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DEGRADATION REACTIONS IN POLYMERS

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CONTRACT F61052-69-C-0026 30TH JUNE 1973.

FINAL SCIENTIFIC REPORT

DEGRADATION REACTIONS IN POLYMERS

70 FEBRUARY 01 - 73 JUNE 30

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THIS RESEARCH HAS BEEN SPONSORED IN PART BY THE AIR FORCE MATERIALS LABORATORY, WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433, THROUGH THE EUROPEAN OFFICE OF AEROSPACE RESEARCH, OAR, UNITED STATES AIR FORCE UNDER CONTRACT F61052-69-C-0026.

FOREWORD

The research work described in this report was carried out during the period 70 February 01 - 73 June 30 under Contract No. F61052-69-C-0026 sponsored by Dr. I.J. Goldfarl and Dr. H. Rosenberg, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

Acknowledgement is made of the many useful discussions with and assistance of members of the Macromolecular Chemistry Research Group of the University of Glasgow and of the clerical work of Miss Ann Matheson.

ABSTRACT

This report is concerned with three distinct aspects of polymer degradation and stability with the general aim of the production of materials of improved stability through a more complete understanding of their degradation mechanism and its relationship to chemical structure.

The photothermal degradation of copolymers of methyl methacrylate and n-butyl acrylate covering the whole composition range has been studied at 165°C. The gaseous and liquid products, which consist of hydrogen, carbon monoxide, methane, methyl methacrylate, n-butyl acrylate, n-butanol and n-butyraldehyde were analysed quantitatively using a gas chromatograph technique and the yields related to copolymer composition. Zip lengths, calculated from molecular weight and volatilisation data, decrease with increasing acrylate content of the copolymer but are higher than those observed during thermal degradation. Infra-red spectral changes in the residue are attributed to lactone formation and associated with the formation of butanol. The "cold-ring" or chain fragment fraction of the products becomes increasingly more abundant as the acrylate content of the copolymer is increased and spectral differences from the original polymer have been accounted for. All the products and principal features of the reaction are explained in terms of a radical process initiated by scission of pendant acrylate units and propagated by a combination of depropagation, intra and intermolecular transfer processes the relative importance of which depends upon copolymer composition. Differences from the thermal reaction and the corresponding reaction in

copolymers of methyl methacrylate and methyl acrylate are discussed.

It is shown that a number of aromatic compounds, both carbocyclic and heterocyclic, may be copolymerized with dimethoxy-p-xylene with stannic chloride as catalyst. Purification of materials and preparations of copolymers are described.

The preparations of a number of poly(dimethyl siloxanes) are described. Thermal analysis using TGA and TVA have shown that thermal decomposition starts at approximately 360°C but this is depressed somewhat by reprecipitation. Neither heating to 130°C to destroy residual catalyst nor the molecular weight of the starting polymer have any significant influence on the threshold degradation temperature or the general characteristics of the thermal degradation reaction. End-blocking lowers the degradation temperature threshold although the subsequent build up in degradation rate is slower. The principal products of degradation are cyclic trimer and tetramer g.l.c. and infra-red methods are being devised for their analysis.

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CHAPTER I

INTRODUCTION

A. Introduction

A great deal of effort has been expended around the world in recent years in the study of the reactions which occur in polymers when they are subjected to a variety of degradative agencies. Although individual polymers in specific applications may require to be resistant to, for example, ozonisation, hydrolysis, high energy radiation, mechanical stress, etc., it is almost certain that in most applications of nearly every polymer it will be important to have the maximum amount of information about their stability to heat and visible or near ultraviolet light.

This report describes work carried out on three different aspects of polymer chemistry which have the common theme of polymer degradation mechanism and stability. Thus Chapter 2 deals with a comprehensive study of the photothermal degradation of copolymers of methyl methacrylate and n-butyl acrylate covering the entire composition range. This is followed, in Chapter 3, by a description of some preliminary investigations into the synthesis of polymers by the reaction of dimethoxy-p-xylene (DMPX) with various aromatic compounds using stannic chloride as catalyst. This was part of a continuing programme of research which is being carried out in this Department and which is concerned with the synthesis of materials of improved thermal stability. It was superceded, as far as the present

contract is concerned and as a result of discussions with the Materials Department, by a programme of study of the degradation reactions of simple polysiloxanes of which progress to date is described in Chapter 4 and which is currently being pursued.

B. Photothermal Degradation of Copolymers of Methyl Methacrylate and n-Butyl Acrylate.

A series of investigations into the thermal degradation of acrylate and methacrylate homopolymers and copolymers has recently culminated in a description of the thermal degradation reactions which occur in copolymers of methyl methacrylate (MMA) and n-butyl acrylate (n-BuA) covering the whole composition range.[1] Currently, in these laboratories, photodegradation studies of some of these systems are being pursued.[2] In order to have relevance to an understanding of the deteriorative processes which occur in polymeric materials in their commercial applications these photodegradation processes are being studied at ambient temperatures in polymer films and solutions.

Although the overall effects of heat on the one hand and of light at ambient temperatures on the other are often superficially different it is clear that there are many close similarities in the basic mechanisms, especially in the sense that the same radicals are usually involved. The differences in overall characteristics thus follow from the different secondary reactions in which these primary radicals participate in the melt and in solid films. In order to assist in a clarification of the relationships which exist between the purely thermal and purely photo reactions it is interesting to study the effects of

ultra-violet radiation on polymers at elevated temperatures such that they are molten, as are thermally degrading materials, but below their threshold for thermal degradation. To emphasise the links with purely thermal and purely photo processes we describe these as photothermal degradations.

Studies of this kind have previously been made on poly (methyl methacrylate)[3] and copolymers of methyl methacrylate with acrylonitrile[4] and methyl acrylate.[5] The work described in Chapter 2 is a sequel to this as well as to the thermal degradation studies on the same system which have recently been published.[1]

C. Synthesis of Friedel-Crafts Polymers.

It has been shown in this laboratory that polymers may be synthesised by the condensation of di(chloromethyl)benzene (DCMB) with a wide variety of aromatic and heterocyclic compounds in presence of Friedel-Crafts catalysts such as $SnCl_4$.[6] Although these materials are structurally comparable with the phenolic resins some of them prove to have superior electrical properties and thermal stability. In the past, work in this laboratory has been specifically directed towards the investigation of relationships between structure and stability in these materials and detailed investigations have been carried out in the DCMB/benzene[7] and DCMB/thiophen[8] systems in order to discover in structural terms why the latter is at least 100° more stable than the former.

Polymers may be similarly prepared by condensation of aromatic compounds with the corresponding ether, dimethoxy-p-xylene (DMPX)

$$CH_3-O-CH_2-\emptyset-CH_2-O-CH_3$$

and these materials are beginning to be applied commercially for electrical applications, being preferred because methanol is the volatile by-product rather than hydrogen chloride from DCMB.

It was intended to synthesise a number of these polymers based on DMPX with the ultimate aim of defining the structural factors necessary for optimum stability and the preparative means of achieving them. It was only possible to carry out some very preliminary experiments along these lines, however, before the contract was redirected towards silicone polymers. It is these preliminary experiments which are described in Chapter 3.

D. Thermal Degradation of Polysiloxanes.

The immediate objective of this work is to characterise the degradation and stability properties of the relatively simple siloxane polymers. When this is achieved emphasis will move towards some of the more sophisticated silicon containing materials which are currently of interest to the Materials Laboratory.

Since polymer structure impurities and additives should be expected to influence degradation and stability properties it was considered desirable to prepare silicone polymers under carefully controlled conditions rather than to depend upon commercial materials. Thus work to date has been concerned with the preparation, handling and characterisation of suitable samples of poly(dimethyl siloxane) and this is being followed by a fundamental study of their thermal degradation using the wide variety of appropriate analytical techniques available to us.

Degradation studies, described in Chapter 4, have been principally concerned with thermal analysis using thermal gravimetric analysis (TGA) and thermal volatilisation analysis (TVA), separation and analysis of volatile products using gas liquid chromatography and infra-red spectroscopy and the influence of polymer preparation and structure on these properties.

CHAPTER II

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

A. Experimental

1. Preparation of Copolymers. 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 it was 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.

The 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.

Pyrex glass dilatometers of approximately 100 ml. capacity with a 5 ml. graduated stem were washed with cleaning solution,

distilled water, and finally Analar acetone before being attached to the vacuum line. The dilatometers were then flamed intermittently for several hours, prior to the addition of the initiator solution.

After degassing and vacuum distillation, pure methyl methacrylate and monomer mixtures of known composition were polymerized in bulk in dilatometers at 60°C ± 0.5°C. Poly n-butyl acrylate homopolymer was polymerized in solution in n-butyl acetate (B.D.H. Ltd.) at 40°C. The initiator concentrations are given in table 1. Polymerization was carried to 8 per cent where possible, but with copolymers of high acrylate content, polymerization 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.[9]

$$r_1 \text{ (M.M.A.)} = 1.80$$
$$r_2 \text{ (nBu.A.)} = 0.37$$

After precipitation of the homopolymers and copolymers by addition to methanol, they 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. Initiator concentrations, copolymer compositions and molecular weights are given in table 1.

Table 1

Copolymer Composition and Molecular Weight Data

Copolymer Composition (mole % n-BuA)	Initiator Conc. (% w/v)	Molecular Weight
1.0	0.17	260,000
3.9	0.17	347,000
16.3	0.042	1,300,000
50	0.084	230,000
82.2	0.084	506,000
93.4	0.002	1,400,000
100	0.11	2,800,000

2. Photothermal Degradation. Photothermal 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 figure 1. The two halves of the cell are joined by a ground glass joint.

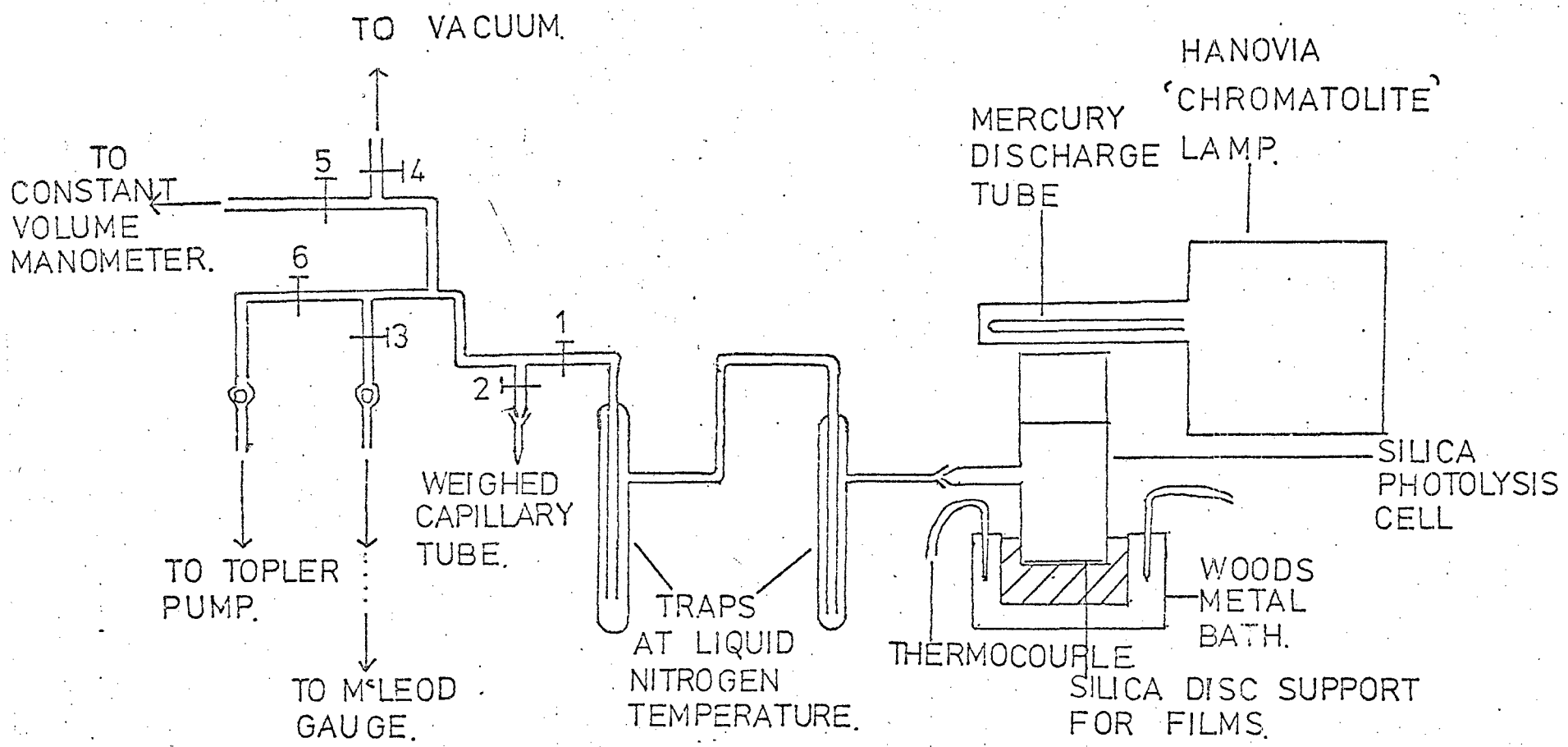
The photolysis cell was heated to the required temperature (165°C) by means of a Woods metal bath controlled by a proportional temperature controller and an isolating transformer. When the reaction vessel was immersed to a depth of half an inch, a temperature control of ± 0.5°C. was attained inside the vessel for 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.

The invariable experimental procedure was to immerse the photolysis cell 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 ultraviolet 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.

3. Polymer Form. In photodegradation studies it is important to use as thin films of polymer as possible but to expose a maximum area so 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.

Fig. 1.

PHOTOLYSIS CELL AND ASSOCIATED VACUUM EQUIPMENT.



a. Rates of diffusion of volatile products from the degrading polymer.

b. Possible temperature gradients in the polymer.

c. Possible skin effects such that the radiation is completely absorbed in the surface layers so that the reaction is not homogenous throughout the polymer.

The use of powdered polymer would be unsatisfactory 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.

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.

4. <u>Source of Radiation.</u> A Hanovia 'Chromatolite' low pressure mercury resonance lamp was used as shown in figure 1. This produces a typical mercury emission spectrum, the intensities of the two resonance lines at 1849 Å and 2537 Å being very much greater than those of all

the other wavelengths present. The output of this lamp is shown in figure 2. 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.

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 will thus be modified to some extent by the absorbing characteristics of silica and air media and it was therefore important to examine these characteristics.

The transmission of fused silica is shown in figure 3. This shows that for light of wavelength 2537 Å, the percentage transmission is 86 per cent.

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 Å, and the more important Schumann-Runge system having a threshold wavelength at 2000 Å and converging towards 1761 Å.[10]

Figure 2 shows that 93 per cent of the output of the lamp is composed of mercury resonance radiation with wavelengths of 1849 Å and 2537 Å. 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

Fig. 2.

OUTPUT OF HANOVIA LAMP

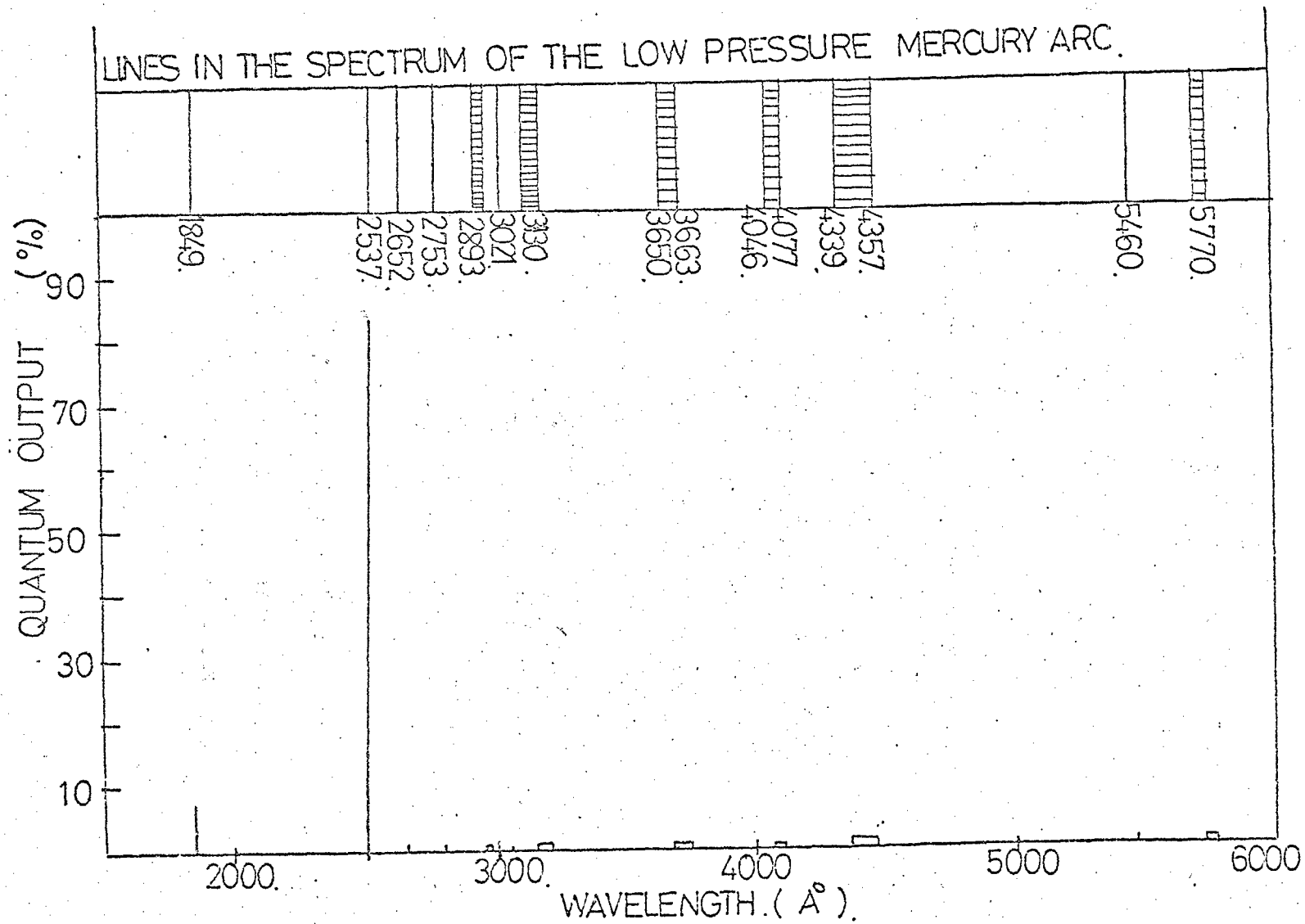
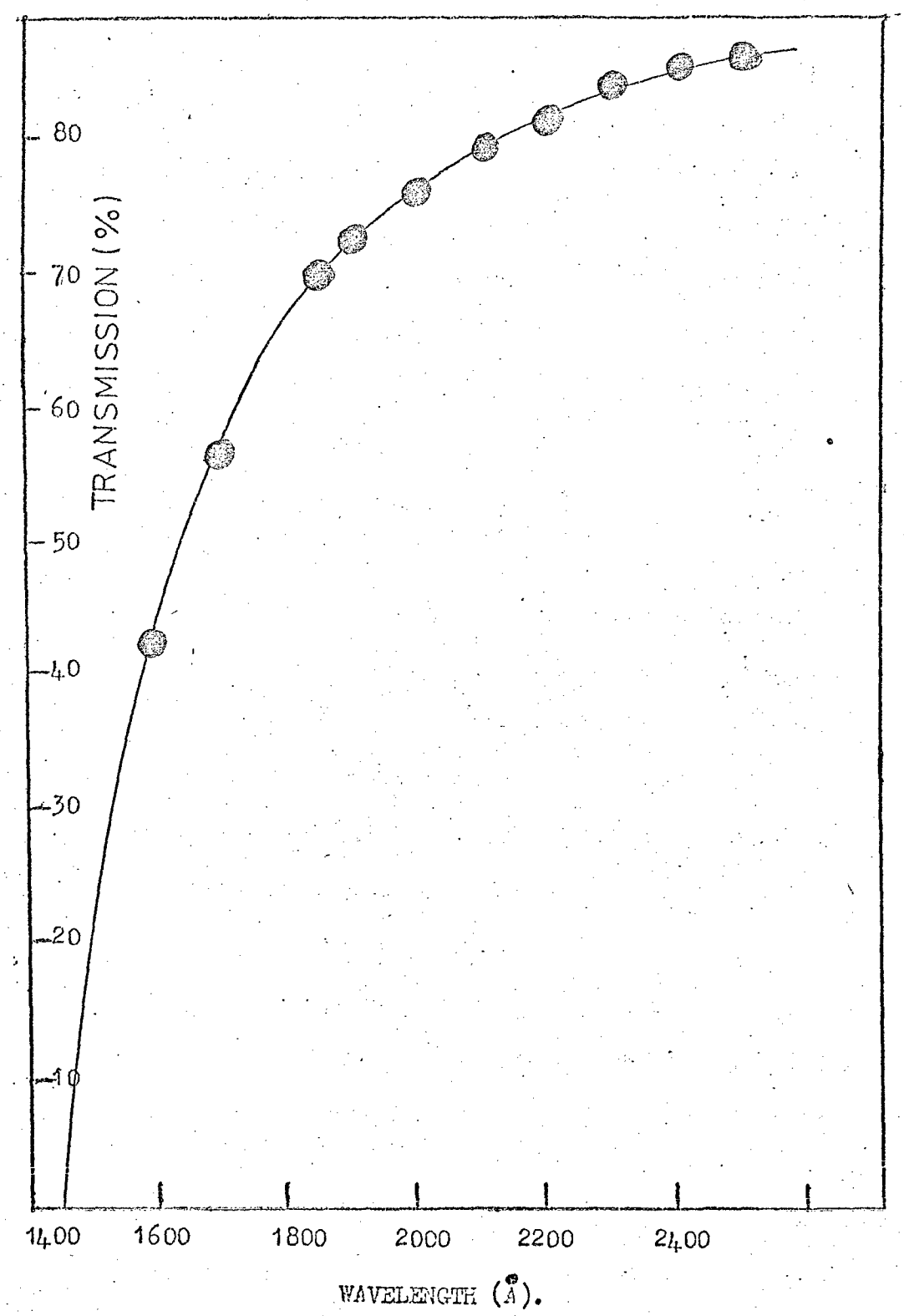


Fig. 3.

ABSORPTION SPECTRUM OF FUSED SILICA (2mm.)



are negligible, the radiation reaching the polymer is virtually monochromatic (2537 Å). It is obvious then that the 1849 Å line has an energy associated with it which exceeds the threhold 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.[11]

5. Measurement of Molecular Weight. Number average molecular weights were measured by means of a Hewlett-Packard High Speed Membrane Osmometer, Model 501, with cellophane membranes.

6. Product Analysis. The terms used to describe the four kinds of products are self-explanatory, namely, permanent gases, liquid condensibles, 'cold ring' (short chain fragments) and residue. For the analysis of the degradation products the silica degradation cell was attached to two small traps immersed in liquid nitrogen. With the traps at liquid nitrogen temperature the permanent gases were removed for analysis by means of a Topler pump. The liquid products retained in the traps were either distilled into an infra-red cell or into a weighed capillary and stored at -18°C. until required. The 'cold ring' formed on the sides and window of the photolysis cell. It was dissolved in chloroform and after evaporation of the solvent on a salt plate, an i.r. spectrum was obtained. Residual polymer on the silica disc was dissolved in toluene for molecular weight measurement.

7. Spectroscopic Measurements. Infra-red spectra were obtained using a Perkin Elmer 257 Grating Spectrophotometer. The soluble residues were run as films deposited on NaCl plates from chloroform solution, the insoluble residues

by means of the standard KCl disc technique.

For ultra-violet spectral measurements a Unicam S.P. 800 instrument was used with the polymer supported on the silica disc on which degradation was carried out.

8. Gas-liquid Chromatography. G.L.C. data for liquid products were obtained using a Microtek G.C. 2000R Research Gas Chromatograph equipped with dual columns, flame ionization 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. The 5% D.N.P., 5% B34. column proved to be most effective in separating the liquid products.

a. Permanent gas sampling apparatus. The gases were first introduced into the sample bulb using a Topler pump with the traps at liquid nitrogen temperature. The sampling system shown in figure 4 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 taps 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.

b. 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

Fig. 4.

INLET SYSTEM OF THERMAL CONDUCTIVITY, G.L.C.

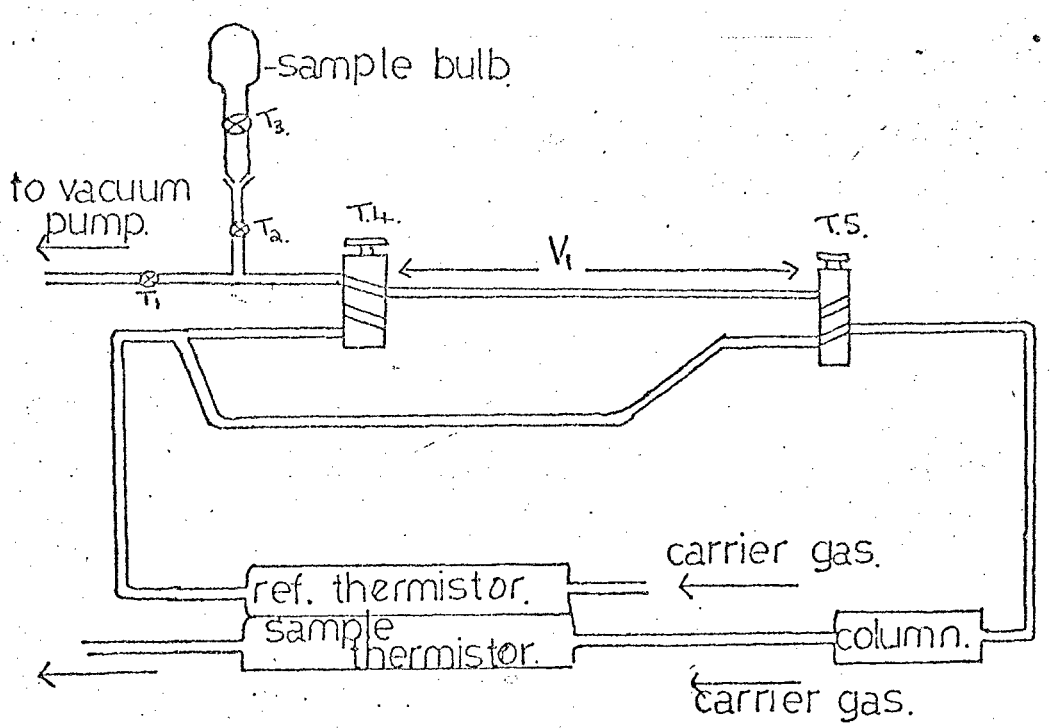


Table 2

G.L.C. Data

COLUMN	PROGRAMME	USE	DETECTOR
10 ft. ¼ 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. ¼ 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. ¼ inch diameter 10%D.N.P. on 100-120 mesh embacel.	Isothermal at 80°C.	Liquid volatiles	Flame ionization
20 ft. ¼ inch diameter 30-60 mesh silica gel.	Isothermal at room temperature	Permanent gases	Thermal conductivity

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

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

c. 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).

9. 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.

B. Results.

1. Choice of Reaction Temperature. A temperature of 165°C was arbitrarily chosen since it was believed that this would be sufficiently above the glass transition and melting points of all the copolymers such that the medium in which reaction was occurring would be reasonably comparable with that of thermal degradation. It was also to be hoped that there would be free enough diffusion of volatile products such that the reaction would be homogeneous throughout the mass of the polymer. At the same time, by reference to thermal studies,[1] 165°C. is clearly well below the thermal degradation threshold.

In order to test for diffusion effects, samples of various thicknesses (weight/unit area) were degraded under standard conditions. A typical result is illustrated in figure 5, which demonstrates that the rate of volatilisation is independent of sample thickness. Similar results were obtained throughout the copolymer composition range.

