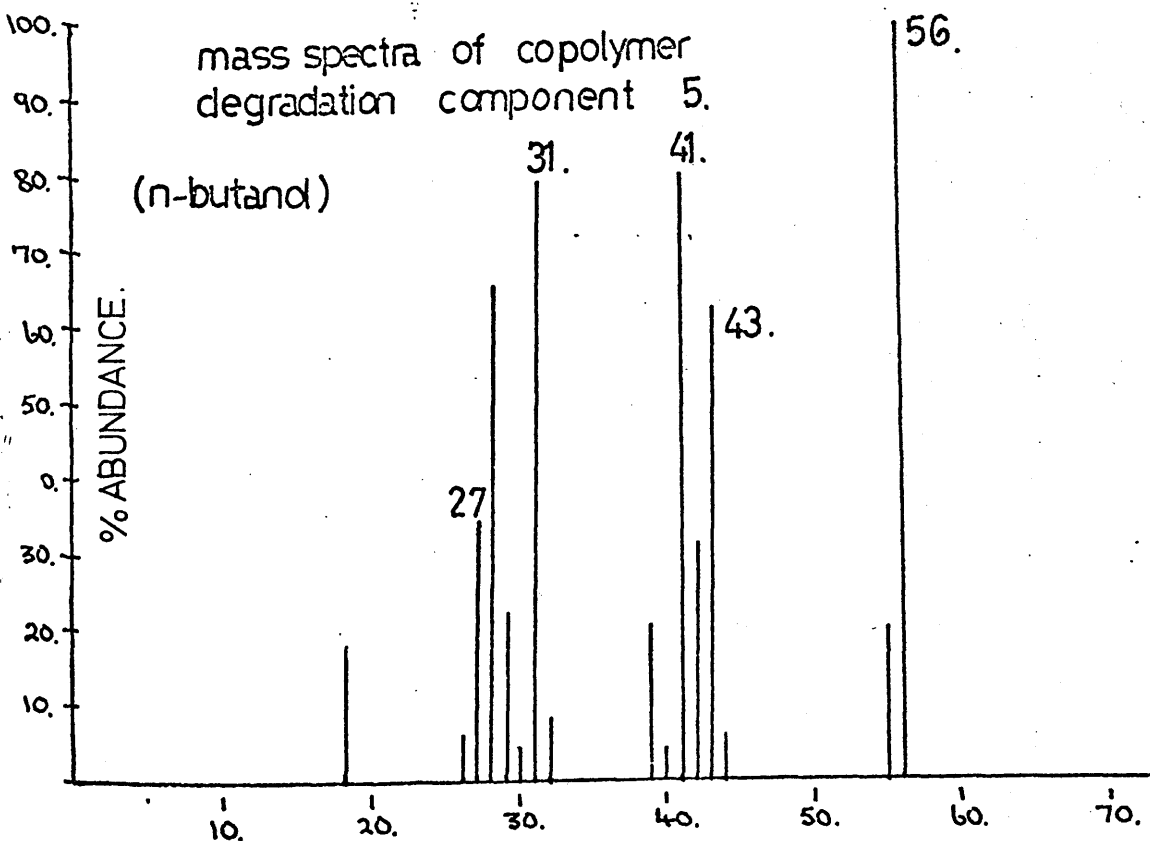
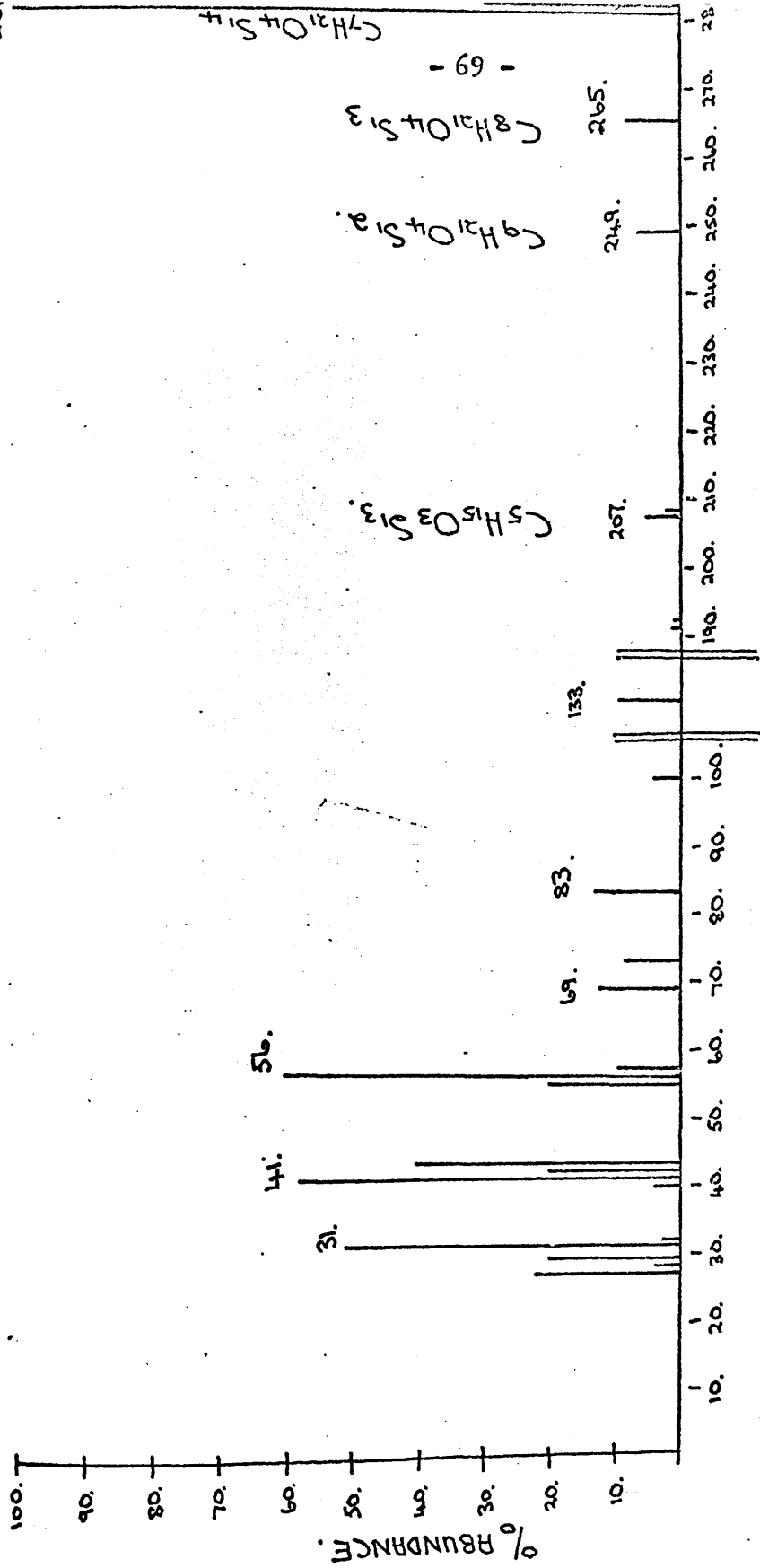


FIG 4.10.



MASS SPECTRA OF COMPONENT 6. (SILOXANE TETRAMER. — $C_7H_{21}O_4Si_4$.)

FIG. 4.11.

MASS SPECTRA OF COMPONENT 7.

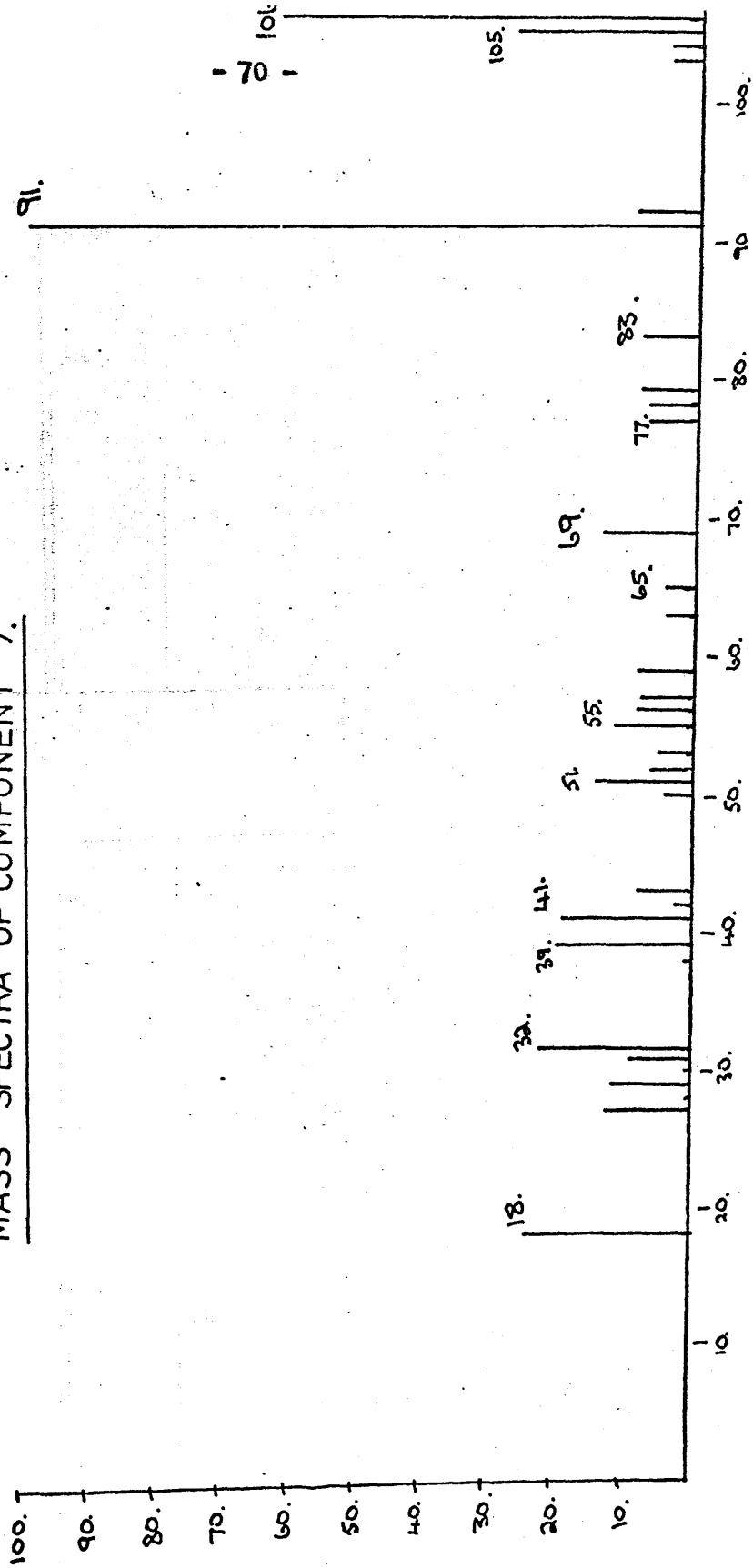
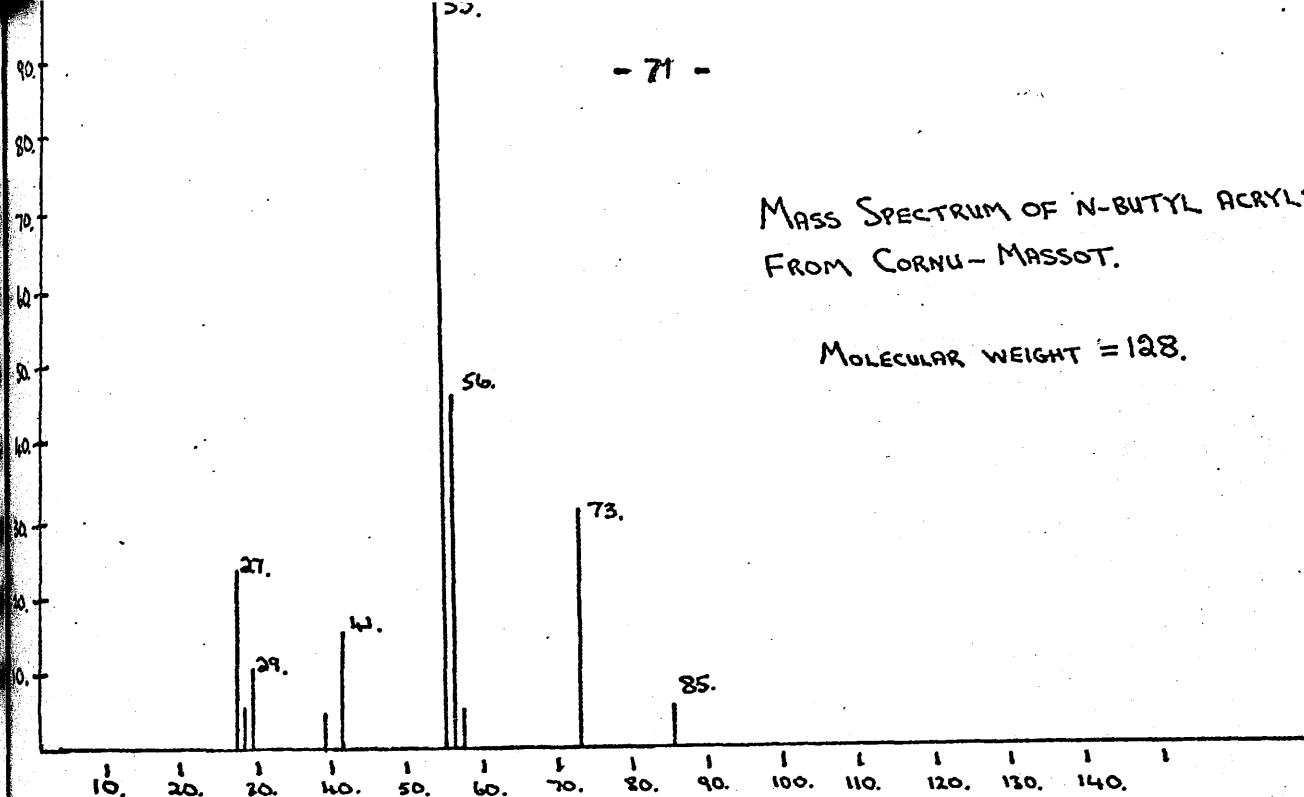


FIG 4.12.

- 71 -

MASS SPECTRUM OF N-BUTYL ACRYLATE,
FROM CORNU - MASSOT.

MOLECULAR WEIGHT = 128.



MASS SPECTRA OF COMPONENT 8.

(N-BUTYL ACRYLATE.)

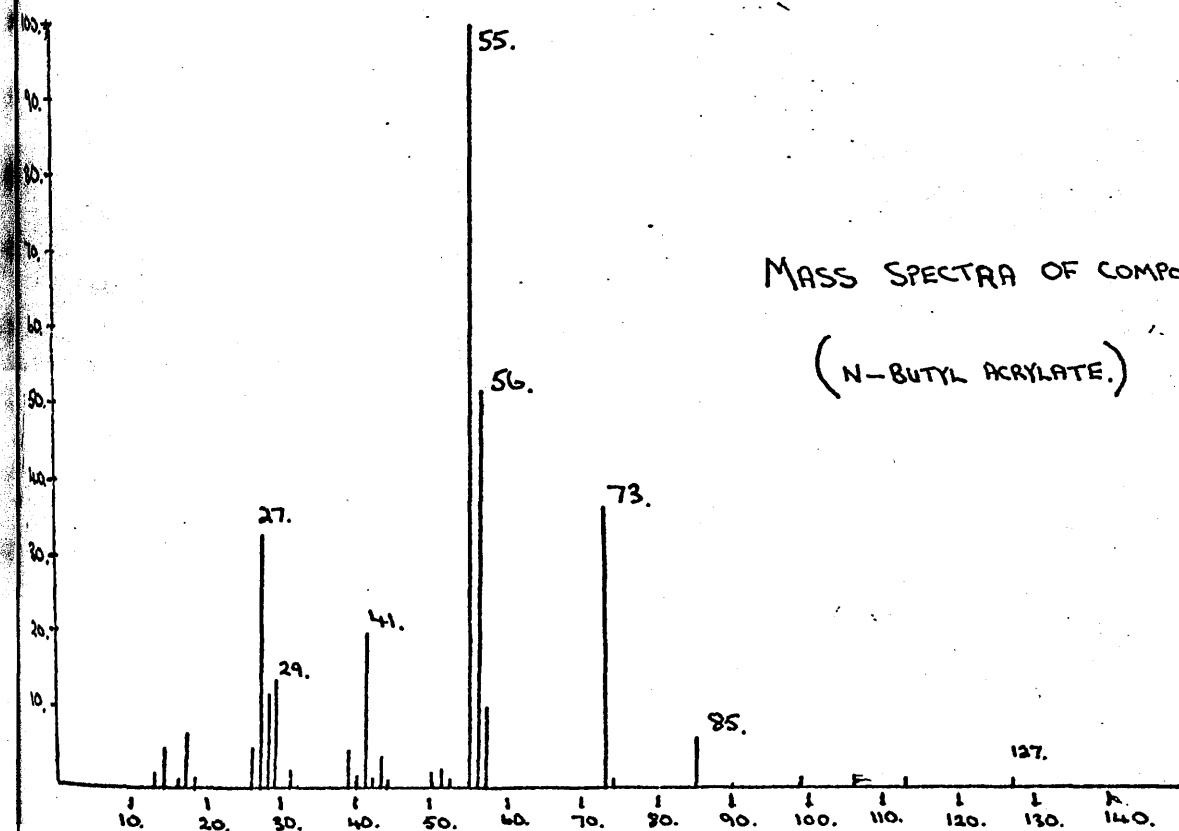


FIG. 4.13.

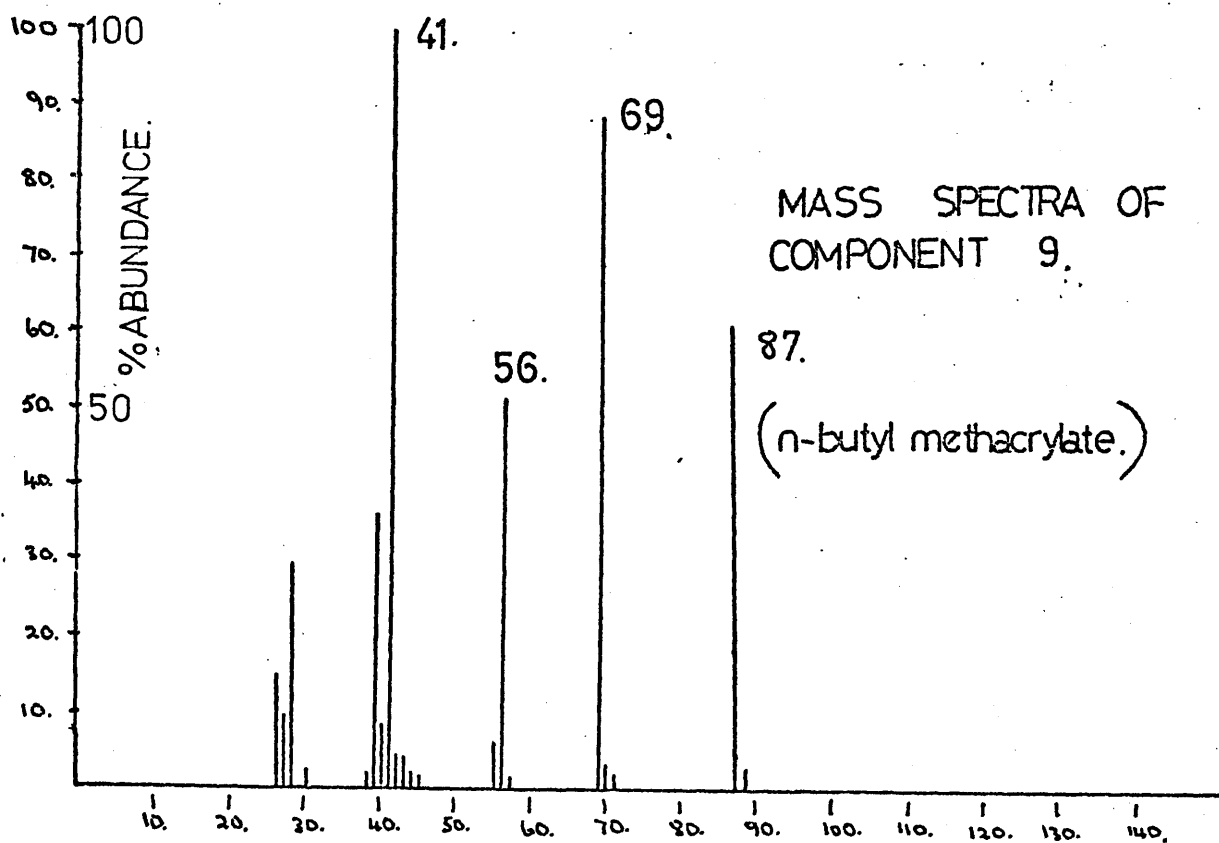
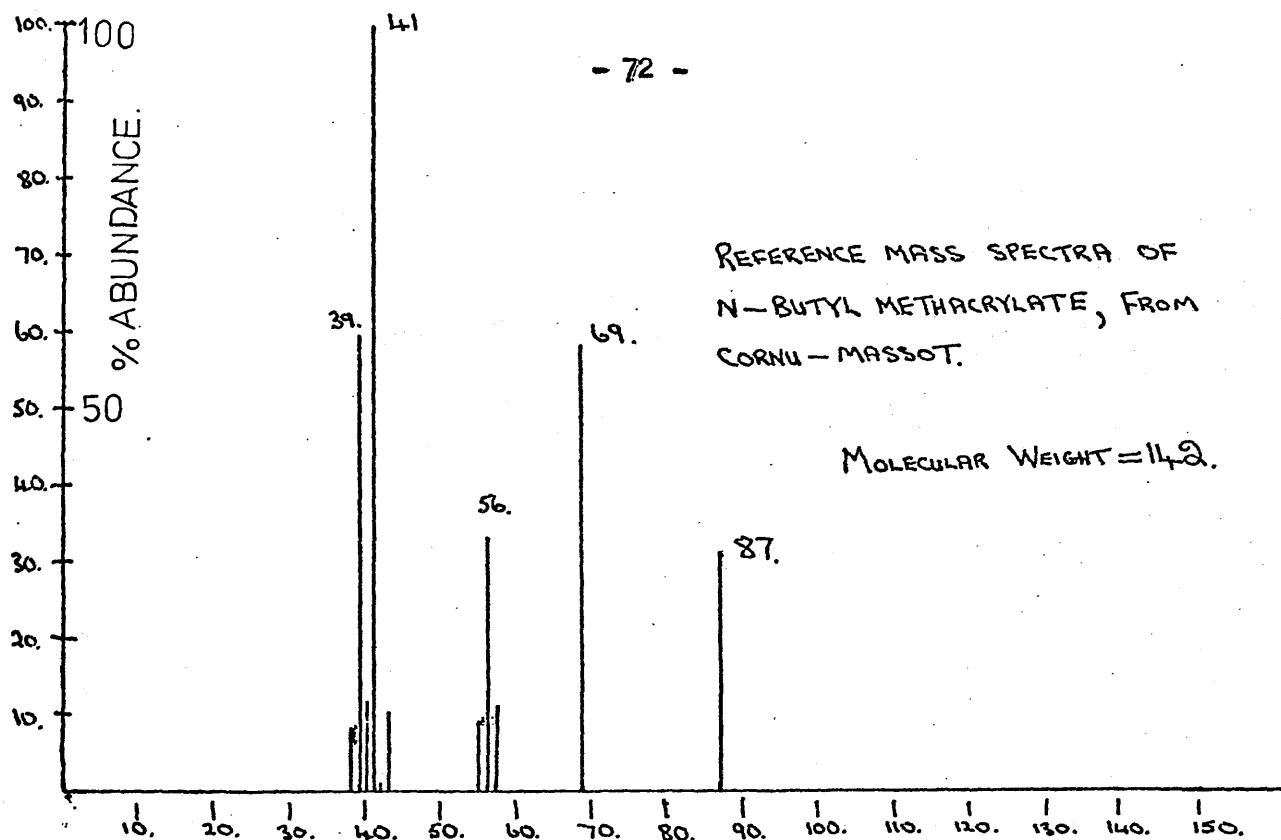


FIG. 4.14.