2. Identification of Products.

a. Liquid condensibles. A typical infra-red spectrum of products condensible in liquid nitrogen is illustrated in figure 6. Assignments of the principal absorptions are given in table 3. Although the polymer films were preheated in a vacuum oven at 40°C. prior to irradiation they clearly still contain residual benzene (solvent). The spectra also suggest that the major fraction of the volatile products is one or other or both of the monomers.

Fig. 5.

INFLUENCE OF FILM THICKNESS ON RATE OF VOLATILISATION OF A 50 MOLE % n-BUTYL ACRYLATE COPOLYMER PHOTOTHERMALLY DEGRADING AT 165°C.

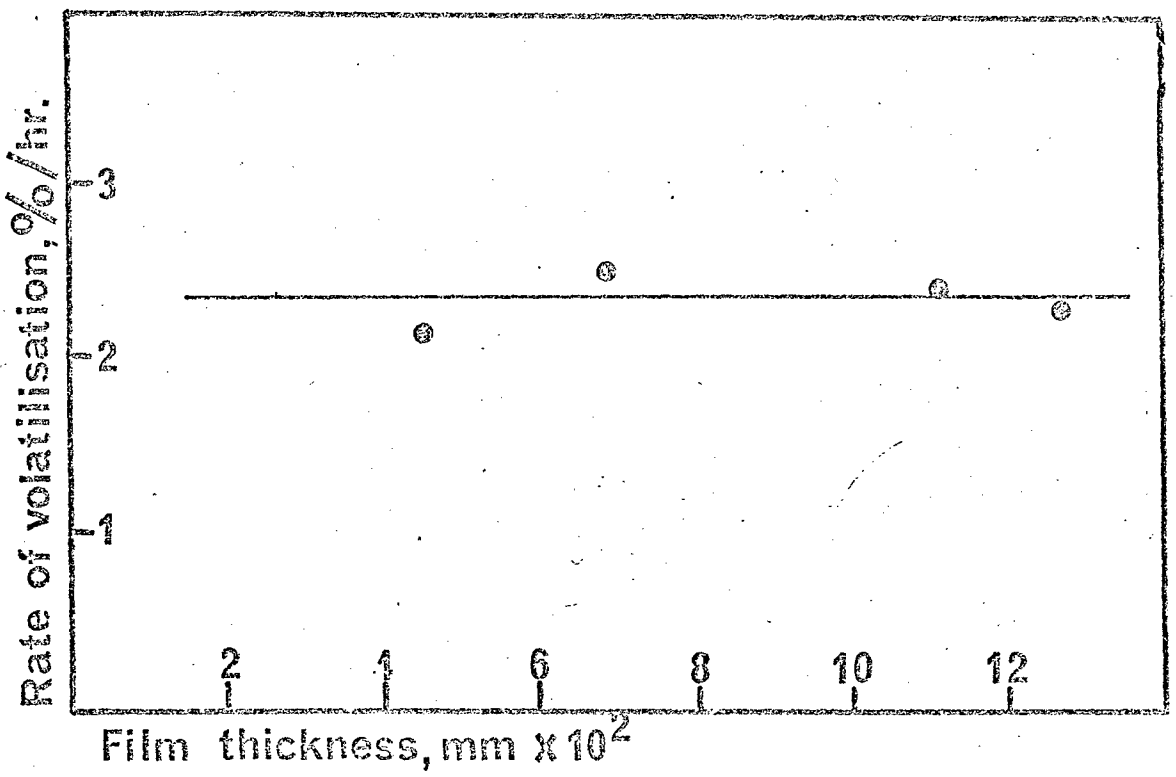
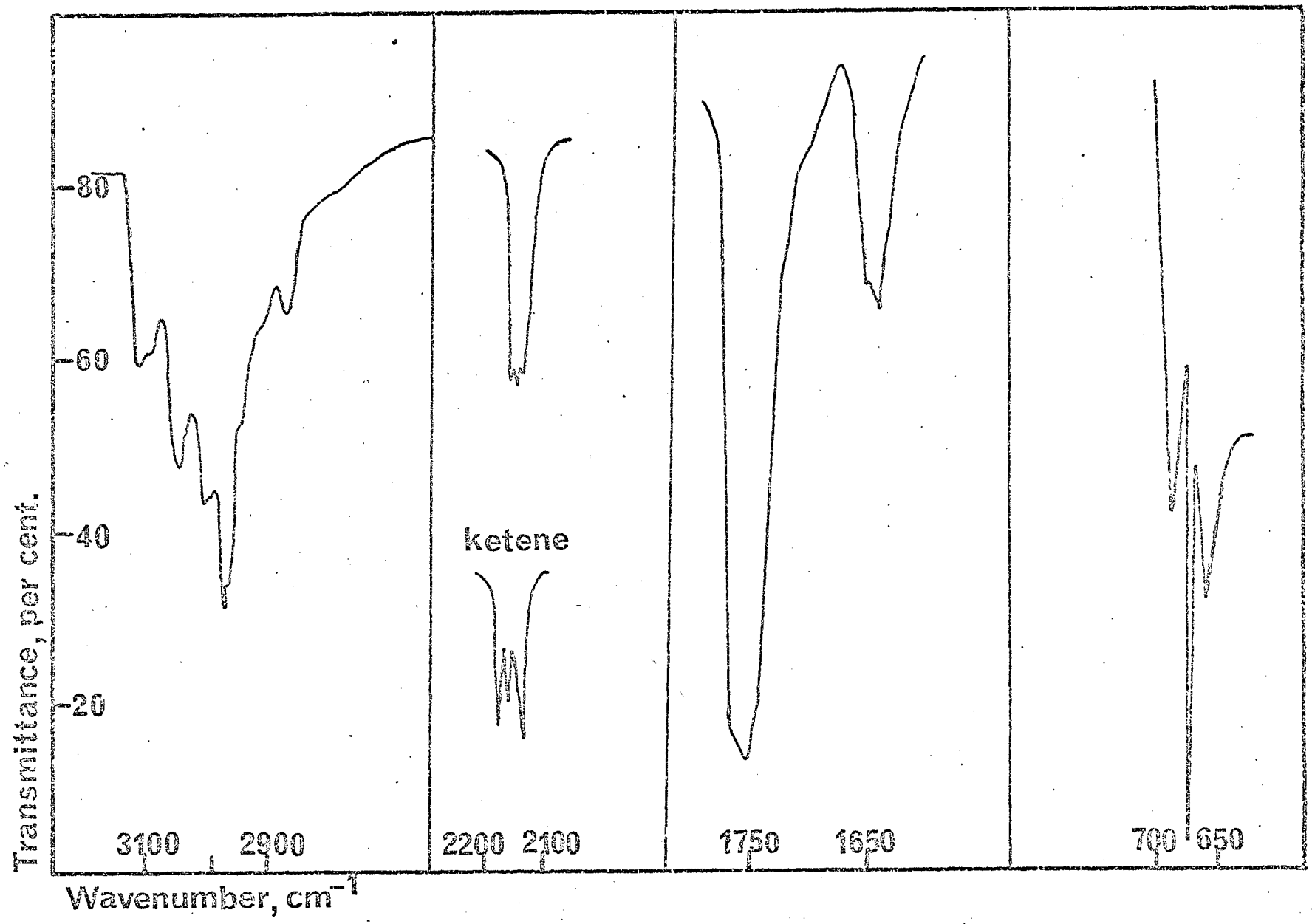


Fig. 6.

INFRA-RED SPECTRUM OF LIQUID CONDENSIBLES FROM A 16.3 MOLE % n-BUTYL ACRYLATE COPOLYMER PHOTOTHERMALLY DEGRADED AT 165°C FOR 23 HOURS.



The absorption at 2138 cm^{-1} is interesting. -C≡C- stretch would give rise to absorption in the region 2140-2100 cm^{-1}. If the structure were H-C≡C-, a peak at 3,300 cm^{-1} due to C-H stretching would appear. Since this is absent, then if absorption at 2138 cm^{-1} is due to alkyne, it can only arise from R-C≡C-R. A reference spectrum of CH_3-C≡C-CH_3 showed absorption at 2135 cm^{-1} but this was not the strongest absorption so it is unlikely that the observed absorption is due to an alkyne. A reference spectrum of ketene ($H_2C=C=O$) is included in figure 6. This has similar absorption and although the shape is rather different it seems likely that the absorption at 2138 cm^{-1} is due to a substituted ketene (RCH=C=O).

Carbon dioxide and but-1-ene were prominent products in the thermal degradation of copolymers of methyl methacrylate and n-butyl acrylate. Neither of these was detected in the photothermal reaction throughout the entire copolymer composition range.

Figure 7 illustrates a typical G.L.C. trace of the liquid degradation products. By the application of combined gas chromatography and mass spectrometry (G.C - M.S) and the use of reference spectra these were identified as in table 4. Components 1, 4, 5, 8 and 9 are obviously genuine degradation products. The benzene is residual solvent, xylene an impurity in the benzene and the siloxane trimer and tetramer are products of photolysis of the tap grease. No peak corresponding to a substituted ketene was observed.

Fig. 7.

G.L.C. TRACE OF THE LIQUID CONDENSIBLES FROM A 50.0 MOLE % n-BUTYL ACRYLATE COPOLYMER PHOTOTHERMALLY DEGRADED AT 165°C (COLUMN TEMPERATURE, 85°C).

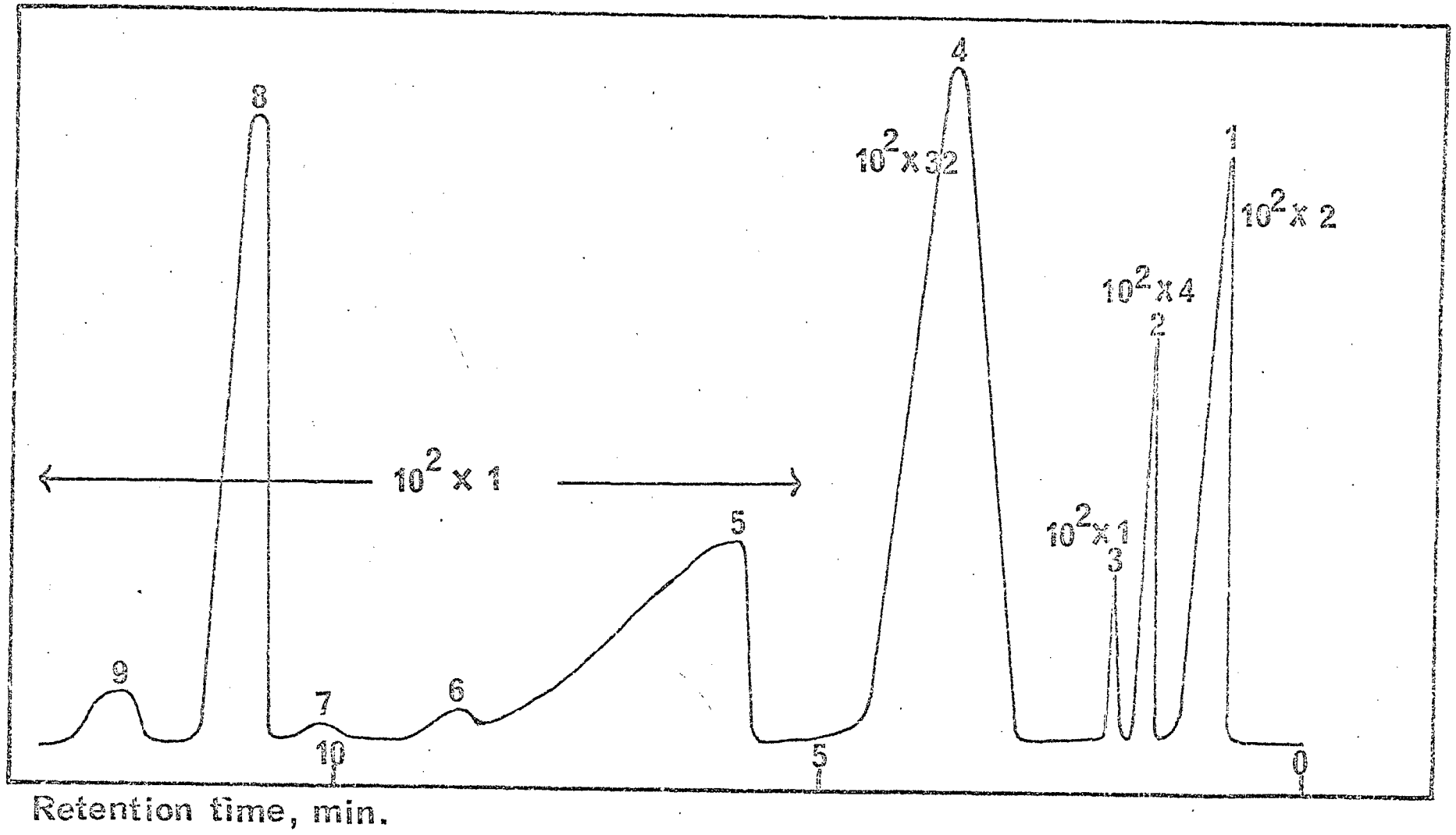


Table 3

Assignment of Infra-red Absorptions of Liquid Condensibles

Frequency (cm^{-1})	Assignment
700 - 650	benzene C-H
1750	$>C = O$ stretch
1644	$>C = O$ stretch
3000 - 2900	C-H stretch in $-CH_3$ or $> CH$
2855	C-H stretch in $-O-CH_3$
3150 - 3000	$= C-H$
2138	ketene

b. Permanent gases. A typical infra-red spectrum and G.L.C. trace of the small proportion of permanent gas products are illustrated in figure 8. These were identified as hydrogen, carbon monoxide and methane.

3. Quantitative Analysis of Degradation Products. The degradation of the copolymers as represented by the weight loss and the formation of products volatile and involatile (cold ring) at room temperature is illustrated in figure 9. As the acrylate content of the copolymer is increased the total rate of decomposition and of production of volatile products decreases while the rate of production of 'cold ring' fraction increases with acrylate content up to 16.3 mole% thereafter decreasing. However the ratio of cold ring to volatiles increases continuously with acrylate content.

Quantitative analysis of the liquid degradation products was carried out using the G.L.C. technique and results are recorded in table 5. All the residual solvent, benzene, was always liberated during the 15 minute period required for the polymer films to attain the operating temperature of 165°C. The total weight of residual benzene, calculated from G.L.C. data was subtracted from the initial polymer weight before calculating the data in table 5. Methyl methacrylate is the predominating product followed in order by butyraldehyde, butyl acrylate, butanol and butyl methacrylate. The order of accuracy for the trace products is obviously low but the results do show interesting general trends.

The total pressure of the permanent gases was very small (approximately 1 torr as measured on a Macleod gauge) so that

Fig.8. INFRA-RED SPECTRUM AND G.L.C. TRACE OF THE PERMANENT GAS PRODUCTS FROM A 50 MOLE % n-BUTYL ACRYLATE COPOLYMER PHOTOTHERMALLY DEGRADED AT 165°C FOR 72 HOURS. (G.L.C. COLUMN AT ROOM TEMPERATURE).

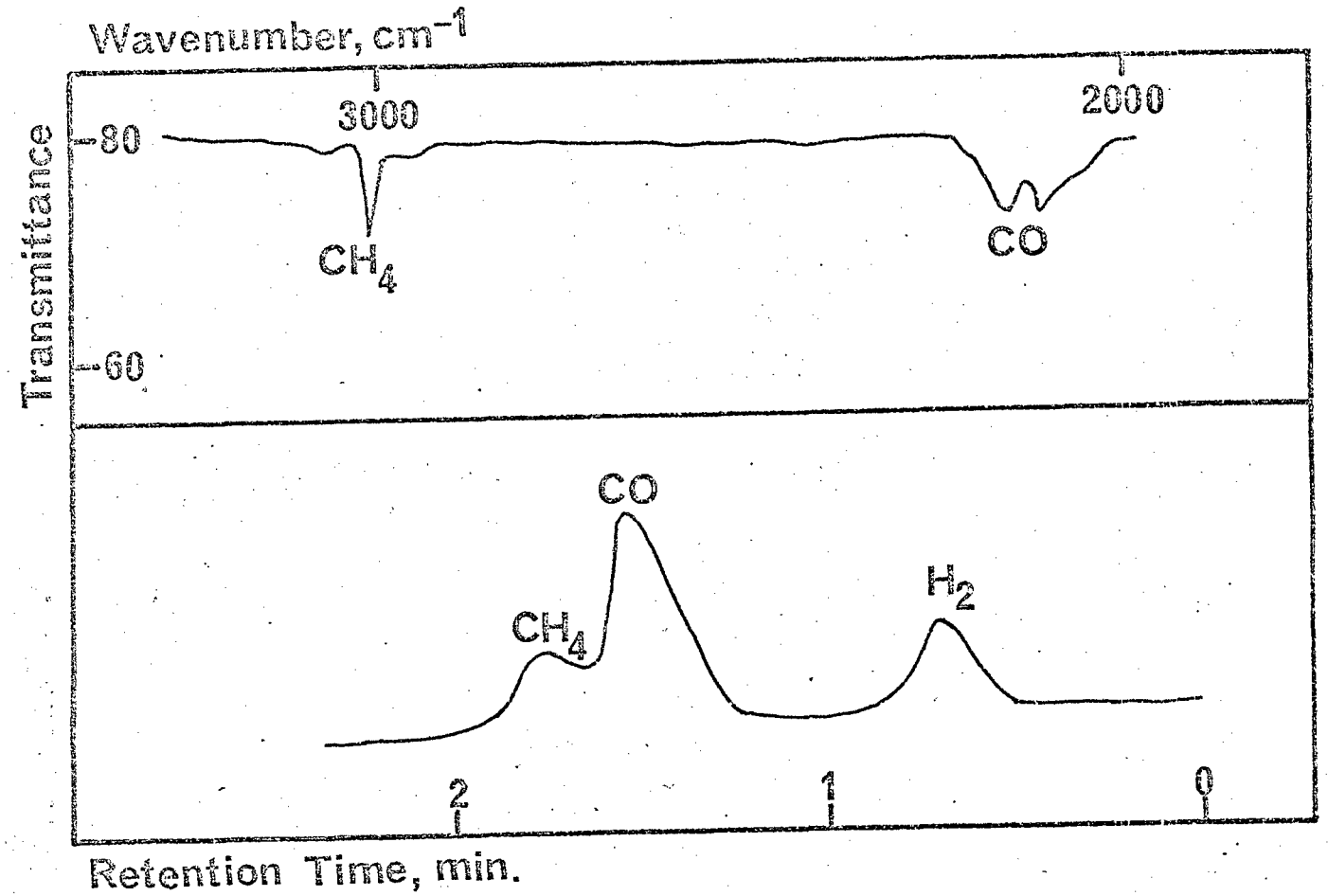


Fig. 9.

WEIGHT LOSS, COLD RING AND LIQUID CONDENSIBLES PRODUCED DURING PHOTOTHERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE AT 165°C. COPOLYMER COMPOSITION, MOLE % n-BUTYL ACRYLATE, O, 1.0; ◐, 3.9; □, 16.3; ▣, 50; Δ, 82; ▲, 93.4; ▽, 100.

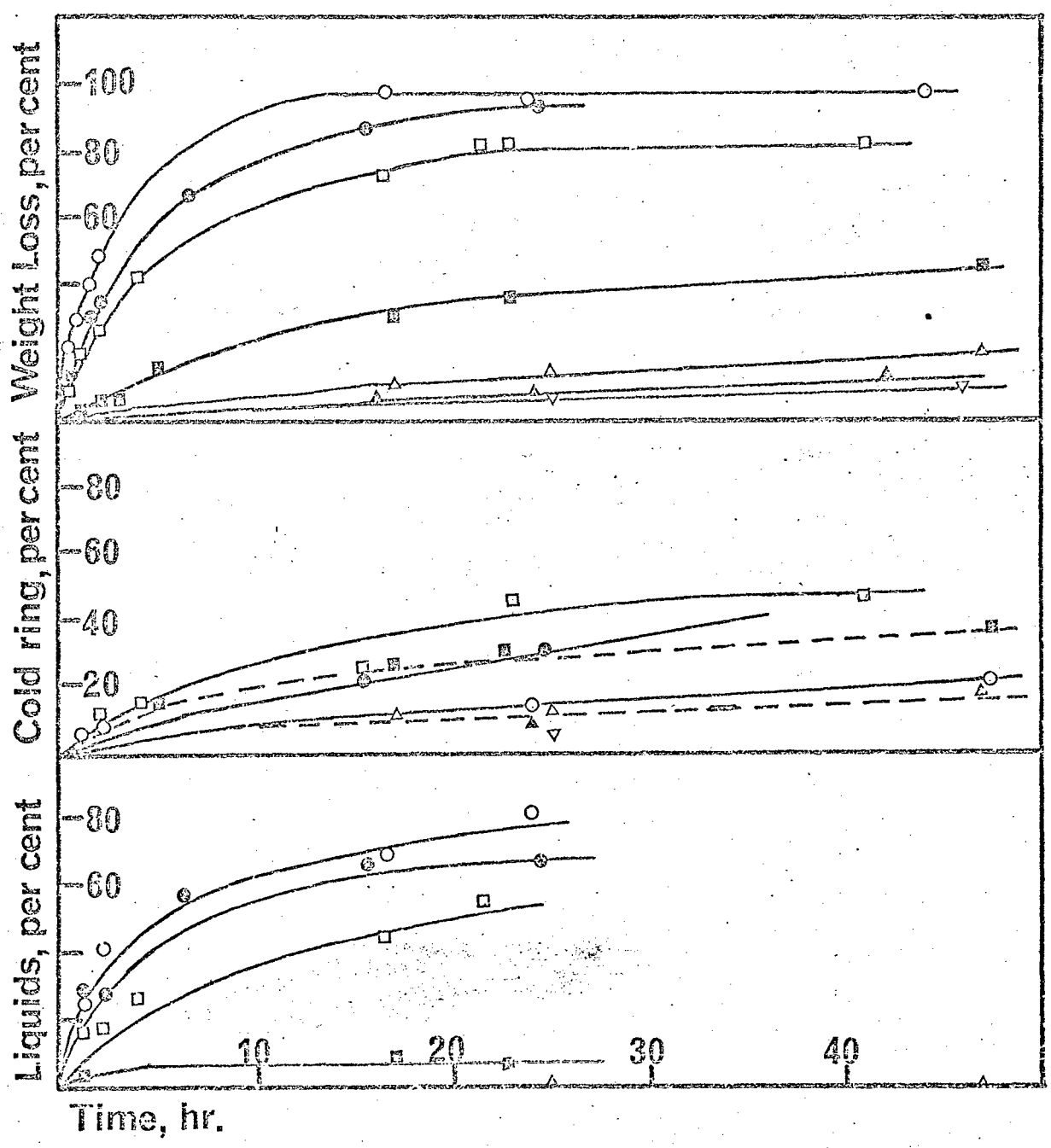


Table 4

G.C-M.S. Identification of the Product Peaks in Figure 3.

Peak No.	Product
1	n-butyraldehyde
2	benzene
3	siloxane trimer
4	methyl methacrylate
5	n-butanol
6	siloxane tetramer
7	xylene
8	n-butyl acrylate
9	n-butyl methacrylate

quantitative measurements were not possible. However the G.L.C. peak ratios for two copolymers, recorded in table 6, represent an approximate measure of their relative importance.

These results demonstrate that, as expected, the amount of methyl methacrylate produced increases with the methacrylate content of the copolymer while the proportion of butyraldehyde decreases. However butyraldehyde is produced even from copolymer containing only 3.9 mole% n-butyl acrylate in which the percentage of acrylate-acrylate linkages, calculated from sequence distribution data, is only 0.1.[1] Thus butyraldehyde production must be associated with single isolated n-butyl acrylate units. While butyl alcohol production also increases with acrylate content it is not detected in the products until the acrylate content of the copolymer is as high as 50 mole % that is until a significant proportion (22%[1]) of acrylate units are present in adjacent sequences. More n-butyl acrylate is formed from 16.3 and 50 mole% copolymer than from 82.2 mole % copolymer. A similar result was observed in the thermal reaction. Acrylate monomer must be produced in the depolymerization reaction initiated and propagated principally through the methacrylate segments of the polymer chain. Apparently a certain proportion of isolated acrylate units can be liberated in this way but adjacent sequences prefer to take part in transfer reactions leading to the formation of large chain fragments at the expense of both monomers. As in thermal degradation,[1] the production of n-butyl methacrylate is greatest in 50 mole % copolymer. The limited

Table 5

Quantitative Analysis of Liquid Products (millimoles/gm of initial polymer)

Copolymer (mole % n-butyl acrylate	Time of Photolysis	M.M.A.	Butyraldehyde	Butyl Acrylate	Butanol	Butyl Methacrylate
1	1.5 2 16.5 24 47.5	2.56 3.36 5.55 5.86 6.97	NIL	NIL	NIL	NIL
3.9	1.5 2 6.5 15.5 24.5	1.54 1.26 4.06 4.81 5.07	NIL NIL 0.006 0.014 0.016	NIL	NIL	NIL
16.3	2 4 16.5 23 41	1.10 1.79 3.91 4.52 3.68	NIL 0.020 0.023 0.036 0.030	0.007 0.020 0.019 0.021 0.016	NIL	NIL

Table 5 (cont'd)

Copolymer	Time	M.M.A.	Butyraldehyde	Butyl Acrylate	Butanol	Butyl Methacrylate
50	4	0.33	.021	.010	.008	.0009
	16.5	0.56	.031	.018	.007	.0008
	45	0.76	.052	.025	.018	.0015
	70	0.88	.053	.029	.014	.0012
82:2	25	0.04	0.056	.006	0.039	.0004
	47	0.08	0.11	.007	0.052	.0006
	71	0.10	0.16	.008	0.061	.0007

Table 6

G.L.C. Peak Ratios for Permanent Gases

Copolymer	Peak Ratio		
	H_2	CO	CH_4
50 mole % acrylate	0.9	2.4	1
82.2 " " "	15.6	1.3	1

data for permanent gases indicate that hydrogen evolution increases with acrylate content but the methane/carbon monoxide ratio remains roughly constant.

4. Molecular Weight Changes and Zip Lengths. All copolymers containing up to 50 mole % n-butyl acrylate remain soluble at all stages of photothermal degradation. Copolymers richer in n-butyl acrylate become insoluble in the later stages of reaction but in all copolymers there is a rapid decrease in molecular weight in the initial stages of reaction. Data are presented in table 7. Molecular weight measurements by themselves can not give a quantitative picture of relative rates of chain scission since starting molecular weights and extents of volatilisation vary. Nevertheless figure 10 demonstrates qualitatively that the rate of chain scission increases with acrylate content for low acrylate copolymers but that for high acrylate copolymers the situation is rather more complicated.

A more quantitative picture may be obtained by calculating the number of scissions per polymer molecule (N) and per chain unit (n) using the formulae[12]

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

$$n = \frac{1-x}{CL} - \frac{1}{CL_o}$$

in which CL_o and CL are the chain lengths initially and after an average of N scissions per polymer molecule have occurred

Fig. 10. MOLECULAR WEIGHT CHANGES IN COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE PHOTOTHERMALLY DEGRADING AT 165°C. COPOLYMER COMPOSITION, MOLE % n-BUTYL ACRYLATE, O, 1.0; ⊘, 3.9; □, 16.3; ▣, 50; Δ, 82; ▲, 95.4.