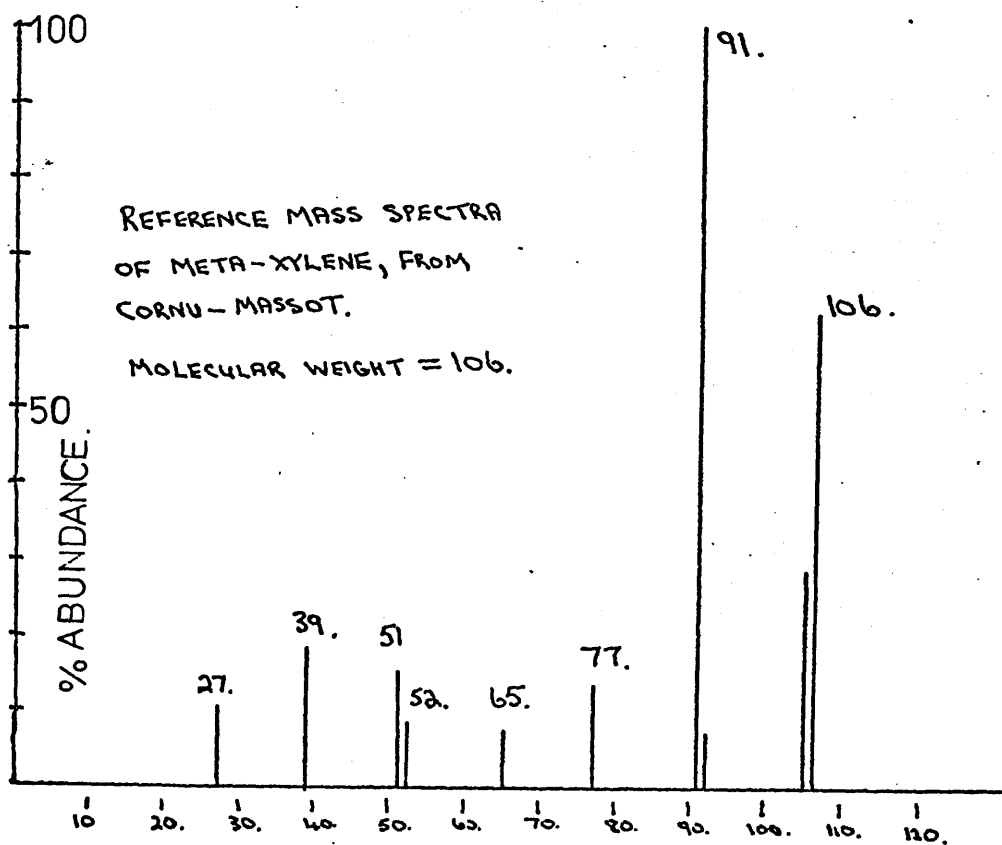
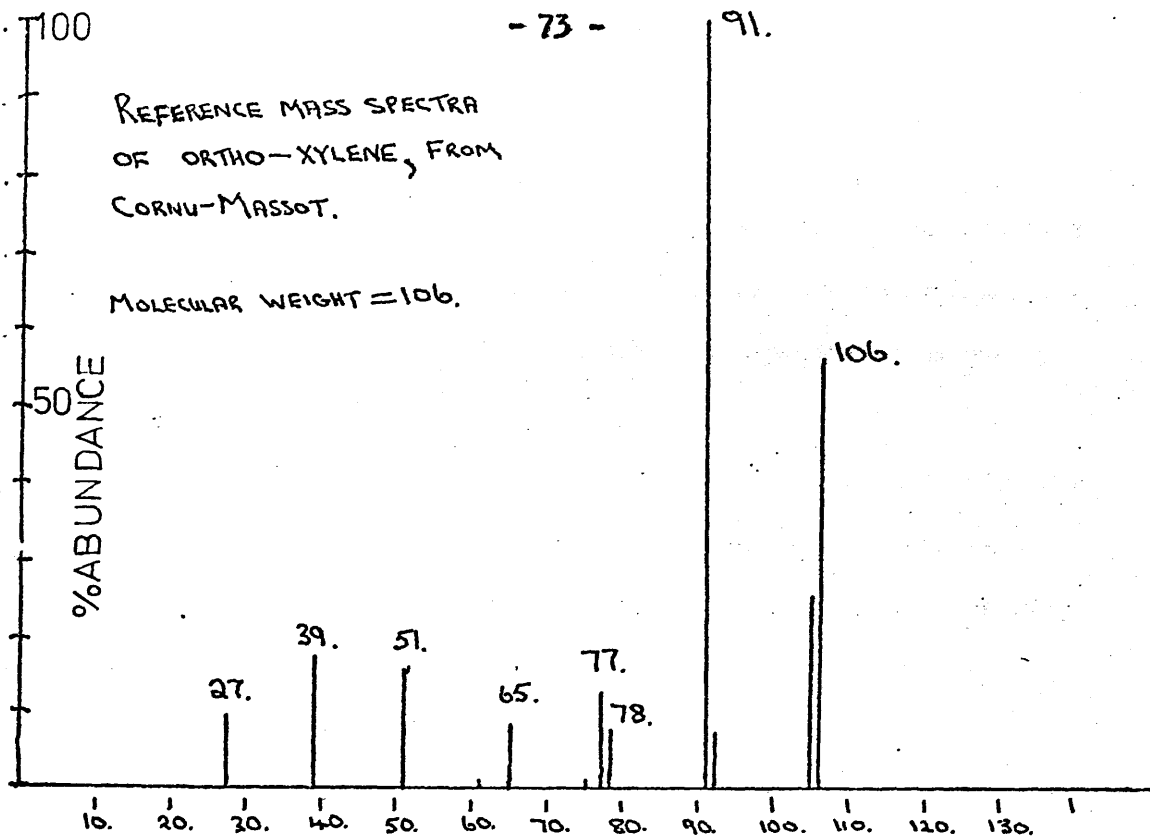


FIG. 4.15.

2a INTERPRETATION OF MASS SPECTRA.

By considering the common fragmentation patterns it is possible to analyse these spectra and propose a structure for each component, and finally compare the spectra with reference spectra of known compounds.

The ion formed by the loss of a single electron from a molecule is called the molecular or parent ion. The position of this peak indicates the molecular weight (M) of the material present. In many cases, however, this peak is of low abundance or not present at all while in esters and some other compounds peaks often occur at mass number $M+1$. 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 (see figure 4.15). The most abundant masses in each spectrum are listed in the order of their relative abundance in Table 4.2.

TABLE 4.2.

SUSPECTED COMPOUND	MASS
n-Butyraldehyde	44, 43, 27, 29, 72, 41
Benzene	78, 52
Siloxane Trimer	56, 41, 31, 87, 149, 207
Methyl Methacrylate	41, 69, 100, 39, 15
n-Butanol	56, 31, 41, 43, 27
Siloxane Tetramer	281, 56, 41, 31, 207, 249, 265
Xylene	91, 106, 105
n-Butyl Acrylate	55, 56, 27, 73, 41
n-Butyl Methacrylate	41, 69, 87, 56, 39

3. PROCESSES OF FRAGMENTATION OF POSITIVE IONS

Mass spectra can be interpreted in terms of the following three processes.⁵⁵

A. Simple Fission

A neutral fragment is lost by the breaking of one bond.

B. Rearrangement

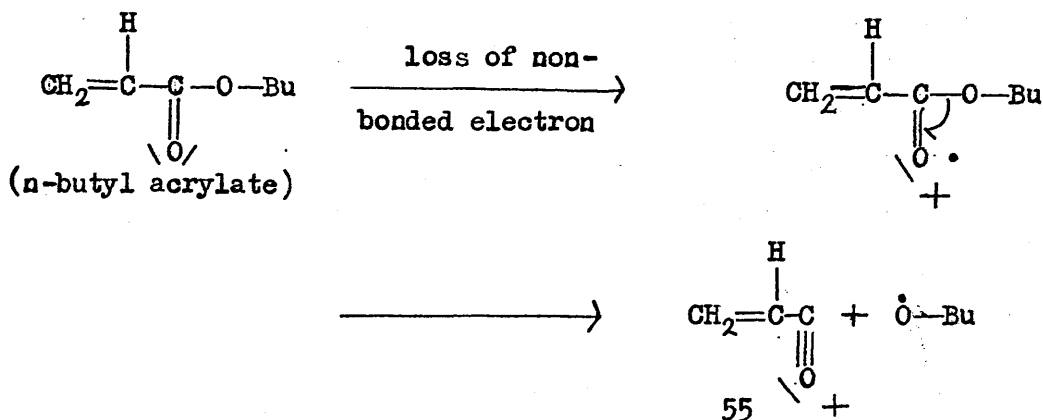
More than one bond fission occurs, accompanied by transfer of one hydrogen from one atom to another within the decomposing ion.

C. Double Rearrangement

Two hydrogen atoms are transferred simultaneously from the neutral fragment being lost to the fragment ion being formed.

ESTER PRODUCTS

Considering the mass spectra of the three esters, n-butyl acrylate, methyl methacrylate and n-butyl methacrylate, the simple fission process can occur as follows:



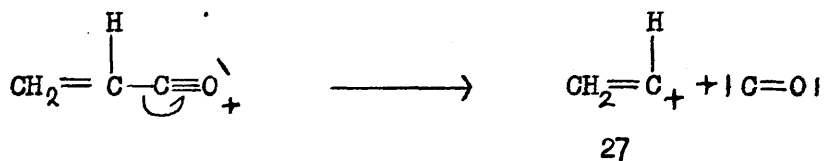
In simple fission, a non-bonded electron is lost from the ester carbonyl oxygen atom followed by transfer of an electron to the positively charged site, from the α bond. This process is therefore called α fission.

Transfer of one electron during bond fission or bond formation is denoted by a single headed arrow \curvearrowright . A double headed arrow \curvearrowleft indicates the movement of two electrons. This is the convention used by Djerassi.⁵⁵

When this process occurs in n-butyl methacrylate (n-BuMA) and methyl methacrylate (M.M.A.) fragments of mass 69 are obtained from both.

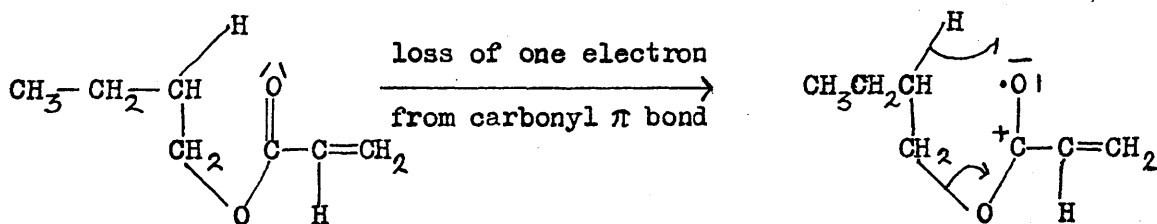
Fragment ion fission can also occur. A neutral molecule is eliminated

from the fragment ion by cleavage of a single bond, the mechanism involving a two electron shift.



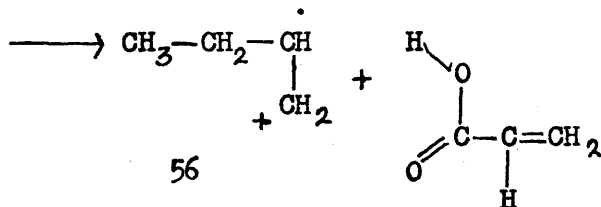
Operating this process on nBu.M.A. and M.M.A. gives fragments of mass 41 from both.

A rearrangement process can be used to explain the ion 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.



nBu.A.

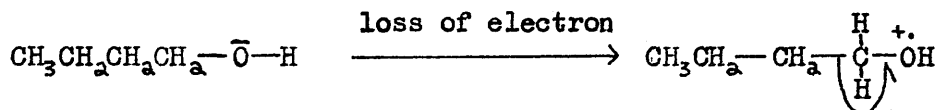
A proton transfer from the γ carbon and a transfer of two electrons completes the process.



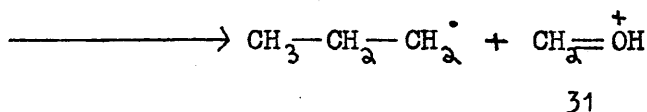
Fragments of mass 56 are also produced when this process operates in nBu.M.A.

THE MASS SPECTRUM OF n-BUTANOL

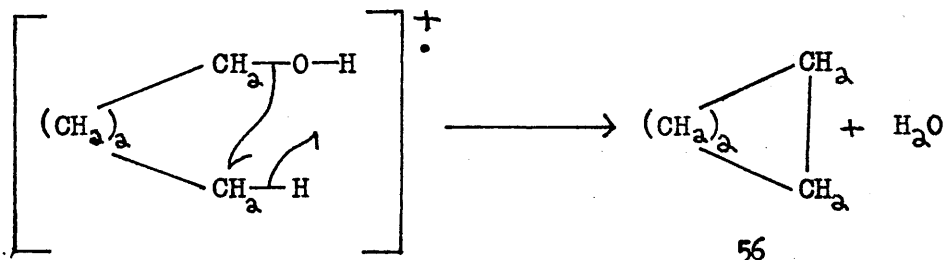
The most favourable ionization process for an alcohol corresponds to the removal of one of the lone pair electrons on the oxygen atom.



The resulting ion radical may then decompose by α cleavage with radical elimination and formation of a stable oxonium ion.



The most characteristic fragmentation of the higher alcohols is associated with the elimination of water, giving a peak at $M-18=56$.

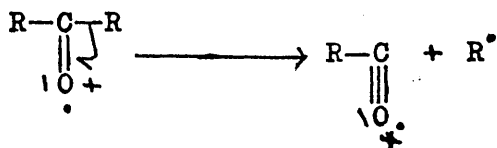


BENZENE

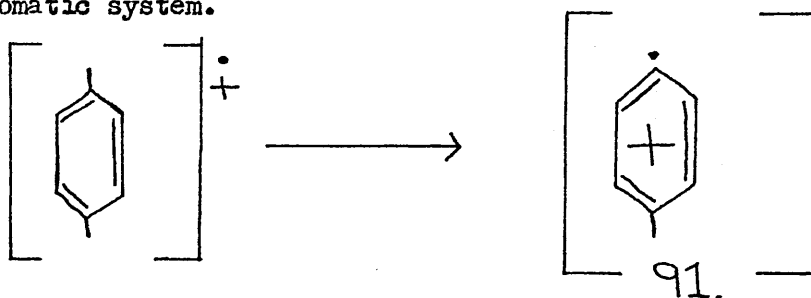
The residual solvent, benzene, gives a high abundance of the molecular ion indicating a very stable molecule.

n- BUTYRALDEHYDE

If simple fission occurs



Simple fission of the bond in the substituent group α to the aromatic system can occur with the charge being preferentially retained on the aromatic system.



Other possible processes in substituted aromatic compounds are;

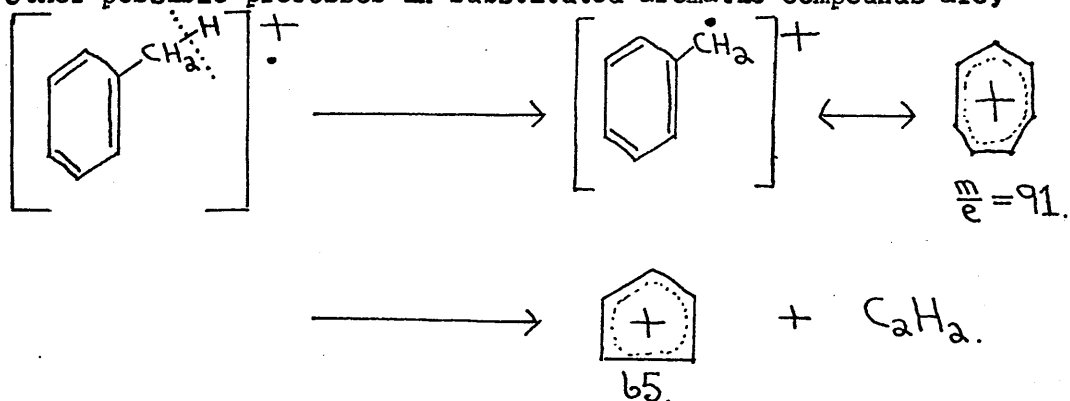


Fig. 4.15 shows the spectra of xylenes. From this evidence, component 7 is a xylene type compound possibly arising as an impurity from benzene.

COMPONENTS 3 and 6.

Slawson and Russell⁵⁶ depolymerised silicone grease with KOH and suggested that peaks at 281 correspond to siloxane tetramer (Si_4O_4 ring with 7 attached CH_3 groups) and that peaks at 265 and 249 could correspond to the substitution of some of the silicone atoms by carbon. Masses have also been observed at 149 (dimer), 207 (trimer) and even

355 (probably an extra $-\text{OSi}(\text{CH}_3)_2$ added to the tetramer.

These observations show that silicones will yield a wide range of decomposition products, either by thermal or photo degradation, or by interaction with reactive chemical species. They complicate the interpretation of mass spectra and present the possibility of decomposition of silicone in embarrassing amounts in regions where ionic reactions may occur.

(d 4.) CONCLUSIONS.

The liquid volatile products have been separated into nine components and identified as in Table 4.2. n-Butyraldehyde, methyl methacrylate, n-butanol, n-butyl acrylate and n-butyl methacrylate are genuine degradation products. The benzene is residual solvent, xylene an impurity in the benzene and the siloxane trimer and tetramer are derived from tap grease.

4.3. ANALYSIS OF PERMANENT GASES.

(a) Infra-red.

Using a Topley pump as described in section 2.8.a,c. the permanent gases were collected in a 'minimum volume' infra-red cell. Typical infra-red spectra for the gaseous degradation products from both a 50 and 82.2 mole % n-butyl acrylate copolymers are shown in Fig. 4.16 and Fig. 4.17 respectively. The characteristic absorption at 2140 cm^{-1} can be attributed to methane.

(b) Gas Chromatography.

After an I.R. spectra of the permanent gas fraction was obtained the infra-red cell was connected to the permanent gas sampling apparatus shown in Fig. 2.6. Using a silica gel column at room temperature and argon as a carrier gas, room temperature g.l.c. as shown in Fig. 4.16. and Fig. 4.17 were obtained for the 50 and 82.2 mole % n-butyl acrylate copolymers. Pure samples of hydrogen, carbon monoxide and methane were passed through the column for comparison of retention times.

100% OF PERMANENT GASES

100% OF PERMANENT GASES

100% OF PERMANENT GASES
n-butyl acrylate copolymer
mole % 50 and 82.2

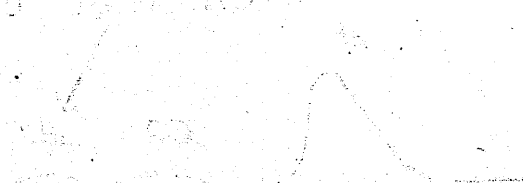
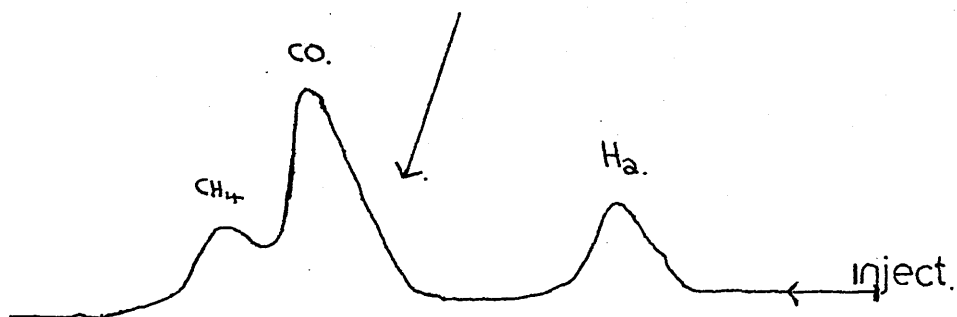
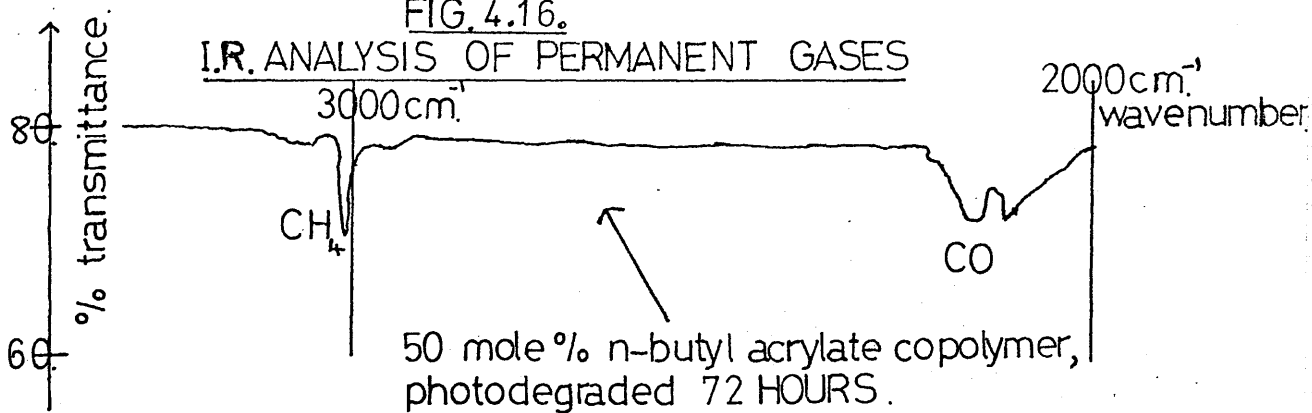
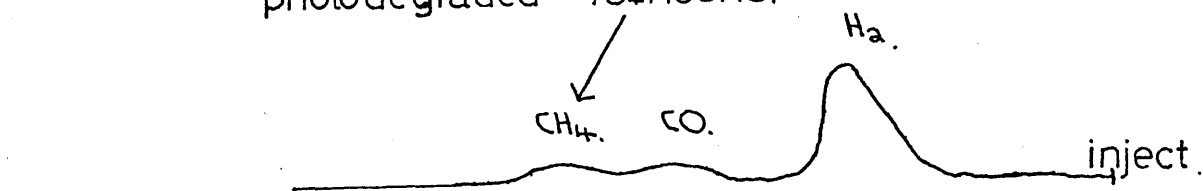
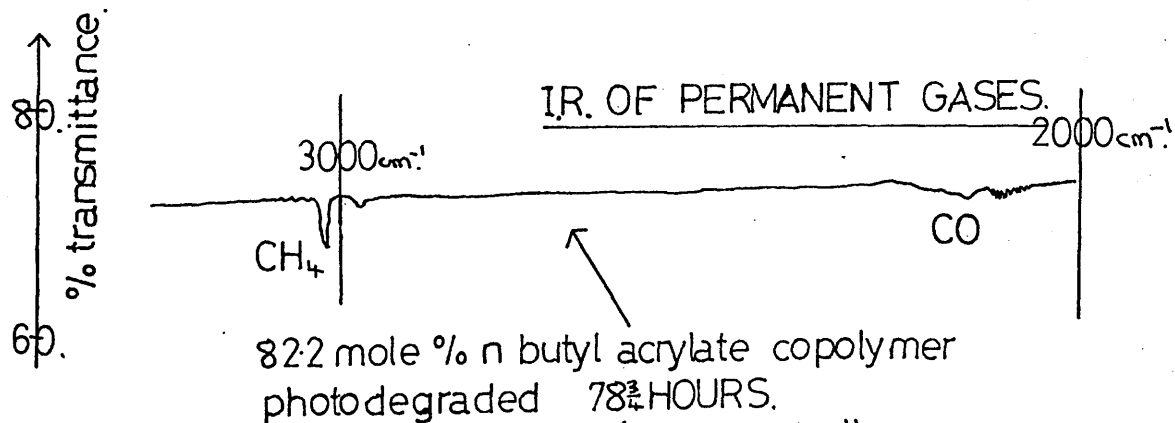


FIG. 4.16.

I.R. ANALYSIS OF PERMANENT GASES



room temp. g.l.c. of permanent gas fraction



room temp. g.l.c. of permanent gas fraction.

FIG. 4.17.

CHAPTER 5.

QUANTITATIVE ANALYSIS OF DEGRADATION PRODUCTS.

5.1. Introduction.

In the last chapter the identification of the products of photolysis was described. A detailed analysis of weight loss, liquid condensibles products, cold ring, residue and permanent gases is described in this section. The notation '25/1' copolymer is used to imply a 3.9 mole per cent n-butyl acrylate copolymer. Similarly the notation '1/5' copolymer implies an 82.2. mole per cent n-butyl acrylate copolymer.

5.2. Quantitative Analysis.

Using the photolysis cell with the polymer supported on the flat silica disc as described in sections 2.2, and 2.3., the analysis of weight loss, cold ring and residue was readily achieved. Data are presented in Table 5.1. and illustrated in Figs. 5.1.-5.7. Fig. 5.8. shows the percentage liquid volatiles resulting from the photolysis of five copolymer samples, and indicates, at a glance, that as the methacrylate content of the copolymers increases, the percentage liquid volatiles evolved also increases. Fig. 5.9. is a representation of the change in cold ring with methyl methacrylate content. This graph was constructed by reading off values of cold ring and weight loss after 20 hours photolysis, from Figs. 5.1. - 5.8.

TABLE 5.1.

COPOLYMER	TIME (HRS)	% WT LOSS	% CONDENS.	% COLD RING	% RESIDUE
100/1	0.5	21.76	—	—	78.24
	1	30.35	24.49	5.86	69.65
	1.5	40.17	32.56	7.61	59.83
	2	48.72	40.79	7.93	51.28
	16.5	98.4	68.05	—	1.6
	24	96.12	81.51	14.61	3.88
	47.5	98.70	76.15	22.55	1.3
25/1	0.5	12.77	—	—	87.23
	1	30.57	27.52	3.05	69.43
	1.58	30.93	28.54	2.38	69.07
	2	35.26	27.80	7.46	67.74
	6.5	65.91	58.61	7.30	34.09
	15.5	87.24	65.95	21.29	12.76
	24.5	97.83	66.89	30.94	2.17
5/1	0.5	8.93	—	—	91.07
	1	19.62	16.03	3.59	80.38
	1.5	21.25	15.63	5.62	78.75
	2	27.01	15.82	11.19	72.99
	4	41.66	26.63	15.03	58.34
	16.5	72.57	44.65	27.92	27.43
	21.5	82.19	55.49	26.70	17.81
	23.	82.56	53.25	46.75	17.44
	41	82.45	—	47.59	17.55

TABLE 5.1. (contd.)

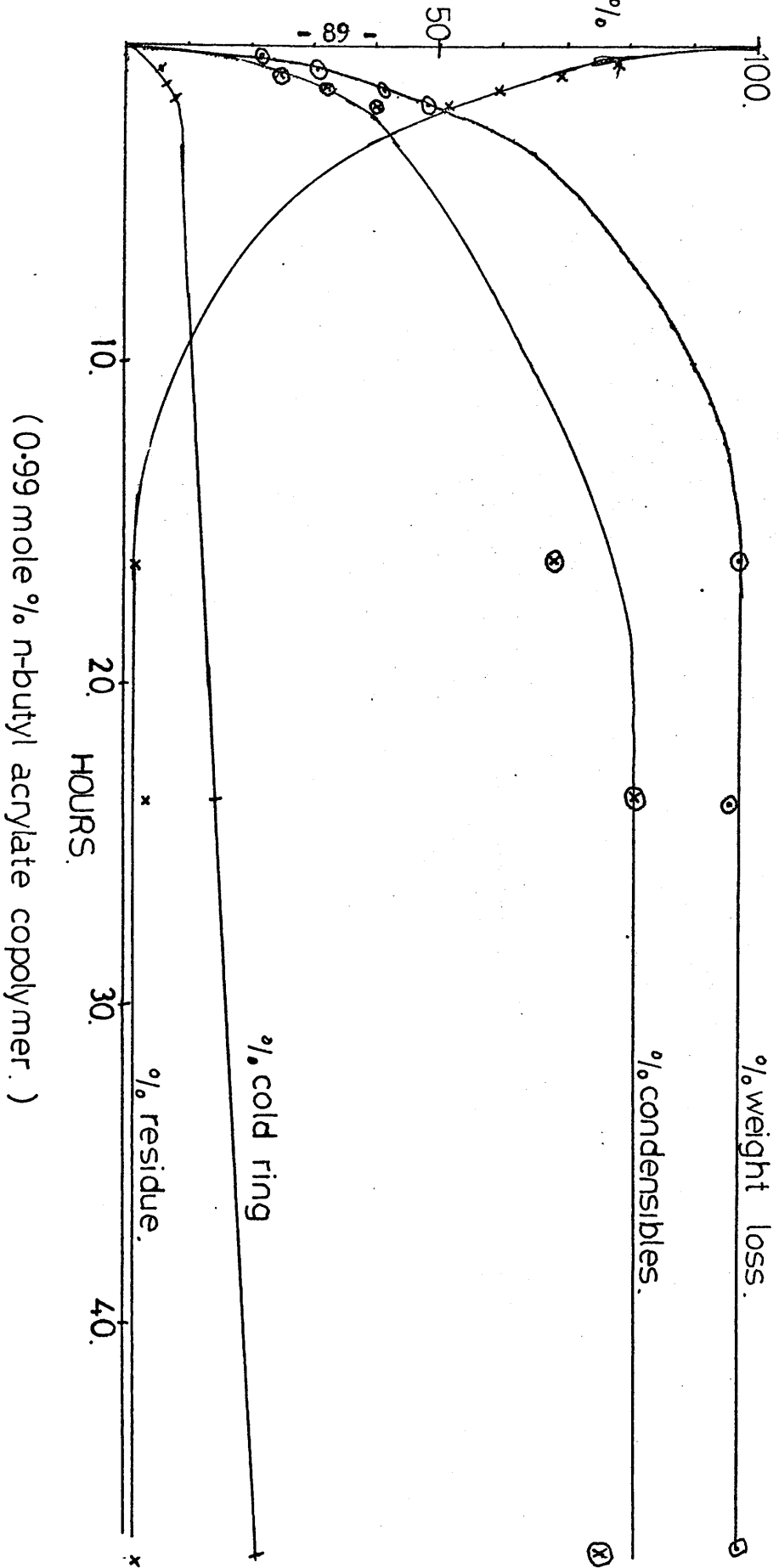
COPOLYMER	TIME	% WT LOSS	% CONDENS.	% COLD RING	% RESIDUE
1/1	1	2.26	—	—	97.74
	1.5	3.41	—	—	96.59
	2	5.23	3.56	1.67	94.77
	3	6.63	—	—	93.37
	5	16.07	1.74	14.33	83.93
	17	32.48	8.25	24.23	67.52
	22.75	36.90	6.62	30.28	63.10
	47	46.14	7.99	38.14	53.86
1/5	2	1.87	—	—	98.13
	17	11.60	—	11.60	88.40
	25	14.63	1.02	13.61	85.37
	47	20.64	0.96	19.67	79.36
	71	21.96	2.49	19.47	78.04

TABLE 5.1. (contd.)

COPOLYMER	TIME (HRS)	% WT. LOSS	% RESIDUE
1/15	3	1.30	98.69
	5	3.53	96.46
	7	4.39	95.60
	16	8.15	91.85
	24	8.63	91.85
	42	14.20	85.80
POLY n-Bu.A.	2	2.10	97.90
	3	2.98	97.02
	7	4.09	95.90
	17	6.92	93.08
	25	6.18	93.82
	46	10.47	89.53.

100/1 COPOLYMER

FIG. 51.



(0.99 mole % n-butyl acrylate copolymer.)

25 | 1 COPOLYMER

FIG.5.2.

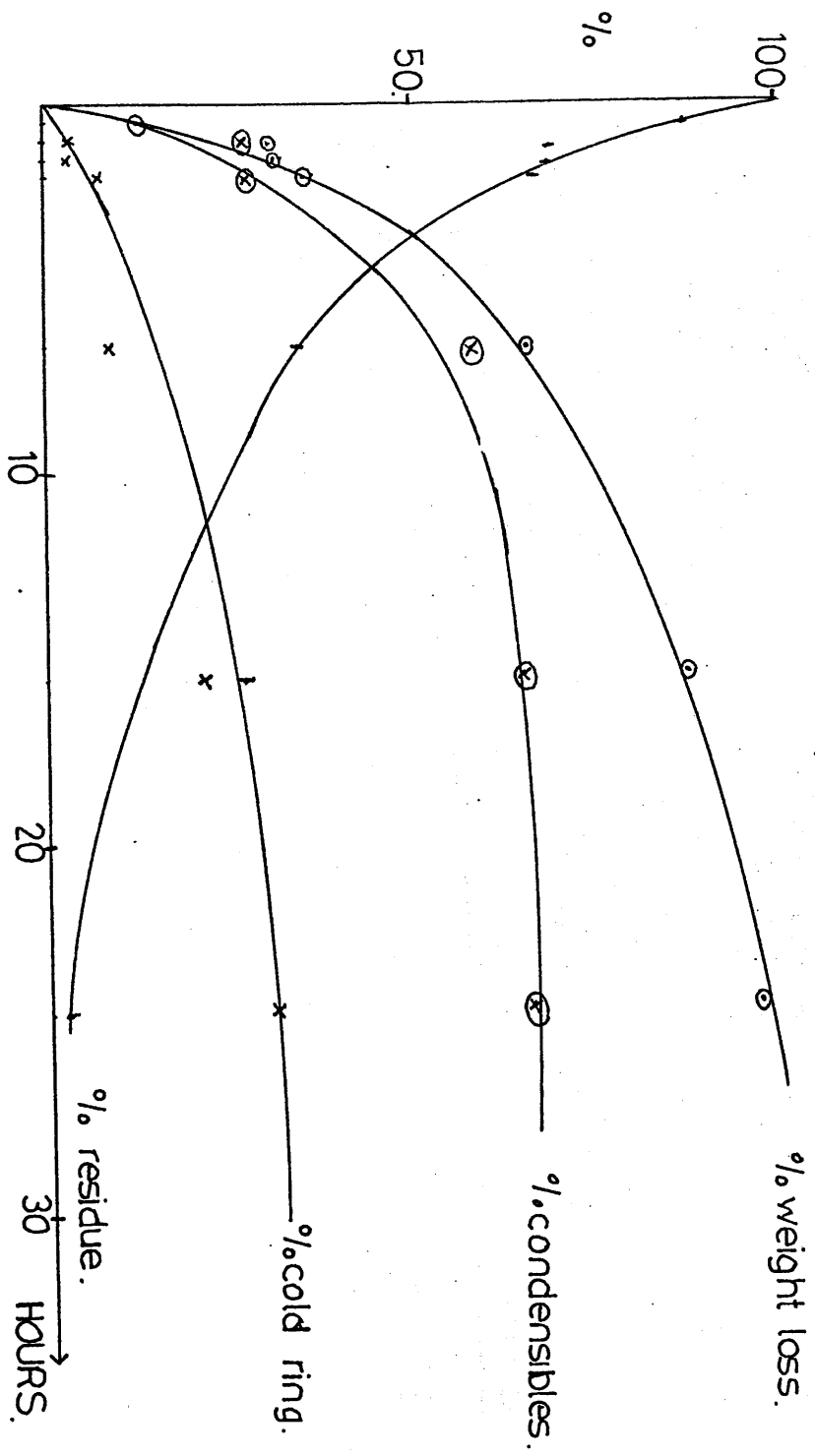


FIG.5.3.

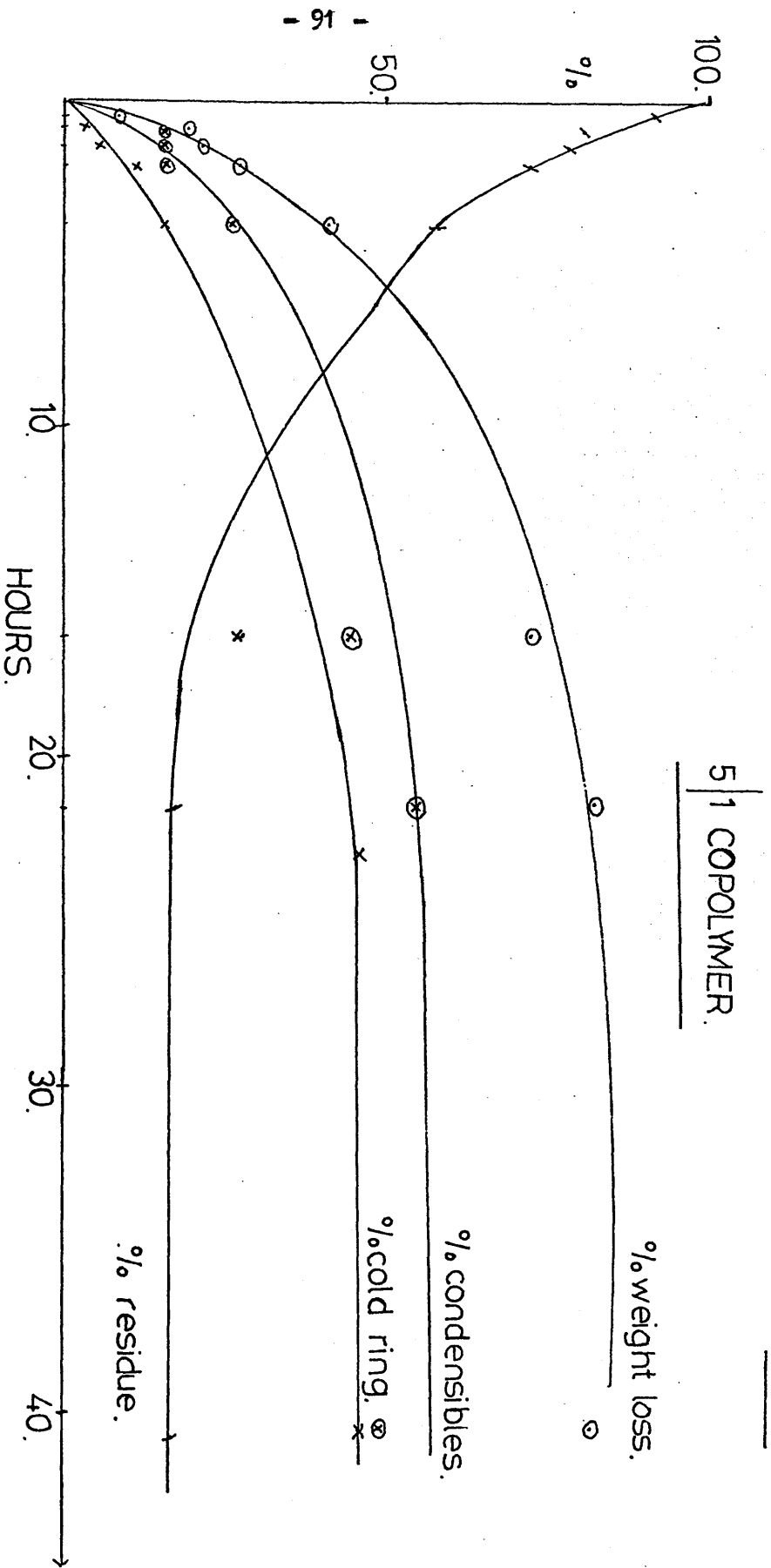


FIG.5.4.

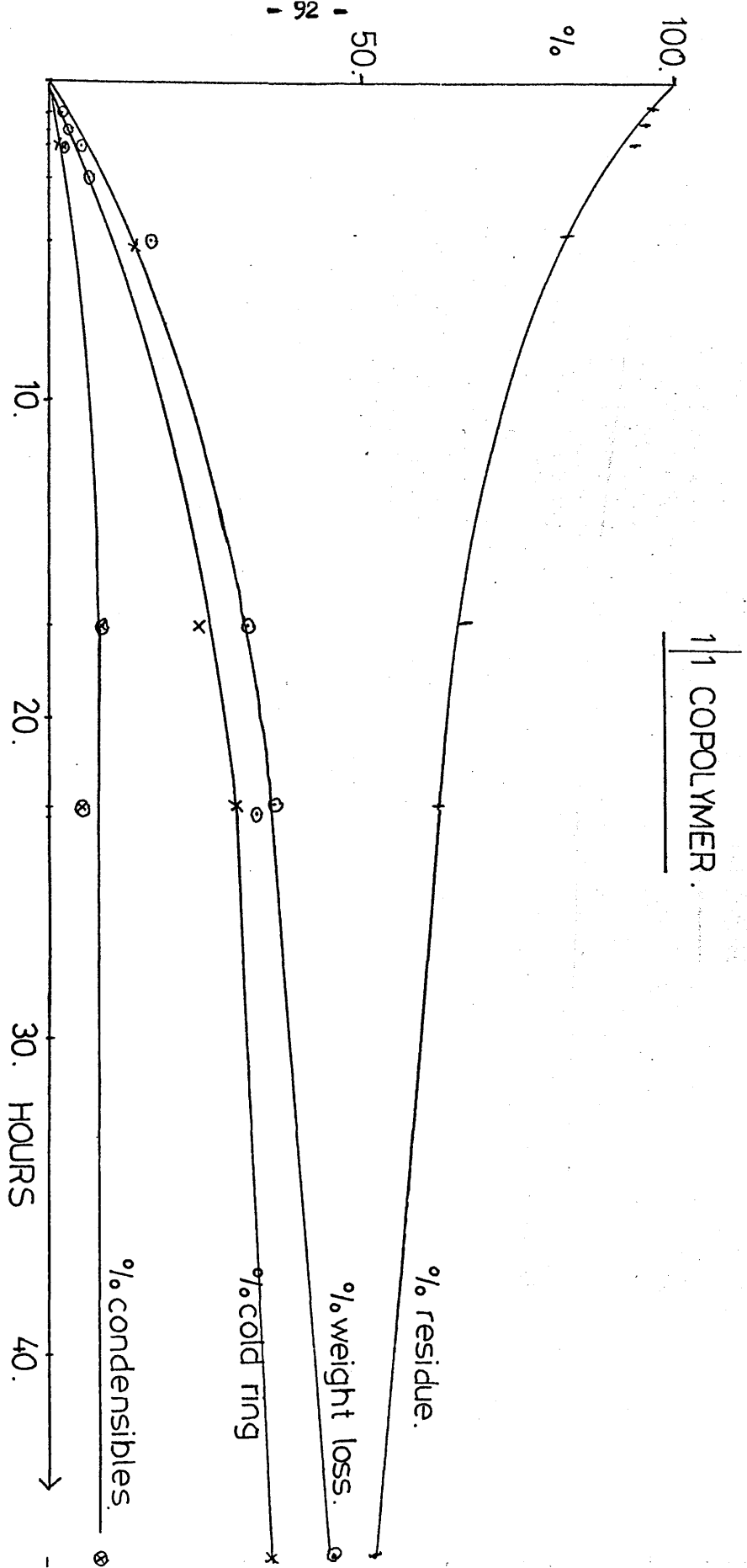


FIG. 5.5.

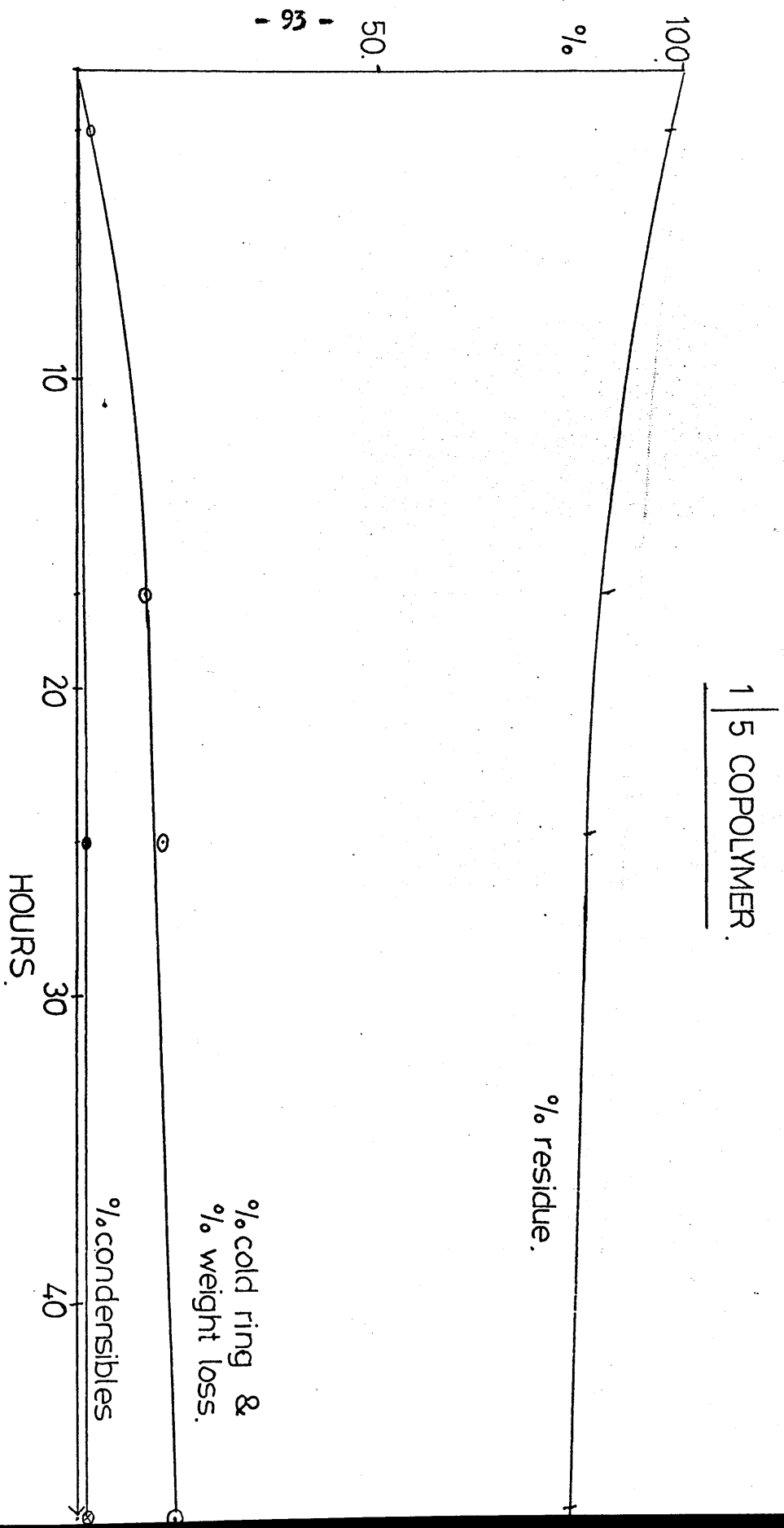


FIG. 5.6.

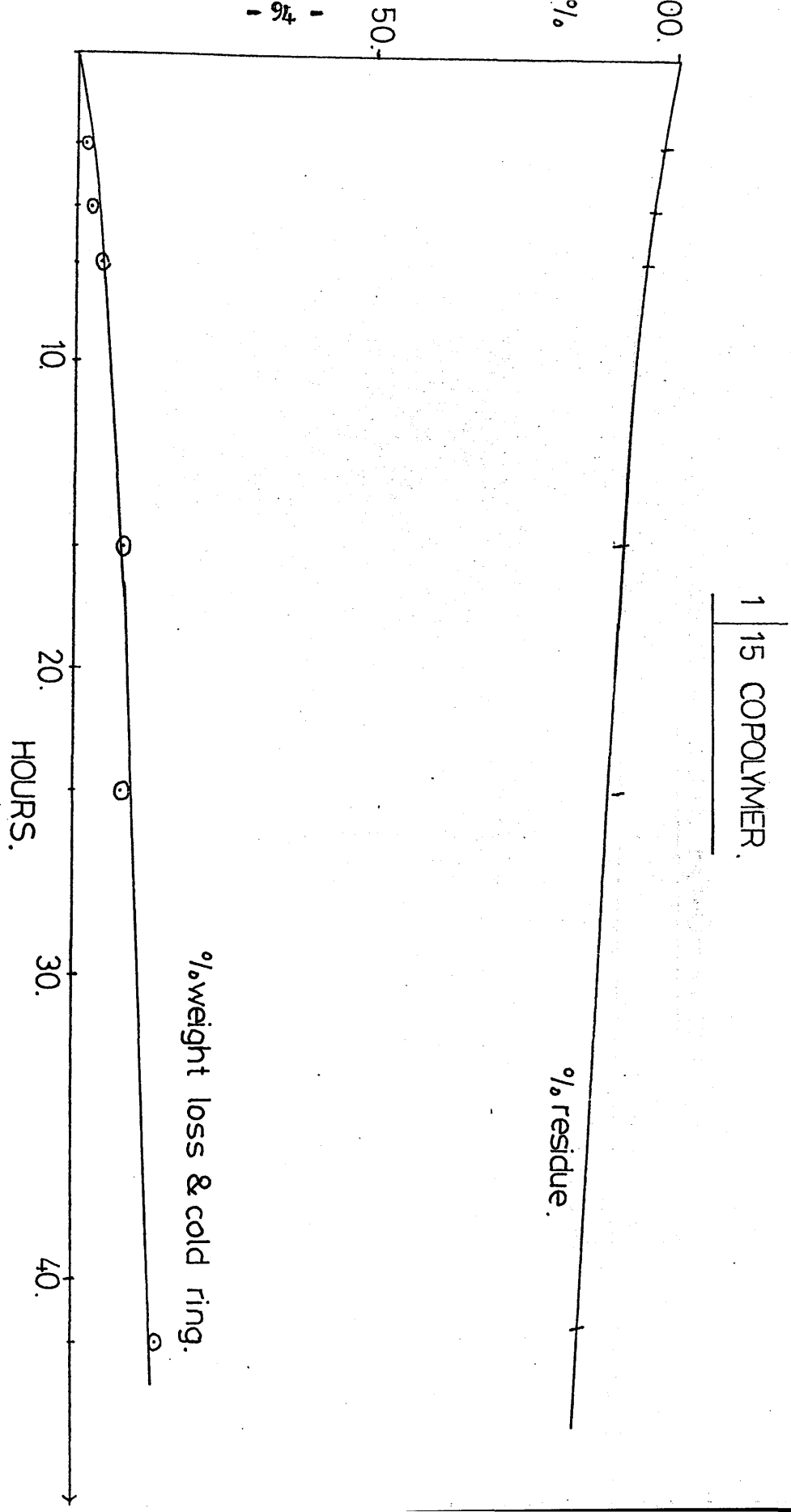


FIG. 5.7.

n-BUTYL ACRYLATE HOMOPOLYMER.

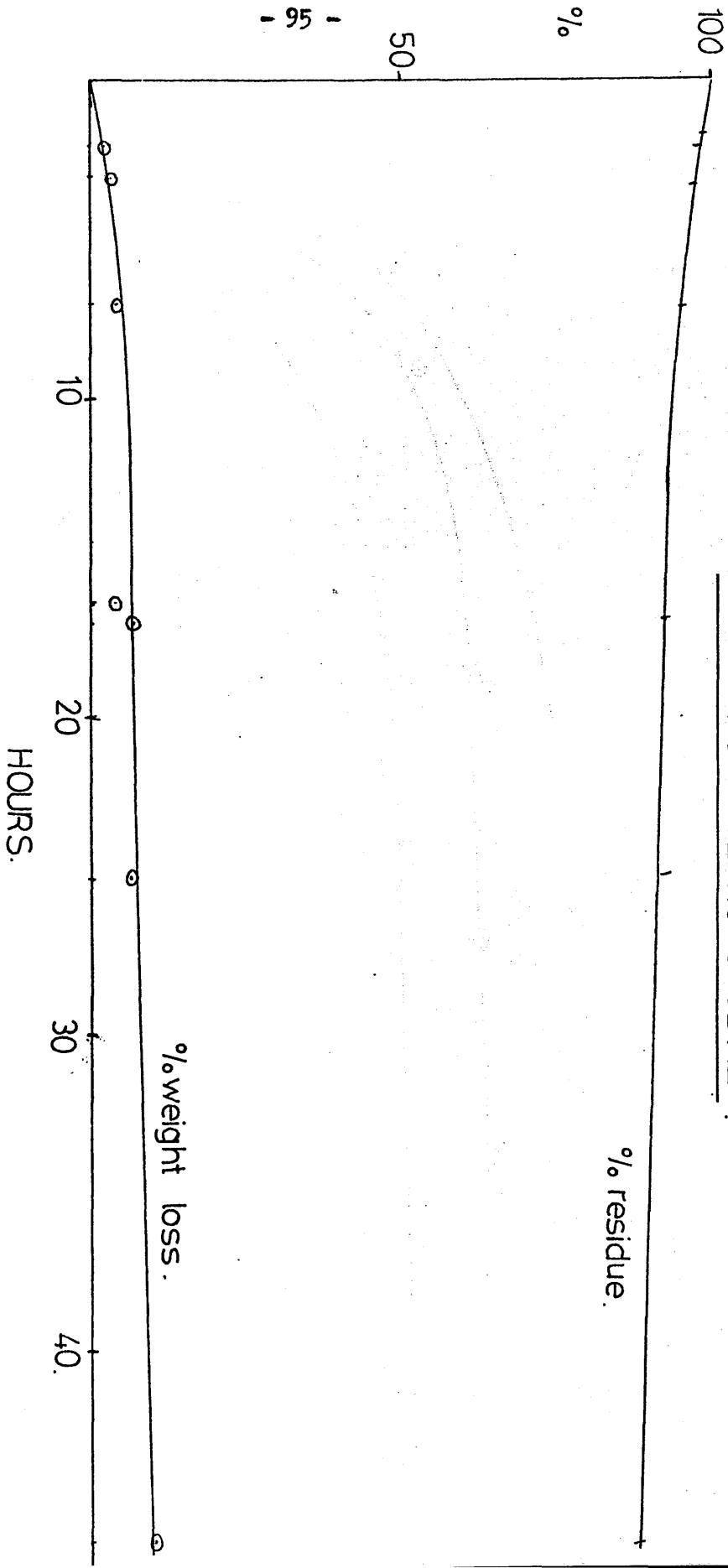


FIG.5.8.

% LIQUID VOLATILES.