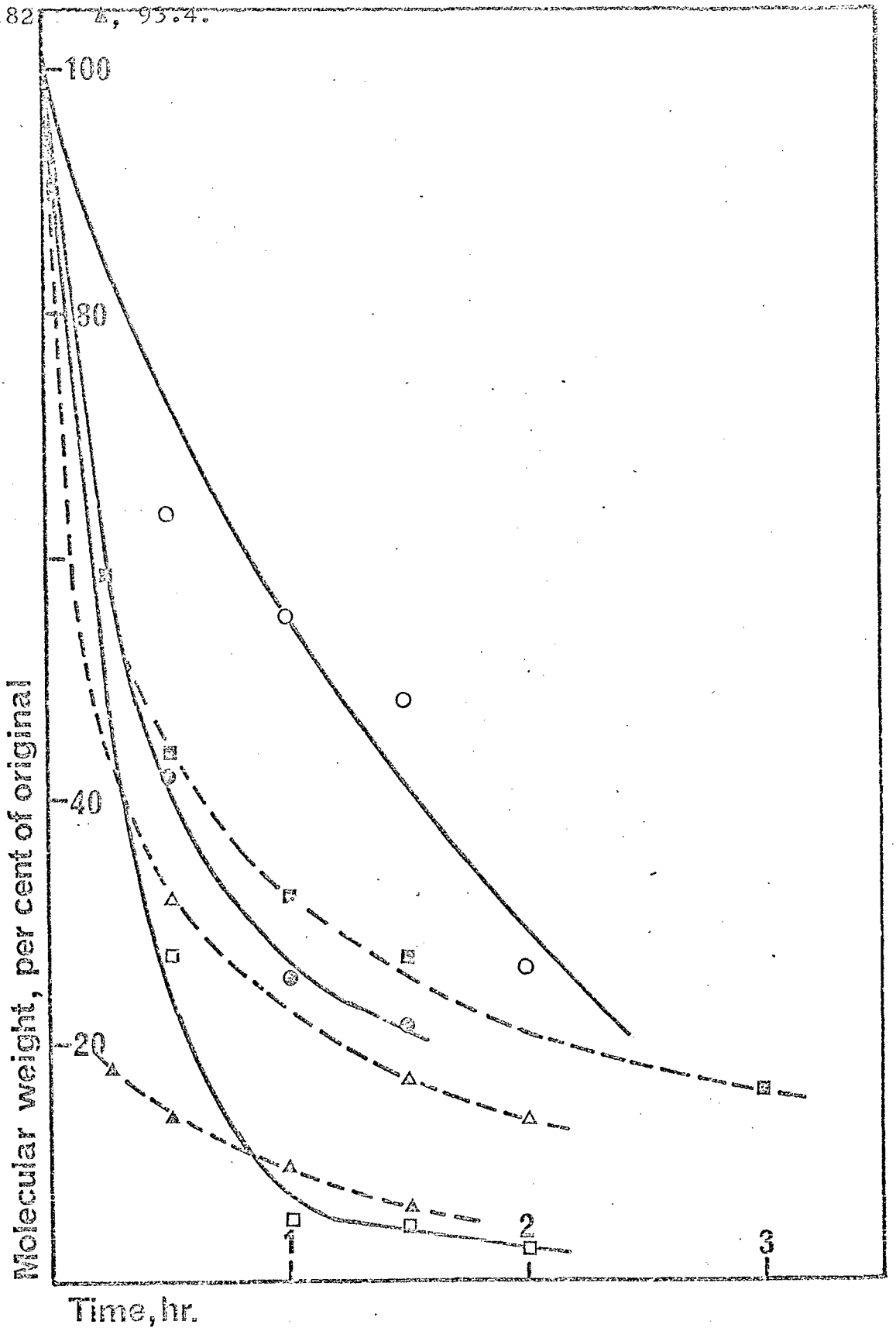


Table 7

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

Copolymer mole % n-butyl acrylate	Time (hrs.)	% Volatilisation	M.W.	M.W. % of original	$n \times 10^4$ scissions per monomer unit.	N scissions per polymer molecule.
1	0	0	260,000	100	0	0
	0.5	21.76	165,000	63.46	0.94	0.24
	1.0	30.35	143,000	54.99	1.02	0.26
	1.5	40.17	125,000	48.07	0.96	0.25
	2.0	48.72	67,600	25.99	3.8	0.99
3.9	0	0	347,000	100	0	0
	0.5	12.77	146,000	42.08	3.13	1.08
	1.0	30.57	87,200	25.13	5.14	1.77
	1.5	31	73,000	21.04	6.60	2.29
16.3	0	0	1,330,000	100	0	0
	0.5	8.93	361,000	27.14	1.86	2.36
	1.0	19.62	68,000	5.11	11.59	14.73
	1.5	21.25	60,000	4.51	12.95	16.45
	2.0	27.01	36,500	2.74	20.14	25.59
	4.0	41.66	25,100	1.84	-	-
	21.5	82.19	9,880	0.74	-	-

Table 7 (cont'd)

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

Copolymer	Time (hrs.)	% Volatilisation	M.W.	M.W. % of original	$nx10^4$ scissions per monomer unit	N scissions per polymer molecule.
50	0	0	230,000	100	0	0
	0.25	0	135,000	58.59	3.48	0.70
	0.5	1	101,000	43.91	6.22	1.25
	1.0	2.26	74,000	32.18	10.14	2.05
	1.5	3.41	61,700	26.83	12.97	2.29
	3	6.63	36,300	15.79	24.57	6.12
	5	16.07	23,900	10.40	-	-
82.5	0	0	506,000	100	0	0
	0.5	0	160,000	31.61	4.18	1.72
	1.5	0	85,000	16.80	11.98	4.92
	2	0	67,700	13.38	15.78	6.47
93.4	0	0	1,410,000	100	0	0
	0.25	0	250,000	17.73	4.15	4.64
	0.5	0	196,000	13.90	5.55	6.19
	1.0	0	138,000	9.78	8.25	9.22
	1.5	0	90,600	6.42	13.03	14.55

and x is the fraction of polymer volatilised. It should be noted that in deriving these formulae the only important assumption is that no polymer molecules have been lost by complete unzipping to volatile fragments. Calculated values of N and n are included in table 7. Plotting n against time as in figure 11, it is clear that while the rate of chain scission increases with copolymer acrylate content up to 16.3 mole %, thereafter the rate is constant within experimental error. A similar result was previously observed for the methyl methacrylate/methylacrylate copolymer system.[9] On the other hand figure 12 demonstrates that the volatile material produced per chain scission is progressively reduced by increasing the n-butyl acrylate content of the copolymer.

By plotting volatilisation against N, as in figure 13, for the four methacrylate rich copolymers, the zip length for each copolymer was calculated as in table 8. These values compare with 1,200 and 9 in the thermal degradation at 313°C. of 0.25% and 50% copolymers, calculated from the data of Grassie and Fortune.[1] Lower zip lengths were also observed in the thermal[13] compared with the photothermal[5] degradation of copolymers of methyl methacrylate and methyl acrylate.

5. Spectroscopic Examination of the Residue. Infra-red spectra of undegraded and degraded 93.4 mole % n-butyl acrylate copolymer are shown in figure 14. The only difference is that the spectrum of the degraded material has a shoulder at 1770 cm^{-1} on the carbonyl peak. There were no significant spectral changes on degradation of any of the other copolymers. Similar

Fig. 11.

CHAIN SCISSIONS PER CHAIN UNIT IN COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE PHOTOTHERMALLY DEGRADING AT 165°C. COPOLYMER COMPOSITION, MOLE % n-BUTYL ACRYLATE, O, 1.0; ⊙, 3.9; □, 16.3; ▣, 50; △, 82; ▲, 93.4.

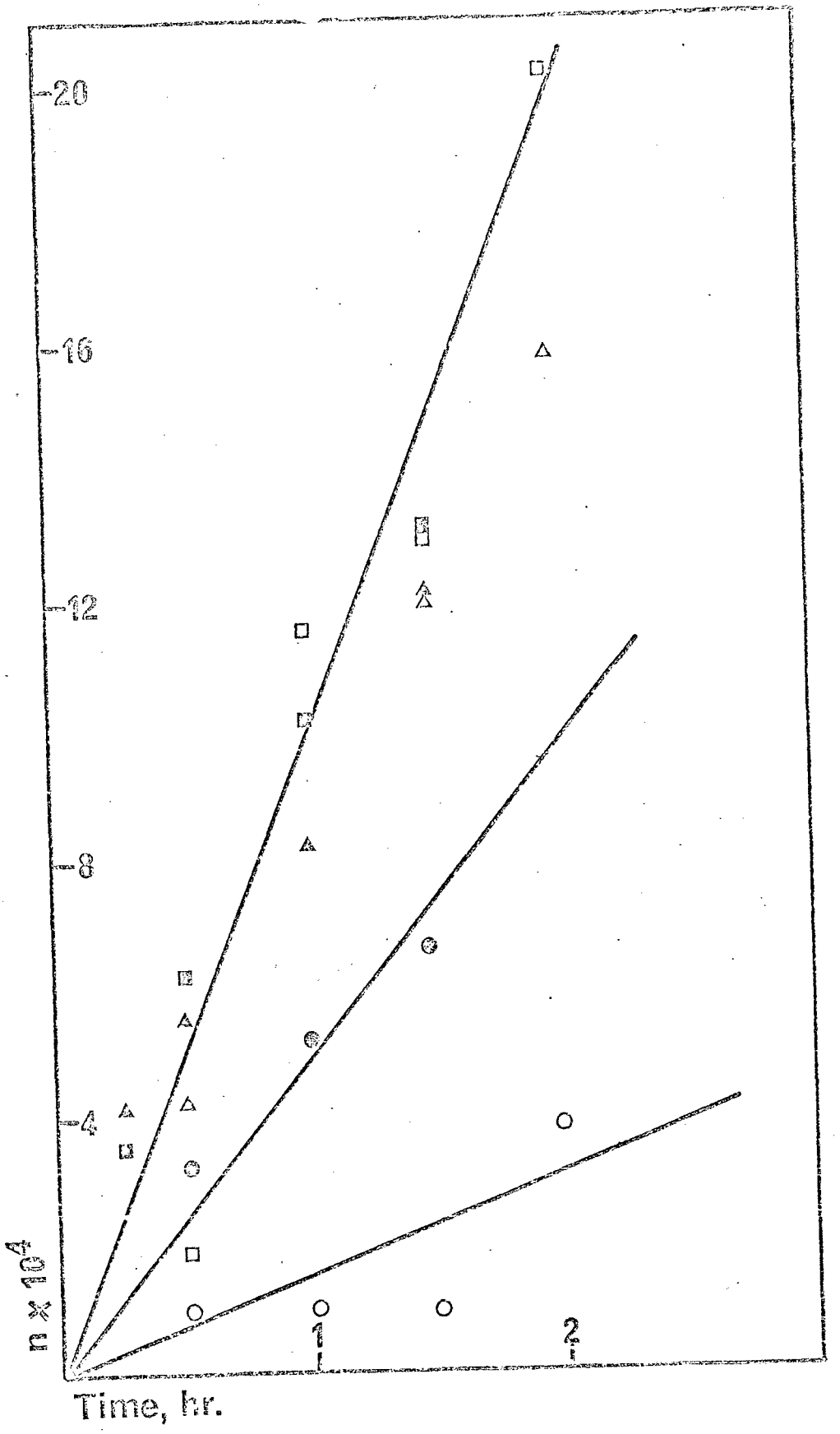


Fig. 12.

RELATIONSHIP BETWEEN CHAIN SCISSIONS PER CHAIN UNIT AND VOLATILISATION IN COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE PHOTOTHERMALLY DEGRADING AT 165°C. COPOLYMER COMPOSITION, MOLE % n-BUTYL ACRYLATE, O, 1.0; ⊙, 3.9; □, 16.3; ⊠, 50.

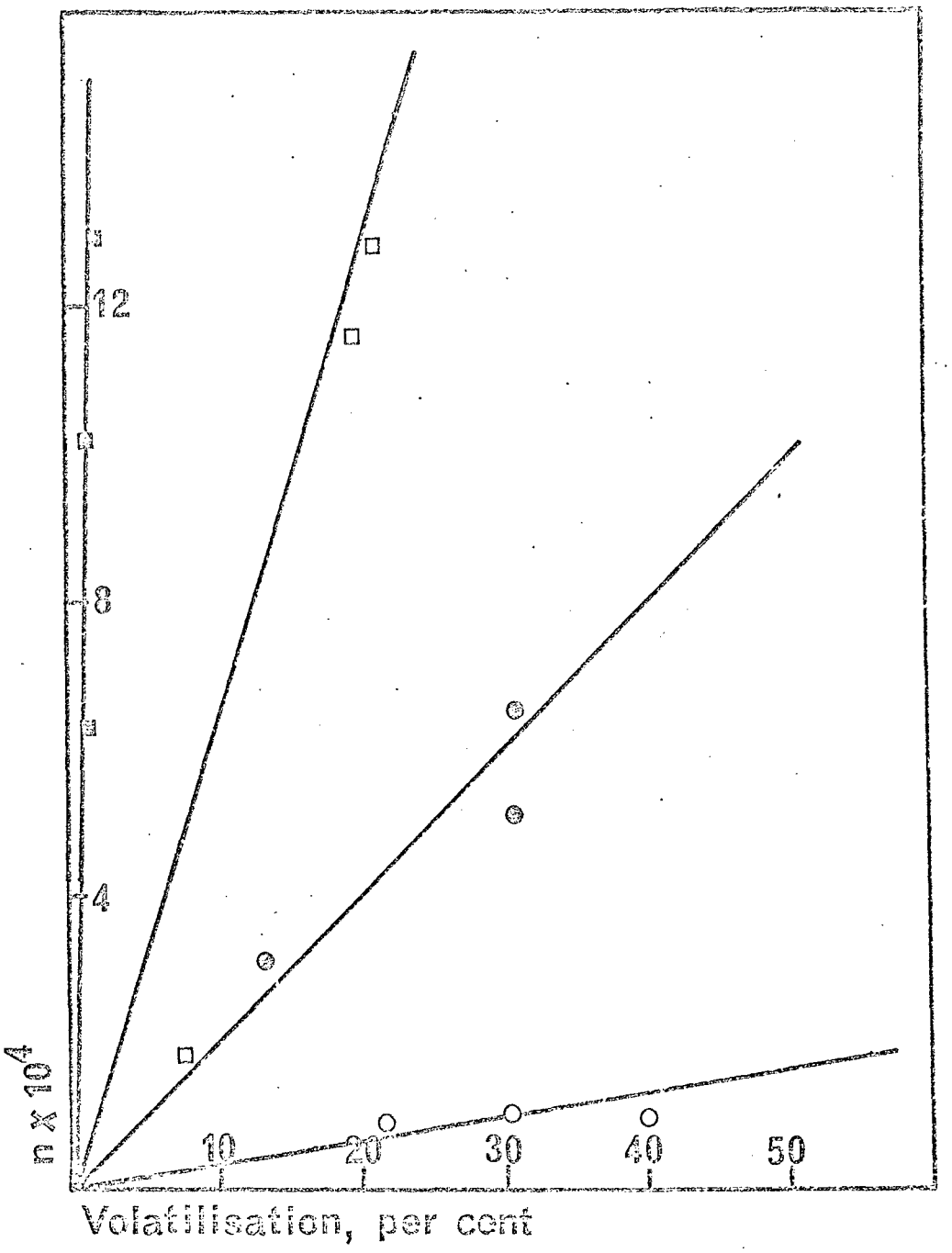
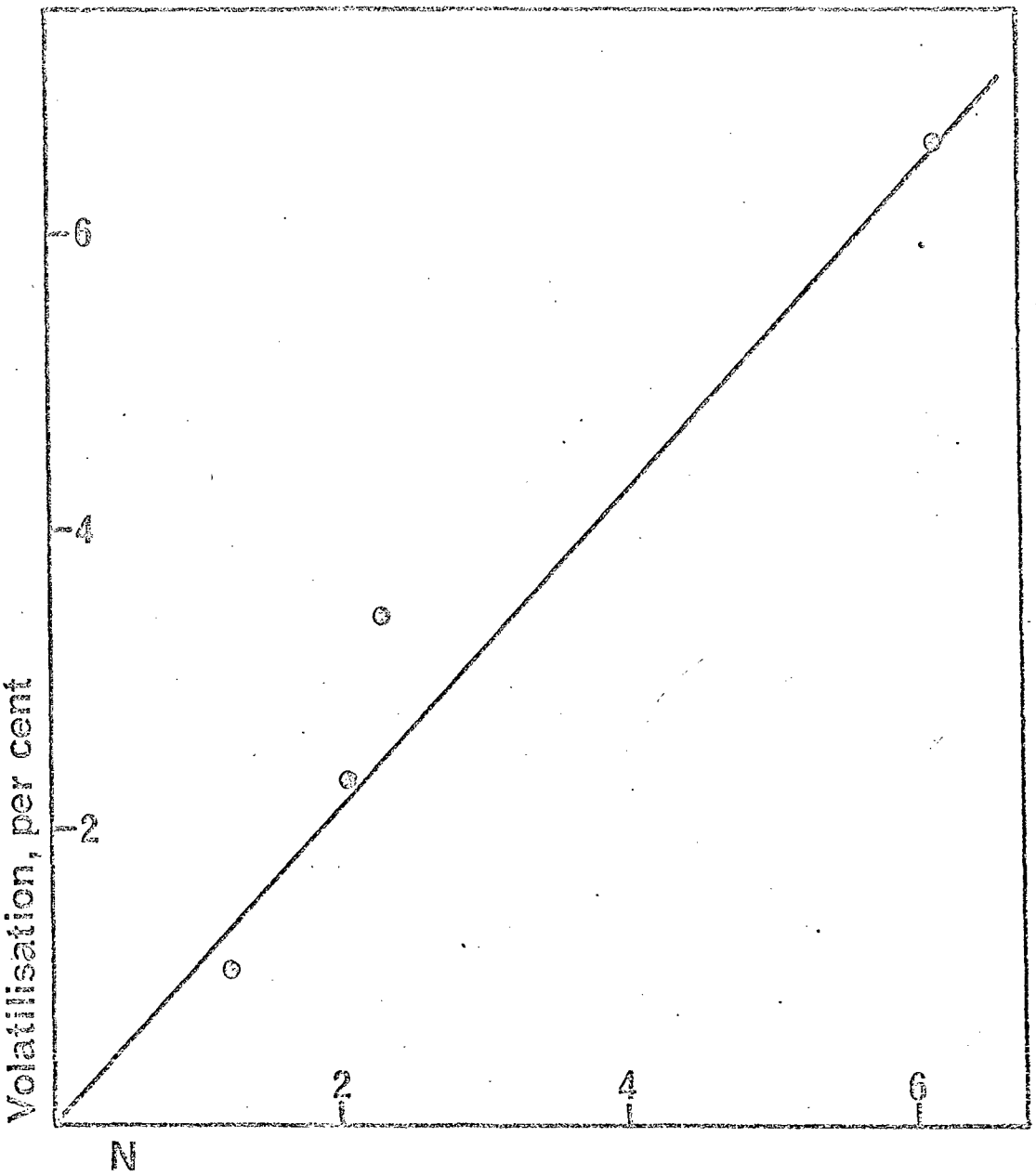


Fig. 13. RELATIONSHIP BETWEEN SCISSIONS PER POLYMER MOLECULE AND VOLATILISATION IN A 50 MOLE % n-BUTYL ACRYLATE COPOLYMER PHOTOTHERMALLY DEGRADING AT 165°C.



absorption at 1760 cm^{-1} during thermal degradation was attributed to lactone formation but absorptions at 1605 and 1560 cm^{-1} during thermal degradation were not observed during the photothermal reaction. These had previously been assigned to carboxylate ion and conjugated carbon-carbon bonds respectively.

There was never any visible change in colour in any of the copolymers during photothermal degradation unlike thermal degradation during which the colour deepened through yellow to brown with increasing decomposition. U.v.-visible spectra were run on photothermally degraded copolymers and a typical result is presented in figure 15. It is important to note that after 40 hours irradiation approximately 50% of the original material had been lost so that the true absorption per unit mass is very much greater than is shown in figure 15. As photothermal degradation proceeds there is a general increase in absorption in the region 400-255 mμ which can be attributed to increasing ethylene conjugation in the polymer chain backbone as in the thermal reaction.

6. <u>The Cold Ring.</u> It has already been demonstrated that the 'cold ring', which consists of short chain fragments, becomes increasingly more abundant as the acrylate content of the copolymers is increased. Comparing the infra-red spectrum of an undegraded copolymer with the spectrum of its cold ring as in figure 16, new absorptions are clearly present. A shoulder at about 1780 cm^{-1} appears, new absorption at 1635 cm^{-1} emerges and the C-O single bond peak

Table 8

Zip Lengths for Photothermal Degradation

Copolymer (mole % butyl acrylate)	Slope (Fig 13) % Volatilisation/ scission/ molecule, A	Initial M.W.	M.W. lost per scission $\frac{M.W. \times A}{100}$	Average wt. of monomer unit, B	Zip Length $\frac{M.W.\ A}{100.B.}$
1	48.6	260,000	126,400	100.27	1260
3.9	15.0	347,000	52,050	101.08	515
16.3	1.20	1,330,000	15,960	104.6	153
50	1.08	230,000	2,484	114	22

Fig. 14. INFRA-RED SPECTRA OF A, UNDEGRADED AND B, PHOTOTHERMALLY DEGRADED (64 hr) 93.4 MOLE % n-BUTYL ACRYLATE COPOLYMER.

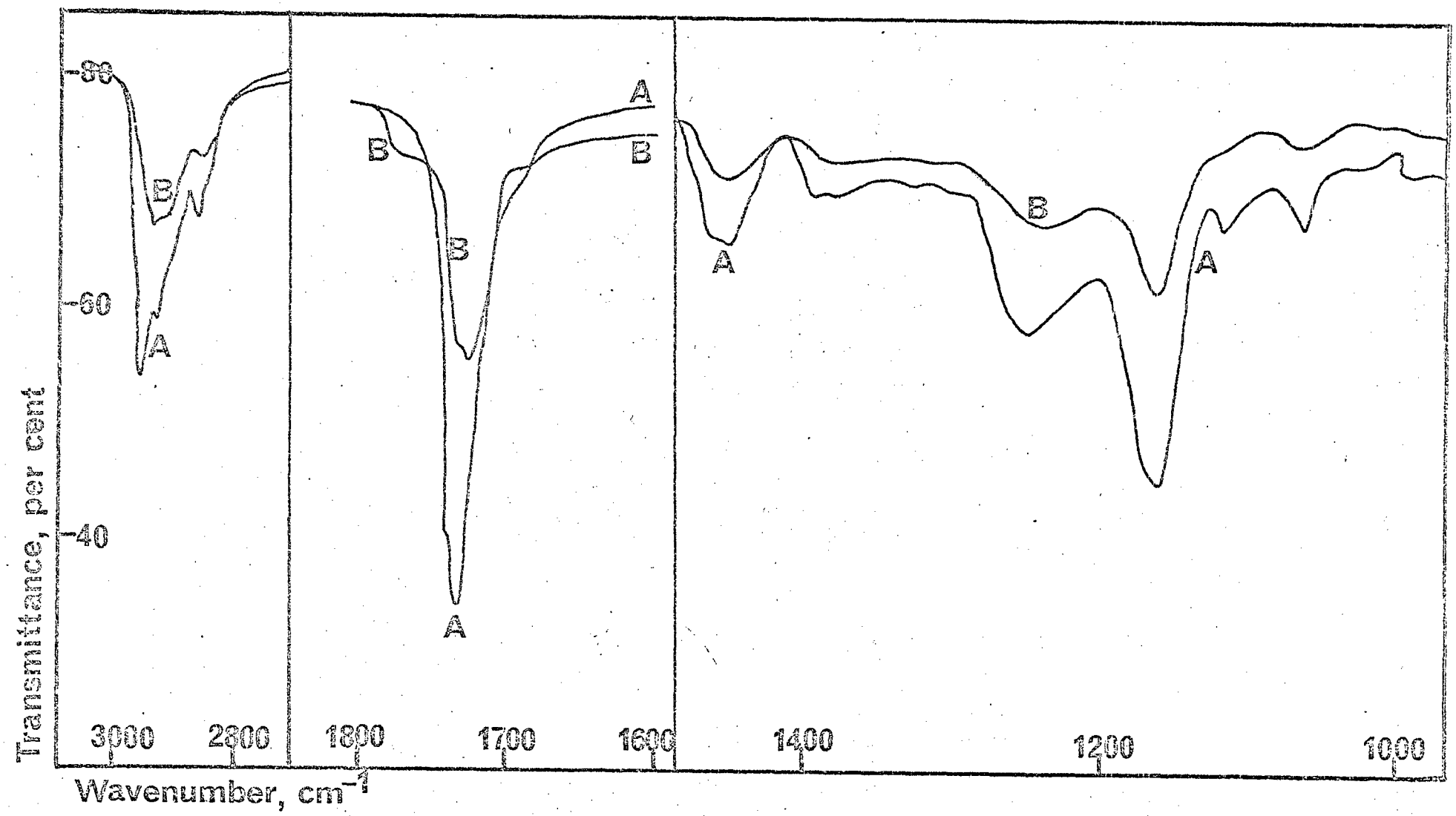


Fig. 15. ULTRA-VIOLET SPECTRA OF PROGRESSIVELY PHOTOTHERMALLY DEGRADED 50 MOLE % ACRYLATE COPOLYMER. 1, undegraded; 2, preheated to 165°C- residual benzene removed; 3, irradiated for 40 hr; 5, 80 hr.

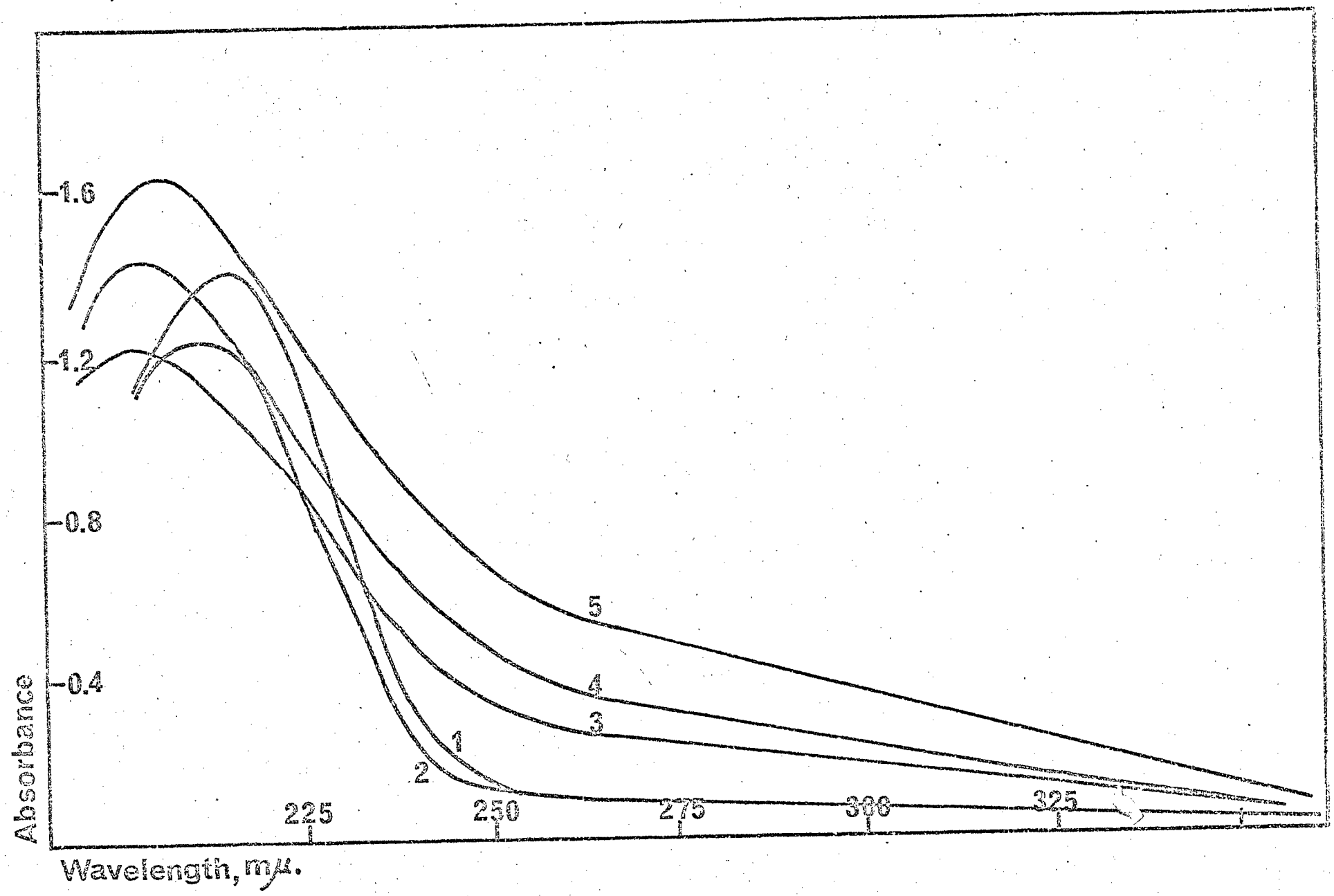
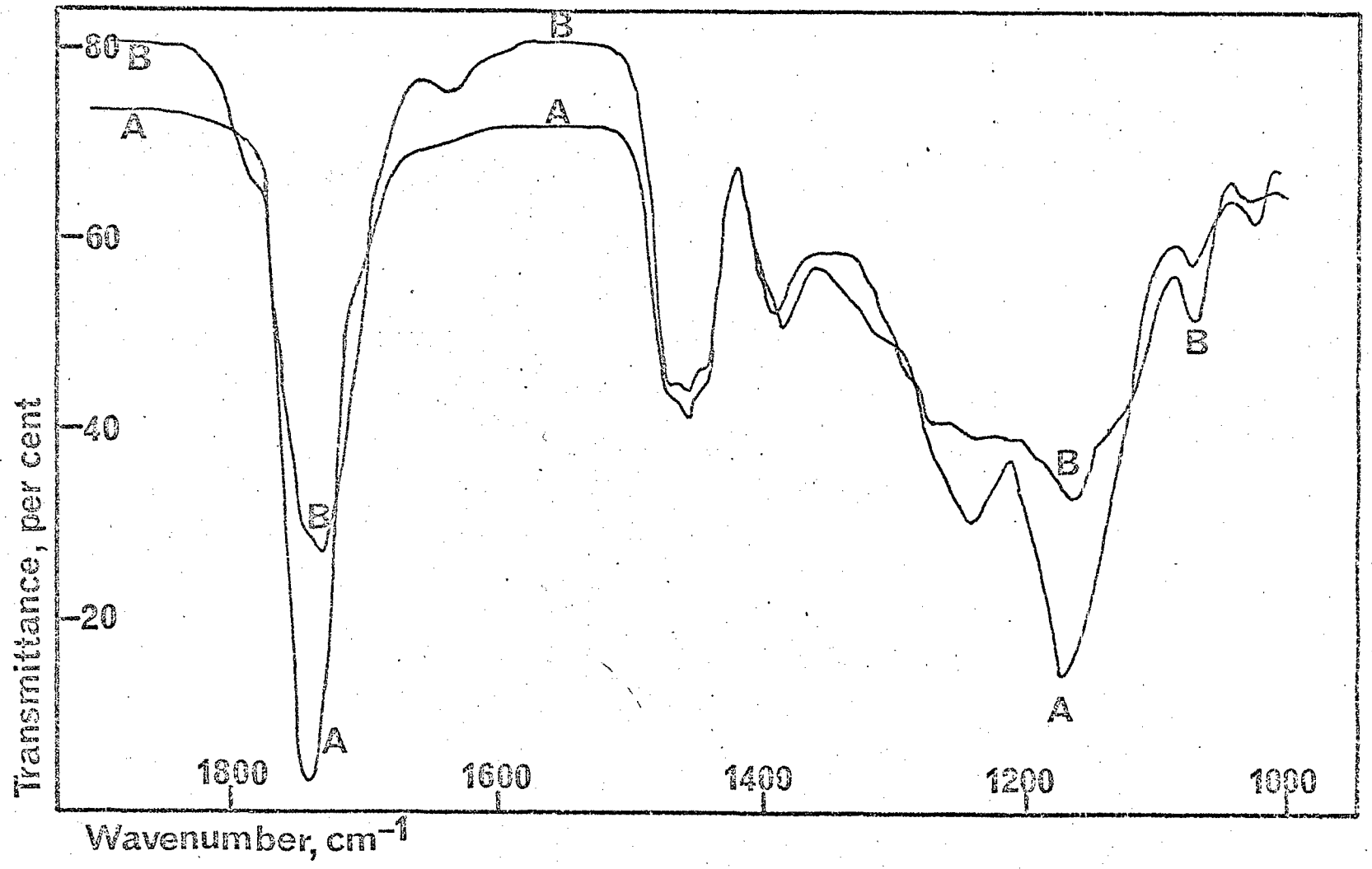
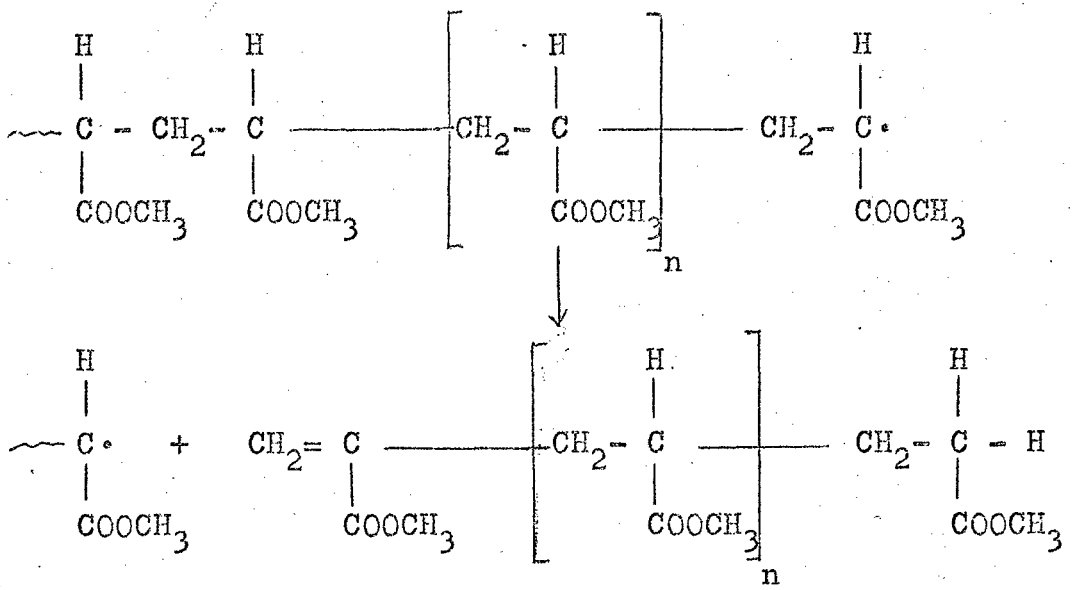


Fig. 16. COMPARISON OF INFRA-RED SPECTRA OF A, UNDEGRADED 50 MOLE % n-BUTYL ACRYLATE COPOLYMER AND B, THE COLD RING FRACTION AFTER PHOTOTHERMAL DEGRADATION FOR 48 HR.



at 1160 cm^{-1} becomes more diffuse.

These chain fragments must be formed in intramolecular transfer processes.

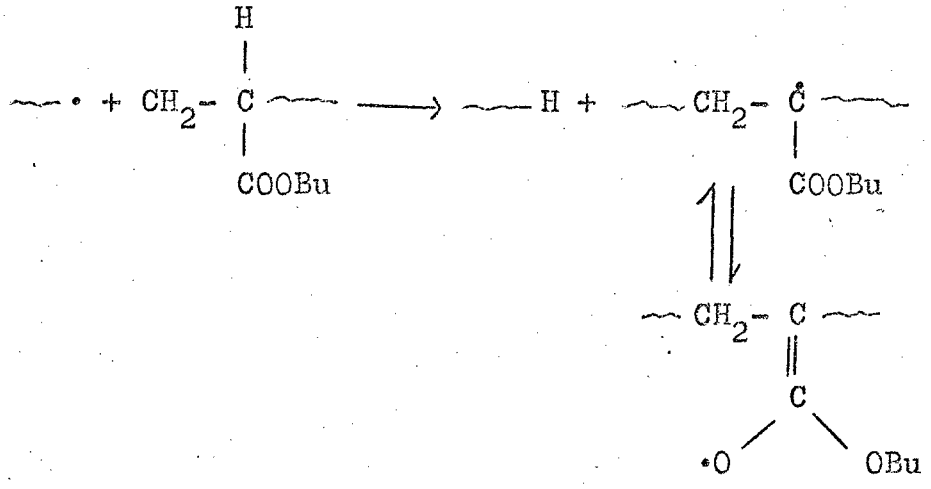


which must introduce terminal carbon-carbon unsaturation which may account for the new absorption at 1635 cm^{-1}. As in the residue the shoulder at 1780 cm^{-1} may be attributed to lactone formation as may also the changes around 1160 cm^{-1}.

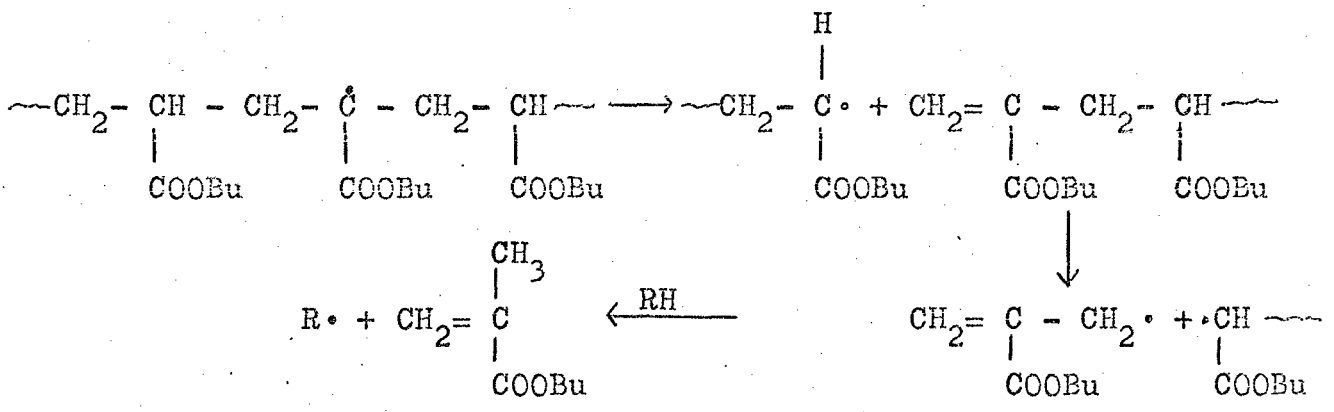
C. Discussion

It is obvious from the foregoing results that the principal features of the photothermal degradation of copolymers of methyl methacrylate and n-butyl acrylate are similar to those of the thermal reaction.[1] Thus chain terminal radicals are formed somehow in the system. These depropagate readily through methacrylate segments of the polymer molecule and rather less readily through acrylate units. Acrylate terminated chain radicals prefer to undergo transfer processes, especially intramolecular transfer which results in short chain fragments.

Thus methacrylate monomer and short chain fragments are by far the most dominant products of decomposition of this copolymer system. Other minor products, butanol, n-butyl methacrylate, methane, hydrogen as well as the appearance of unsaturation and lactone ring formation in the residue and short chain fragments may also be explained as in thermal degradation[1] by reactions of chain side radicals formed by intermolecular transfer

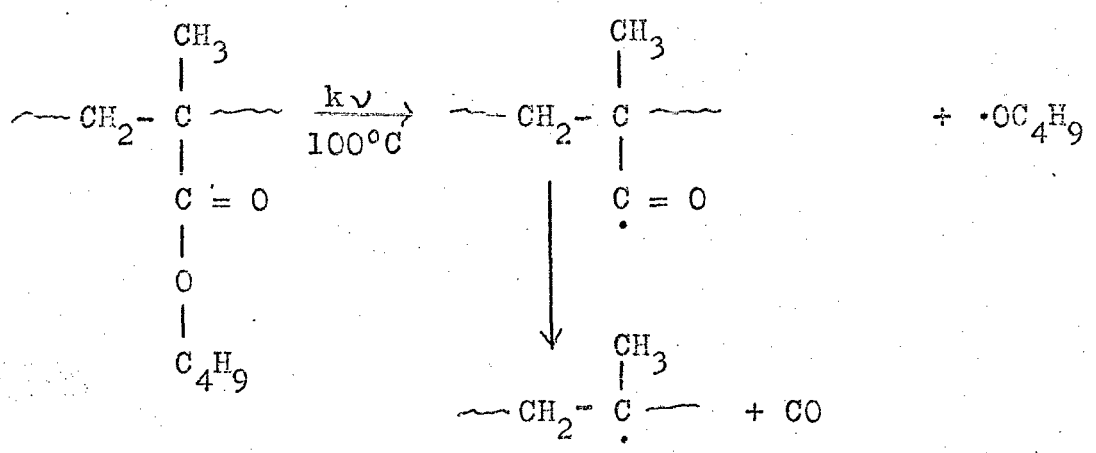


Grassie and Fortune[1] proposed two possible mechanisms for the production of n-butyl methacrylate in the thermal reaction. One of them involved the simultaneous production of carbon dioxide. Since carbon dioxide is not a product of photo-thermal degradation, the second of Grassie and Fortune's mechanisms, which they favoured, would appear to be confirmed.



There are however some very significant differences in the pattern of products of the photothermal reaction compared with the thermal reaction. Thus butyraldehyde, which is completely absent from the products of thermal degradation, is produced in the photothermal reaction while but-1-ene and carbon dioxide, which are significant products of thermal degradation, are not produced photothermally.

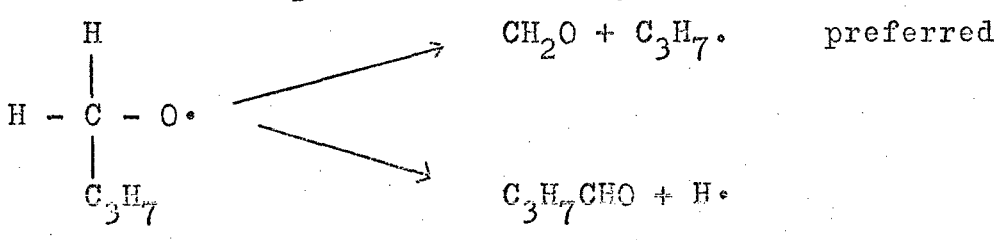
It is possible to formulate reactions of chain terminal or chain side radicals, of the type believed to be present in this degrading system, which would result in butyraldehyde, but it is difficult to justify their occurrence in the photothermal process and their exclusion from the thermal reaction. Instead, it is suggested that the presence and absence of butyraldehyde is a manifestation of different initiation steps in the two reactions. It was proposed[1] that thermal initiation consists of random scission of the polymer chain backbone. On the other hand, there is strong evidence that the primary effect of u.v. radiation on acrylate and methacrylate polymers is to cause scission reactions in the pendant ester groups.[14] It has been suggested[15] that butyraldehyde is produced in the photodegradation of poly(n-butyl methacrylate) by disproportionation of butoxy radicals,



$$2\ C_4H_9O \longrightarrow C_4H_9OH + C_3H_7CHO$$

This reaction sequence would account for the production of carbon monoxide but would result in equimolar yields of n-butanol and n-butyraldehyde. However the characteristics of formation of butyraldehyde and butanol are found experimentally to be quite different. Butyraldehyde formation increases with increasing acrylate content of the copolymers and is a degradation product even from 3.9 mole % acrylate copolymer. Thus the evolution of butyraldehyde is a function of single acrylate units. On the other hand, butanol is not a product until the acrylate content of the copolymer reaches 50 mole % and is associated with acrylate sequences rather than with single units.

It seems more likely that butyraldehyde is produced by fragmentation of butoxy radicals. It is known that alkoxy radicals fragment to form a carbonyl function,[16] the formation of the carbonyl group providing the driving force for cleavage. Primary and secondary alkoxy radicals have been studied mainly in the gas phase and under these conditions loss of an alkyl radical predominates over loss of a hydrogen atom. Thus butyraldehyde formation would be preferred to formaldehyde formation in the decomposition of butoxy radicals.



In the previous thermal degradation studies of copolymers of methyl methacrylate and n-butyl acrylate[1] and of poly(n-butyl acrylate)[17] mechanisms proposed for the production of but-1-ene and carbon dioxide involved the same types of chain side radicals

as are believed to participate in the photothermal reaction under discussion. An independent molecular reaction seemed out of the question in view of the fact that the characteristics of the formation of but-1-ene and carbon dioxide were similar to those of the other products. It is therefore somewhat surprising that but-1-ene and carbon dioxide are completely absent from the products of photothermal degradations. Perhaps the formation of the steric configuration necessary for the production of but-1-ene in a radical process[1] is inhibited by the very much greater viscosity of the medium in which the photothermal reaction is occurring due to the very much lower temperature at which it is being carried out. The absence of the butyl group decomposition products, ethane, ethylene, propane, propylene and butane in the photothermal reaction may also be an indication that they were formed as a by-product of the reaction in which but-1-ene was formed in the thermal reaction.

In addition to these differences in the products of the thermal and photothermal reactions there are also minor differences concerning the zip lengths and the relative amounts of acrylate and methacrylate monomers produced. The values of 1200 and 9 for the zip lengths in 0.25 and 50 mole % acrylate copolymers calculated from Grassie and Fortune's thermal degradation data[1] clearly indicate a tendency to lower zip lengths than those quoted for the photothermal reaction in table 8. Bearing in mind the method of calculation, these zip lengths are a measure of the number of monomer units lost by depropagation and intramolecular transfer between each act of intermolecular transfer. Thus it may be concluded that intermolecular transfer becomes

relatively more important compared with depropagation and intramolecular transfer at the higher temperature of thermal degradation (313°C), all the photothermal degradation data having been obtained at 165°C. This is reasonable since it is to be expected that intermolecular interactions should be favoured by the greater mobility of the polymer molecules at the higher temperature.

Molar ratios of the two monomers, calculated from the present and previous data[1] are presented in table 9 which demonstrates 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 indicating the greater tendency at the higher temperature to depropagation of acrylate units at the expense of intramolecular transfer.

These zip length and monomer ratio data thus give a qualitative indication of the effect of temperature on the relative tendencies for depropagation, intra and intermolecular transfer at acrylate terminated chain radicals.

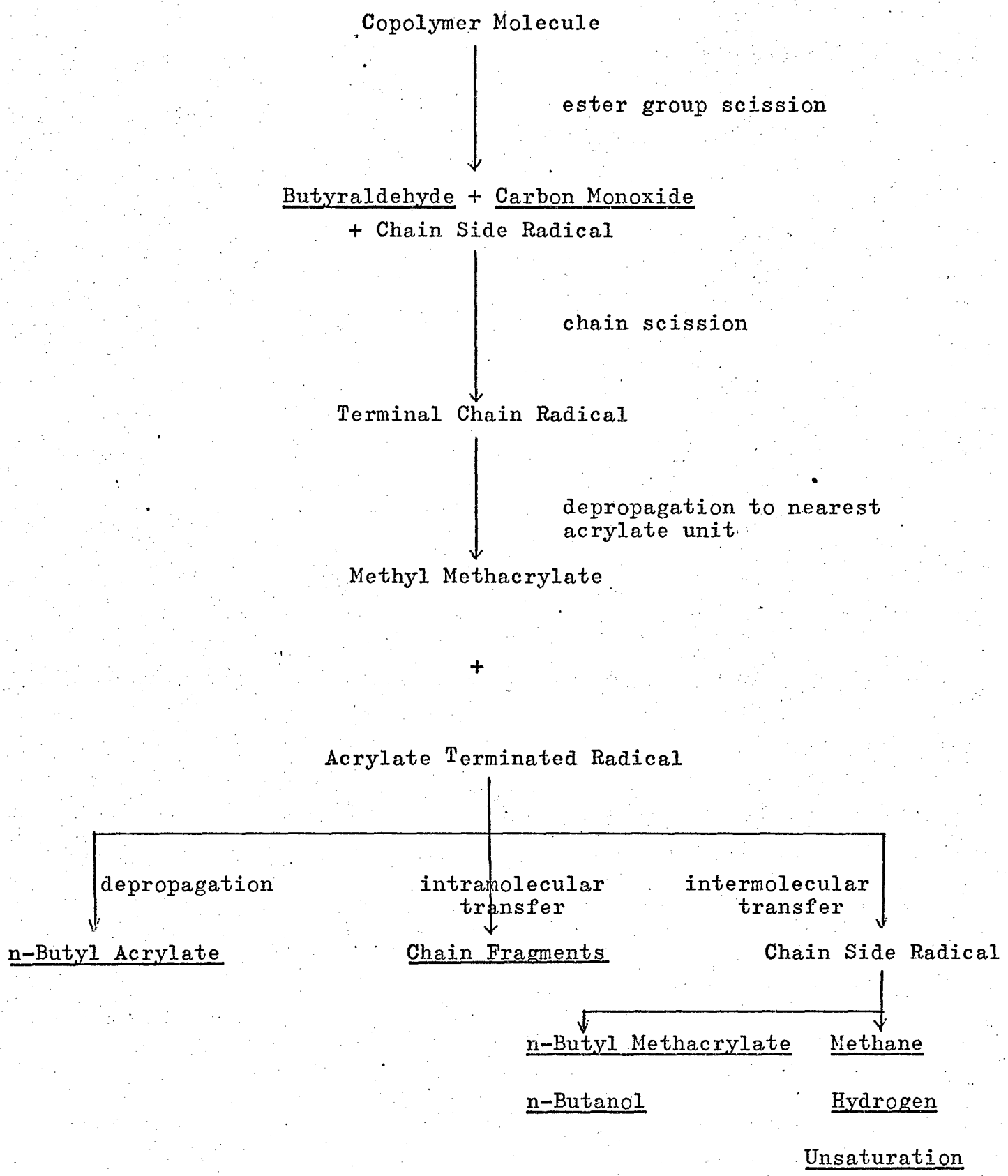
It may also be worthy of note that zip lengths for n-butyl acrylate copolymers are very much less than those for methyl acrylate copolymers which demonstrates a lower relative tendency for n-butyl acrylate units to depropagate. This will undoubtedly also be influenced, however, by the different viscosities of the two polymers at the temperature at which the photothermal degradations were carried out.

Bearing in mind the various mechanisms which have been proposed, the overall photothermal degradation process may be represented qualitatively by the following reaction sequence in which the various observed products are underlined.

Table 9

Molar Ratios of Monomeric Products

Copolymer (mole % n-BuA.)	Monomer Ratio (M.M.A./n-BuA.)	
	Photothermal	Thermal
16.3	215	23
50	30	4
82.2	10	1


Copolymer Molecule
ester group scission
Butyraldehyde + Carbon Monoxide
+ Chain Side Radical
chain scission
Terminal Chain Radical
depropagation to nearest acrylate unit
Methyl Methacrylate
+
Acrylate Terminated Radical
depropagation
intramolecular transfer
intermolecular transfer
n-Butyl Acrylate
Chain Fragments
Chain Side Radical
n-Butyl Methacrylate
Methane
n-Butanol
Hydrogen
Unsaturation

CHAPTER III

SYNTHESIS OF FRIEDEL-CRAFTS POLYMERS

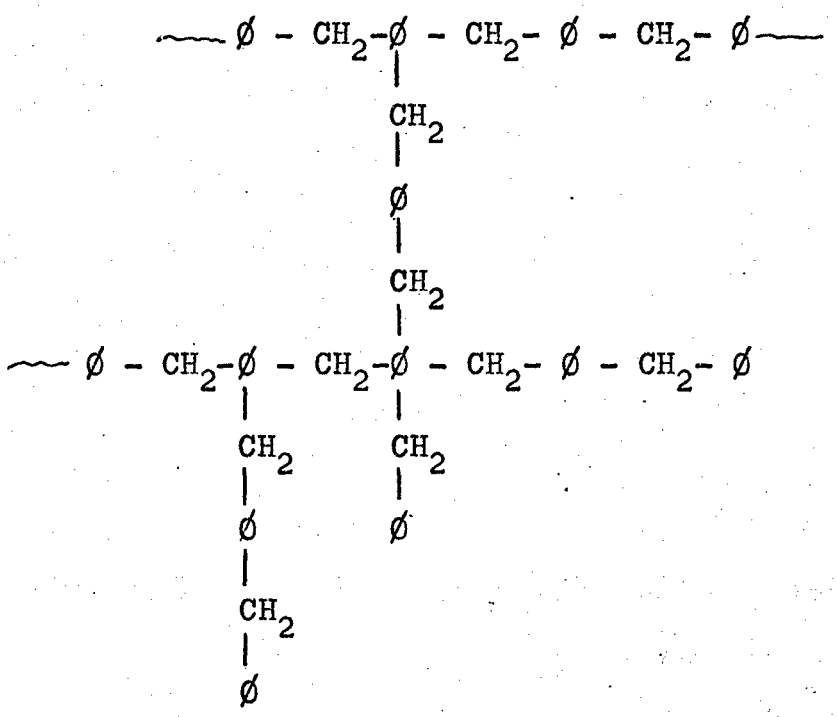
A. Introduction

Phillips,[18] in 1964, showed that polymers prepared by the condensation of p-di(chloromethyl)benzene with benzenoid aromatic substances, in presence of Friedel-Crafts catalysts, can be considerably more thermally stable than conventional phenolic resins and hence might have considerable potential commercial application. Grassie and Meldrum[6] subsequently demonstrated that the range of polymers could be further extended by replacing the benzenoid aromatic component by heterocyclic aromatic components. They used thiophen, pydridine, indole, quinoline and pyrrole with stannic chloride as catalyst and found that the resulting polymers had widely differing stabilities. In particular, the thiophen polymer was considerably more stable than the benzene polymer.

To investigate the reasons for these differences in stability and with the long term objective of defining conditions for optimum stability, a comprehensive investigation of the DCMB/benzene/$SnCl_4$ system was undertaken.[7] Each individual product, up to a molecular weight of approximately 1000, was separated using g.l.c. or g.p.c., identified, and rate constants for its formation and further reaction deduced. Since material of molecular weight 1000 represents more than 90% reaction as defined by acts of condensation and measured by HCl librated, it is clear that the principal structural

features of the final insoluble, infusible, polymer already exist and it is a relatively simple matter to extrapolate to 100% reaction.

The ultimate picture of the DCMB/benzene polymer was of a highly branched structure of the type,



the finer structure being defined by the ratio of mono: di: tri: tetra substituted benzene rings.

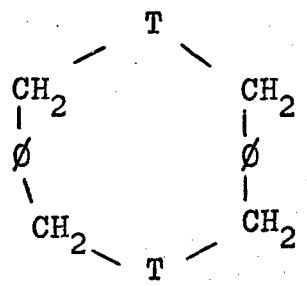
A similar investigation of the DCMB/thiophen/$SnCl_4$ system was subsequently reported.[8] Differences from the DCMB/benzene/$SnCl_4$ system were immediately obvious. The first two steps in the reaction are strictly comparable, (T represents a thiophen nucleus)

$$Cl - CH_2 - \emptyset - CH_2 - Cl$$
$$\downarrow T$$
$$Cl - CH_2 - \emptyset - CH_2 - T$$
$$\downarrow T$$
$$T - CH_2 - \emptyset - CH_2 - T$$

The thiophen nucleus is very much more reactive than the benzene nucleus, however, so the next product in the thiophen system is almost exclusively

$$T - CH_2 - \emptyset - CH_2 - T - CH_2 - \emptyset - CH_2 - Cl \qquad A.$$

rather than a mixture of linear and branched isomers as in the benzene system. In the thiophen, but not in the benzene system the stereochemistry of A is such that the two ends of the molecule react to form



B.

Thiophen nuclei being more reactive than benzene nuclei further reaction with DCMB occurs preferentially at the former so that what is in effect a partial ladder structure is rapidly built up and it is to this that the superior stability of the thiophen polymer has been attributed.

Polymers may be similarly prepared by replacing DCMB by α,α'-dimethoxy-p-xylene (DMPX) in which case methanol, rather than HCl is the volatile condensation product. By the time the work described above was complete it was clear that materials based on DMPX rather than DCMB were more appropriate for commercial exploitation and it was with this knowledge and background that a programme of research was proposed, "to study the products and mechanism of polymerization of DMPX with benzene and thiophen as a first step towards the elucidation of the relationships between structure and stability in this class of polymers so that the factors for

the achievement of optimum stability may ultimately be determined".

It was only possible to carry out some very preliminary experiments before the contract was directed towards the work described in Chapter 4. These preliminary experiments are described in the following section.

B. Experimental and Results.

1. Preparation of Polymers under Nitrogen. For precise kinetic measurements it is, of course, necessary to use highly purified materials, but in order to establish suitable experimental conditions for the preparation of these materials as well as to get some feel for the range of aromatics which may be copolymerized with DMPX, a number of preliminary experiments were carried out under nitrogen using stannic chloride as catalyst. Using the general experimental method, which follows, the following carbocyclic and heterocyclic aromatic compounds were copolymerized with DMPX and satisfactory copolymers were obtained in each case.