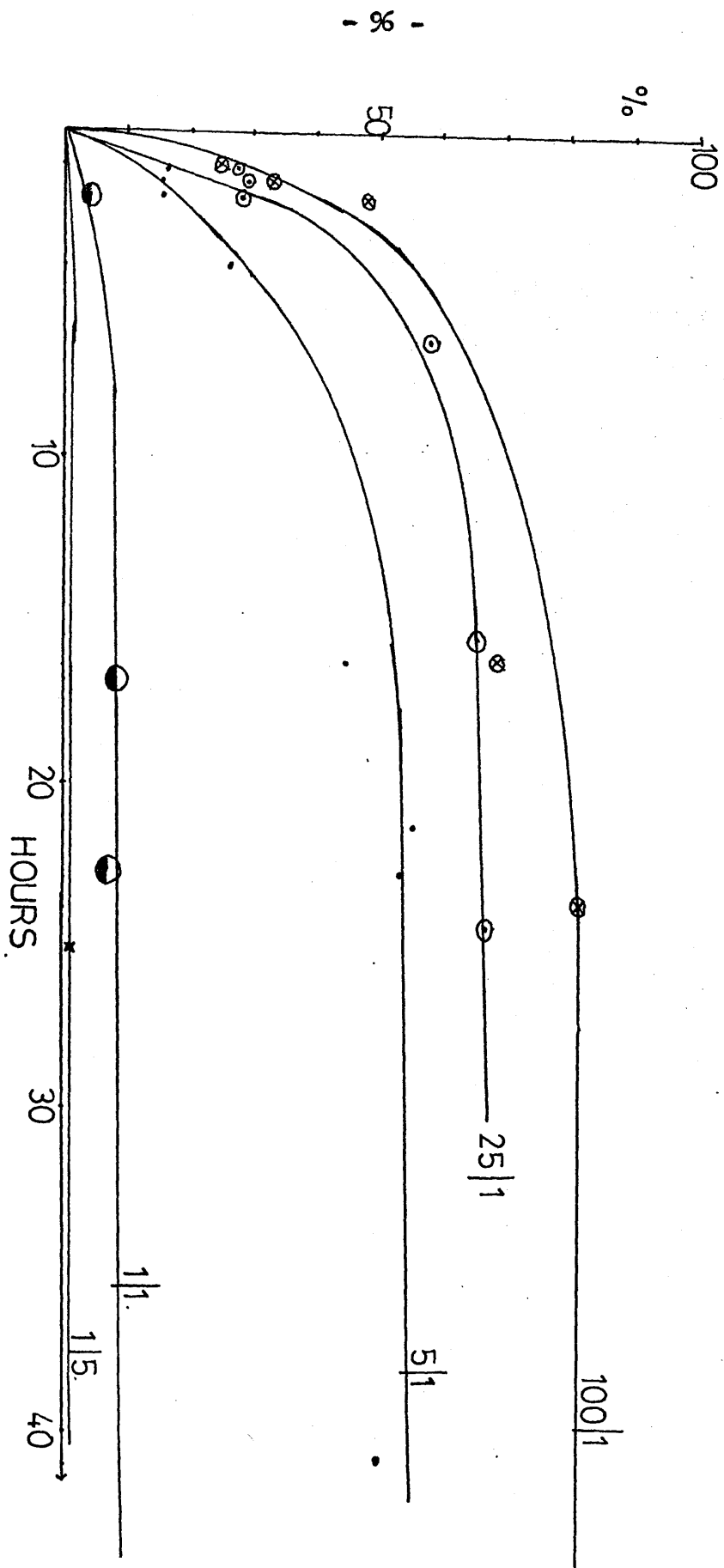
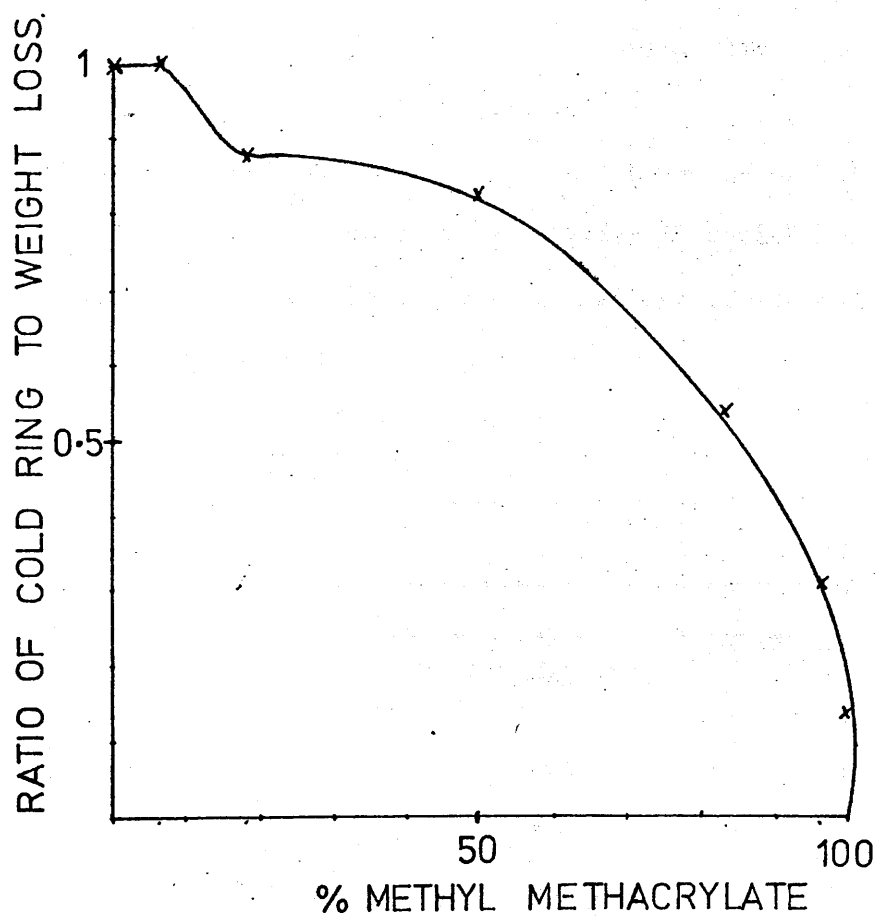


FIG 5.9.

CHANGE IN COLD RING—WT. LOSS RATIO.



5.3. Analysis of Liquid Degradation Products.

(a) Analytical Techniques.

The condensible liquid products were analysed by infra-red spectroscopy (4.2 a.) and g.l.c. (4.2 c.). Using a 5 % D.N.P., 5 % B.34 column good separation of the nine well defined degradation products was achieved, as shown in Fig. 4.5. All quantitative measurements were carried out using this column.

As described in section (2.8e) cyclohexane was chosen as an internal standard, and the sensitivity of each product relative to cyclohexane was calculated. Table 5.2. shows the sensitivity factors of the major components relative to cyclohexane.

TABLE 5.2.

5 % D.N.P., 5 % B. 34 .	
COMPONENT	SENSITIVITY FACTOR (k) RELATIVE TO CYCLOHEXANE.
n-Butyraldehyde	0.25
Benzene	1.06
n-butanol	0.47
n-butyl acrylate	0.71
n-butyl methacrylate.	0.81
methyl methacrylate	0.73

Using these sensitivity factors the percentage by weight of any product can be calculated as described in section 2.8 e.

(b) Treatment of Results

With methacrylate rich copolymers residual solvent (benzene) was present among the liquid volatile products. This benzene was evolved during the 15 minute period which was required for the polymer films to attain the operating temperature of 165°C. Since the polymer films were not irradiated until this temperature was attained, benzene is therefore not a photolysis product.

The total weight of residual benzene, calculated from g.l.c. data, was subtracted from the initial polymer weight before calculating the number of millimoles of each product per gram of polymer. Table 5.3. lists the concentrations of the five products in units of millimoles of product per gram of polymer. The term 'trace' is used to imply less than 0.02 millimoles of product per gram of polymer. The percentage of each of the components analysed for, with respect to the total weight of the liquid fraction, did not change in any systematic fashion as the reaction proceeded. The difference between the sum of the weights of the components and the total weight of liquid products can be accounted for in terms of grease degradation products, (see Table 4.2.), and short chain fragments which distilled into the weighed capillary tube.

Using the data of Table 5.3., the graph of methylmethacrylate production (millimoles/gm. polymer) with time of irradiation was

TABLE 5.3.

Data given in terms of millimoles of product per gram initial polymer.

COPOLYMER	TIME OF PHOTOLYSIS	M.M.A.	BUTYRALDEHYDE	BUTYL ACRYLATE	BUTANOL	BUTYL METHACRYLATE
100/1	1.5 2 16.5 24 47.5	2.56 3.36 5.55 5.86 6.97	NIL	NIL	NIL	NIL
25/1	1.5 2 6.5 15.5 24.5	1.54 1.26 4.06 4.81 5.07	NIL NIL TRACE TRACE TRACE	NIL	NIL	NIL
5/1	2 4 16.5 23 41	1.10 1.79 3.91 4.52 3.68	NIL 0.02 0.023 0.036 0.030	TRACE TRACE TRACE TRACE TRACE	NIL	NIL

TABLE 5.3.

Data given in terms of millimoles of product per gram initial polymer.

COPOLYMER	TIME	M.M.A.	BUTYRALDEHYDE	BUTYL ACRYLATE	BUTANOL	BUTYL METHACRYLATE
1/1	4	0.33	.021	TRACE	TRACE	TRACE
	16.5	0.56	.031	TRACE	TRACE	TRACE
	45	0.76	.052	.025	TRACE	TRACE
	70	0.88	.053	.029	TRACE	TRACE
1/5	25	0.04	0.056	TRACE	0.039	TRACE
	47	0.08	0.11	TRACE	0.052	TRACE
	71	0.10	0.16	TRACE	0.061	TRACE.

constructed (Fig. 5.10.), showing an increase in methyl methacrylate monomer production with increasing time of irradiation and methacrylate content of the copolymers, as expected. Fig. 5.11. shows the relative importance of the two largest components, methyl methacrylate and n-butyraldehyde, for a 50 mole per cent n-butyl acrylate copolymer.

The data for the analysis of the trace degradation products is given in Tables 5.4. - 5.7. These data were obtained by the standard g.l.c. technique. Since the g.l.c. peak areas of the trace products were small the data are not highly accurate, but the results can be used to show the general trends. The relative importance of the photolysis products is shown for a 50 mole per cent n-butyl acrylate copolymer. (Fig. 5.12.). Using this figure along with Fig. 5.11., it is observed that the order of importance of products is methyl methacrylate > butyraldehyde > butyl acrylate > butanol. The production of n-butyraldehyde for four copolymers is shown in Fig. 5.13. Butyraldehyde production is shown to increase with acrylate content of the copolymers. The production of n-butyl acrylate and n-butanol is shown graphically in Figs. 5.14 and 5.15. respectively. No data are given for the 1/15 copolymer in Table 5.3. since systematic measurement of the production of volatiles was impossible.

5.4. Analysis of Gaseous Degradation Products.

Figures 4.16 and 4.17 show the g.l.c. and I.R. analysis of the permanent gas fraction. Since the total pressure of these gases, as

FIG. 5.10.
methyl methacrylate production.

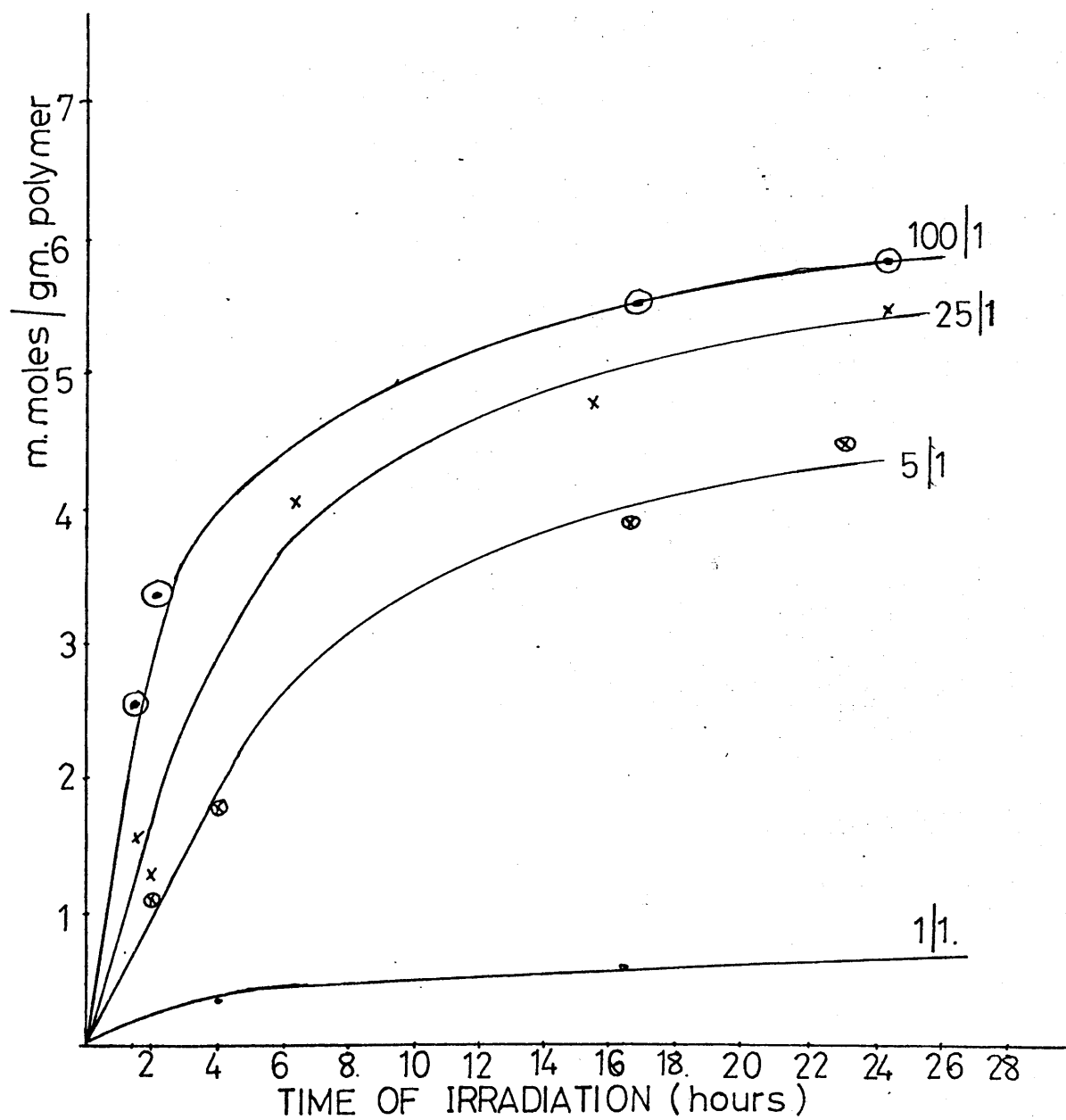


FIG. 5.11.
photolysis of 50mole% n-butyl acrylate copolymer.

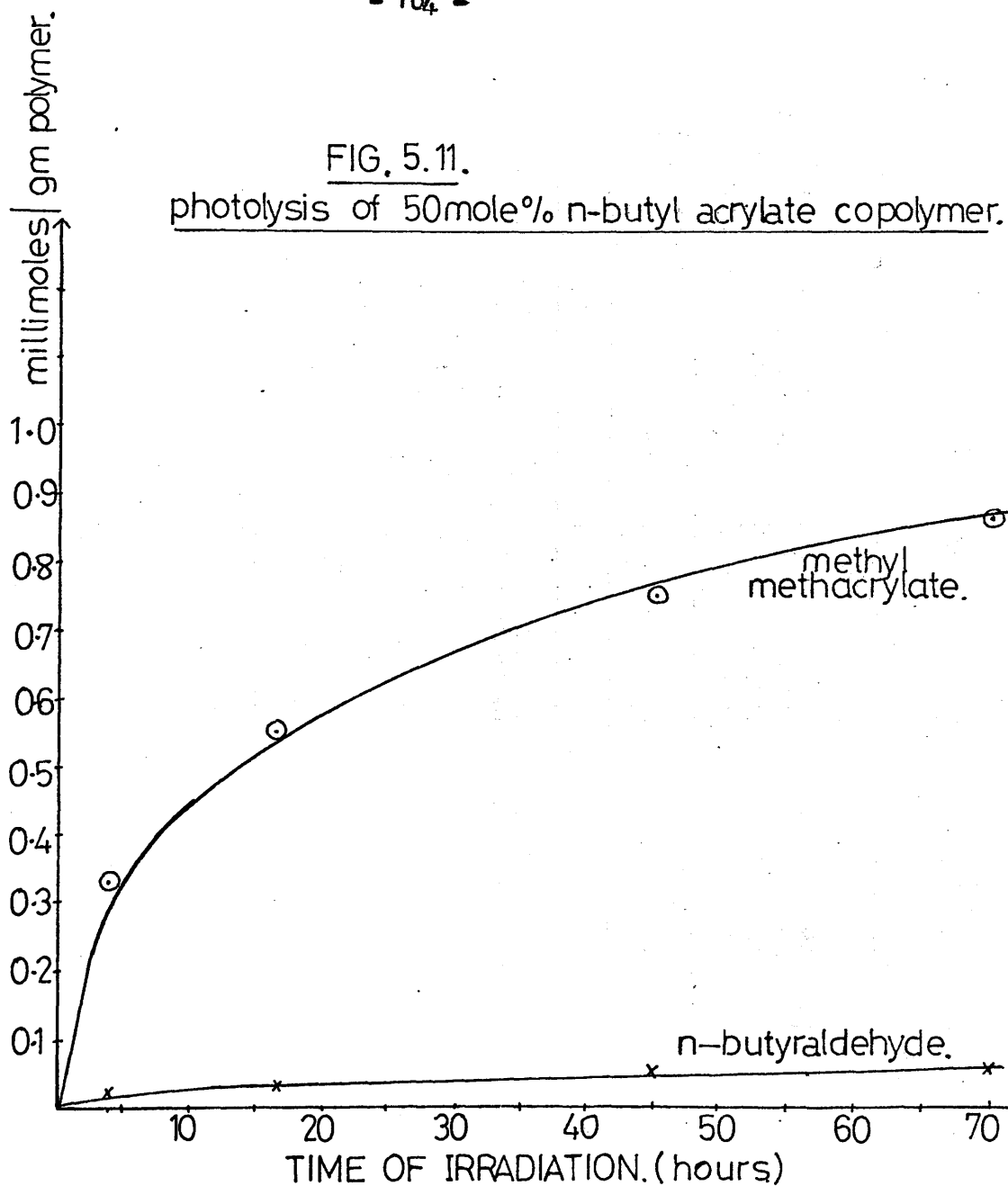


TABLE 5.4.

Data for Butyraldehyde Production (Fig. 5.13.)

25/1			5/1			1/1			1/5		
Time (hrs.)	No. of millimoles /gm. polymer		Time (hrs.)	No. millimoles /gm. polymer		Time (hrs.)	No. millimoles /gm. polymer		Time (hrs.)	No. millimoles /gm. polymer	
1.5	0		2	0		4	.021		25	.056	
2	0		4	0.020		16.5	.031		47	.11	
6.5	0.006		16.5	0.023		45	.052		71	.16	
15.5	0.014		23	0.036		70	.053				
24.5	0.016		41	0.030							

- 105 -

TABLE 5.5.

Data for Butyl Acrylate Production.

5/1			5/1			1/5		
Time (hrs.)	No. millimoles /gm. polymer		Time	No. millimoles /gm. polymer.		Time	No. millimoles /gm. polymer.	
2	.007		4	.01		25	.006	
4	.020		16.5	.018		47	.007	
16.5	.019		45	.025		71	.008	
23	.021		70	.029				
41	.016							

TABLE 5.6.

Data for Butyraldehyde Production (Fig. 5.15.)

1/1		1/5	
TIME	No. millimoles /gm. polymer.	TIME	No. millimoles /gm. polymer
4	.008	25	.039
16.5	.007	47	.052
45	.018	71	.061
70	.014		

TABLE 5.7.

Data for Butyl Methacrylate Production.

1/1		1/5	
TIME	No. millimoles /gm. polymer	TIME	No. millimoles /gm. polymer.
4	.0009	25	.0004
16.5	.0008	47	.0006
45	.0015	71	.0007
70	.0012		

FIG. 5.12.

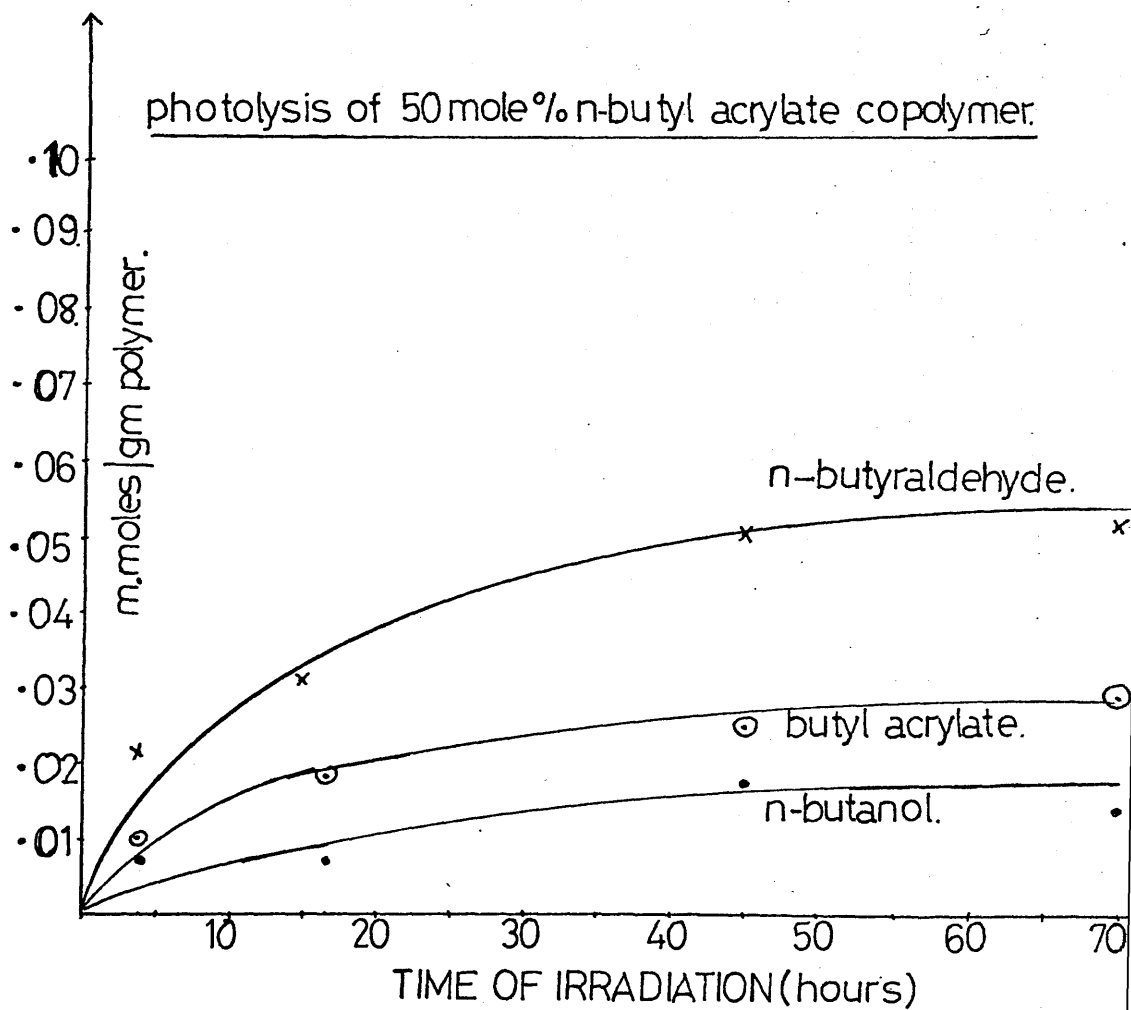
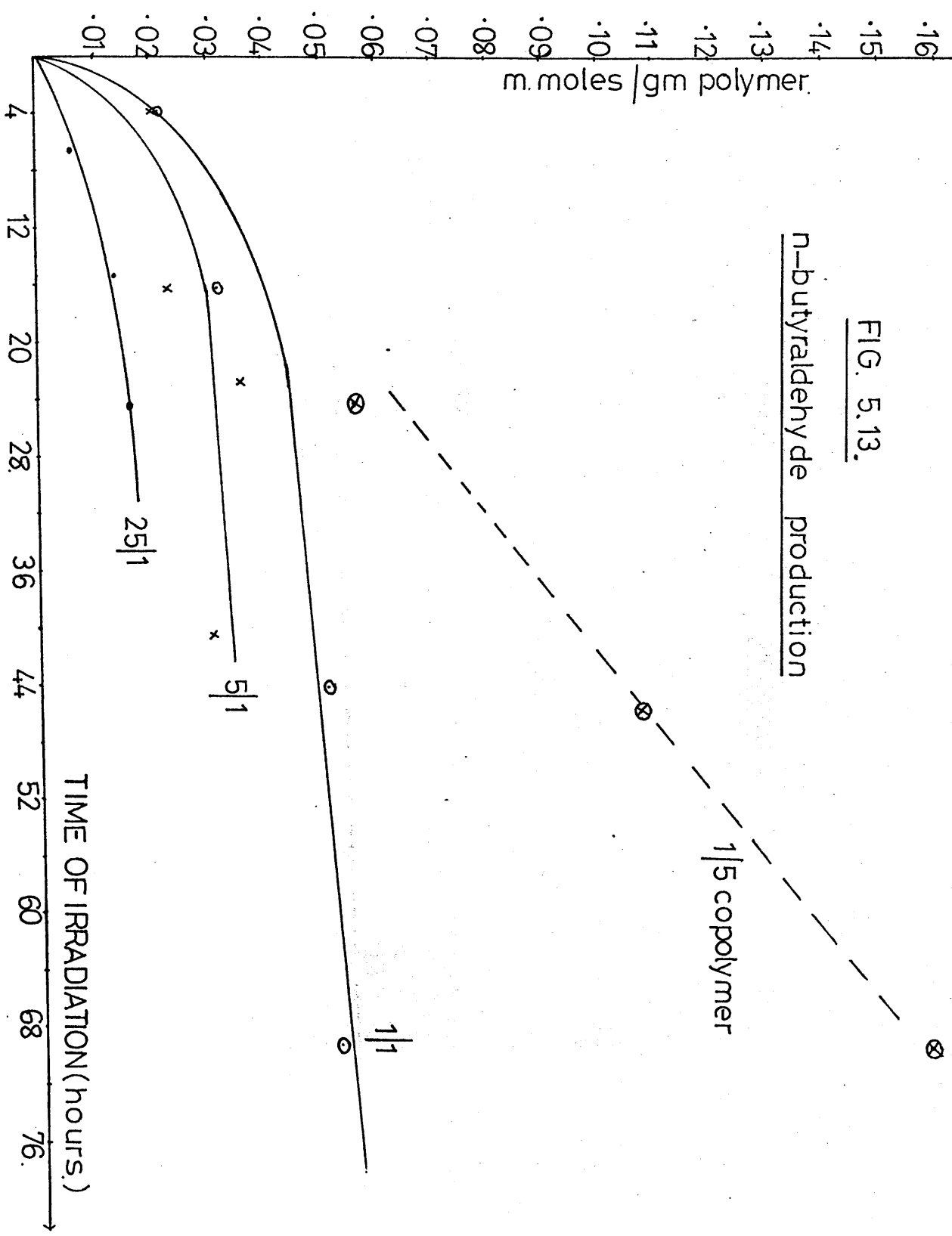


FIG. 5.13.