Benzene	thiophene
dimethylbenzene	DCMB
pyridine	styrene
furan	phenol
toluene	p-xylene
2-methyl thiophen	m-xylene
2-chloro thiophen	dimethyl terephthalate

terephthalic acid.

The preparations were carried out in a round-bottomed flask fitted with a thermometer, nitrogen outlet and reflux condenser fitted with a drying tube.

The aromatic compound, solvent (1,2-dichlorethane) and DMPX were added to the flask and the apparatus flushed out with dry oxygen-free nitrogen while it was heated to just below the reflux temperature (83°C). The stannic chloride, in solution in 1,2-dichlorethane, was added. The usual recipe was,

4-10 gm aromatic compound
2-4 ml DMPX
0.2 ml $SnCl_4$
40-50 ml DCE

Solutions were refluxed for periods of 2 to 24 hours from the time of addition of $SnCl_4$, most runs being of 6 hours duration. In some of the copolymerization reactions, especially those with benzene, dimethyl benzene, thiophene and DCMB, several molar feed ratios were used. Otherwise the most common were 1:4 and 1:5, DMPX: aromatic. After the desired polymerization time the reaction was stopped by adding water, the organic layer was separated and dried, and the polymer was precipitated in an excess of Analar methanol. The precipitated polymer was filtered, dried, and twice reprecipitated from Analar chloroform solutions. The resultant pure polymer was dried under vacuum and stored. In a few cases the polymer in solution was not precipitated by methanol. In these cases the solvent was removed by distillation under vacuum.

2. Preparation of Polymers under Vacuum. Having established, in general, that a variety of polymers can be prepared by replacing DCMB by DMPX it was then important to devise suitable methods of purification of reagents and

techniques for carrying out the reactions under vacuum for kinetic purposes. The following methods were found to be generally applicable.

a. Purification and drying of reagents. Since small quantities of water or other impurities could have a considerable effect upon the polymerizations, great care was taken to insure dryness and absence of contamination.

i. Dimethoxy-p-xylene

$\alpha\alpha'$ Dimethoxy-p-xylene (DMPX) (Albright and Wilson) was purified by passing a 100 ml aliquot twice through a large basic alumina column (diameter 3.5 cm, height 40 cm) using diethyl ether as the elutant. This removes acid impurities formed by oxidation and any peroxides that may be present. A stream of nitrogen was directed into the receiving flask to keep out oxygen and to help evaporate the ether. The purified DMPX could be stored for several days under nitrogen without the reappearance of impurity peaks (1270, 1310, 1580, 1610, 1690, 1710 cm^{-1}) in the I.R. spectrum but should be kept under vacuum to avoid oxidation.

Diethyl ether was removed from the DMPX by distillation under vacuum. The apparatus was constructed as follows. Freshly ground calcium hydride was added to a 250 ml flask with a break-seal tube and side-arm attached. The DMPX-Et_2O solution was added. The apparatus was attached to the vacuum line and degassed at least three times by the freezing and thawing technique. The diethyl ether was then distilled from the mixture using ice/water for the cold trap rather than liquid nitrogen so as to minimise bumping. The distillation was completed with liquid nitrogen, however, in order to

remove the last traces of diethyl ether. The DMPX was again degassed several times, sealed off and stored for at least a week in the dark with periodic shaking. The CaH_2 was removed by filtering under vacuum. The filtered DMPX was sealed off and the flask used as a storage ampoule.

ii. Benzene Benzene (Hopkins and Williams Analar) was pre-dried over freshly ground calcium hydride. It was attached to the vacuum line, degassed three times, distilled onto fresh CaH_2, and stored for at least a week.

This process was repeated, the benzene was degassed three times, distilled under vacuum in all glass apparatus and redistilled two more times. Extra degassing was often necessary since the drying process resulted in the production of hydrogen and the CaH_2 also seemed to degas slowly. The pure, dry benzene was stored in a sealed ampoule under vacuum until used.

iii. Stannic chloride Phosphorus pentoxide (BDH laboratory reagent) was first sublimed under vacuum into an ampoule which was sealed off. Stannic chloride, anhydrous (BDH Reagent Grade) was transferred quickly from its ampoule to a flask, degassed several times under vacuum and distilled onto the freshly sublimed phosphorus pentoxide. The flask was sealed off and stored in the dark for at least one week. After redistillation under vacuum onto freshly sublimed phosphorus pentoxide, followed by storage for one more week in the dark, the stannic chloride was twice vacuum distilled in all glass apparatus and stored under vacuum in a sealed ampoule wrapped in a black plastic bag in the dark.

iv. 1,2-Dichloroethane The purification and drying of 1,2-dichloroethane (DCE) (BDH Reagent Grade) was similar to that for stannic chloride. DCE was vacuum distilled three times in all glass apparatus before being stored.

b. Preparation of Glassware. Pyrex glass was used throughout. It was cleaned before use by washing in a solution of Pyroneg, rinsing with distilled water, Analar acetone, and Analar chloroform, then dried in air at 100°C. Before use glassware was evacuated on the vacuum line to a pressure of 10^{-4} torr or less and flamed out to remove all traces of moisture.

c. Preparation and Distribution of Solutions. Several types of solutions were made up and distributed. They included the "standard solutions" for polymerizations in which the same initial reagent concentrations were used but the length of time of reaction was varied. A single "standard solution" was used for a whole series of polymerizations. These solutions were employed in runs to determine the rate of reaction and the time of appearance of various products. Other reactions such as those used for kinetic determinations, involved the use of different initial reagent concentrations. Thus individual reagent solutions had to be prepared.

i. "Standard Solutions" "Standard solutions" of benzene and stannic chloride in DCE were prepared as follows. Exact amounts of each reagent were poured under vacuum from their storage flasks into previously calibrated graduated ampoules fitted with break-seals. 1 ml ampoules were used for $SnCl_4$, 10 ml or 25 ml for benzene, and 100 ml for DCE. The

graduated ampoules containing the reagents were then attached to a large storage flask, the break-seals broken and the reagents distilled into the flask.

A typical "standard solution" recipe would be 0.2 ml $SnCl_4$, 10.0 ml benzene, 84.8 ml DCE.

The "standard solution" was then thoroughly shaken and distributed under vacuum into 10 ml calibrated ampoules. The apparatus used consisted of a 250 ml central reservoir surrounded by a periphery of ten calibrated 10 ml graduated ampoules and one inlet tube. The storage flask containing the standard solution was sealed onto the inlet tube and the apparatus was evacuated and sealed off. The standard solution was introduced into the central reservoir via the break-seal and poured into each ampoule in turn. After each addition the ampoule was sealed off at a constriction.

ii. DMPX Approximate amounts of DMPX were distributed from the storage flask into a number of small ampoules ($\sim$ 10 ml) using apparatus similar to that mentioned above. Since DMPX could not be distilled and proved impossible to pour accurately, the small ampoule had to be broken open and the necessary amount pipetted into the reaction flasks. Five aliquots (usually 0.50 ml) of DMPX at a time were pipetted into 10 ml ampoules having stems 6-8 in. long. Care was taken to avoid getting any DMPX on the upper part of the stem as this would have been oxidised on heating. A break-seal tube with side-arm was then attached to the stem without blowing (to prevent possible oxidation) and a constriction formed at this point. This apparatus was attached to the vacuum line, degassed several times, pumped down to a pressure of 10^{-4} torr or less,

and sealed off. The sample was then stored in the dark until needed.

iii. Individual Samples of Stannic Chloride, Benzene, and DCE. In kinetic determinations the initial concentrations of reagents would have to be varied from run to run. Thus standard solutions as defined above could not be used. The most straight-forward method of doing these polymerizations would be to distil the reagents directly onto the DMPX. This worked well enough for benzene and DCE but the exceedingly small amounts of stannic chloride needed for a given reaction could not be measured with any accuracy. Thus a solution of $SnCl_4$ in DCE was prepared. Measured amounts of the two reagents were transferred to calibrated ampoules. The contents of these ampoules were then distilled into a flask and the resulting solution was distributed into calibrated ampoules as described above. These ampoules were stored in the dark until needed. Measured quantities of benzene and DCE were transferred and distributed in a similar fashion.

CHAPTER IV

THERMAL DEGRADATION OF POLYSILOXANES

A. Preparation of Polymers.

1. Introduction. Poly(dimethyl siloxanes) are prepared by the hydrolytic conversion of dimethyldichlorosilane to the cyclic tetramer, octamethylcyclotetrasiloxane, followed by polymerization of the tetramer in presence of suitable catalysts to form the linear polymer.

According to Patnode and Wilcock[19] the relative proportions of the compounds formed by hydrolysis of dimethyldichlorosilane depend upon the conditions of hydrolysis but there is a very strong tendency toward the formation of the cyclic tetramer which is generally formed in the greatest amount. Their method was used with variations in the silane/water ratio. Since the hydrolysis reaction is exothermic, the reaction vessel must be cooled. Water to silane ratios of 2:1 to 3:1 were used without noticably affecting the yield of short chain cyclic polymer. The products of this hydrolysis are principally the cyclic trimer (b.p. 134°C), tetramer (b.p. 175°C) and pentamer (b.p. 210°C) with the tetramer predominating. The tetramer may thus be separated in high purity by distillation.

Cyclic tetramer was polymerized by the method of Gilbert and Kantor[20] using tetramethylammonium hydroxide as catalyst. This system was chosen since the catalyst may be deactivated simply by heating to 130°C when it decomposes to trimethylamine and methyl alcohol.[20]

2. Hydrolysis of dimethyldichlorosilane. Distilled water (750 ml) in an R.B. flask equipped with magnetic stirrer and thermometer was cooled in an ice/water bath. Dichlorodimethylsilane (Merck) (250 ml) was added dropwise, the temperature of the reaction mixture being maintained below 20°C. The reaction mixture was vigorously stirred throughout the hydrolysis.

The oil formed by hydrolysis was separated from the excess water and dried over magnesium sulphate. The liquid was separated by filtration and distilled under reduced pressure to separate the low molecular weight cyclic siloxanes from the non-volatile products of hydrolysis. The distillate, which was contaminated with HCl, was washed with aqueous sodium bicarbonate, separated and dried over magnesium sulphate.

The liquid was then distilled through a 10" Vigreux column at ordinary pressure giving approximately 50 ml of material distilling at 168-173°C, and redistilled a number of times to give progressively purer cyclic tetramer (b.p. 170-174°C).

3. Polymerization of octamethylcyclotetrasiloxane. A typical polymerization of the cyclic tetramer was carried out as follows. Octamethylcyclotetrasiloxane (30 ml) in an R.B. flask was heated to 115-116°C in an oil bath. Several drops of a 25% aqueous solution of tetramethylammonium hydroxide were added with stirring. After 25 minutes the liquid became obviously more viscous. Heating was continued for a further 20 minutes and the mixture allowed to cool to a tacky gum.

Benzene and anhydrous toluene are suitable solvents for the polymer with methanol a suitable precipitating agent.

4. Polymer Samples. The material described above has been designated polymer 1. Further samples have been prepared at different temperatures using pure catalyst rather than an aqueous solution (polymers 2, 3 and 4) and a large sample has been prepared from tetramer of very high purity (confirmed by g.l.c.) obtained by five successive fractional distillations (polymer M). Full details are given in table 10.

The catalyst decomposes to trimethylamine and methanol at 130° and briefly heating to this temperature after reaction is complete has been used to destroy residual catalyst which can influence the stability of the polymer. Gilbert and Kantor[20] have reported that the amine has no effect on polymer stability. The residual amine may be easily removed by methanol.

All these polymerizations have been carried to high conversion and probably, in most cases, to equilibrium. Polymerizations have been in air. The molecular weight is obviously an inverse function of polymerization temperature but there is insufficient data to indicate possible effects of impurities and catalyst concentration on molecular weight.

5. Preparation of End-Blocked Polymer. An attempt has been made to block the active end groups of a sample of polymer 4 (0.5g) by refluxing with excess 1,1,1,3,3,3-hexamethyldisilazane (1.2 ml) in toluene (20 ml) for 24 hours. The polymer was reprecipitated from methanol. No characterisation of this material has been carried out but its thermal degradation characteristics have been observed using TGA (see below)

Table 10

Preparations of Poly(dimethylsiloxanes)

Polymer	Tetramer	Temp(°C)	Catalyst	M_n	Subsequent Treatment
1	impure	115	few drops of 25% aqueous solution	258,000	None
2	impure	110-130	dry, 0.02%	94,500	None
3	impure	108-110	dry, 0.01%	141,000	Heated to 130°C
4	impure	97-98	dry, 0.02%	183,000	(a-None (b-heated to 130°C
M	pure	100	dry, 0.01%	269,000	(a-None (b-heated to 130°C and reprecipitated

B. Measurement of Molecular Weight.

Molecular weights were measured in toluene solution using a Hewlett-Packard 501 High Speed Membrane Osmometer with cellophane 300 membrane. The osmotic plot for polymer 1, which is quite typical, is illustrated in figure 17 from which a molecular weight of 258,000 was deduced. This measurement was perfectly normal and straight-forward and it is clear that polymers can be prepared with molecular weights in a range ideally suitable for the use of molecular weight as a tool for the investigation of degradation reactions.

C. Gas-Liquid Chromatography.

Gas-liquid chromatography has been vital in two phases of this work. First in checking the purity of the cyclic tetramer formed in the first stage of the preparation of polymer. Second in the analysis of degradation products. In both cases the principal constituent of the mixture to be analysed is the cyclic tetramer and the minor constituents are expected to be principally smaller and larger cyclic analogues and closely related compounds. Thus the problems associated with the application of g.l.c. to the two phases of the work are almost identical and are most conveniently considered together.

All g.l.c. data have been obtained using a Microtek G.C. 2000R instrument with flame ionization detector. Two columns have proved suitable, namely, 1% S.E. 30 and 20% D.C.560 on gas chrom Q and their separation characteristics have been established. Typical chromatograms, shown in figures 18-20, demonstrate the high quality of separation attainable. The

Fig. 17.

A TYPICAL OSMOTIC PLOT.

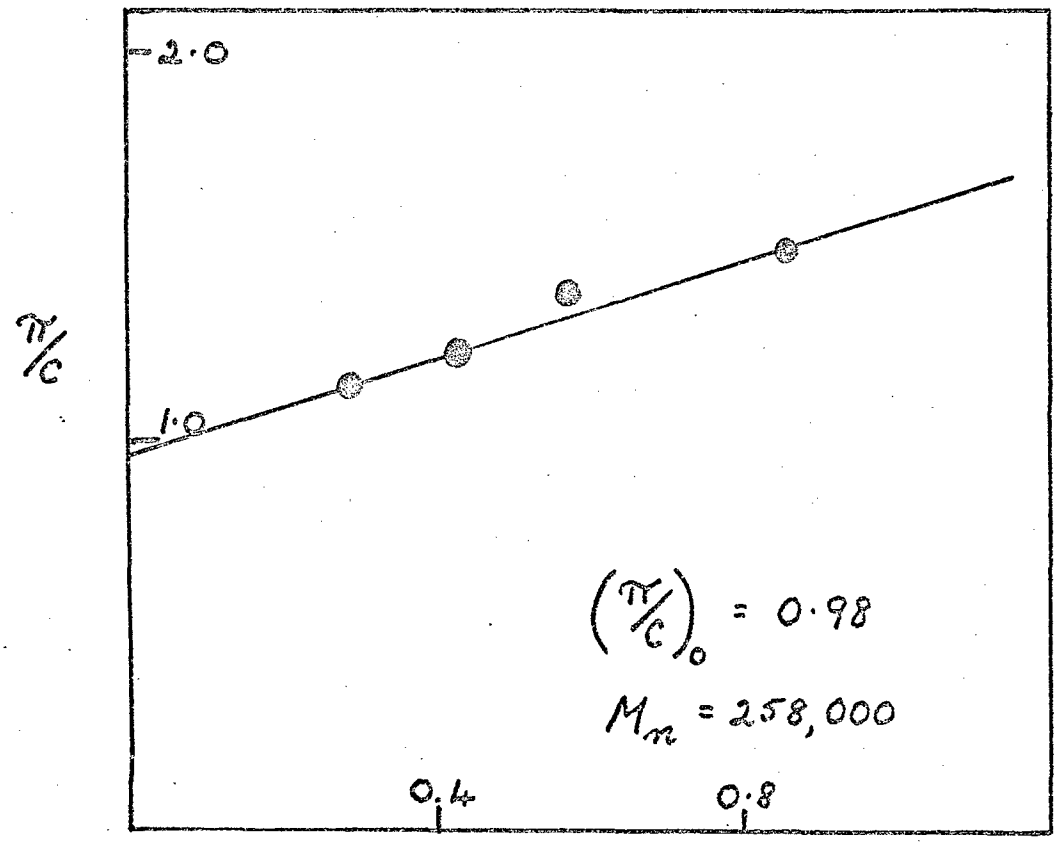


Fig. 18. G.L.C. ON DC 560 ON GAS-CHROM Q COLUMN SHOWING TETRAMER AND PENTAMER.

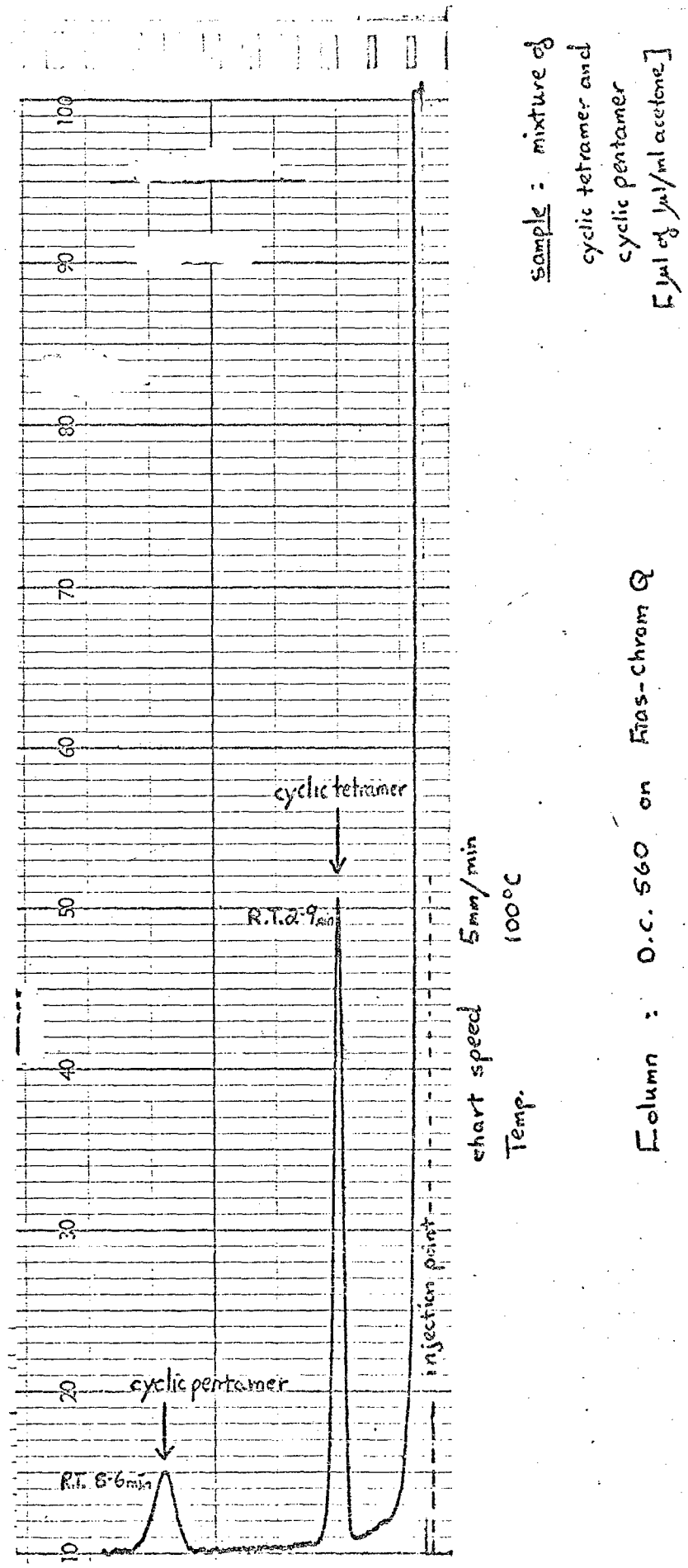


Fig. 19. G.L.C. ON 1% SE-30 COLUMN SHOWING TRIMER, TETRAMER AND PENTAMER.

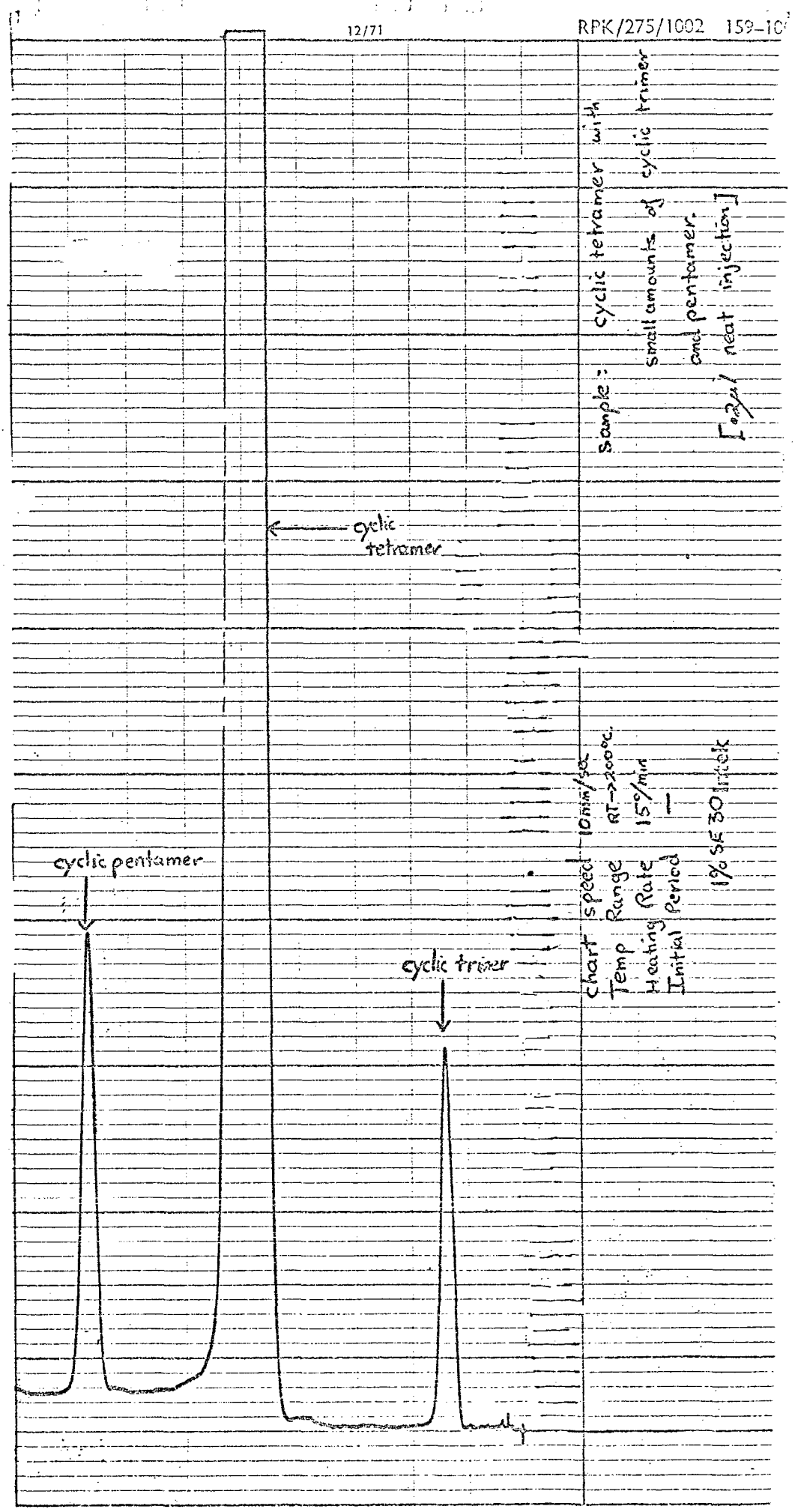
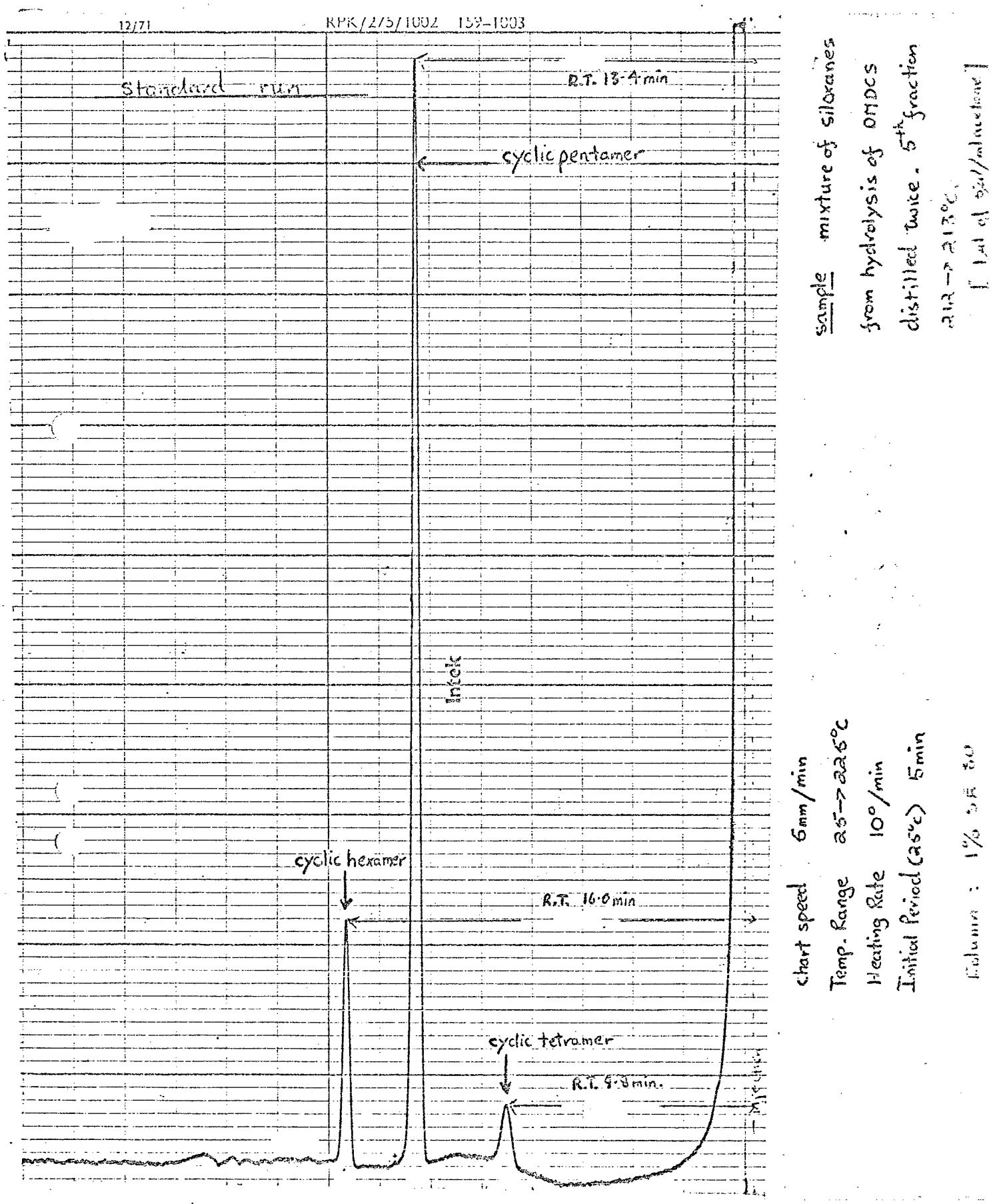


Fig. 20.

G.L.C. ON 1% SE 30 COLUMN SHOWING TETRAMER, PENTAMER AND HEXAMER.



assignment of tetramer peaks presents no difficulty since it is the major product of hydrolysis of dichlorodimethylsilane in the first stage of the preparation of polymer. The other peaks were preliminarily assigned according to the order of molecular weights of the species which are known to be present in the tetramer as impurities, namely trimer (0.5%), pentamer (6.7%) and hexamer (1.6%). The 1% S.E. 30 column is generally the more useful and convenient but the D.C. 560 column is better for the separation of trimer.

In order to calibrate the instrument for the quantitative estimation of degradation products pure samples of as many of the potential volatile degradation products as possible will be necessary. Thus a pure sample of the dimer, hexamethyldisiloxane,

$$(CH_3)_3\text{-Si-O-Si-}(CH_3)_3$$

has been prepared by hydrolysis of trimethylchlorosilane. The chromatogram in figure 21 illustrates its high purity and a retention time of 2.4 min. on a standard column.

Cyclic trimer has been prepared by pyrolysis, at temperatures in excess of 400°C, of the residues from the preparation of cyclic tetramer. Figure 22 demonstrates a retention time of 9.2 min. on a standard column.

Pure tetramer is available as the intermediate in the preparation of polymer and pure pentamer and hexamer are gradually emerging from successive fractional distillations of the residues remaining after fractional distillation of impure tetramer. Progress towards pure pentamer and hexamer are illustrated in figure 20 which represents some of the residual products after two distillations.

Fig. 21.

G.L.C. OF SILOXANE DIMER ON DC 560 ON GAS-CHROM Q COLUMN.

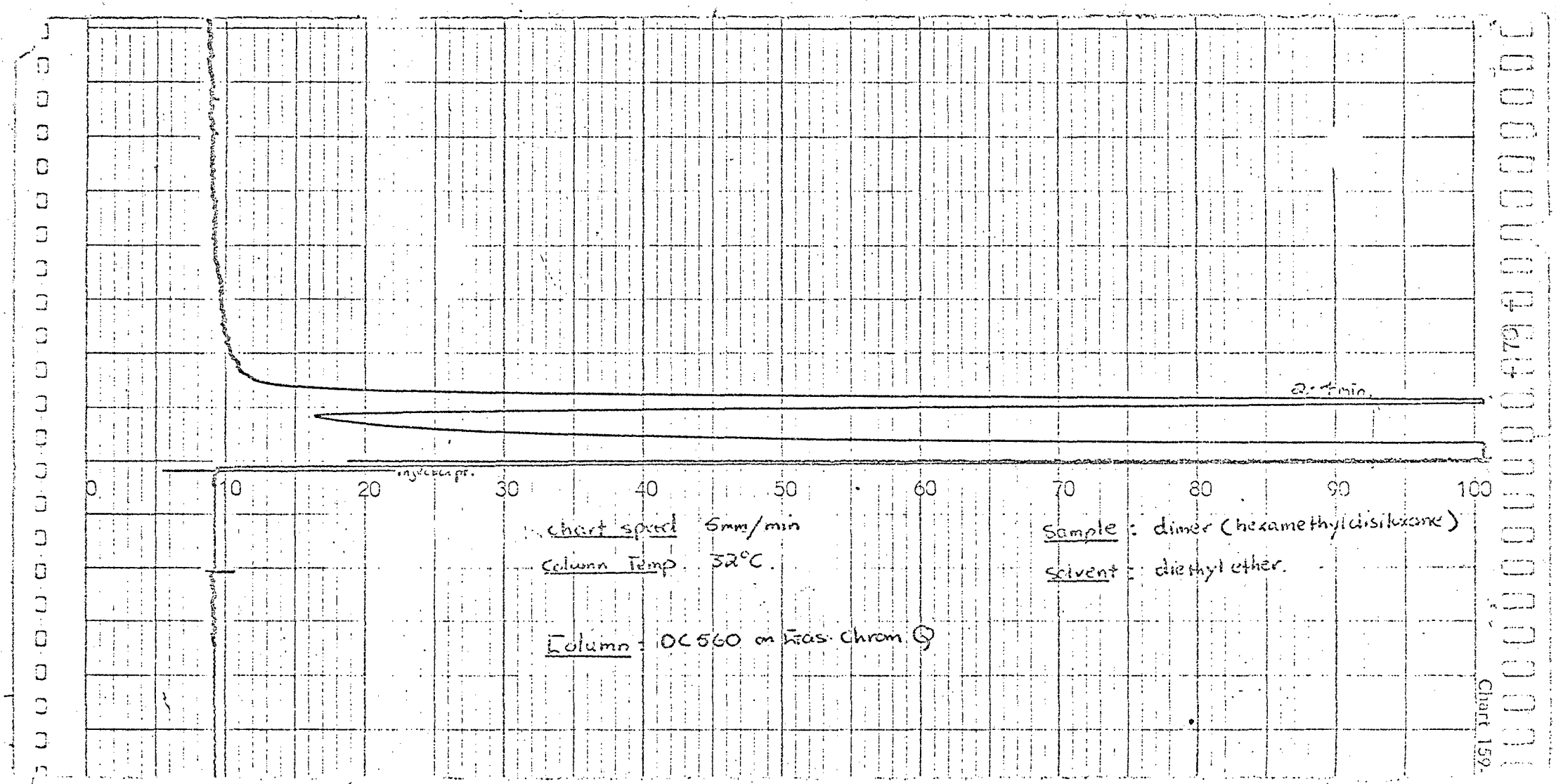
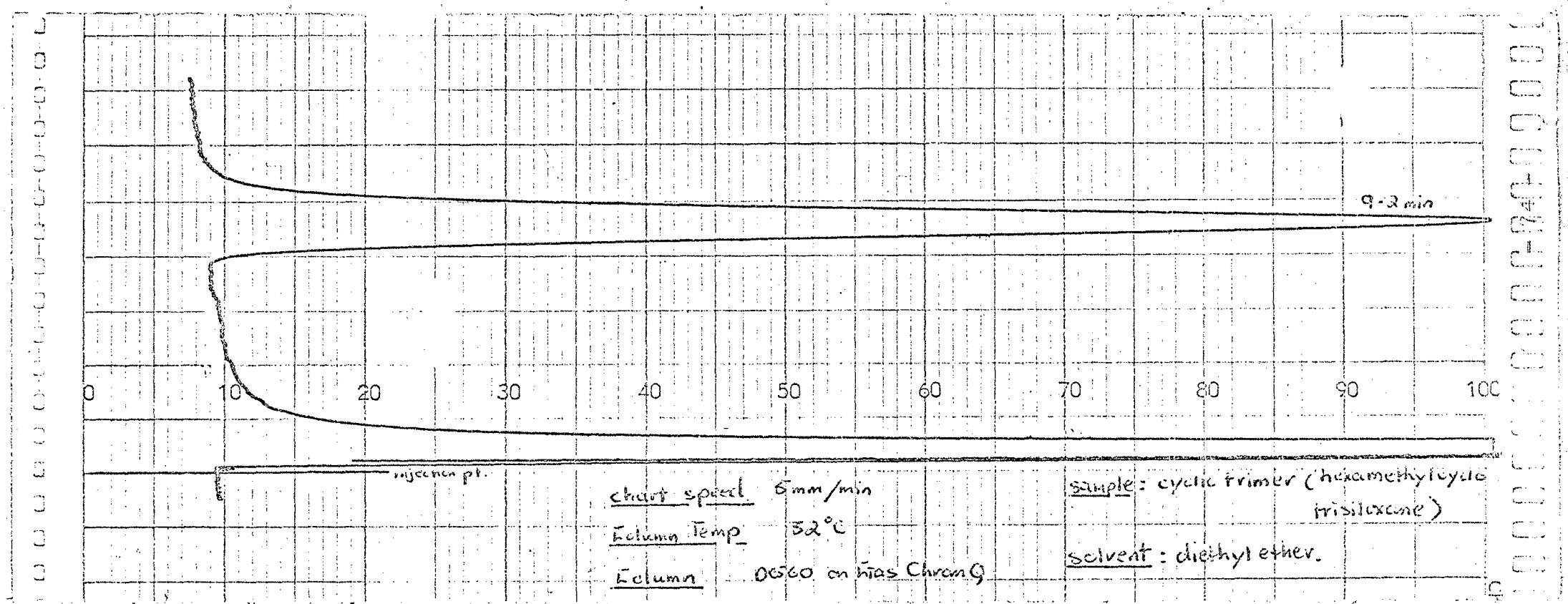


Fig. 22. G.L.C. OF TRIMER ON DC 560 ON GAS-CHROM Q COLUMN.



D. Thermal Analysis of Polymers.

1. Introduction. Thermal analysis can be used to provide a rapid preliminary picture of the principal characteristics and products of the thermal degradation of polymers. Thermal Gravimetric Analysis (TGA) and Thermal Volatilsation Analysis[21] have been applied in the present instance.

TGA demonstrates the progressive weight loss as the sample is heated through a linear temperature programme. The Du Pont 950 instrument has been used for this purpose, degradations being carried out, unless otherwise mentioned, in a nitrogen atmosphere (80 ml/min.) at a heating rate of 10%/min. to 485°C.

TVA demonstrates the evolution of volatile products as the sample is heated through a linear temperature programme. In the apparatus, as devised by McNeill[22] the stream of volatile products is divided into four, each passing through a trap at a different temperature (normally 0°C, -45°C, -75°C and -100°C) A Pirani gauge measures the pressure of products passing through each trap. Finally the gas streams are recombined and passed through a trap at -196°C which is also associated with a Pirani gauge. The Pirani gauge responses are fed into a pen recorder so that the thermogram displays a qualitative picture of the products volatile at each of these temperatures. A further trace provides a check of the linearity of the temperature programme.

2. Thermal Gravimetric Analysis. Thermograms are presented in figures 23-31 and additional details in table 11. It is clear from these thermograms that neither heatingto 130°C to destroy the catalyst nor the molecular weight of the starting polymer have any significant influence on the threshold degradation

Fig. 21. T.G.A. OF POLYMER 1. (reprecipitated)

SAMPLE: Polymer 1 (reprecipitated)	X-AXIS	Y-AXIS	RUN NO. _____ DATE 26-4-75
	TEMP. SCALE *50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR _____
	SHIFT _____ inch		HEATING RATE 10 °C / min.
			ATM. N2
SIZE _____ mg.	TIME SCALE (ALT.) _____	SUPPRESSION _____ mg.	TIME CONSTANT _____ sec.

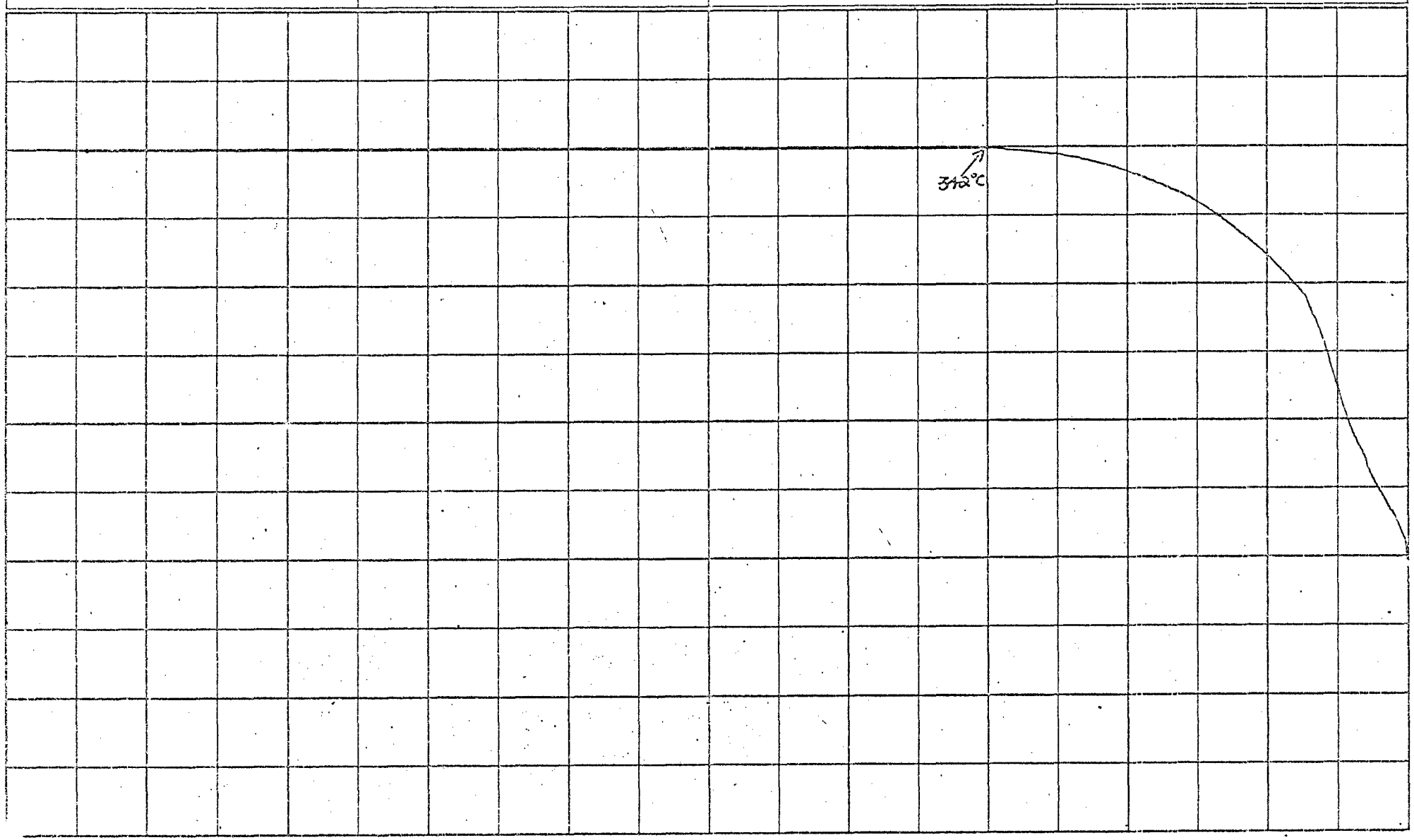


Fig. 24. T.G.A. OF POLYMER 2. (reprecipitated)

(DUPONT) EXPERIMENTAL

SAMPLE: Polymer 2 (reprecipitated)	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
	TEMP. SCALE *50 °C inch	SCALE 2 mg. inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

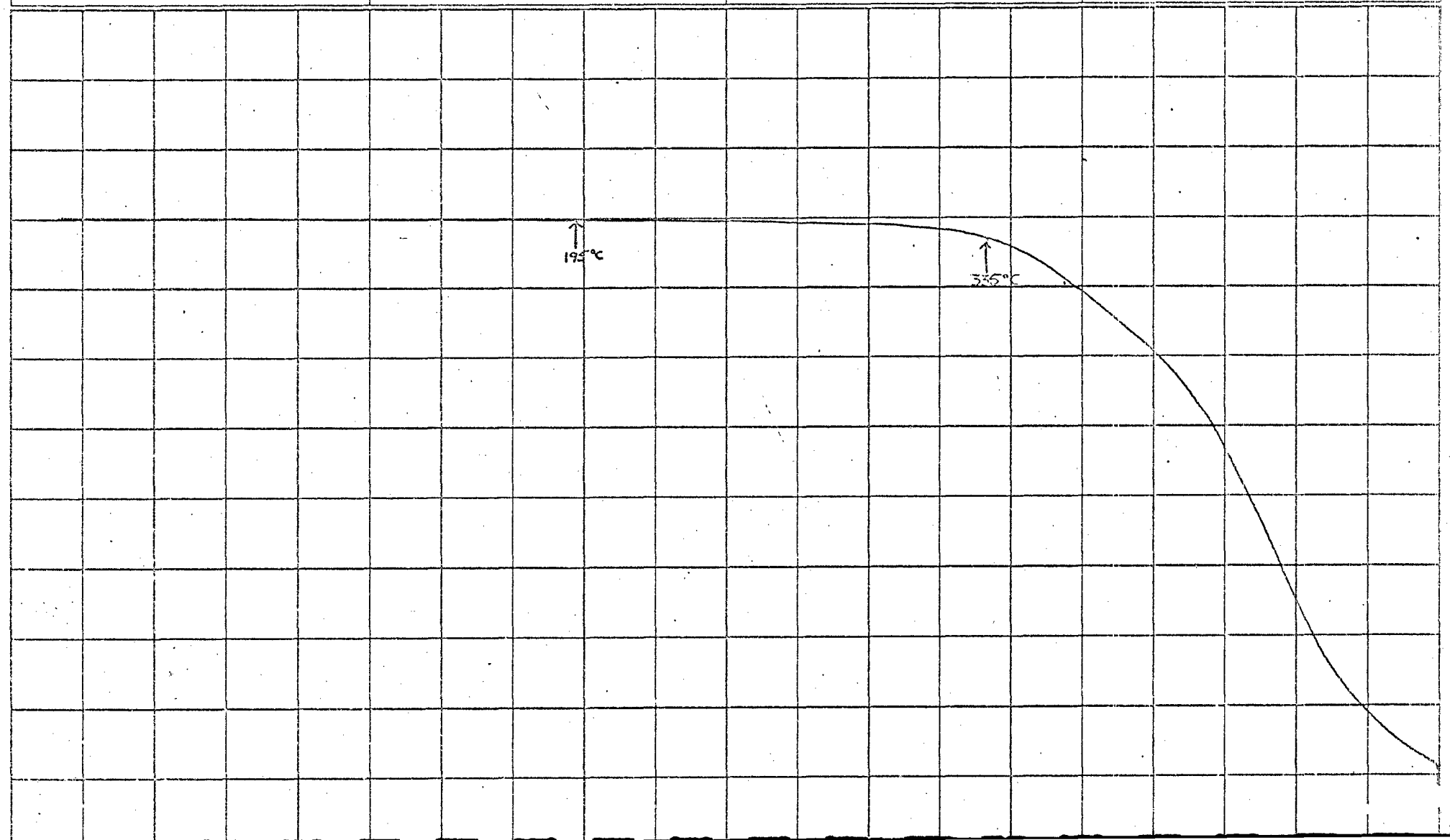


Fig. 25. T.G.A. OF POLYMER 3 (reprecipitated and heated to 130°C)

DU PONT INSTRUMENTS

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE 26 4 73
Polymer 3 (reprecipitated & heated to 130°C)	TEMP. SCALE *50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C / min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

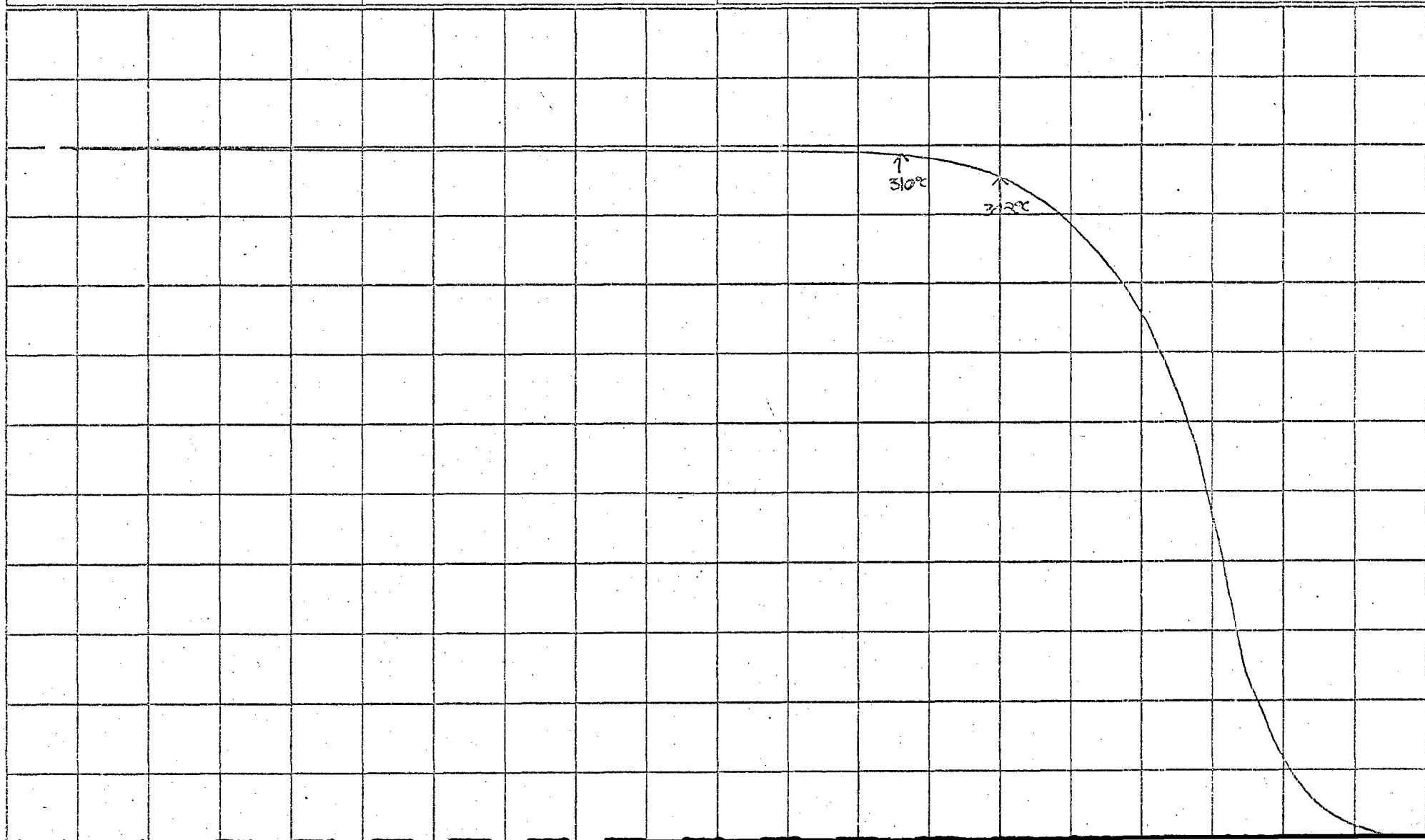


Fig. 26. T.G.A. OF POLYMER 4 (reprecipitated)

DU PONT INSTRUMENTS

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
Polymer 4 (reprecipitated)	TEMP. SCALE *50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C / min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

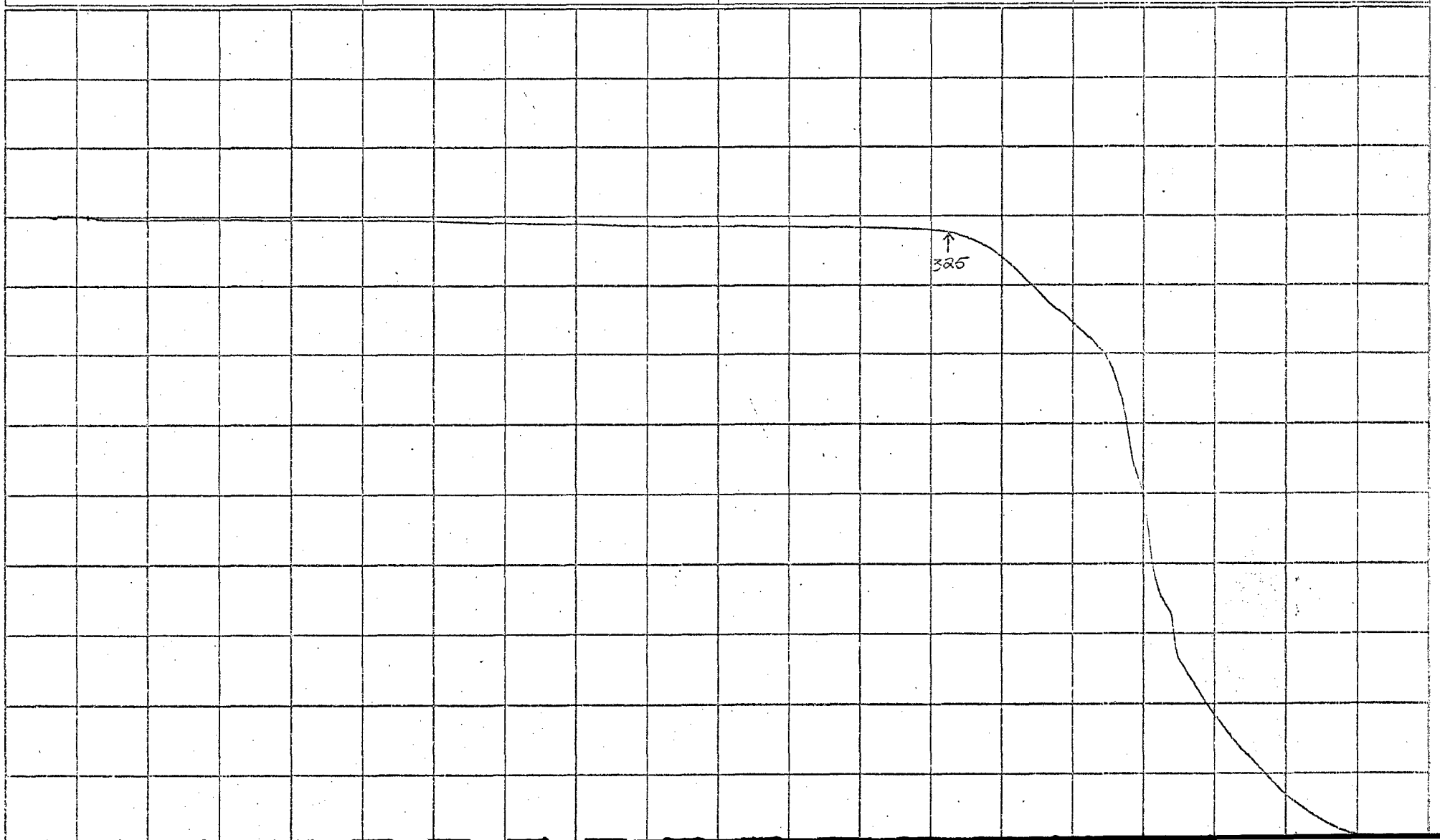


Fig. 37. T.G.A. OF POLYMER 4 (reprecipitated and heated to 130°C)

DUPONT INSTRUMENTS

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
Polymer 4 (reprecipitated and heated to 130°C)	TEMP. SCALE *50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C / min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

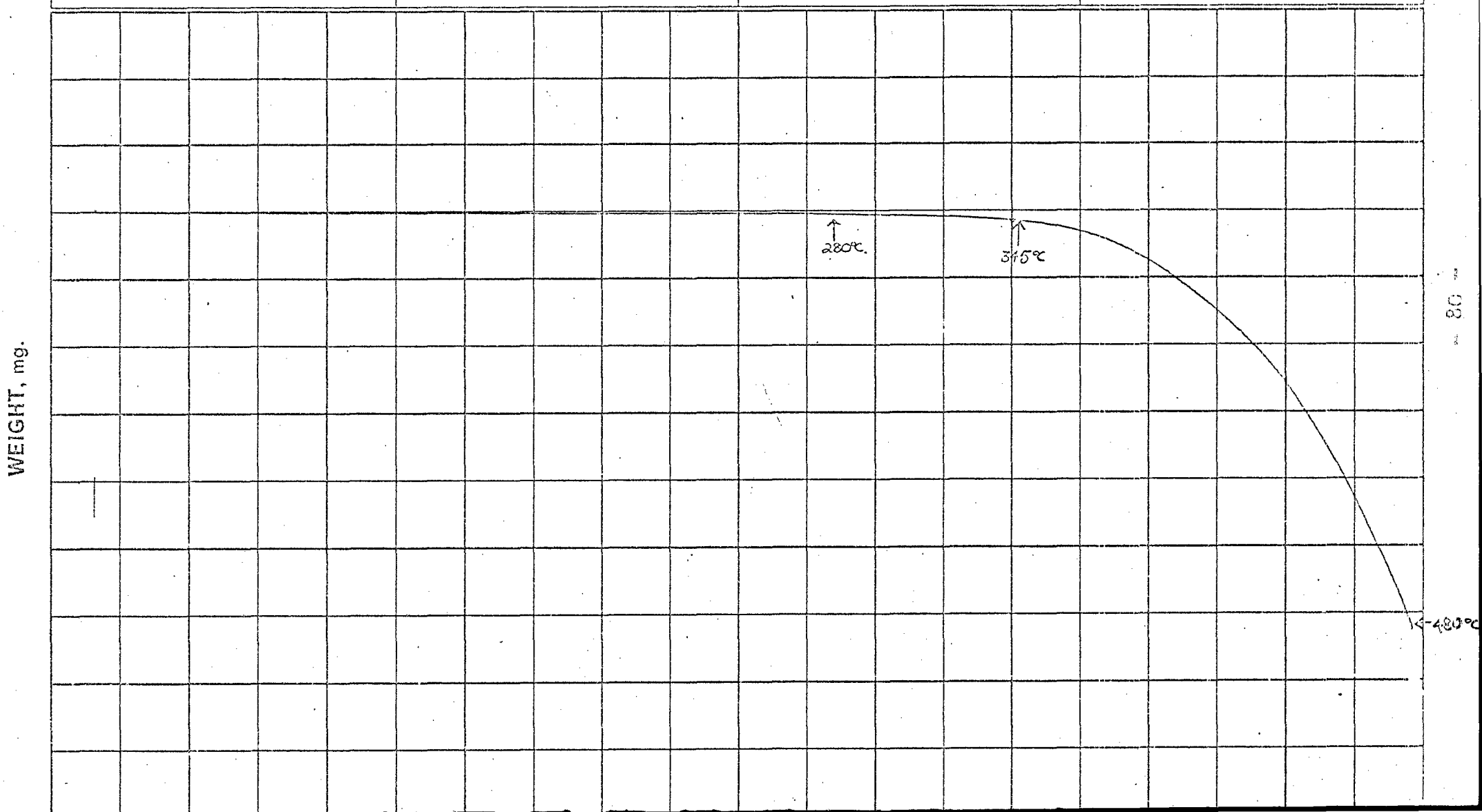


Fig. 28. T.G.A. of POLYMER 4 (reprecipitated)