n-butyraldehyde production



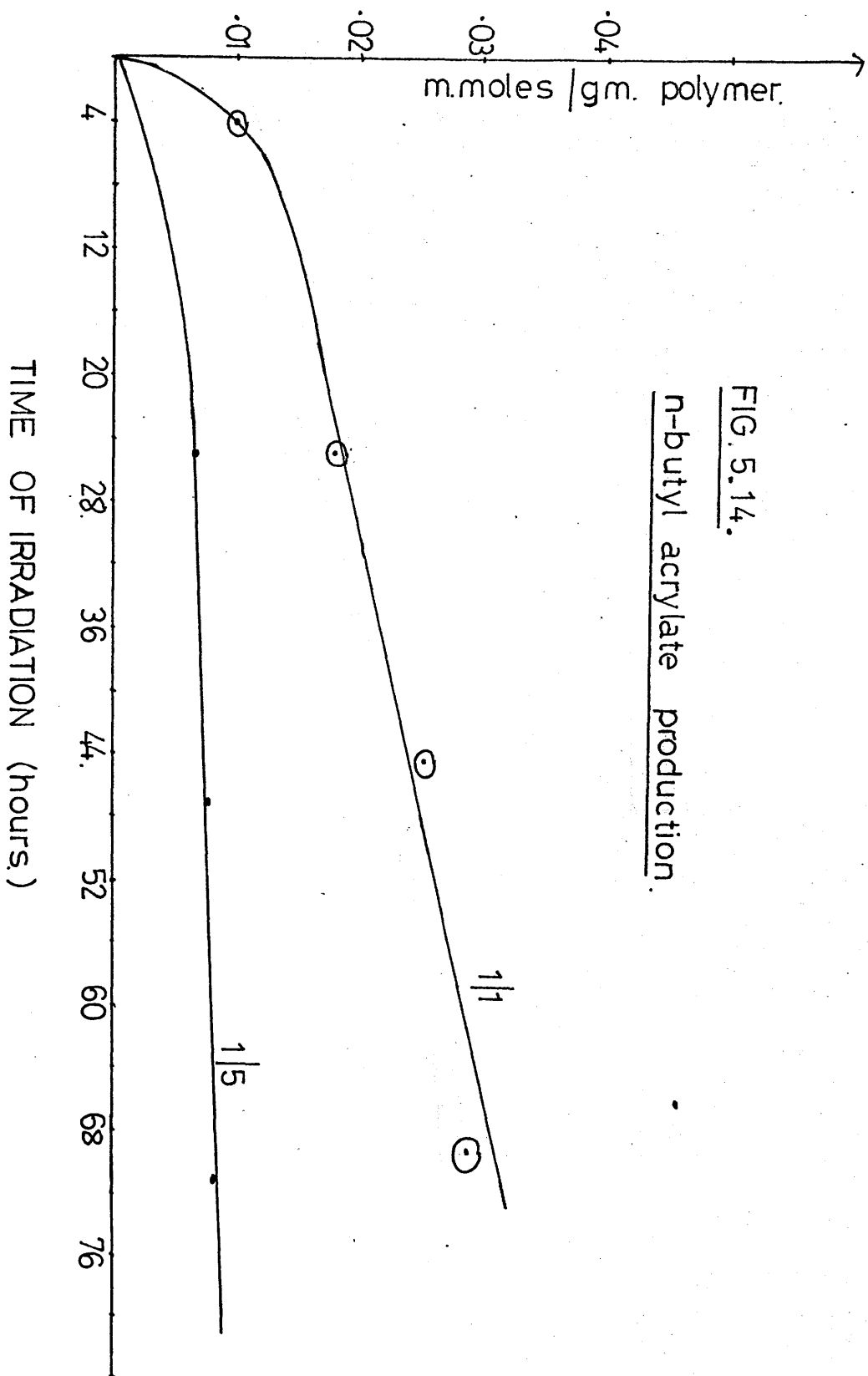
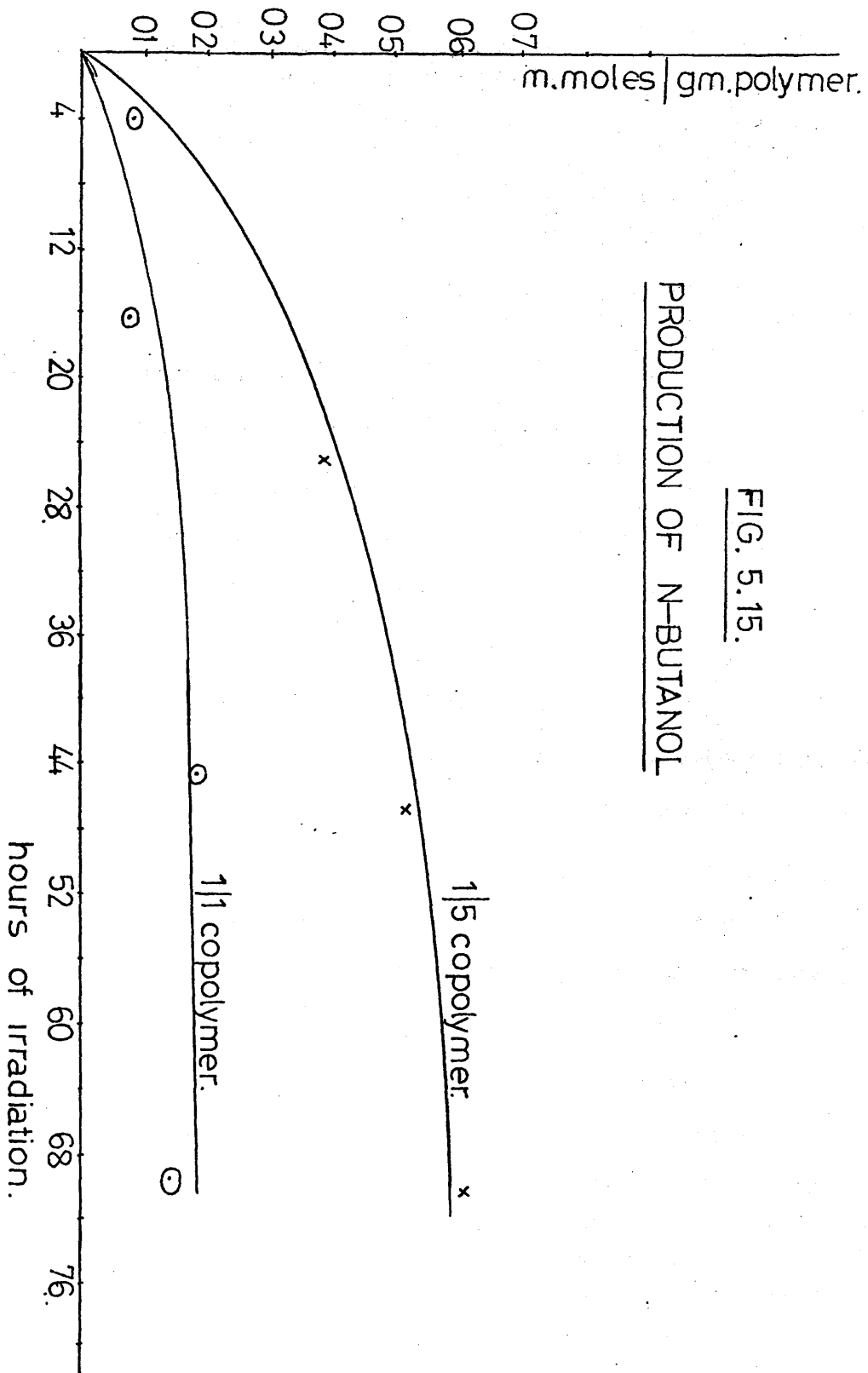


FIG. 5.15.

PRODUCTION OF N-BUTANOL



measured by the McLeod gauge, was so small (1-2 mm Hg.) no detailed pressure measurements were carried out. Using the g.l.c. peak areas of Figure 4.16 and 4.17., a semi-quantitative measurement is possible.

	Peak Ratio		
	H	CO	CH ₄
50 mole% n-butyl acrylate copolymer	0.9	2.4	1
82.2 " " " "	15.6	1.3	1

5.5. Discussion of Results.

As expected the percentage weight loss and liquid condensibles decreases with increasing acrylate content, whilst the percentage residue increases with acrylate content. The copolymers become more stable with increase in acrylate content. The short chain fragments (cold ring) become important with increasing acrylate content consistent with the increasing predominance of transfer reactions..

The amount of methyl methacrylate found in the liquid condensibles increases with methacrylate content while the amount of butyraldehyde decreases. Butyraldehyde is present as a degradation product even in a 3.9 mole per cent n-butyl acrylate copolymer where the percentage acrylate-acrylate linkages, as calculated by sequence distribution data , is 0.1. (Section 7.2.). Thus butyraldehyde is evolved from single butyl ester side chains. The alcohol production increases with increasing acrylate content but it is not present until the acrylate content reaches 50 mole per cent, that is until a reasonable proportion

of units are present in adjacent sequences.

The data of table 5.5. and Fig. 5.14. indicate that more n-butyl acrylate monomer is evolved from both the 16.3 and 50 mole per cent n-butyl acrylate copolymers than from the 82.2 mole per cent n-butyl acrylate copolymer. Thus increase of acrylate content appears to result in a decrease of the acrylate monomer production. A similar result was found for the purely thermal degradation of M.M.A./nBuA. copolymers.^{4a} Acrylate monomer must be produced in a depolymerisation reaction initiated at methacrylate chain units. The depolymerisation must be capable of unzipping through some of the acrylate units before termination occurs. If no methacrylate units are available to initiate the process the acrylate radicals will take part in transfer reactions and very little acrylate monomer will be evolved.

As in the thermal degradation,^{4a} n-butyl methacrylate production is greatest in a 50 mole per cent n-butyl acrylate copolymer, where there are the greatest number of acrylate - methacrylate linkages. (Section 7.2.).

The permanent gas results indicate that hydrogen evolution increases with increasing acrylate content and is associated with the polymer backbone. Methane and carbon monoxide are evolved in roughly the same proportions in the two copolymers studied.

CHAPTER 6.

CHAIN SCISSION AND THE RESIDUE.

6.1. INTRODUCTION.

The measurement of the number average molecular weight of the residue at various stages of the reaction is often a useful method of elucidating the mechanism of a degradation process.⁵⁷ There are three general mechanisms by which degradation can proceed. (1) Random scission, with little monomer production, will result in a rapid drop in the molecular weight. (2) Step wise degradation, in which monomer is eliminated progressively from the ends of the long chain molecules, will result in a linear relationship between the residual molecular weight and the amount of monomer produced. (3) Depolymerisation, the reverse of chain propagation in polymerisation, results in complete disintegration to monomer, the molecular weight of the residue remaining unchanged.

6.2. Molecular Weight of Residue.

The copolymer films were degraded under standard conditions as described in Chapter 2. The weight of material lost by volatilisation was obtained by weighing the silica disc and polymer film before and after degradation. The residue was dissolved in toluene for molecular weight determinations. The results are presented in Table 6.1. The plot of volatilisation against molecular weight (% of original) is shown in Fig. 6.1., which is similar to the plot obtained previously

for the thermal degradation of this copolymer system. ⁴²Grassie ⁵⁸ has shown that, for this type of plot, if the degradation is a depolymerisation process, the curve will be above the diagonal AC, while a curve along ABC implies a random scission process. Although the change in molecular weight with progressing degradation is useful in elucidating the mechanism of degradation, it should be noted that this evidence alone is insufficient to decide finally whether a polymer molecule suffers random or chain end initiation. ⁵⁹

It is evident that for high acrylate content copolymers photo-thermal degradation proceeds by a random scission process, and that as the acrylate content is decreased the mechanism tends towards the depolymerisation process of pure poly methyl methacrylate.

Table 6.1.

Molecular Weight / Volatilisation Data for Methyl Methacrylate /
n-Butyl Acrylate Copolymers.

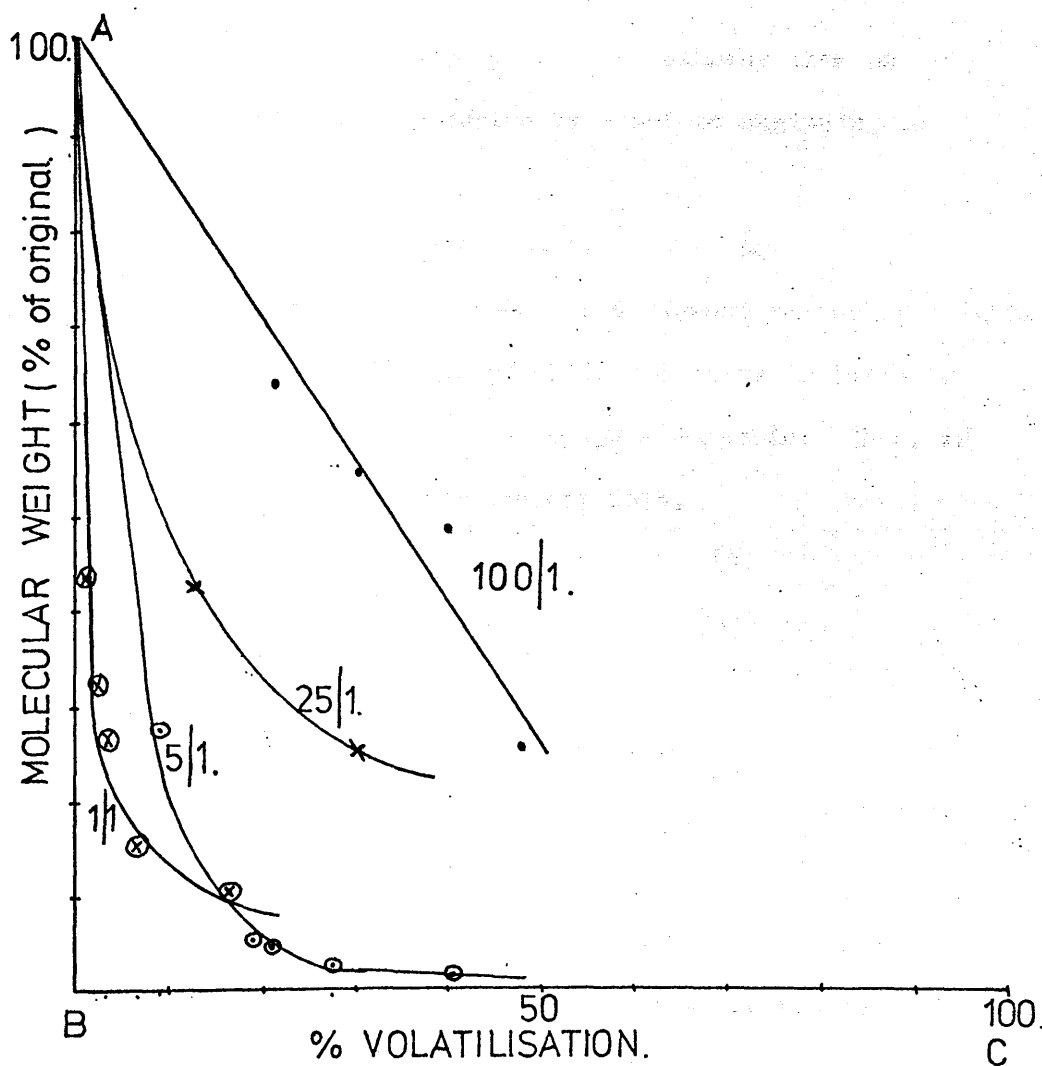
Copolymer	Time (hrs.)	% Volatilisation	M.W.	M.W. % of original
100/1	0	0	260,000	100
	0.5	21.76	165,000	63.46
	1.0	30.35	143,000	54.99
	1.5	40.17	125,000	48.07
	2.0	48.72	67,600	25.99
25/1	0	0	347,000	100
	0.5	12.77	146,000	42.08
	1.0	30.57	87,200	25.13
	1.5	31	73,000	21.04
5/1	0	0	1330,000	100
	0.5	8.93	361,000	27.14
	1.0	19.62	68,000	5.11
	1.5	21.25	60,000	4.51
	2.0	27.01	36,500	2.74
	4.0	41.66	25,100	1.84
	21.5	82.19	9,880	0.74

Table 6.1.

Molecular Weight / Volatilisation Data for Methyl Methacrylate /
n-Butyl Acrylate Copolymers.

Copolymer	Time (hrs.)	% Volatilisation	M.W.	M.W. % of original
1/1	0	0	230,000	100
	0.25	0	135,000	58.59
	0.5	1	101,000	43.91
	1.0	2.26	74,000	32.18
	1.5	3.41	61,700	26.83
	3	6.63	36,300	15.79
	5	16.07	23,900	10.40
1/5	0	0	506,000	100
	0.5	0	160,000	31.61
	1.5	0	85,000	16.80
	2	0	67,700	13.38
1/15	0	0	1,410,000	100
	0.25	0	250,000	17.73
	0.5	0	196,000	13.90
	1.0	0	138,000	9.78
	1.5	0	90,600	6.42

FIG. 6.1.
MOLECULAR WEIGHT VERSUS % VOLATILISATION.



6.3. Calculation of Chain Scission in the Presence of Volatilisation.

If N is the number of chain scissions which has occurred per polymer molecule and CL_0 and CL are the chain lengths at zero time and after N breaks respectively, then provided that no material is lost by volatilisation,

$$N = \frac{CL_0}{CL} - 1. \quad \dots \quad (1)$$

If the fraction of polymer volatilised is χ , but assuming that no polymer molecules are lost from the system by complete unzipping to volatile fragments,^{as}

$$N = \frac{CL_0}{CL} (1-\chi) - 1. \quad \dots \quad (2)$$

For the purpose of comparison of copolymers of different molecular weights, it is convenient to express the number of chain scissions in terms of scissions per monomer unit rather than per polymer molecule. Thus, if n is the number of chain scissions per monomer unit,

$$N = nCL_0 \quad \dots \quad (3)$$

$$\text{and} \quad n = \frac{1-\chi}{CL} - \frac{1}{CL_0} \quad \dots \quad (4)$$

Values of n and N are calculated in Table 6.2.

(a) Relation between Volatilisation and Chain Scission.

Using equation (4), the number of chain scissions, n, per monomer unit can be calculated, taking into account the material lost by volatilisation. The relationship between volatilisation and chain scission is shown in Fig. 6.2. This plot must be interpreted in

Table 6.2.

Data for Calculation of n and N.

Copolymer	Time hrs.	M.W.	% Volat.	$n \times 10^4$ scissions per monomer unit.	N scissions per polymer molecule.
100/1	0	260,000	0	0	0
	0.5	165,000	21.76	0.94	0.24
	1	143,000	30.35	1.02	0.26
	1.5	125,000	40.17	0.96	0.25
	2	67,600	48.72	3.8	0.99
25/1	0	347,000	0	0	0
	0.5	146,000	12.77	3.13	1.08
	1	87,000	30.57	5.14	1.77
	1.5	73,000	31.00	6.60	2.29
5/1	0	1,330,000	0	0	0
	0.5	361,000	8.93	1.86	2.36
	1	68,000	19.62	11.59	14.73
	1.5	60,000	21.25	12.95	16.45
	2	36,500	27.01	20.14	25.59

TABLE 6.2.

DATA FOR CALCULATION OF n and N .

Copolymer	Time Hrs.	M.W.	% Volat.	$n \times 10^4$ scissions per monomer unit.	N scissions per polymer molecule.
1/1	0	230,000	0	0	0
	0.25	135,000	0	3.48	0.70
	0.5	101,000	1	6.22	1.25
	1	74,000	2.26	10.14	2.05
	1.5	61,000	3.41	12.97	2.29
	3	36,300	6.63	24.57	6.12
1/5	0	506,000	0	0	0
	0.5	160,000	0	4.18	1.72
	1.5	85,000	0	11.98	4.92
	2	67,700	0	15.78	6.47
1/15	0	1,410,000	0	0	0
	0.25	250,000	0	4.15	4.64.
	0.5	196,000	0	5.55	6.19
	1	138,000	0	8.25	9.22
	1.5	90,000	0	13.03	14.55

accordance with the restriction that no polymer molecules are lost by complete unzipping. If complete molecules are lost, in high methacrylate copolymers, by unzipping this would give an anomalously high value of the volatiles produced by chain scission. The plot clearly illustrates that the amount of volatiles produced per chain scission decreases as the proportion of acrylate in the copolymer is increased.

By plotting % volatilisation against (N) scissions per polymer molecule as in Figure 6.3., for the four methacrylate rich copolymers, the zip length for each copolymer was calculated as in Table 6.3.

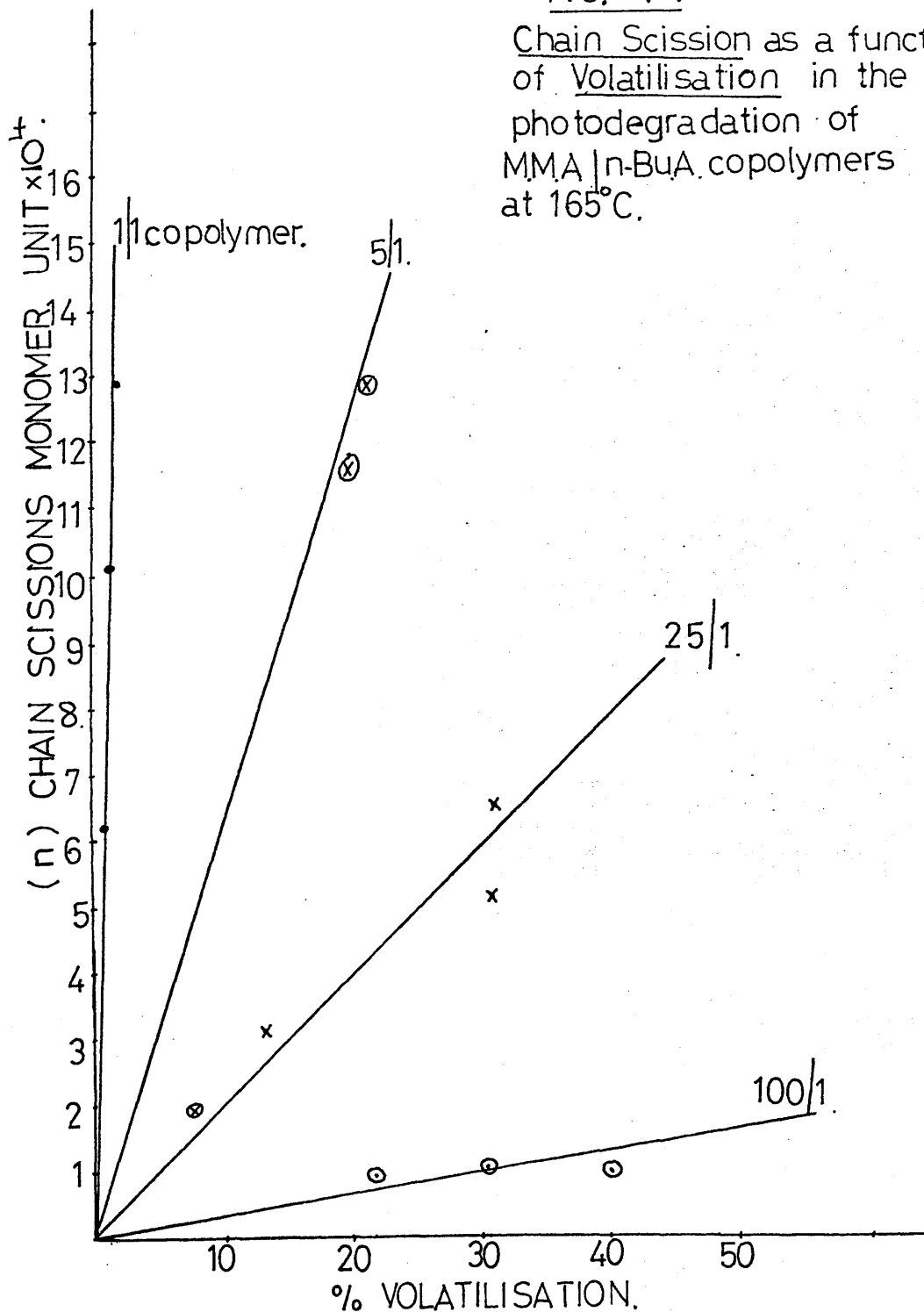
TABLE 6.3.

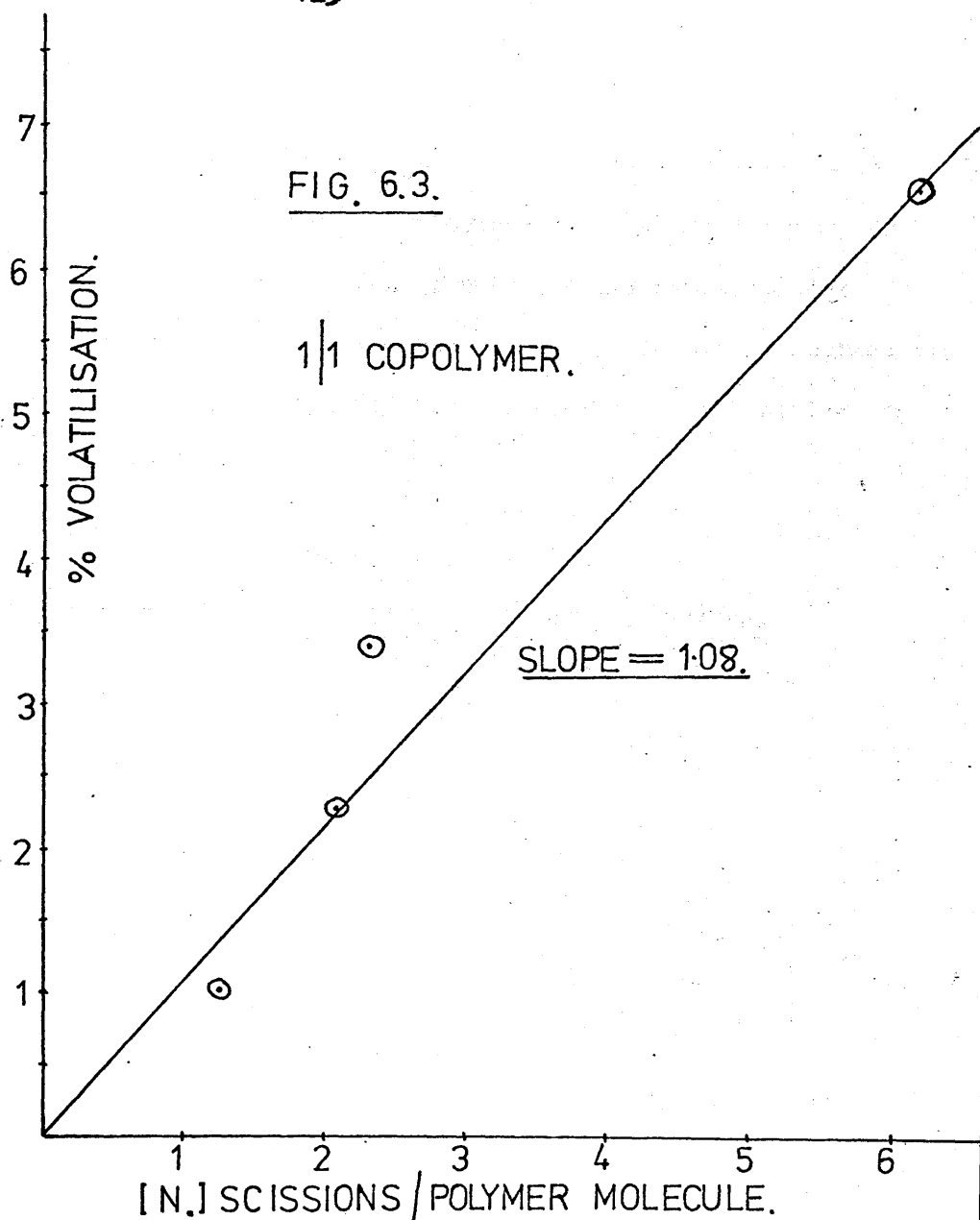
Zip Lengths for Photothermal Degradation. (MMA - nBuA)

Copolymer	Slope (Fig 6.3) % Volatilisation per scission/ molecule [A]	Initial M.W. M.W. ₀	M.W. lost per scission $\frac{M.W \times A}{100}$	Average wt. of monomer [B] unit.	Zip Length $\frac{M.W_0 \cdot A}{100 \cdot B}$
100/1	48.6	260,000	126,400	100.27	1260
25/1	15.0	347,000	52,050	101.08	515
5/1	1.20	1,330,000	15,960	104.6	153
1/1	1.08	230,000	2,484	114	22

FIG. 6.2.