SAMPLE: Polymer 4 (reprecipitated)	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
	TEMP. SCALE 50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C / min.
			ATM. Static air
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

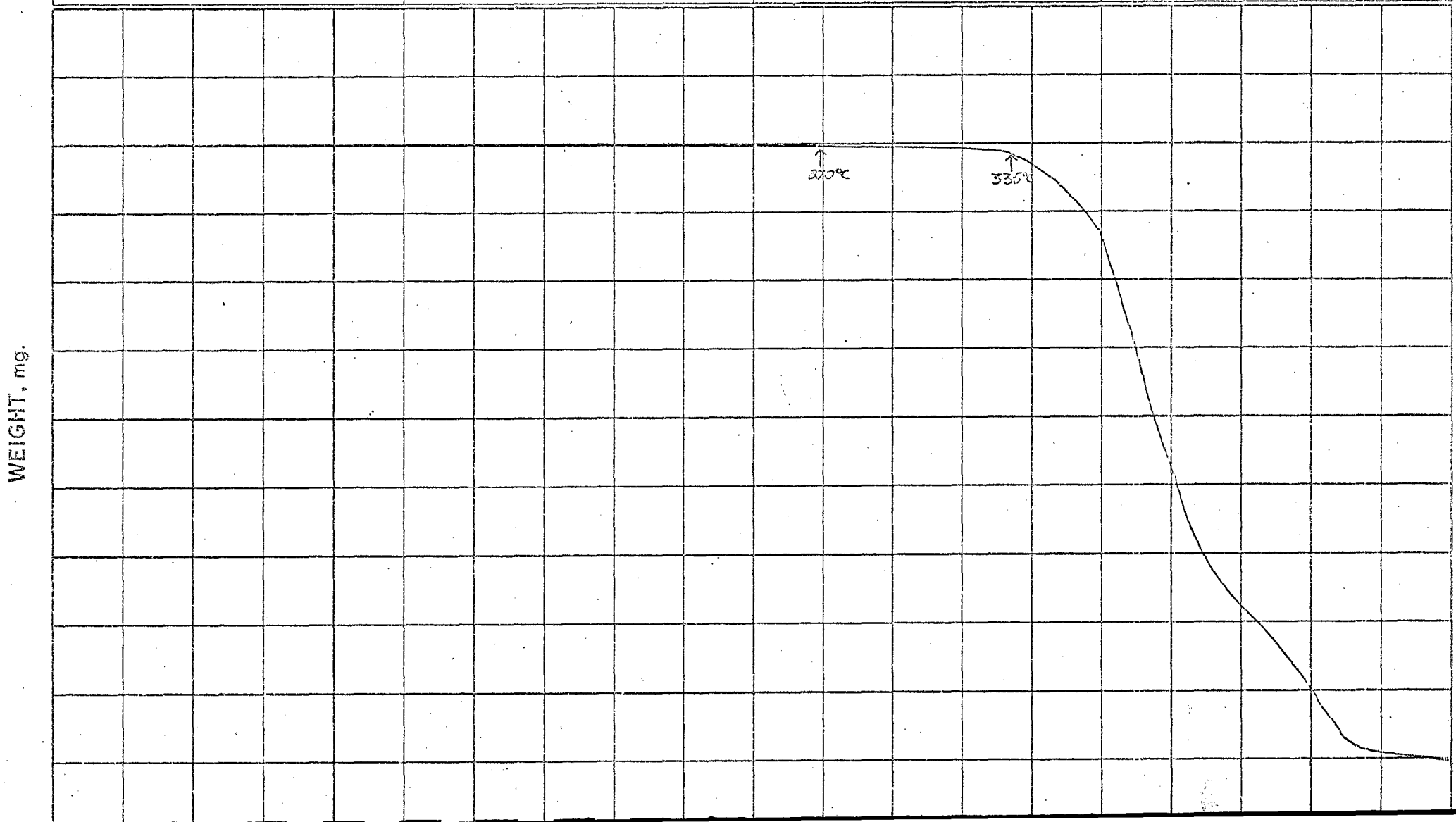


Fig. 29. T.G.A. OF POLYMER M (reprecipitated)

DUPONT INSTRUMENTS

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
Polymer M (reprecipitated)	TEMP. SCALE *50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C / min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

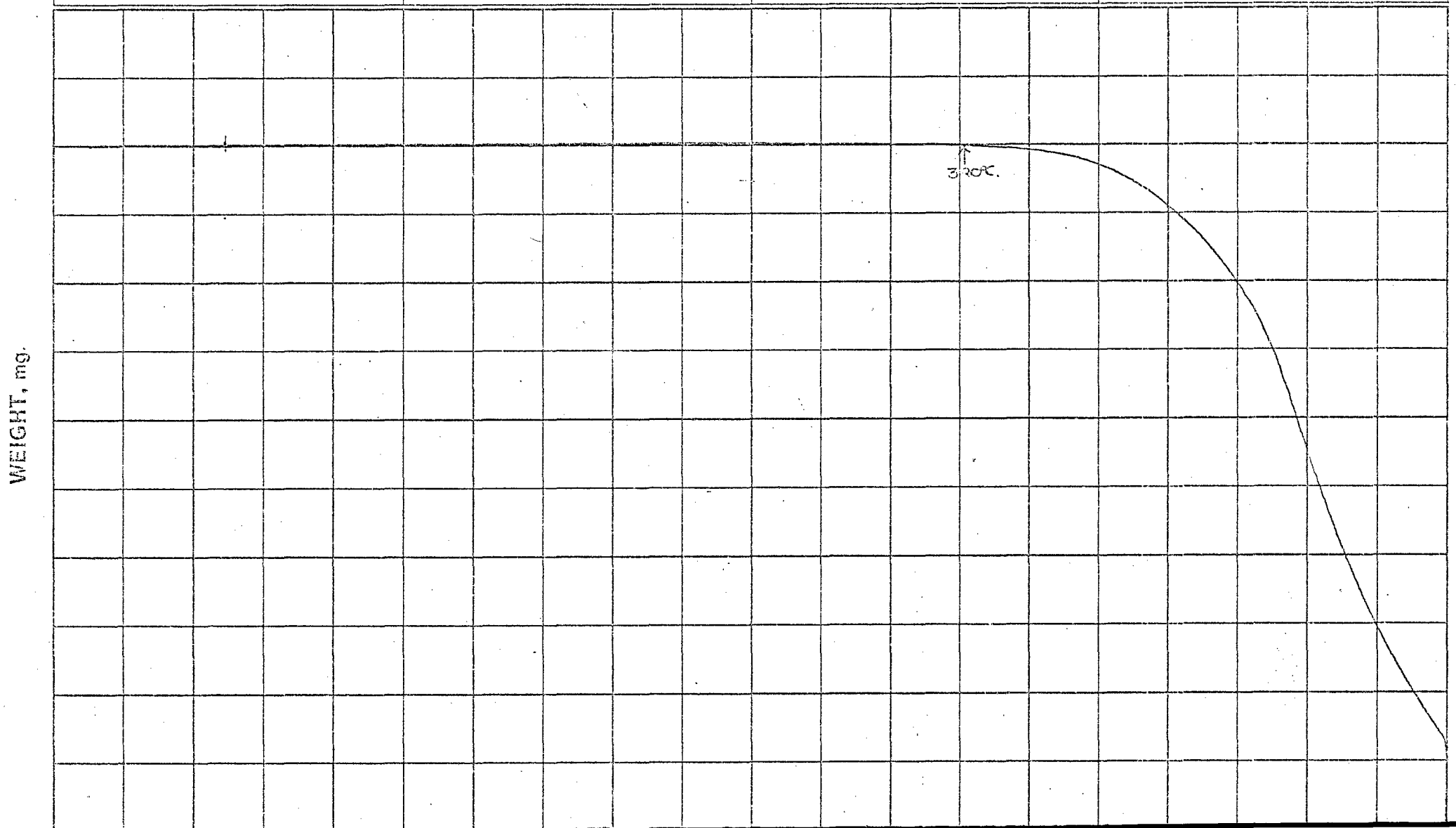


FIG. 10. T.G.A. OF POLYMER M (reprecipitated and heated to 130°C)

INSTRUMENTS

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
Polymer M (reprecipitated and heated to 130°C)	TEMP. SCALE *50 °C / inch	SCALE 2 mg. / inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C / min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

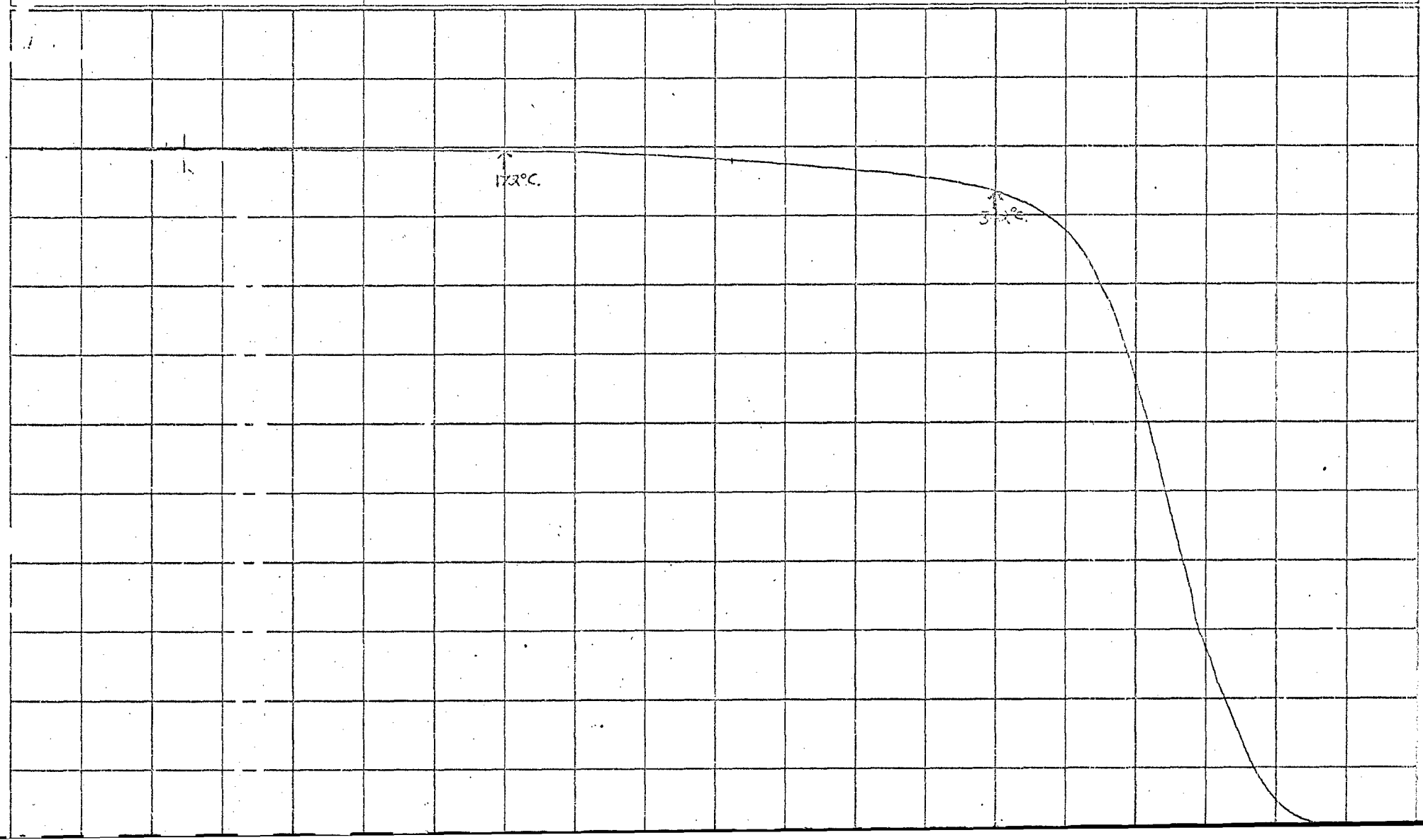


Fig. 31. T.G.A. OF POLYMER 4 (end blocked)

DUPONT INSTRUMENTS

SAMPLE: Polymer 4 (end-blocked)	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
	TEMP. SCALE 50 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR ____
	SHIFT ____ inch		HEATING RATE 10 °C/min.
			ATM. Nitrogen
SIZE ____ mg.	TIME SCALE (ALT.) ____	SUPPRESSION ____ mg.	TIME CONSTANT ____ sec.

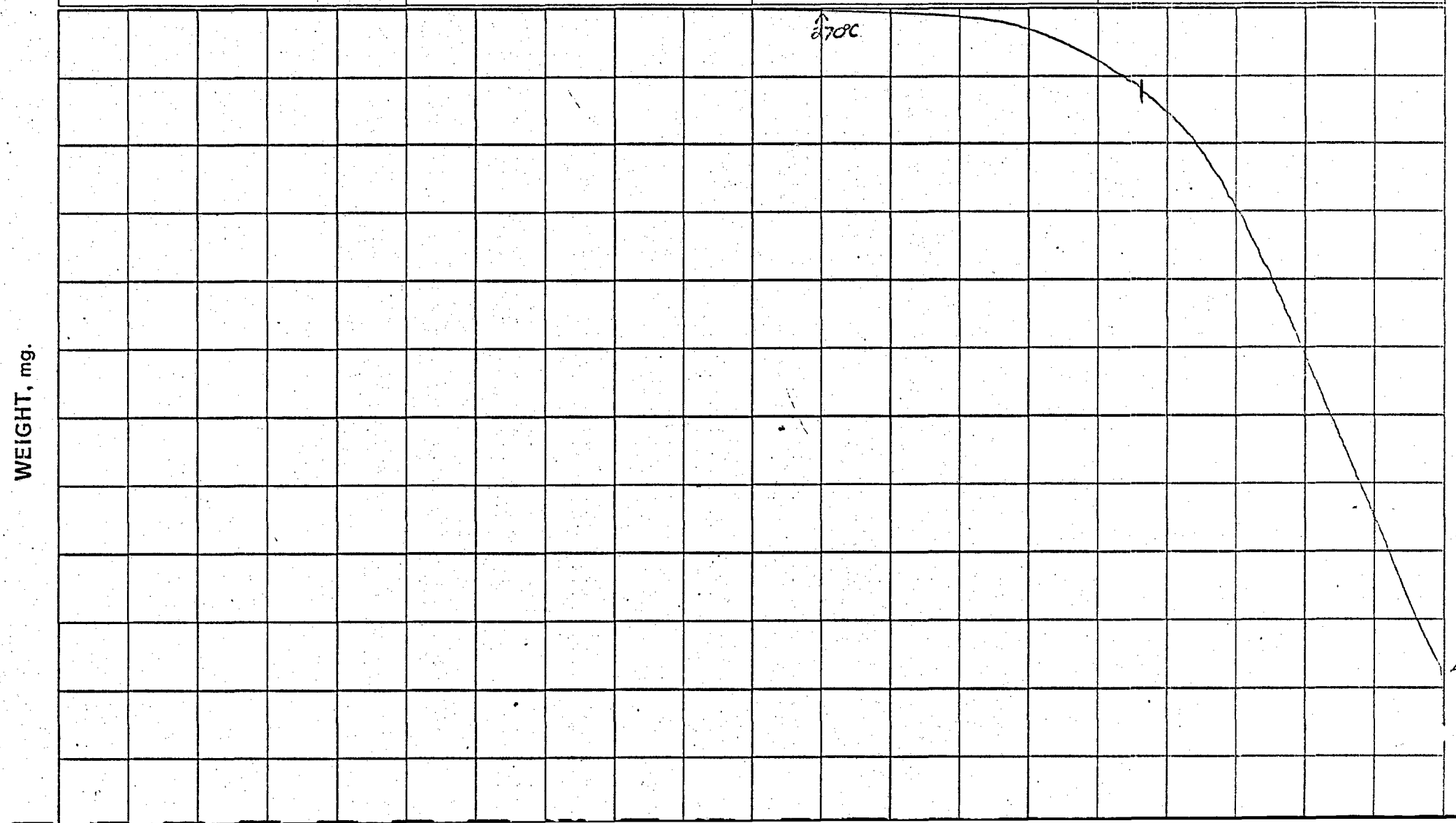


Table 11

Details of TGA Thermograms-Figures 23-31

Fig. No.	Polymer	Pretreatment	Threshold Degrad. Temperature	Atmosphere
23	1	reprecipitated	342	nitrogen
24	2	reprecipitated	335	nitrogen
25	3	reprecipitated and heated to 130°C	342	nitrogen
26	4	reprecipitated	325	nitrogen
27	4	reprecipitated and heated to 130°	345	nitrogen
28	4	reprecipitated	335	static air
29	M	reprecipitated	320	nitrogen
30	M	reprecipitated and heated to 130°	342	nitrogen
31	4	End-blocked	270	nitrogen

temperature or the general characteristics of the thermal degradation reaction. It is surprising that the end-blocked polymer appears to have a lower degradation threshold although the subsequent build up in degradation rate is slower.

3. Thermal Volatilisation Analysis. It is known that polymers, as prepared, are in equilibrium with the starting material, cyclic tetramer. This shows up as a peak in the TVA thermogram around 175-190°C as shown in figure 32 for polymer M but is eliminated by reprecipitation as shown in figure 33. However, the reprecipitated polymer is very much less thermally stable, beginning to degrade at 343°C compared with 398°C for the polymer as prepared.

A further sample of polymer M was heated to 150°C, to destroy residual catalyst, and cooled. The thermogram in figure 34 demonstrates that degradation once again occurs at the lower temperature. Further experiments will be required to clarify these observations.

E. Infra-Red Spectra of Products of Degradation

Further preliminary information about the products of degradation have been obtained by comparing the infra-red spectra of polymer M (figure 35), cyclic trimer (figure 36) and cyclic tetramer (figure 37) with those of the TVA condensibles obtained from polymer M preheated to 150°C (figure 38), reprecipitated (figure 39) and as prepared (figure 40) and the "cold ring" or chain fragment fraction from polymer M as prepared (figure 41)

All the spectra are similar. The information available is not sufficient for a detailed analysis but it is clear that the main products are cyclic trimer and tetramer or closely

10 / min

19

Fig. 32. T.V.A. OF POLYMER M (as prepared)

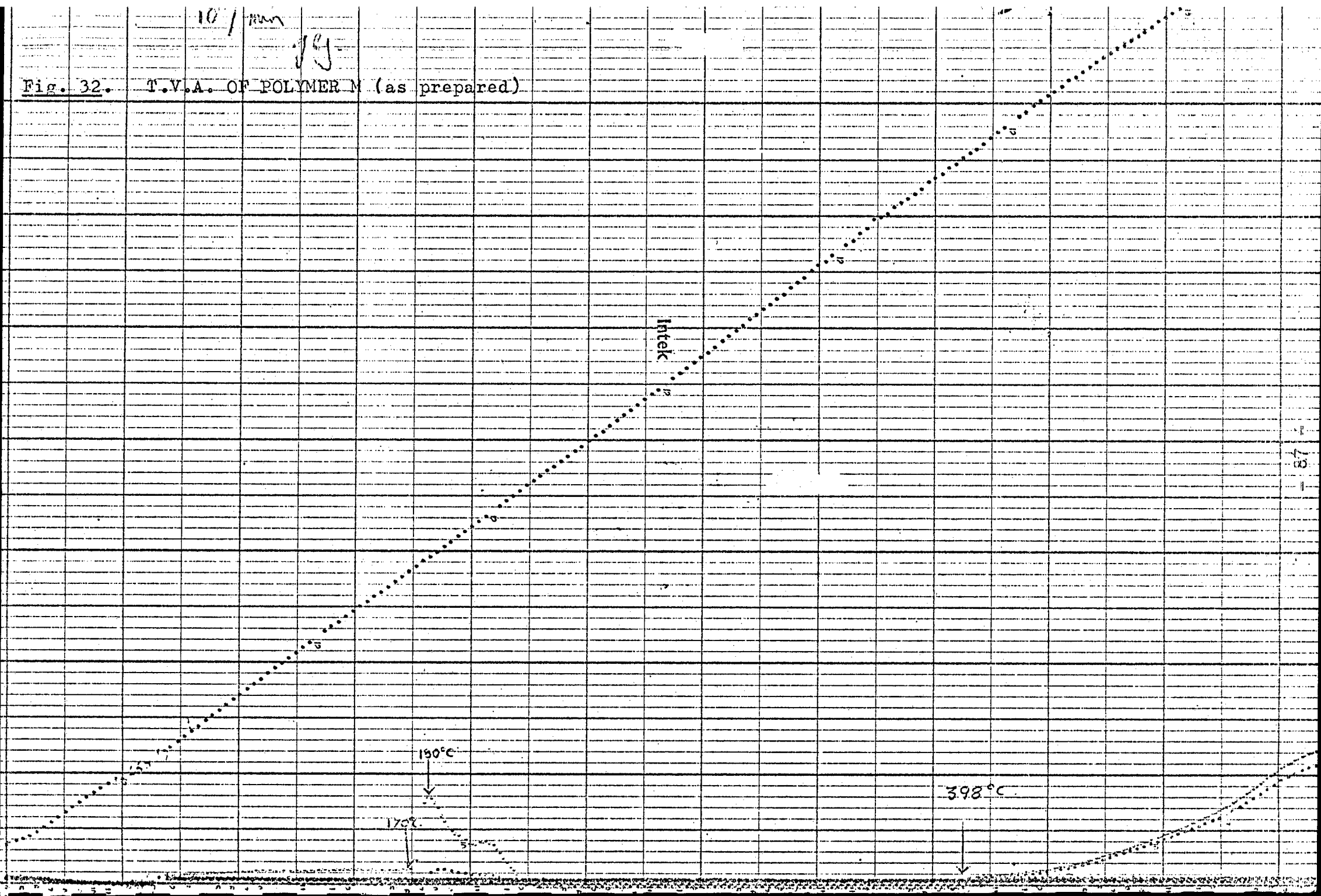


Fig. 33. T.V.A. OF POLYMER M (reprecipitated)

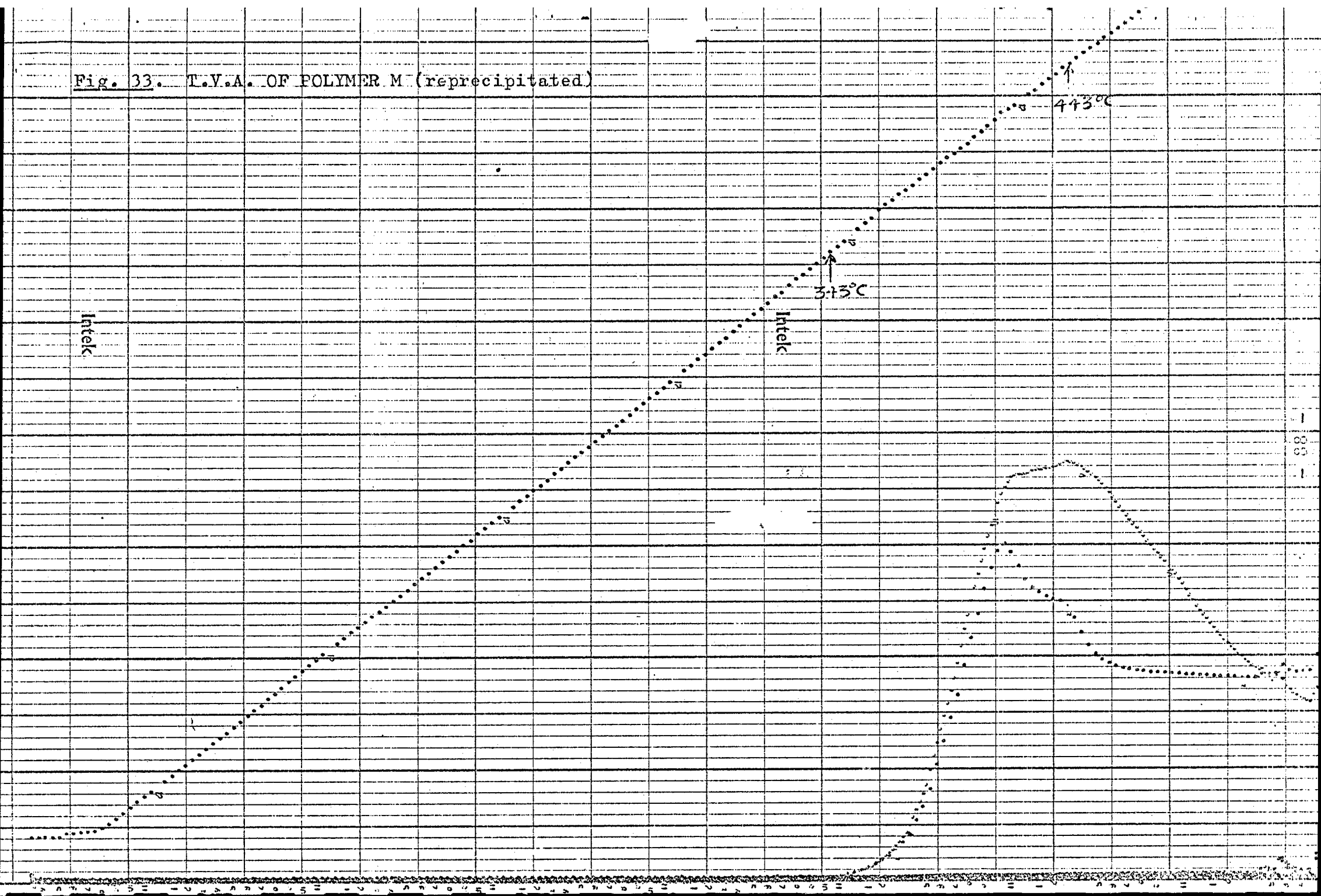


Fig. 34. T.V.A. OF POLYMER M (heated to 150°C)