Chain Scission as a function of Volatilisation in the photodegradation of MMA/n-BuA copolymers at 165°C.





RELATIONSHIP BETWEEN SCISSIONS AND
VOLATILISATION FOR 1/1 COPOLYMER.

The blockage of the depropagation reaction by the n-butyl acrylate units is clearly shown by Table 6.3., since zip lengths decrease with increasing methyl acrylate content. Unfortunately, no zip lengths were calculated in the thermal degradation of poly (methyl methacrylate/n-butyl acrylate) copolymers. In the thermal and photothermal degradation of copolymers of methyl methacrylate/methyl acrylate the calculated zip lengths were as shown in Table 6.4.^{32,33.}

TABLE 6.4.

Zip Lengths for Thermal Degradation of poly MMA/MA.

Copolymer	Zip Length.	
	Photothermal	Thermal
MMA/MA		
26/1	1327	74
7.7/1	741	74
2/1	214	34

The zip length of the thermal reaction is very much less than in the photo reaction.

Previously, the data in Fig. 5.8. (chapter 5) illustrated that for the photodegradation volatilisation decreased with increasing acrylate content.

(b) Chain scission with Time of Degradation.

When n (scissions per monomer unit) is represented as a function of time of degradation as in Fig. 6.4., it is evident that the rate of chain scission increases with the acrylate content of the three copolymers. (100/1, 25/1, 5/1.) A similar plot was found by Grassie and Farish for 4 methyl methacrylate / acrylonitrile copolymers, with molar ratios 410/1, 40/1, 16/1, and 8/1, photodegraded by 2537 Å. at 160°C. ^{35,36.}

However, Fig. 6.5 shows the change in chain scission with time of irradiation for the whole copolymer composition range, and it is evident that the rate of chain scission is independent of the n-butyl acrylate content for copolymers of acrylate content greater than 16.6 mole per cent. (5/1 copolymer) Grassie and Colford^{3a} have previously shown that for the photodegradation of methyl methacrylate/methyl acrylate copolymers, the rate of chain scission was independent of the methyl acrylate content of the polymer, although the plot did exhibit a large scatter of points.

FIG 6.4.

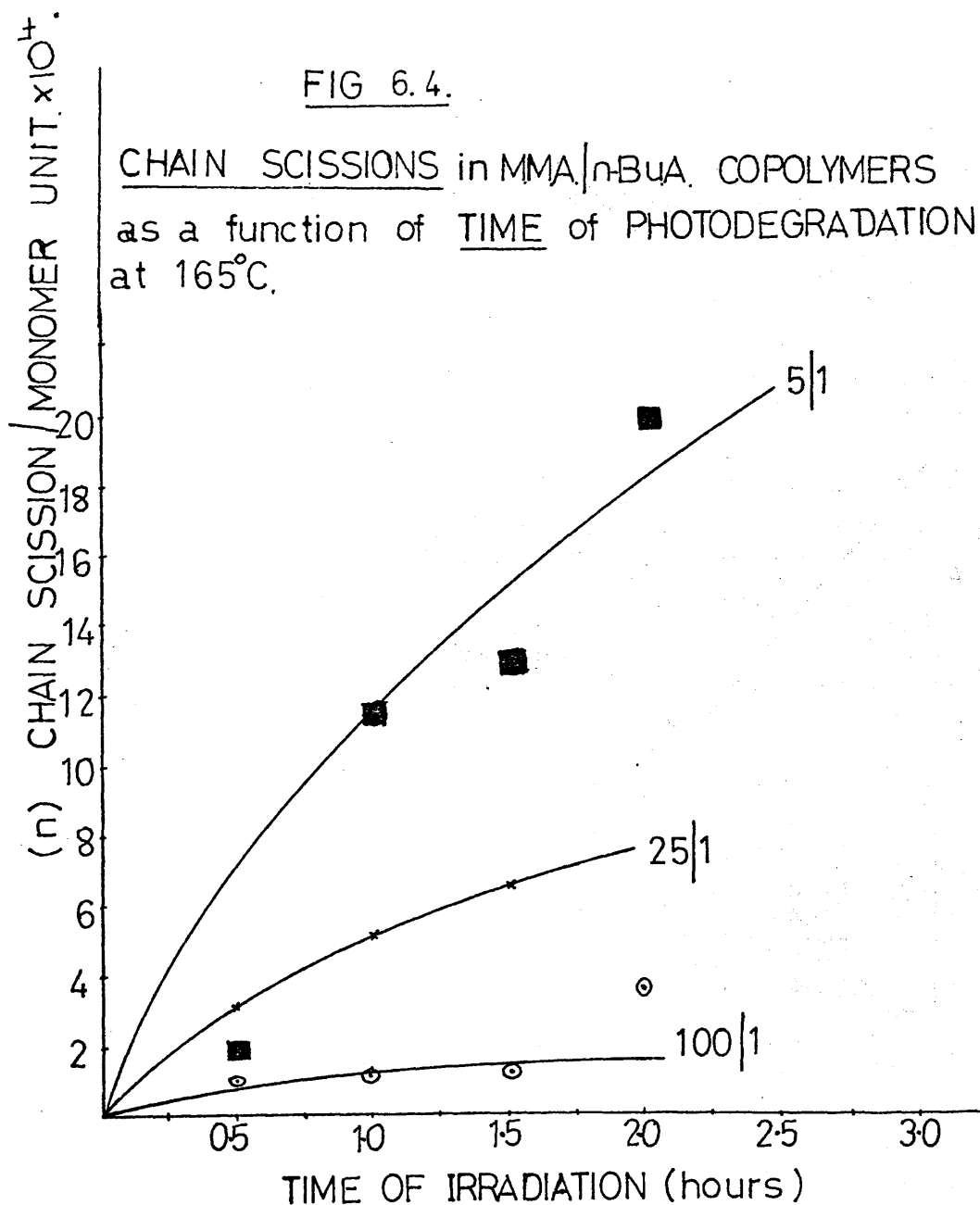
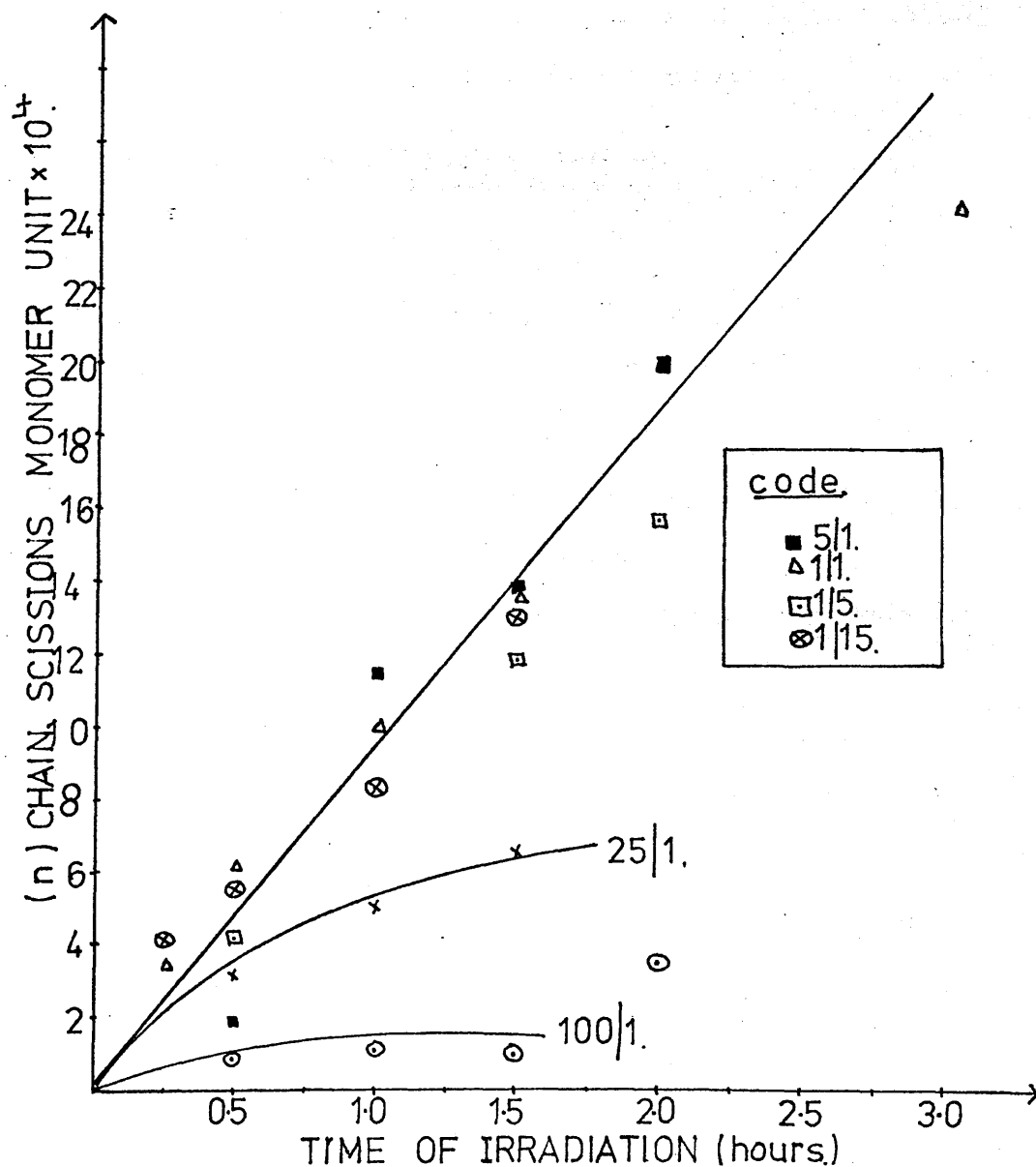


FIG. 6.5.

CHAIN SCISSION in MMA/ n Bu.A. COPOLYMERS
as a function of TIME of PHOTODEGRADATION
at 165°C.



6.4. Sol-Gel Analysis.

(a) Introduction.

Using the Soxhlet extraction technique (2.9) the soluble and insoluble portions of the polymeric residues were investigated. For each degradation the weight of gel, the weight of sol (soluble fraction) and the total weight of residue were determined. The percentage insolubility (% I) was calculated along with the percentage conversion (% C).

$$\% C = \left[1 - \frac{\text{weight of residue}}{\text{initial weight of polymer}} \right] \times 100$$

(b) Results.

Using the data of Table 6.5., the progression of insolubility with time of irradiation is illustrated in Fig. 6.6. This clearly shows that insolubility increases with time of irradiation. For any fixed time of irradiation the amount of gel formation (insolubility) in the acrylate homopolymer is always greater than in the copolymers. Clearly, insolubility increases with increasing acrylate content and irradiation time.

Fig. 6.7. is a plot of insolubility as a function of conversion. As the percentage conversion increases, the percentage insolubility also increases. Increasing the acrylate content of the system increases gelation at any given conversion. Insolubility only develops in the three materials of highest acrylate content, namely copolymers with molar ratios 1/5, 1/15, and the acrylate homopolymer.

TABLE 6.5.

POLYMER (MMA/n-BuA.)	TIME (HRS.)	% INSOLUBILITY	% CONVERSION.
1/5	17	.07	11.6
	25	15.47	14.63
	47	36.89	20.64
	71	39.90	21.96
1/15	3	2.37	1.30
	7	18.45	4.39
	16	40.29	8.15
	24	46.37	8.63
	42	54.95	14.20
Poly n-BuA.	2	1.85	2.10
	3	4.34	2.97
	7	22.56	4.10
	16.25	40.59	4.04
	25	47.32	6.2
	46	56.03	10.46

CHANGE IN % INSOLUBILITY WITH TIME AND ACRYLATE CONTENT

FIG. 66.

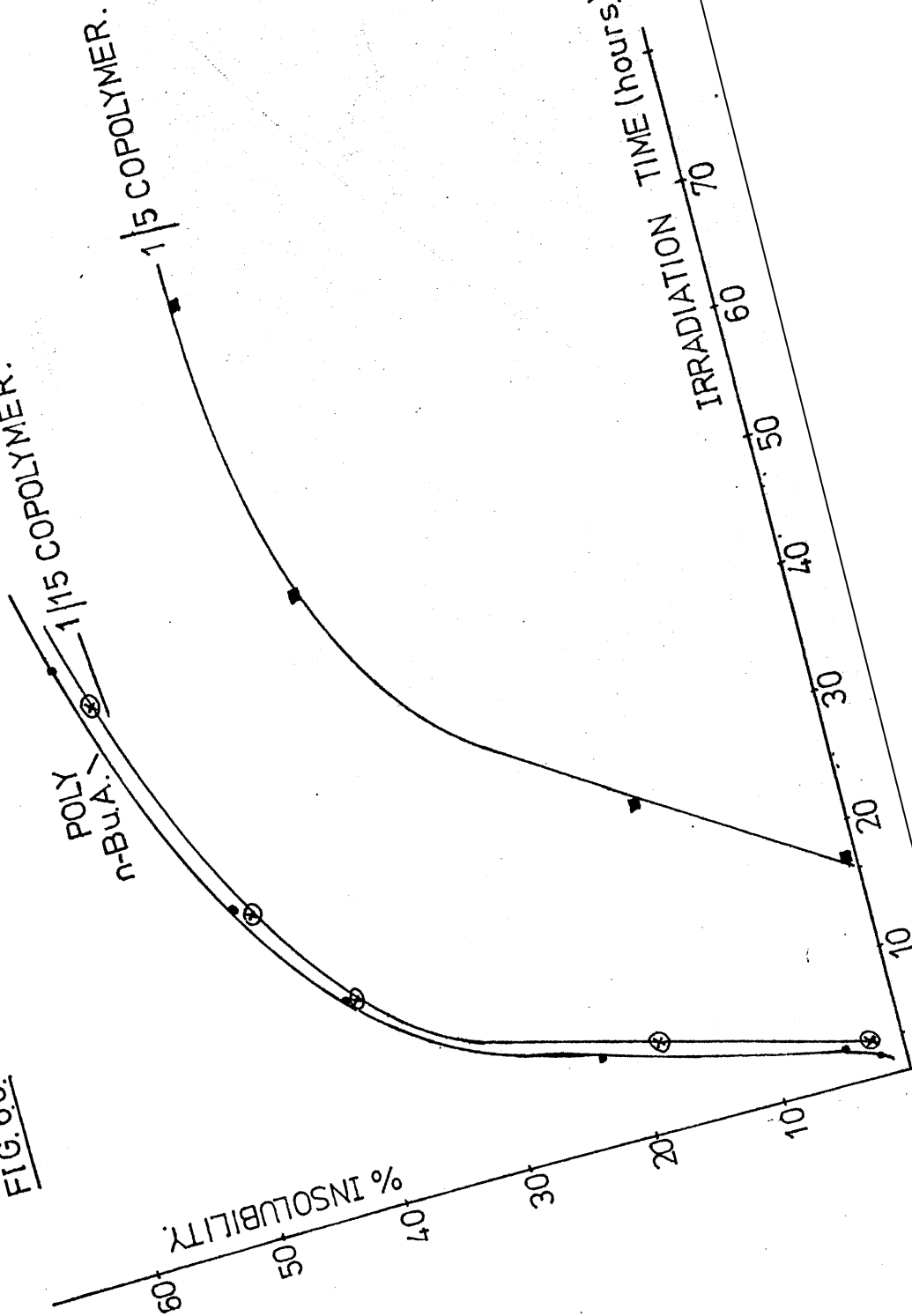
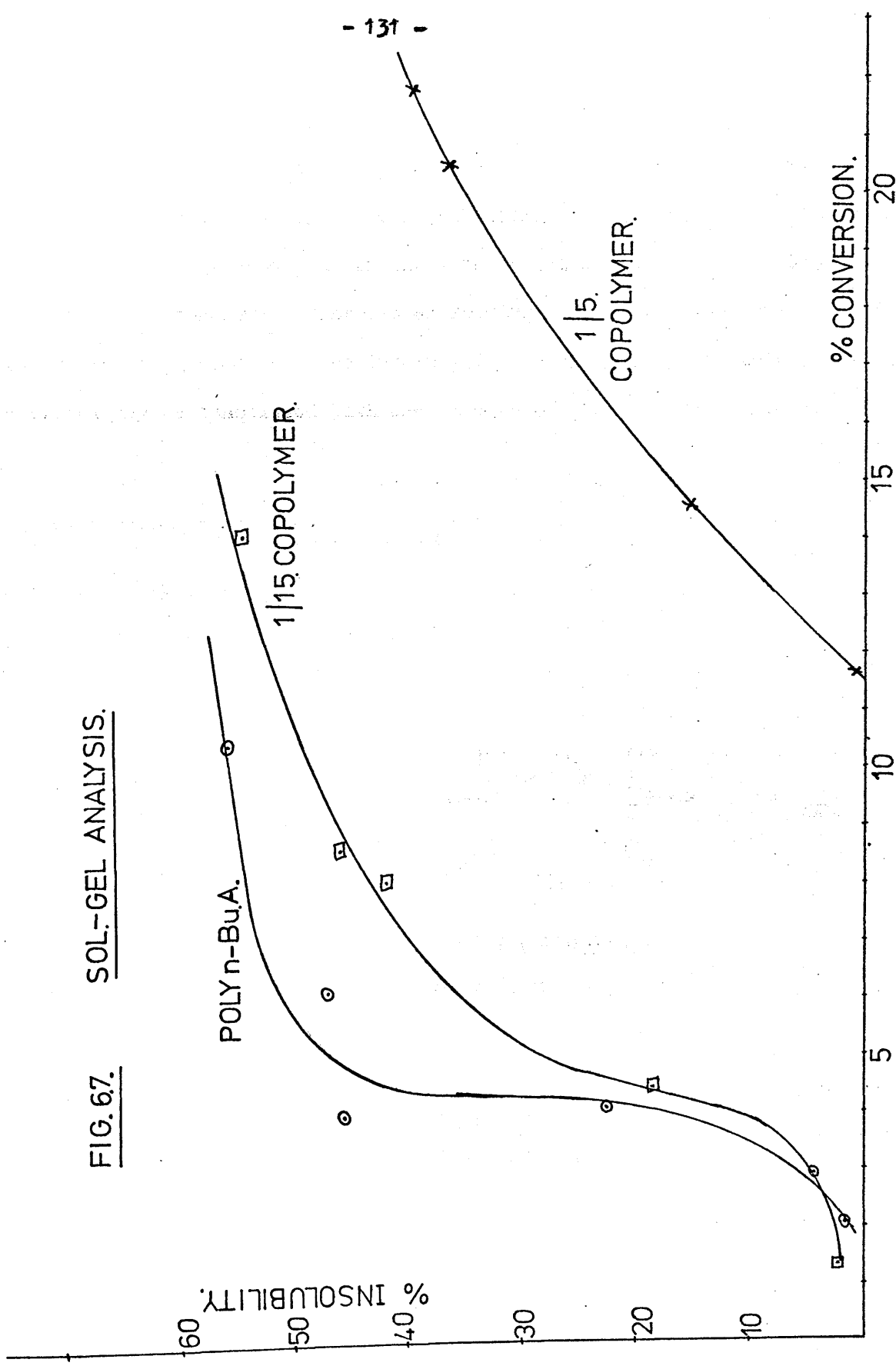


FIG. 6.7. SOL-GEL ANALYSIS.



- 131 -

The spectroscopic examination of the residue (6.6a.) produced no evidence for the existence of inter or intra molecular anhydride groups, thus it must be deduced that insolubility in the photothermal degradation results by crosslinking of the n-butyl acrylate units through their tertiary carbon atoms. Grassie and Fortune^{4a} also reached similar conclusions for the purely thermal degradation of methyl methacrylate/n-butyl acrylate copolymers, and further concluded that for a given degree of conversion the higher the molecular weight of the initial polymer the greater the quantity of insolubility. By thermally degrading copolymers at 313°C. and 329°C, they also showed that there was greater insolubility at the lower temperature of decomposition. Insolubility developed thermally even in a 52.4 mole per cent n-butyl acrylate copolymer. Comparing the data of the photothermal and purely thermal degradations it is obvious that insolubility occurs at much lower conversions in the photothermal degradations for copolymers of high acrylate content. This difference may be accounted for by the temperature of the degradation and not by the method of initiation of degradation. The lower temperature used in the photothermal degradations will have a direct influence on the depolymerisation, random scission and crosslinking processes.

6.5. Crosslinking and Scission.

(a) Introduction.

An important part of the study of radiation effects on polymers is the crosslinking and scission of polymer chains. Crosslinking, in moderate amounts is usually considered advantageous, whereas scission causes polymer degradation. The theoretical aspects of crosslinking, scission and their side effects on gel formation have been treated by several authors⁶¹⁻⁶⁴, but the most lucid explanation has been given by Charlesby and Pinner⁶⁴. For a polymer with an initial random distribution of chain lengths, they developed the equation:

$$S + \sqrt{S} = \frac{P_0}{Q_0} + \frac{1}{Q_0 U \sqrt{r}} \quad \text{..... (1)}$$

in which S is the sol fraction, P_0 and Q_0 are the rates of scission and crosslinking respectively, U is the number average degree of polymerisation of the starting material and r is the radiation dose. This has shown to be the case for crosslinking by high energy irradiation. There is no apparent reason why it should not also hold for ultraviolet radiation if r is replaced by T, the time of irradiation. Thus a straight line should be obtained by plotting $S + \sqrt{S}$ against $\frac{1}{\sqrt{T}}$, the intercept being $\frac{P_0}{Q_0}$ the ratio of scission to crosslinking, and the slope being $\frac{1}{Q_0 U}$.

(b) Results.

The result for poly n-butyl acrylate homopolymer is shown in Fig. 6.8. Using the graph of $S + \sqrt{S}$ against $\frac{1}{\sqrt{T}}$ a straight line can be

FIG. 6.8. PLOT OF $S + S^{\frac{1}{2}}$ AGAINST $1/T$ FOR POLY n-BuA.

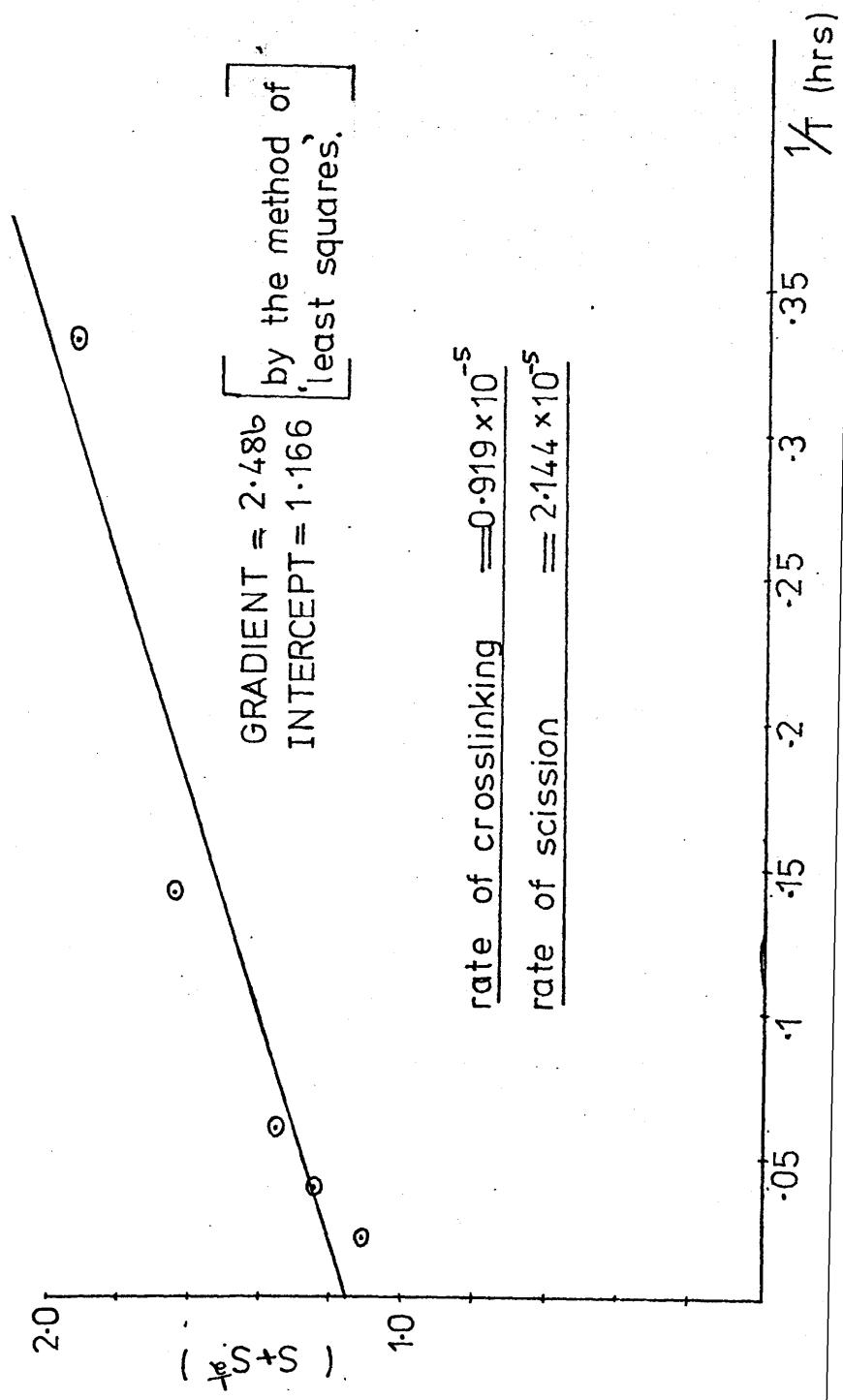


TABLE 6.6.

COPOLYMER	S + \sqrt{S}	(hours)	FROM LEAST SQUARES METHOD.
1/5	1.999	.058	intercept = 1.139
	1.765	.040	gradient = 14.45
	1.426	.021	\therefore rate of crosslinking = 0.863×10^{-5}
	1.376	.014	and rate of scission = 1.965×10^{-5}
1/15	1.964	.333	intercept = 1.168
	1.719	.143	gradient = 2.601
	1.337	.063	\therefore rate of crosslinking = 1.722×10^{-5}
	1.269	.042	and rate of scission = 4.023×10^{-5}
	1.122	.024	
Poly n-Bu.A. Homopolymer	1.935	.333	intercept = 1.166
	1.654	.143	gradient = 2.486
	1.365	.062	rate of crosslinking = 0.919×10^{-5}
	1.253	.040	and rate of scission = 2.144×10^{-5}
	1.103	.022	

obtained using the 'least squares' method. This plot was obtained using values of S calculated using the weight of residue and not the original weight of polymer degraded. Equation (1) is only true where no weight loss occurs, hence the tendency towards a 'curve' shape in Fig. 6.8. Under the photothermal conditions used volatilisation to cold ring, resulting in weight loss, occurs. This means that the accuracy of the results in Table 6.6. is reduced especially for extended degradation periods.

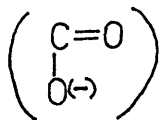
(c) CONCLUSIONS.

From the data listed in Table 6.6., the ratio of scission to crosslinking, as given by the intercept $\frac{p_0}{q_0}$, for the three polymers studied does not appear to alter as the acrylate content is increased. The actual ratio of scission to crosslinking for each is 1.1 (i.e. the intercept). No obvious trend appears to exist for the rates of scission and crosslinking for the three polymers, although the rate of scission is always greater than the rate of crosslinking.

6.6. Spectroscopic Examination of the Residue.

(a) Infra-red.

It was found that for copolymers of high acrylate content the residue is insoluble in organic solvents. Thus it was impossible to compare the spectra of both the degraded and undegraded materials by the usual technique of solution infra-red spectroscopy. Grinding the residue with potassium bromide and pressing the mixture to form a KBr disc was also found to be unsatisfactory because of the 'rubbery' nature of the high acrylate copolymers. The method most satisfactory for the whole copolymer range consisted of preparing a thin film of the copolymer on a clean salt plate and preheating the material to 165°C. for ten minutes, to remove residual solvent, before running an infra-red of the sample. The film and salt plate were then placed inside the photolysis cell and degradation carried out in the normal way. After the photolysis the salt plate and residue were examined. Fig. 6.9. shows the spectra of undegraded and degraded 93.4 mole per cent n-butyl acrylate copolymer. These differ in that the spectrum of the degraded material has a shoulder at 1770 cm⁻¹ on the carbonyl peak. However the spectra of undegraded and degraded copolymers of all other molar ratios are almost identical. In the purely thermal degradation^{4a} of methyl methacrylate/n-butyl acrylate copolymer new absorptions at 1760 cm⁻¹, 1605 cm⁻¹, and 1560 cm⁻¹ were noted. The absorption at 1560 cm⁻¹ was assigned to the structure



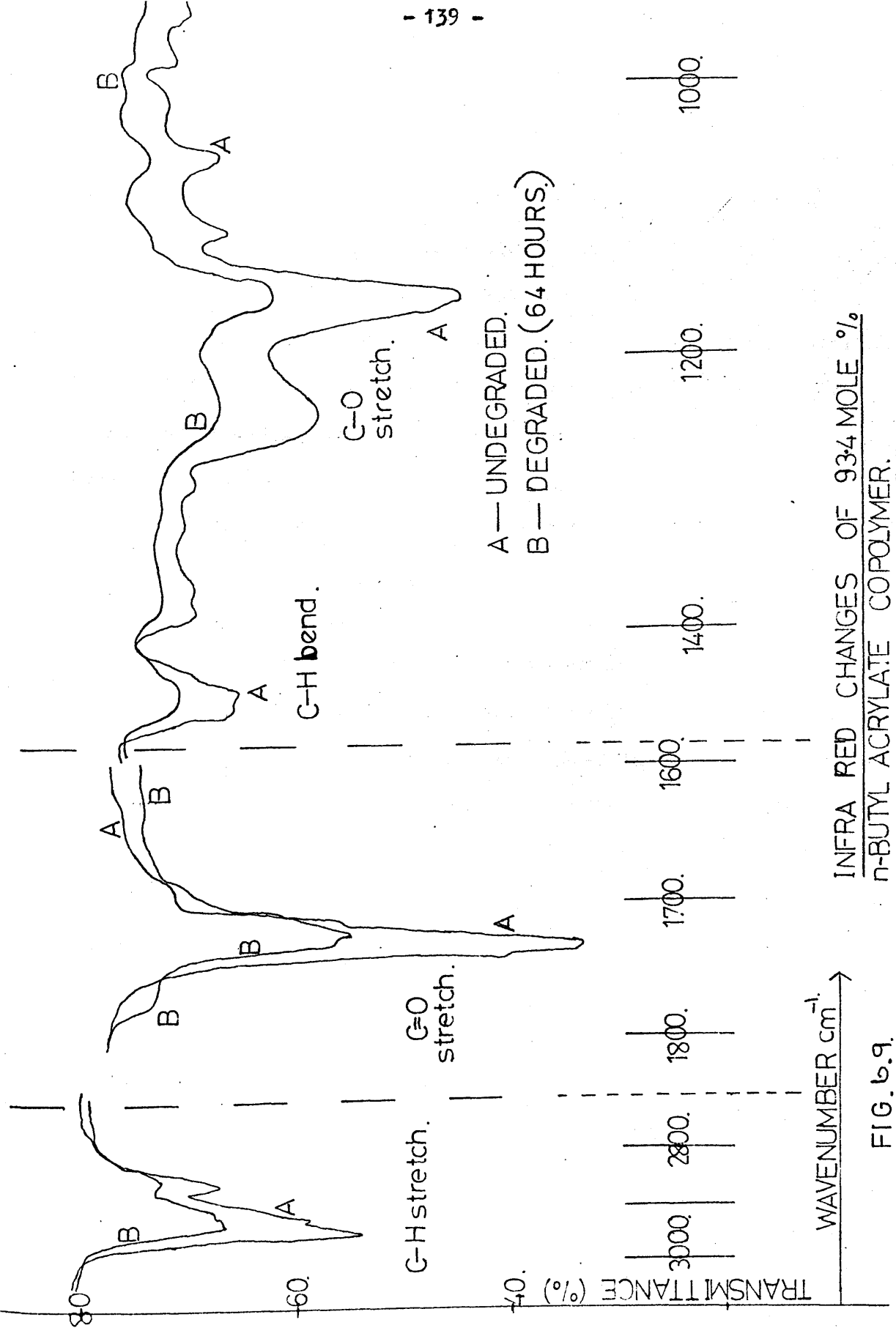


FIG. 6.9.

The shoulder on the carbonyl peak at 1760 cm^{-1} was ascribed to a γ lactone, an $\alpha\beta$ unsaturated γ lactone, or a $\beta\gamma$ unsaturated δ lactone. No evidence for the production of anhydride groups in the residue has been found in either the thermal or photothermal degradations. Anhydride groups have a doublet absorption at about 1800 cm^{-1} and 1760 cm^{-1} . No peak was observed at 1800 cm^{-1} in the degraded materials. The absorption at 1605 cm^{-1} produced in the thermal degradation was attributed to conjugated carbon-carbon double bonds.

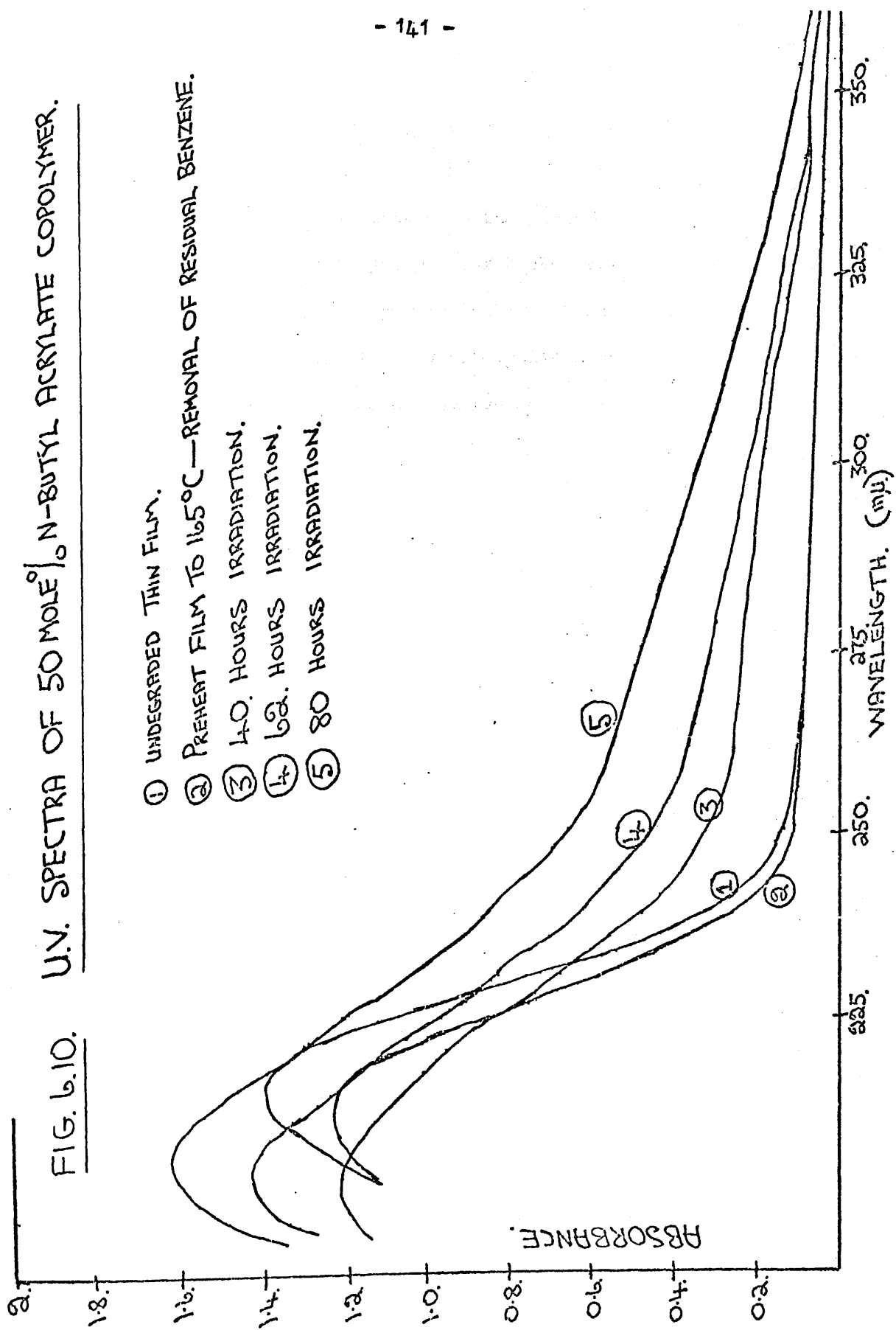
(b) U.V. Visible.

No colour change visible to the eye occurs in the residue as the photothermal degradation proceeds. In the purely thermal degradation^{4a} the residual polymer changed through yellow to brown with increasing decomposition. U.V. -visible spectra were run on the photothermally degraded polymer films deposited on the optically flat silica disc, used in the photolysis cell. The difficulty of finding a suitable solvent, whose absorption characteristics did not obscure that of the polymeric film, was thus avoided. Fig. 6.10. shows the u.v. spectra of a 50 mole per cent n-butyl acrylate copolymer as it is progressively photothermally degraded. It is important to note that after 40 hours of irradiation approximately 50 per cent of the original polymer has been lost by volatilisation. Hence the true absorption per unit mass is much greater than that depicted in Fig. 6.10. The absorption around $225\text{ m}\mu$ corresponds to the absorption by the ester group. As the polymer is

U.V. SPECTRA OF 50 MOLE% N-BUTYL ACRYLATE COPOLYMER.

FIG. 6.10.

- ① UNDEGRADED THIN FILM.
- ② PREHEAT FILM TO 165°C — REMOVAL OF RESIDUAL BENZENE.
- ③ 40. HOURS IRRADIATION.
- ④ 62. HOURS IRRADIATION.
- ⑤ 80 HOURS IRRADIATION.



photothermally degraded there is a general increase in absorption in the region from 400 m μ down to 225 m μ . This new absorption has no characteristic maximum and may be attributed to the presence of varying lengths of ethylenic unsaturation in the polymer backbone. A similar effect was observed for all the copolymers studied. Grassie and Fortune^{4a} have previously shown that a similar new absorption results from the purely thermal degradation of this copolymer system.

(c) N.M.R.

The soluble residues from the photothermal degradation were examined by N.M.R.. No new absorptions appeared on decomposition. A typical N.M.R. trace for this copolymer system has been presented by Grassie and Fortune^{4a}, and shall not be included here.

6.7. Short Chain Fragments.

(a) Introduction.

When all of the copolymers were photothermally degraded the sides and top silica window of the photolysis cell were coated with a material referred to as the 'cold ring'. The cold ring deposited on the silica window was a disadvantage of the system since this screened the polymer film from the radiation. Thus the amount of light impinging on the polymer film could not be constant, and almost certainly intensity decreased with increasing time of irradiation. This made the measurement of quantum yields impossible.

(b) Analysis.

The quantitative analysis of the cold ring or chain fragments has been described in detail (in chapter 5, table 5.1.) Fig. 5.9. clearly illustrates that these short chain fragments become increasingly important as the acrylate content of the copolymers is increased.

On comparing detailed infra-red spectra of the undegraded 50 mole per cent n-butyl acrylate copolymer with the spectra of its cold ring, (fig 6.11) new absorptions are clearly present. A shoulder at about 1780 cm^{-1} appears on the carbonyl peak and a new peak at 1635 cm^{-1} emerges. Also the C-O single bond peak at 1160 cm^{-1} becomes more diffuse. Outside the $1800 - 1000\text{ cm}^{-1}$ region there are no significant changes. The infra-red spectra of the cold ring fraction was run as a liquid film between salt plates.

(c) Discussion.

Grassie, Speakman and Davis,⁶⁵ studying the purely thermal degradation of poly alkyl acrylates, found that poly n-butyl acrylate degraded to chain fragments with an average molecular weight of 470 which corresponds to a chain length of 3.6. The trace obtained by injecting the chain fragments into a g.l.c. instrument confirmed that the retention time was similar to $\text{C}_{18} - \text{C}_{24}$ n-alkanes.

From the large amount of chain fragments produced (Fig. 5.9.) and the rapid decrease in molecular weight with photothermal degradation it is obvious that transfer reactions occur.

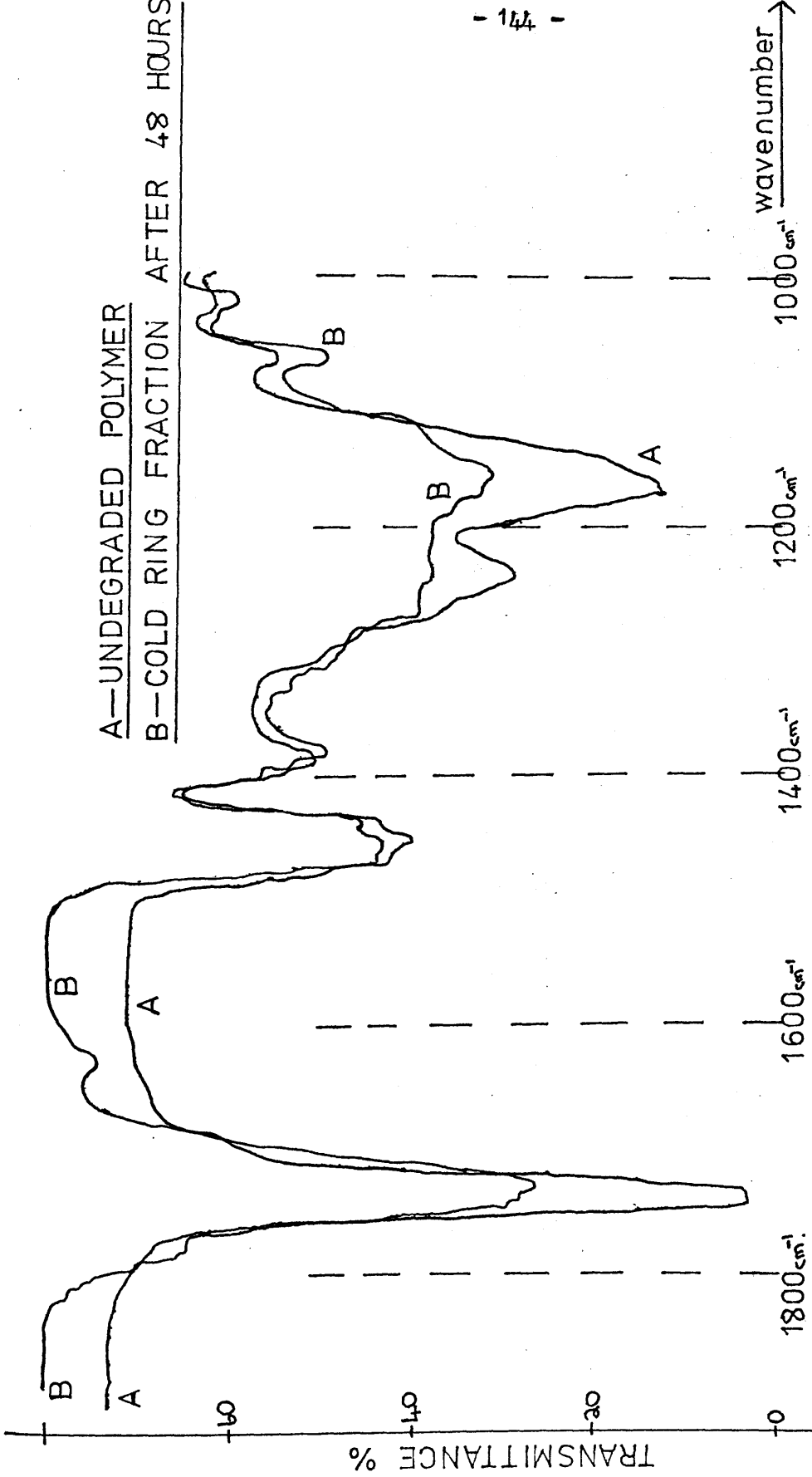
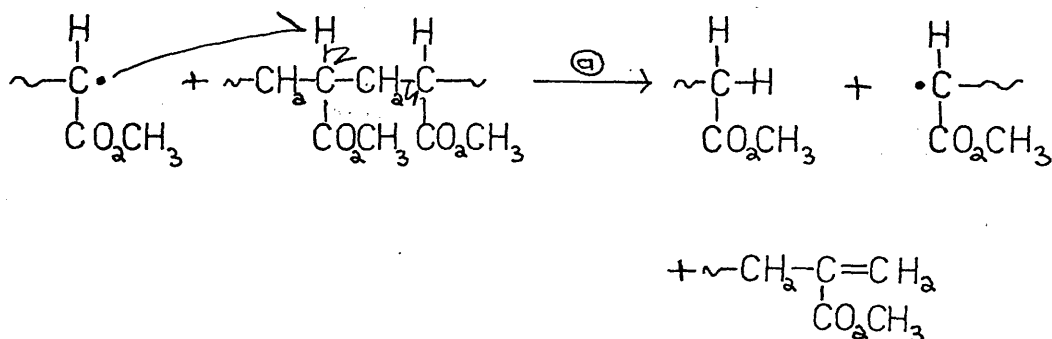


FIG 6.11.

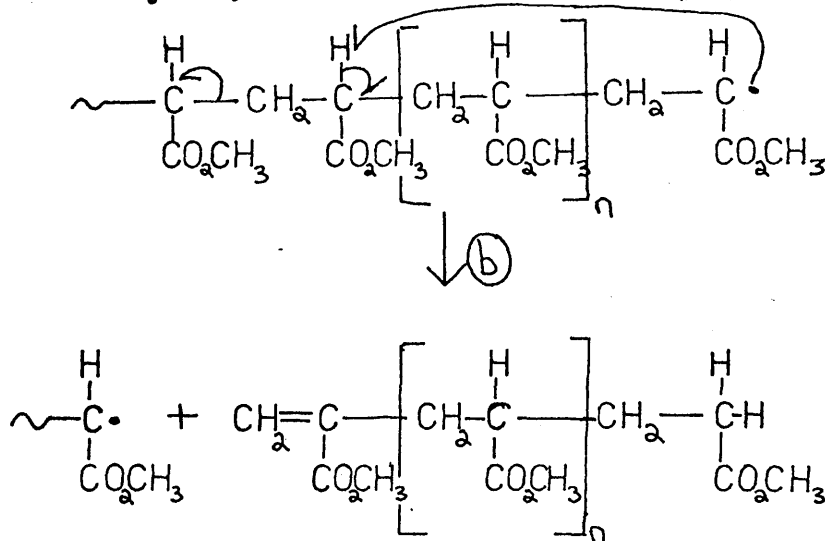
CHANGE IN IR. SPECTRA OF 50 MOLE % N BUTYL ACRYLATE
COPOLYMER AND COLD RING

Cameron and Kane⁶⁰ have demonstrated the radical nature of the thermal degradation of poly methyl acrylate. Two types of transfer reactions can occur. Firstly, intermolecular transfer results in the production of long chain fragments



(a) Intermolecular Transfer.

Intramolecular transfer may also occur resulting in the production of small chain fragments. Cameron and Kane⁶⁰ have described this process as 'unbuttoning', since the radical moves along the chain eliminating small molecules. This is in contrast to 'unzipping' in poly methyl methacrylate, in which monomer units are progressively eliminated.



(b) Intramolecular Transfer.

Such transfer reactions would introduce terminal double bonds in half of the newly formed chain fragments. The new absorption at 1635 cm^{-1} may originate from such a terminal structure.

CHAPTER 7.

GENERAL DISCUSSION.

7.1 Introduction.

The principal features of the photothermal degradation of the methyl methacrylate - n-butyl acrylate copolymer system have been described in previous chapters. It is of interest to compare these results with those previously obtained for the thermal degradation of this system and for the thermal and photothermal degradation of the methyl methacrylate/methyl acrylate copolymer systems. The interpretation of the results obtained is also discussed in more detail in this chapter and mechanisms are proposed to account for the degradation products.

7.2. Sequence Distribution Data.

In any investigation on the degradation of copolymers a knowledge of the sequence distribution data as well as the composition is fundamental. When two different monomer units are copolymerised their distribution in the copolymer is complex. Harwood's^{66, 67} method of calculating sequence distribution data uses the concept of run numbers of uninterrupted monomer sequences which occur in a copolymer chain per hundred monomer units. This distribution has previously been calculated for the methyl methacrylate - n-butyl acrylate copolymer system by Grassie and Fortune.⁴² Their results are directly applicable to the present work since our copolymer compositions are identical to theirs. Table 7.1. shows the

TABLE 7.1.
Sequence Distribution Data for Copolymers of n-Butyl Acrylate and Methyl Methacrylate.

Copolymer Composition (mole % n-butyl acrylate)	Diads			% Acrylate in centre of triads			Number av. run length. \bar{A}_n	Relative total % acrylate in AAA triads, A_{tp}
	% A-A linkages	% M-M linkages	% A-M linkages	MMA 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

sequence distribution data found by Grassie and Fortune, where A and M denote acrylate and methacrylate units respectively. The first seven columns in Table 7.1. are self-explanatory. \bar{A}_n represents the number average length of acrylate sequences. The percentage of A in the centre of AAA triads, relative to all possible triads including those centred on methacrylate units is also given in Table 7.1., as the relative total percentage in AAA triads, A_{tp}

7.3. Blocking Efficiency.

(a) Zip lengths.

The zip lengths for the depolymerisation of each copolymer (6.3.a) indicate that the presence of an n-butyl acrylate unit causes a blockage of the depropagation step. Blocking of this kind is not complete however since monomeric n-butyl acrylate is a product of the photothermal degradation. The zip length for depolymerisation decreases from 1,260 to 22 as the acrylate content changes from 0.99 to 50 mole per cent. It has been shown (table 6.4.) that for the methyl methacrylate-methyl acrylate system,^{3a,33} the zip length of the purely thermal reaction was very much less than in the photothermal reaction at 170°C.

Although Fortune^{4a} did not calculate zip lengths of the thermal degradation of methyl methacrylate - n-butyl acrylate copolymers it is possible to do so using his molecular weight versus percentage volatilisation data. Thus Table 7.2. was constructed in this way.

Table 7.2.

Zip Lengths for Thermal Degradation (313°C.) of Poly(M.M.A. - nBu.A.)

COPOLYMER	SLOPE % VOLATILISATION PER SCISSION/ MOLECULE [A]	INITIAL M.W. M.W. ₀	M.W. LOST PER SCISSION	AVERAGE WT. MONOMER UNIT [B]	ZIP LENGTH.
					$\frac{\text{M.W.}_0 \cdot \text{A.}}{100 \cdot \text{B.}}$
250/1	33.3	361,000	120,100	100.1	1,200
1/1	1.2	100,000	1,200	114	9

Comparison of the data in Table 6.3. and Table 7.2., demonstrates that the zip lengths for the purely thermal degradation are much less than those in the photothermal reaction at 165°C. The greater zip length in the photo reaction can be accounted for by the fact that at 165°C. , in the photo reaction, the polymer is in the form of a highly viscous mass, while at 313°C. in the thermal reaction it is a relatively mobile liquid. Thermal motion will be suppressed in the viscous medium favouring intramolecular transfer at the expense of intermolecular transfer.

From the photo-depolymerisation zip length data for methyl^{3a} and butyl acrylate copolymers it would seem that, since the zip lengths for the n-butyl acrylate copolymers are much less than those for the methyl acrylate copolymers, the n-butyl acrylate unit is a much more effective blocking agent. However, any final interpretation of the

data must take account of the fact that the n-butyl acrylate copolymers were photodegraded at 165°C. while the methyl acrylate copolymers^{3a} were photodegraded at 170°C. In addition, the influence of the two acrylates on the viscosities of the two copolymers may be different.

(b) Molar Ratios of Monomers in the Degradation Products.

The molar ratios, calculated by g.l.c. analysis, of the two monomers, methyl methacrylate and n-butyl acrylate formed in the photothermal and thermal (313°C.) degradation are given in Table 7.3.

TABLE 7.3.

MOLAR RATIOS OF MONOMERIC PRODUCTS.

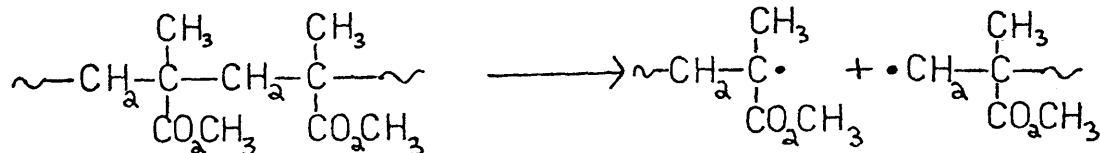
COPOLYMER (M.M.A./nBu.A.)	MONOMER RATIO (M.M.A./nBu.A.)	
	PHOTOTHERMAL	THERMAL
5/1	215	23
1/1	30	4
1/5	10	1.

It is clear that approximately one in forty of the n-butyl acrylate units is liberated as monomer in the photothermal reaction compared with one in five in the thermal reaction. With the methyl methacrylate-methyl^{3a,33.} acrylate copolymer system it was found that approximately one in ten of the methyl acrylate units were liberated in the photothermal reaction compared with one in four in the thermal reaction.

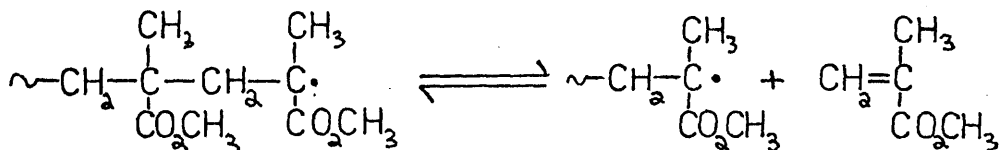
7.4. Mechanistics.

(a) Production of Methyl Methacrylate.

This can be accounted for by a depolymerisation process in which polymer radicals peel off monomer units. The primary influence of ultraviolet radiation on poly (methyl methacrylate) is to cause chain scission¹



The reactions of these radicals and the temperature of the medium control the characteristics of the photolysis. When the polymer is in the liquid state monomer produced in the equilibrium,



can escape easily. Thus the reaction will tend to the right resulting

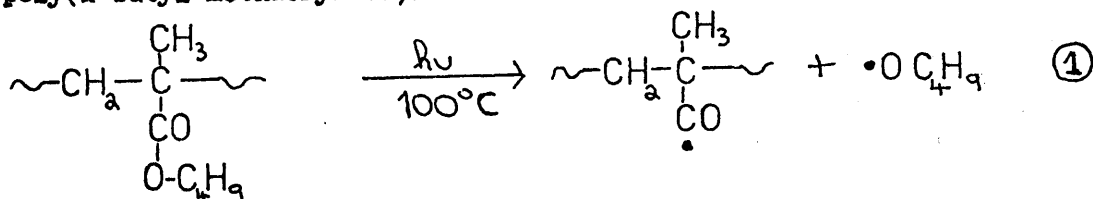
in quantitative conversion to monomer. At lower temperatures when the polymer is a rigid solid the escape of monomer is inhibited. Therefore, monomer production is a characteristic of a high temperature photolysis, while chain scission predominates at lower temperatures.

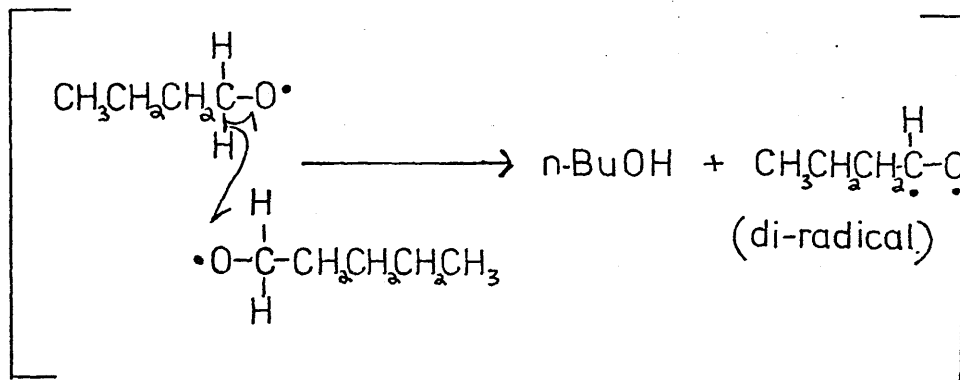
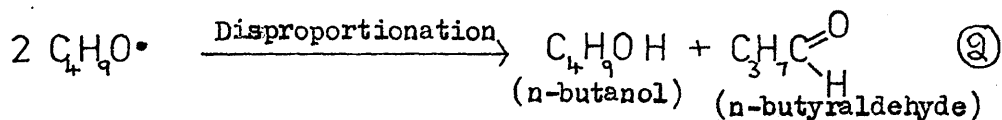
(b) Production of n-Butyl Acrylate.

As stated previously, (section 5.5.) acrylate monomer must be produced in a depolymerisation reaction initiated at methacrylate chain units. The depolymerisation reaction can apparently pass through some of the acrylate units before termination occurs.

(c) Production of n-Butyraldehyde.

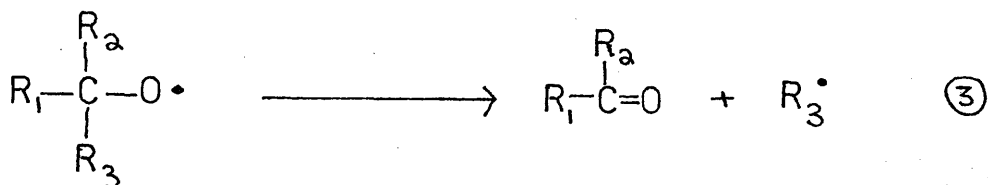
The quantity of butyraldehyde was shown (Fig. 5.13.) to increase with increasing acrylate content of the copolymers, and was present as a degradation product even in a 3.9. mole per cent n-butyl acrylate copolymer (25/1) where the percentage of acrylate-acrylate linkages, as calculated by sequence distribution data, is 0.1. Thus, the evolution of butyraldehyde is a function of single acrylate units rather than of sequences. Isaacs and Fox²⁶ postulated that butyraldehyde was produced by disproportionation of a butoxy radical in the photodegradation of poly(n-butyl methacrylate).





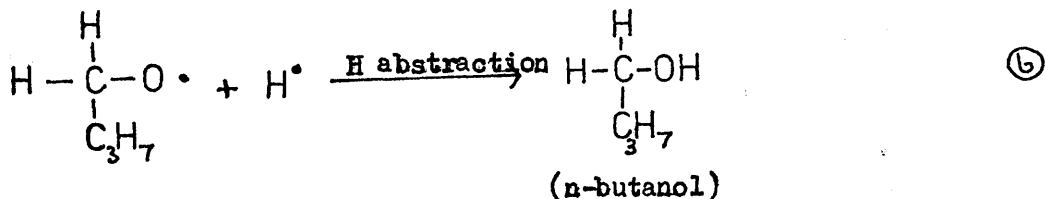
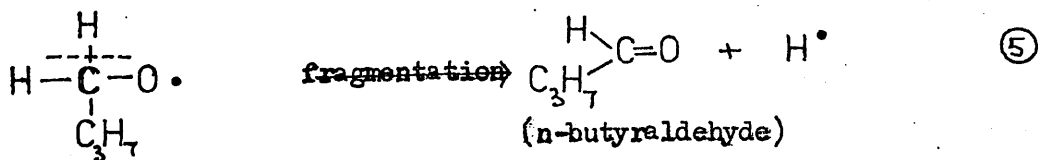
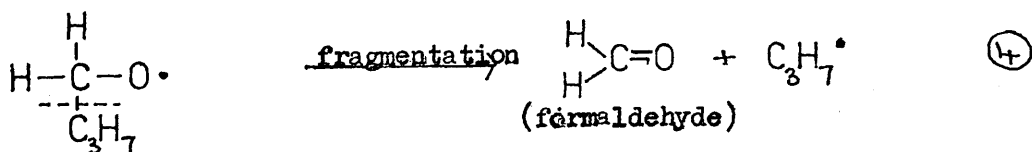
However, such a reaction would result in equimolar yields of n-butanol and n-butyraldehyde. From the data in Table 5.3. it is clear that n-butanol is not a product of degradation until the acrylate content reaches 50 mole per cent., whereas n-butyraldehyde is detectable in both the 3.9 and 16.3 mole per cent n-butyl acrylate copolymers. Also since the molar ratio of n-butyraldehyde to n-butanol for the 50 mole per cent n-butyl acrylate copolymer is approximately 3:1, the disproportionation mechanism does not account satisfactorily for the production of n-butyraldehyde.

It is known that alkoxy radicals fragment to produce a carbonyl function.⁶⁸ The formation of the carbonyl group provides the driving force for cleavage.



(alkoxy radical)

When the radical is primary ($R_1 = R_2 = H$) or secondary ($R_1 = H$) fragmentation can occur by loss of either an alkyl radical or of a hydrogen atom. Primary and secondary alkoxy radicals have been studied mainly in the gas phase and under these conditions the loss of an alkyl radical is the predominant reaction. If the butoxy radical (C_4H_9O) is formed as in reaction (1), then the following reactions could occur.

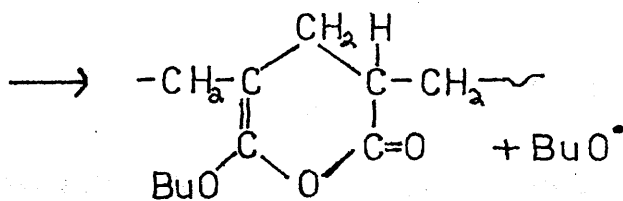
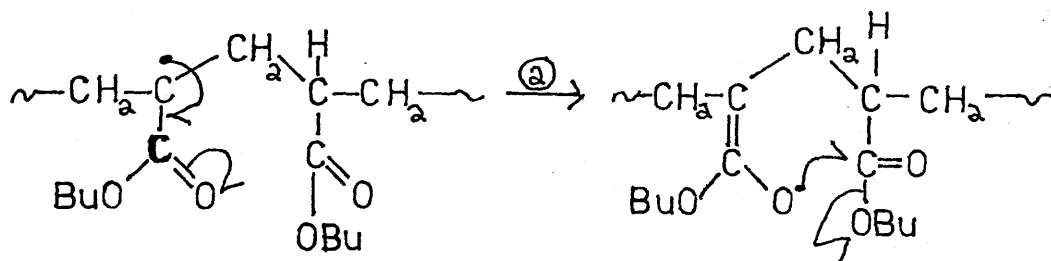
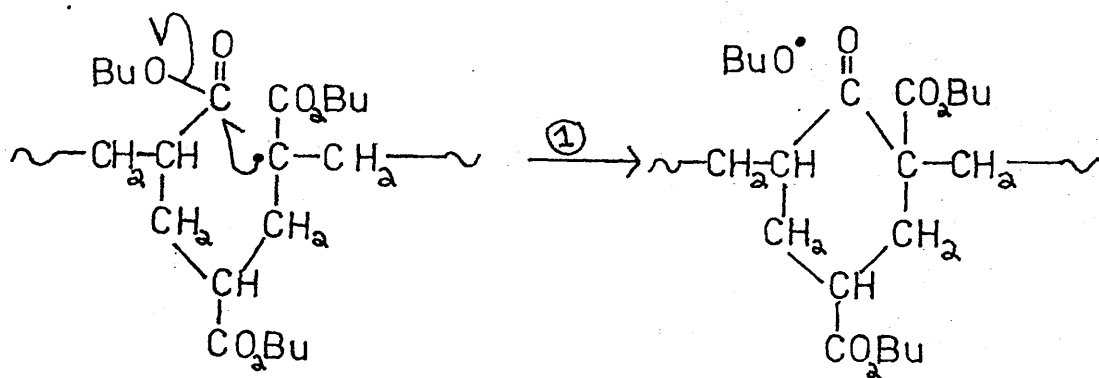


Since no formaldehyde was detected, the loss of the alkyl radical must not occur and it seems that in the viscous polymer, degrading under photothermal conditions, reaction (5) predominates.

(d) Production of n-Butanol.

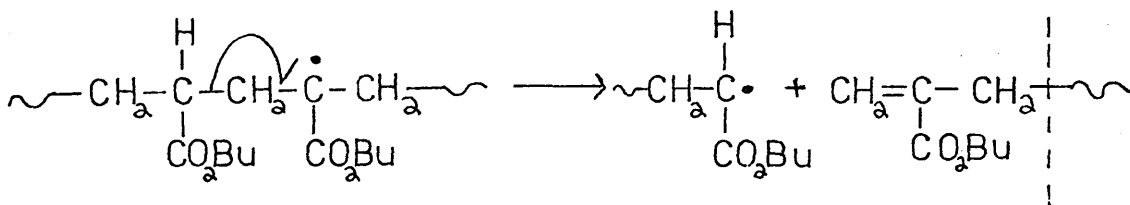
The production of n-butanol (Fig. 5.15) increases with increasing acrylate content, but it is not present as a degradation product until the acrylate content reaches 50 mole per cent, that is, until a reasonable proportion of acrylate units are present in sequences. Grassie and Fortune^{4a} also found that in the thermal degradation of copolymers of methyl methacrylate and n-butyl acrylate at least 50 mole per cent of n-butyl acrylate was required in the copolymer in order that n-butanol should appear on pyrolysis, but it was not certain whether the sequence length required was three or only two acrylate units. Grassie, Torrance and Colford^{3a} found no methanol produced in the photothermal degradation of copolymers of methyl methacrylate and methyl acrylate containing up to 33.3 mole per cent acrylate, but this was the highest acrylate copolymer examined.

Various mechanisms have been postulated in thermal degradations to account for alcohol production, taking into account the need for sequences of acrylate units.^{4a,6a} Two of these may be represented as follows :



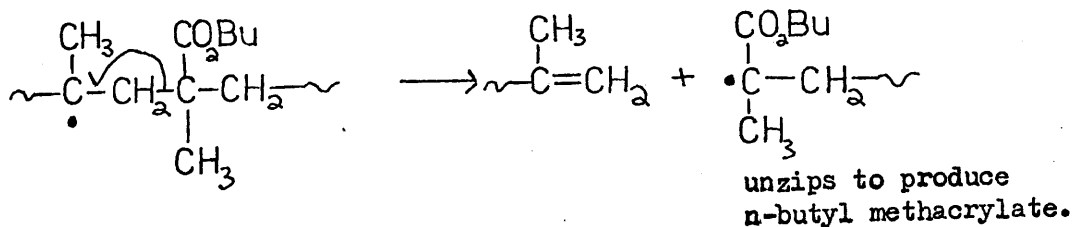
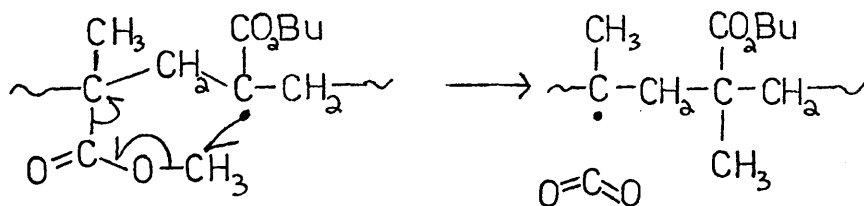
(e) Production of n-Butyl Methacrylate.

This product may be produced by a reaction such as



n-butyl methacrylate produced
by scission of the bond indicated.

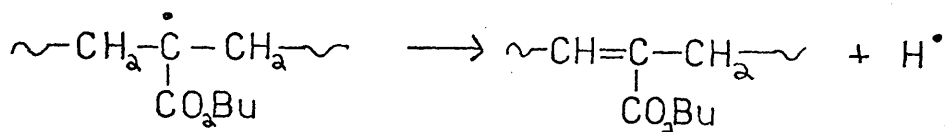
For the thermal reaction Grassie and Fortune^{4a} also suggested the following reaction scheme.



But this cannot apply in the photothermal degradation since no carbon dioxide is produced.

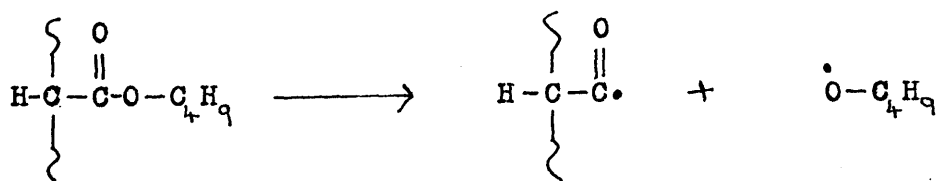
(f) Production of Permanent Gases.

Ultraviolet spectral studies on the polymeric residue suggest the existence of varying lengths of ethylenic unsaturation in the polymer backbone. The initial double bond can be formed in the process.⁶⁰

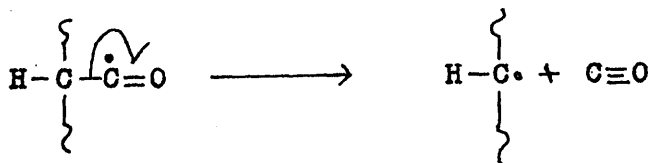


The presence of this double bond will tend to weaken the carbon - hydrogen bond in the β position, thus making it more vulnerable to attack by a free radical or U.V. radiation. Scission of this bond and abstraction of a hydrogen atom from the adjacent methylene group can account for molecular hydrogen production.

When acyl-oxygen fission occurs as previously shown in section 7.4.c1., a butoxy radical is produced, leaving a carbonyl radical on the polymer chain.



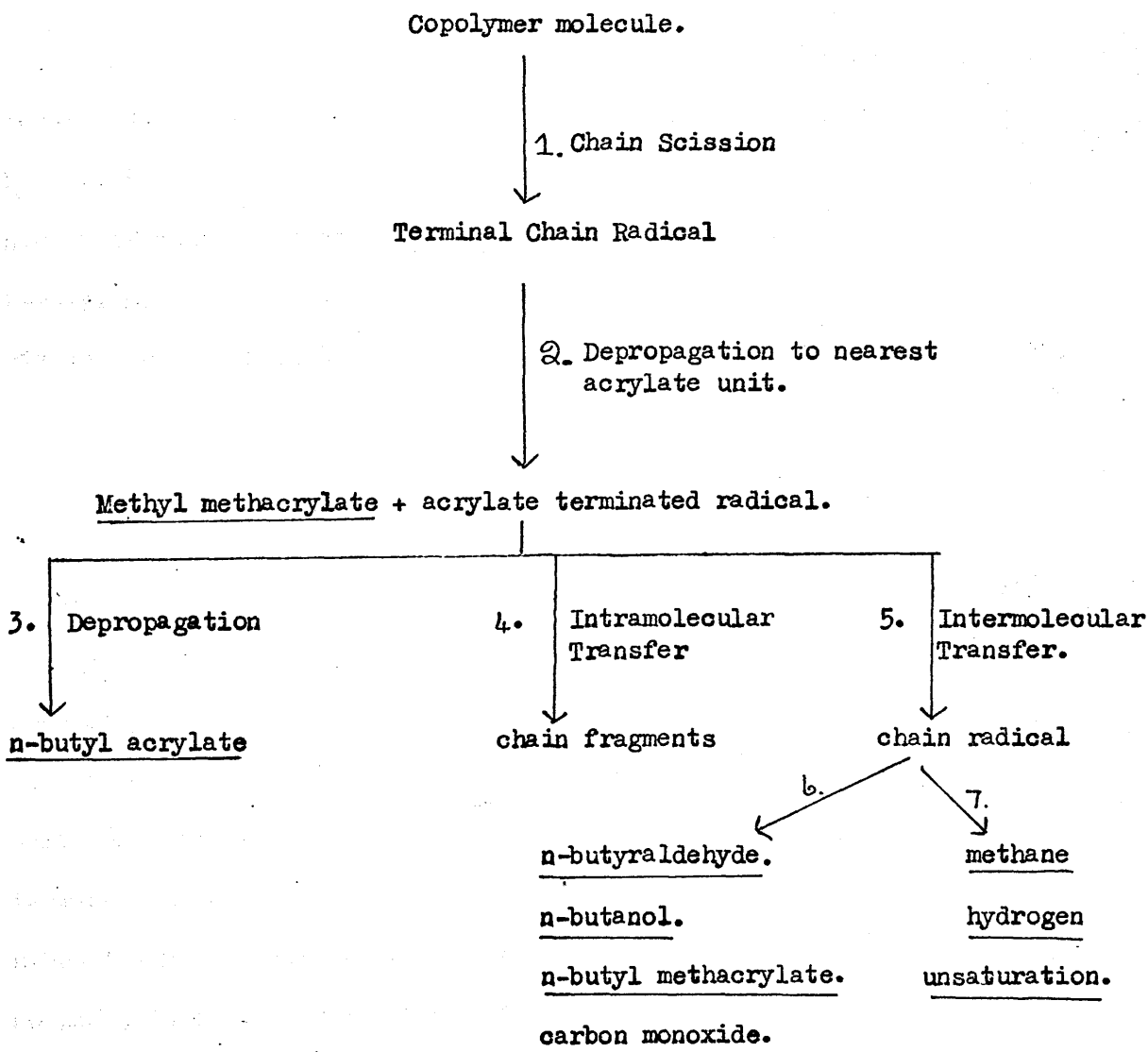
Carbon monoxide may be formed by the breakdown of these carbonyl radicals.



The mechanism of the formation of methane is probably similar to that of hydrogen elimination causing ethylenic unsaturation in the polymer backbone. This will involve the α methyl group of methyl methacrylate units. Methane could also be derived from the methyl ester group of methyl methacrylate or from the breakdown of the n-butyl ester side group.

(g) Reaction Pathway.

Bearing in mind the mechanisms which have been proposed above for the production of the various products the overall process may be represented qualitatively by the following reaction sequence.



After chain scission (1) occurs, depropagation (2) occurs in methyl methacrylate sequences as far as the first acrylate unit. The acrylate terminated radical can depropagate (3) or abstract a hydrogen atom further along its own chain in an intramolecular transfer process (4). Scission at this point would result in a chain fragment and a new chain terminal radical. On the other hand, intermolecular transfer (5) would result in a chain radical of the type believed to be primarily formed by U.V. radiation. It is believed that this radical may undergo a number of complex reactions to produce n-butyraldehyde, n-butanol, n-butyl methacrylate and carbon monoxide. A further reaction (7), similar to the liberation of hydrogen chloride from poly(vinyl chloride) may result in the evolution of hydrogen and methane.

7.5. Summary.

The exact nature of the initiation step can only be speculated upon, but since the reaction is initiated by ultraviolet light, it is likely that the site of the initial reaction is near the ultraviolet absorbing group in the ester side chain. Using molecular weight data it was deduced that the photothermal degradation proceeds by a random scission process. Depolymerisation occurs from methyl methacrylate terminal chain radicals which unzip along the polymer chain until an n-butyl acrylate unit is encountered. Blocking, by the acrylate monomer, is certainly not complete since monomeric n-butyl acrylate is a product of the photothermal degradation. The rate of volatilisation

only becomes appreciable when the methacrylate content of the copolymer is greater than 50 mole per cent. This suggests that although the depropagation process can pass through single acrylate units, it is very much more efficiently inhibited when significant concentrations of sequences of two or more acrylate units occur in the polymer molecule. The rate of chain scission is independent of the n-butyl acrylate content for copolymers of high acrylate content, and analysis of the monomeric degradation products show that approximately one in forty of the n-butyl acrylate units is liberated as monomer. Insolubility, associated with a crosslinking reaction, increases with acrylate content and irradiation time. The products of the photothermal degradation were identified and mechanisms for their production were discussed.

SUMMARY.

This investigation of the photothermal degradation of copolymers of methyl methacrylate and n-butyl acrylate is an extension of an earlier study of the purely thermal degradation of the same system.

A series of copolymers covering the whole composition range was synthesised and degradation was carried out using 2537 \AA radiation. The copolymers were degraded in the form of thin films (100μ in thickness) at a temperature of 165°C . The acrylate monomer has a strong inhibiting effect on the unzipping reaction initiated at methacrylate terminal chain radicals and the rate of volatilisation only becomes appreciable when the methacrylate content of the copolymers is greater than 50 mole per cent.

The liquid degradation products, gaseous products, chain fragments and residue were each examined separately, using among other techniques, combined gas chromatography-mass spectrometry and infra-red spectroscopy. The liquid degradation products were methyl methacrylate monomer, n-butyraldehyde, n-butyl acrylate monomer, n-butanol and n-butyl methacrylate. Condensable gaseous products such as carbon dioxide and but-1-ene were not present. The trace permanent gases were hydrogen, carbon monoxide and methane. Where possible, quantitative analysis of the degradation products was carried out.

Using molecular weight data it was deduced that the photothermal degradation proceeds by a random scission process. The zip length for depolymerisation decreases from 1,260 to 22 as the acrylate content changes from 0.99 to 50 mole per cent and it was shown that the zip lengths for the purely thermal degradation of the same copolymer system were much less than in the photothermal reaction. From the molar ratios of the monomeric products it is clear that approximately one in forty of the n-butyl acrylate units is liberated as monomer in the photothermal reaction compared with one in five in the purely thermal reaction. The rate of chain scission is independent of the n-butyl acrylate content for copolymers of high acrylate content and insolubility only develops when the acrylate content is greater than 50 mole per cent. The chain fragments were only briefly examined.

The mechanisms for the production of the degradation products are discussed although the mechanism of the formation of n-butyraldehyde and n-butanol is not really satisfactorily explained.

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