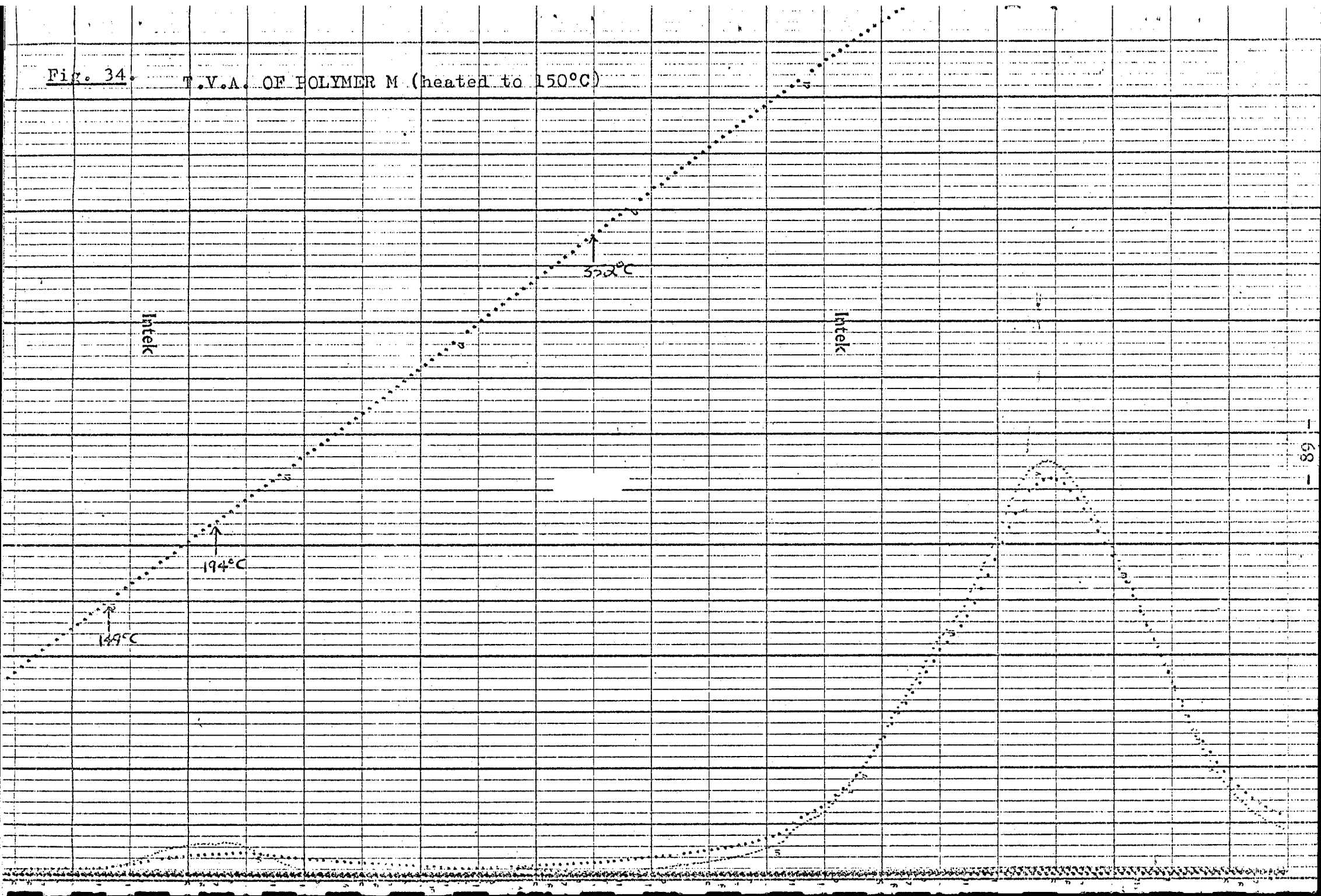
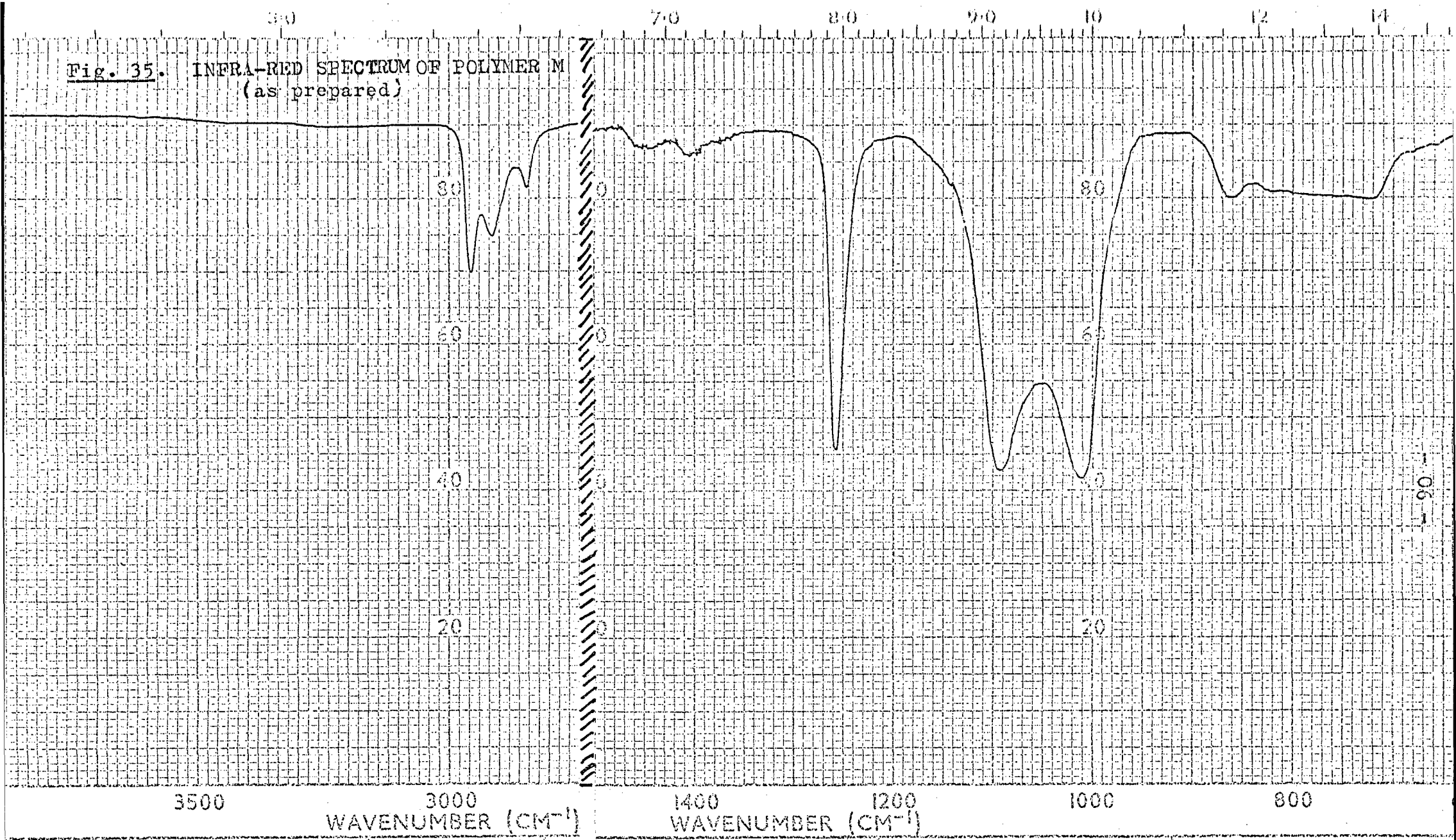
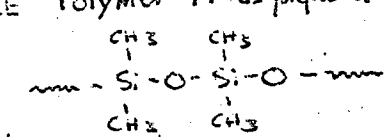


Fig. 35. INFRA-RED SPECTRUM OF POLYMER M (as prepared)



E Polymer M as prepared (not heated) (6)



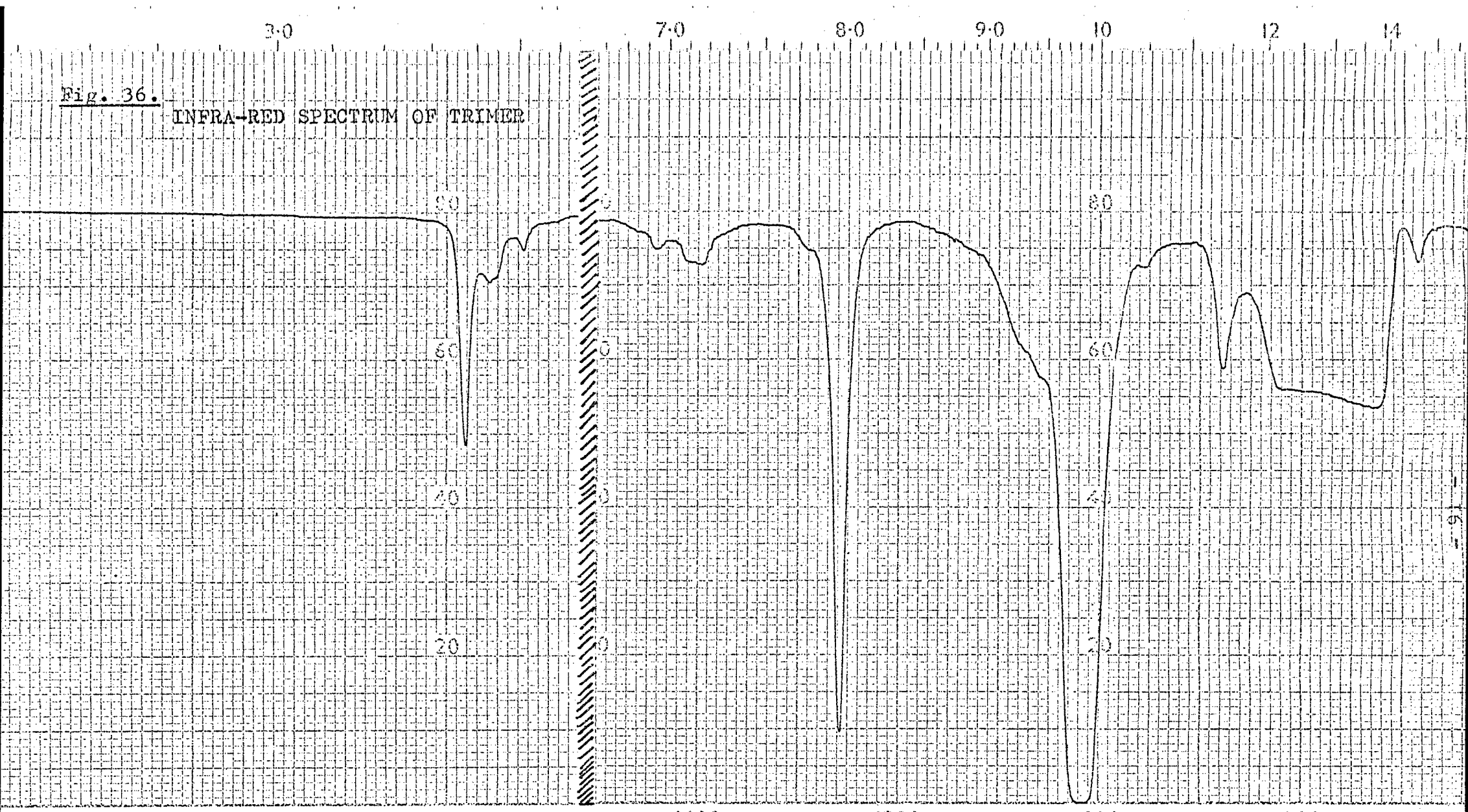
N

SO
CO
CE
RE

SCAN SPEED F
SLIT N
Intek
RPK/215/1001 472-5089

OPERATOR
DATE 14·7·73.
REF. NO.

Fig. 36. INFRA-RED SPECTRUM OF TRIMER



LE cyclic trimer hexamethylcyclotrisiloxane (C)

SO

CO

CEI

REF

N

SCAN SPEED M

SLIT N

Intek

RPK/215/1001 472-5089

OPERATOR

DATE 13·7·73

REF. NO. (A)

Fig. 37.

INFRA-RED SPECTRUM OF TETRAMER.

Cyclic tetramer. (D)

In chst x of sample 2 dated 27-3-73.

SOL
COL
CEL
REF

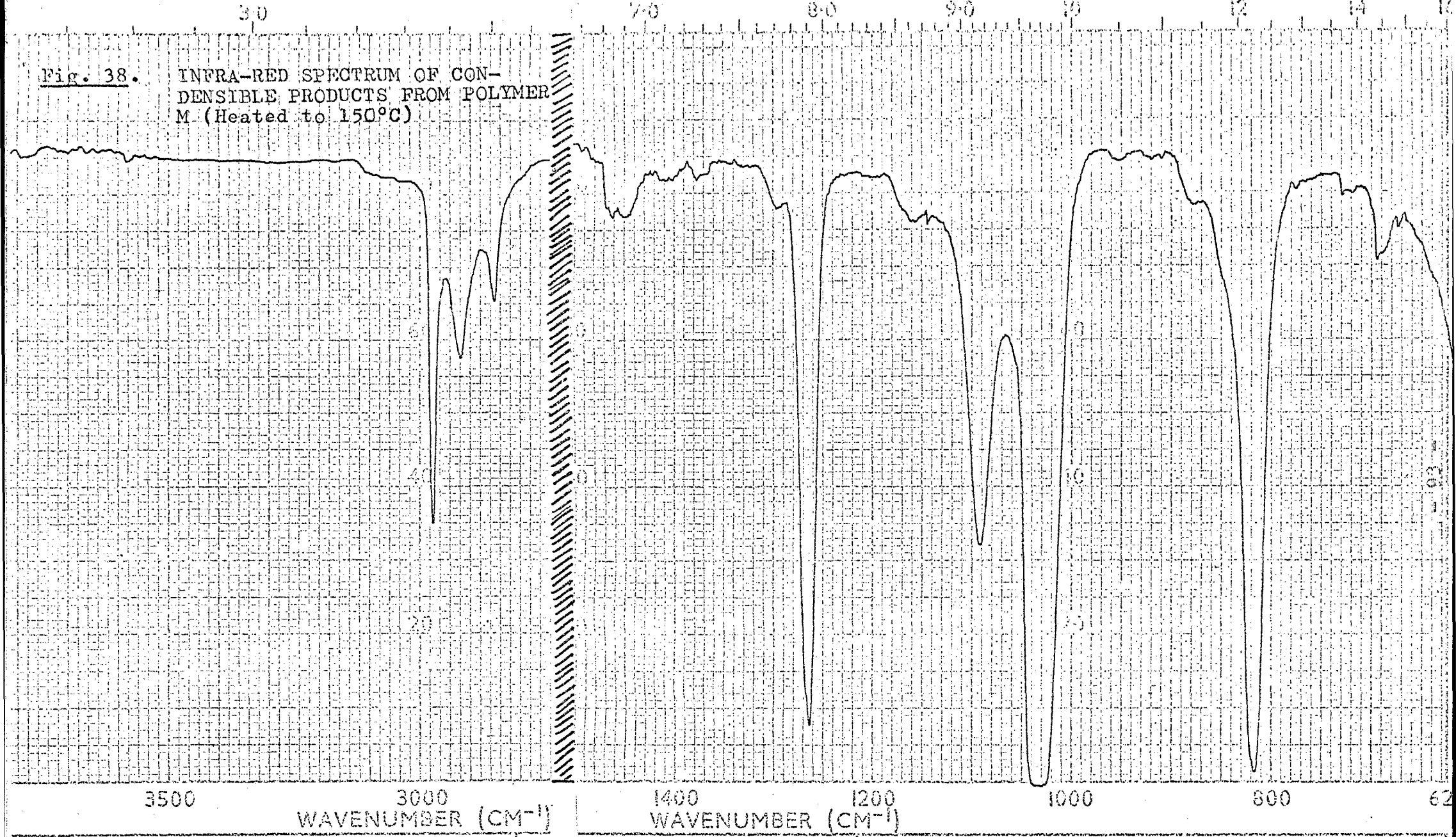
SCAN SPEED Slow.
SLIT N.

Intek
RPK/215/1001 472-5089

OPERATOR [illegible]
DATE 30-3-73

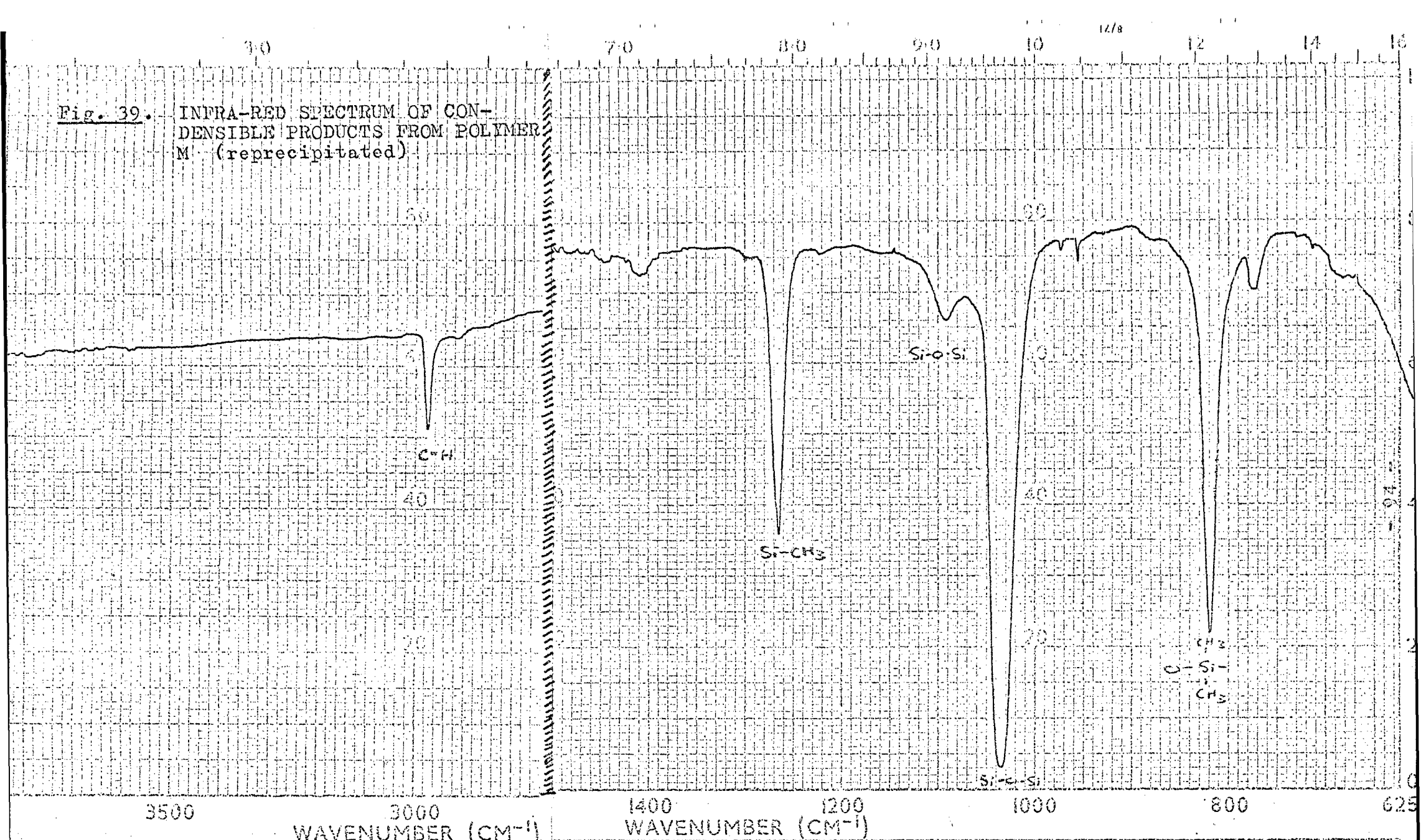
REF. NO.

Fig. 38. INFRA-RED SPECTRUM OF CONDENSIBLE PRODUCTS FROM POLYMER M (Heated to 150°C)



2(1M. heated to 150°C & cooled. bottle 1. (E) VA. condensibles.	SOI CO CEI REF	SCAN SPEED SLIT	OPERATOR J. Gomian DATE 5.7.75
		Intek RPK/215/1001 472-5089	REF. NO.

Fig. 39. INFRA-RED SPECTRUM OF CONDENSIBLE PRODUCTS FROM POLYMER M (reprecipitated)



I.R. of gas cell from degradation (TVA) of M reprecip.

(F)

SOI
CO
CEL
REF

SCAN SPEED M
SLIT 10

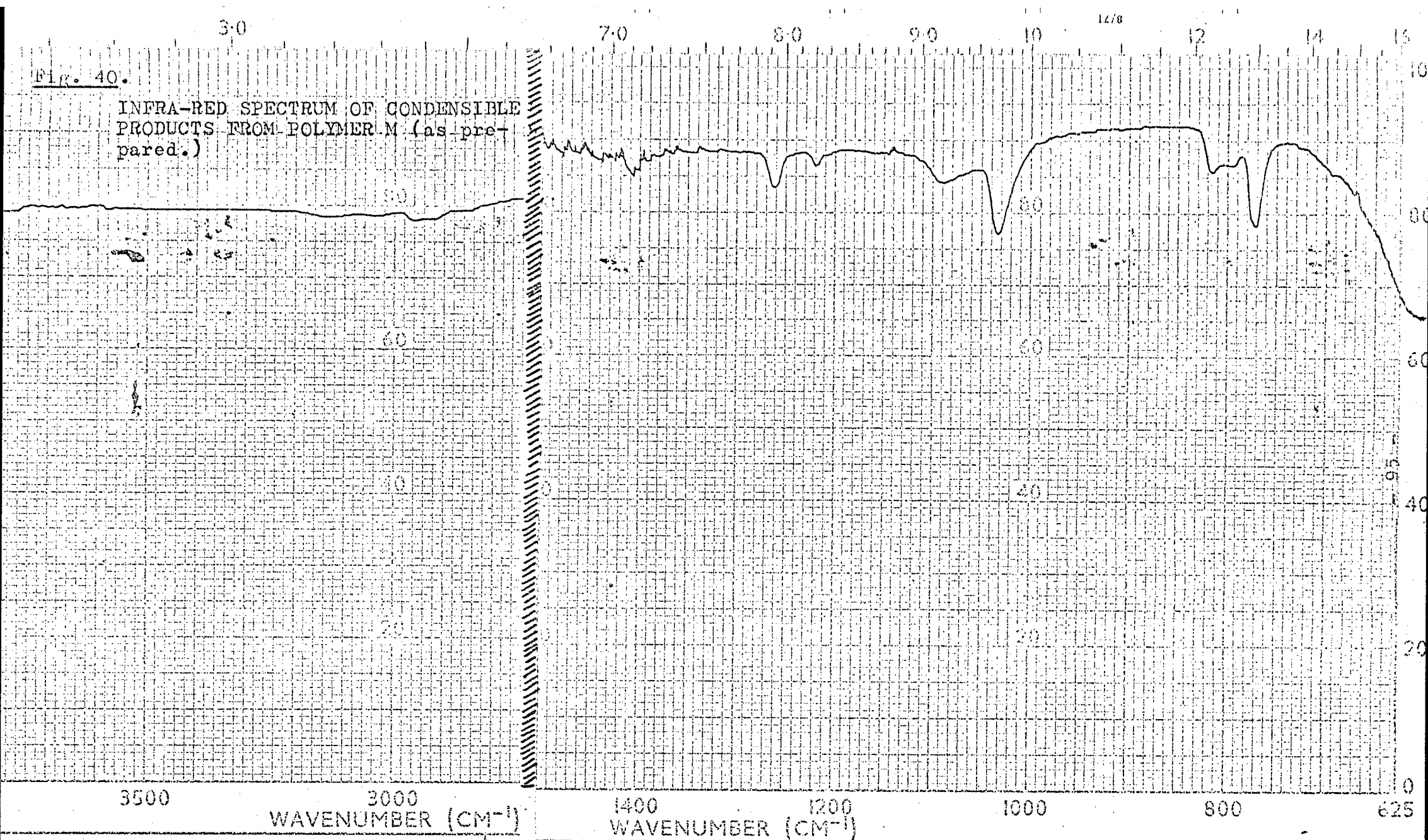
Intek
RPK/215/1001 472-5089

OPERATOR [illegible]
DATE 28·4·73

REF. NO.

FIG. 40.

INFRA-RED SPECTRUM OF CONDENSIBLE PRODUCTS FROM POLYMER M (as prepared.)



POLYMER M (NOT HEATED) (F)

F.V.A.

SOI
CO
CEI
REI

TOTAL
IND. PRODUCTS @ 195°C

SCAN SPEED M
SLIT N

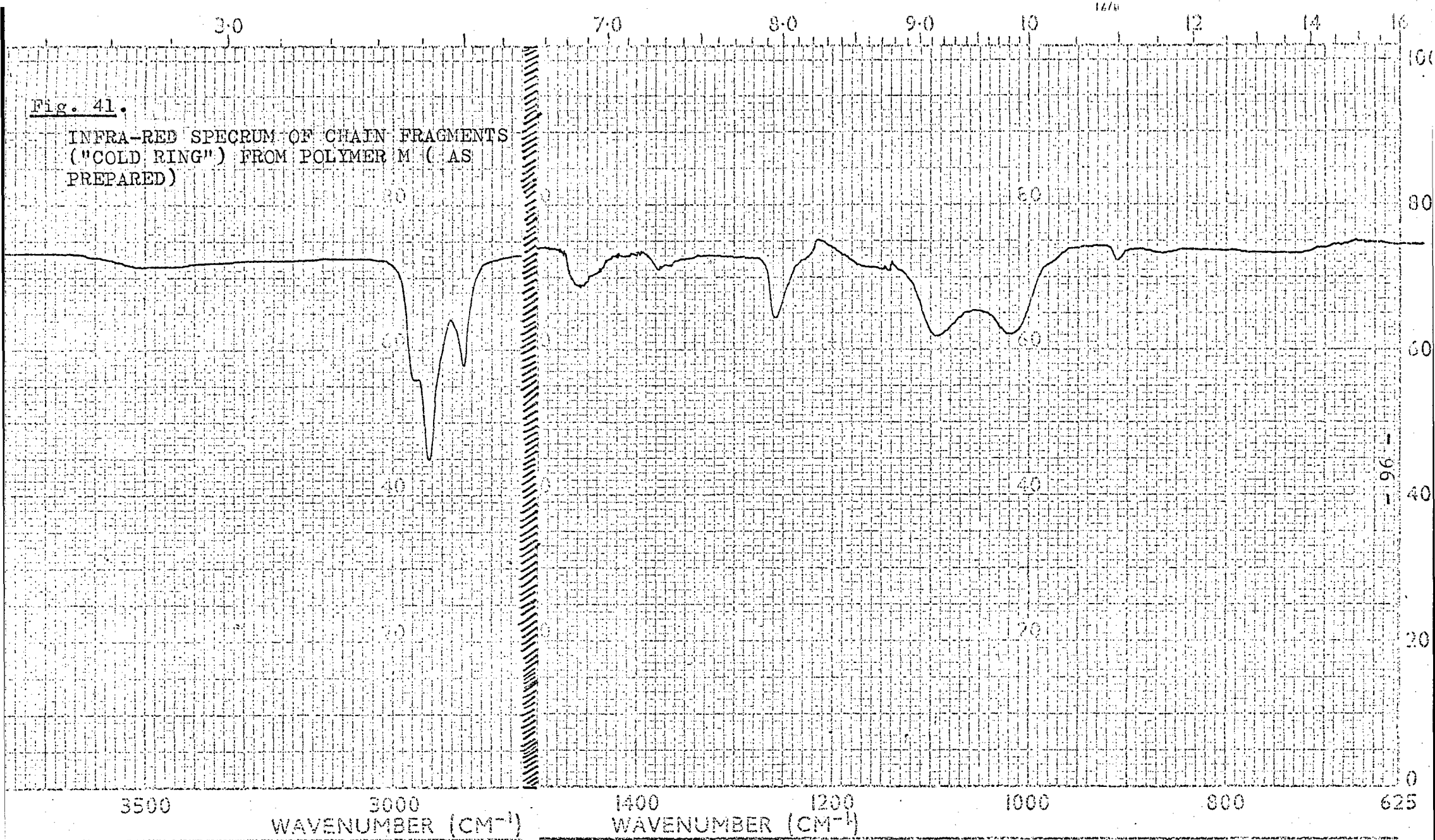
OPERATOR R.G.
DATE 28/4/73

Intek
RPK/215/1001 472-5089

REF. NO.

Fig. 41.

INFRA-RED SPECRUM OF CHAIN FRAGMENTS ("COLD RING") FROM POLYMER M (AS PREPARED)



Cold ring fraction from polymer "M" as prep"
ed by TVA

(H)

SO
CO
CE
RE

SCAN SPEED M
SLIT N

Intek
RPK/215/1001 472-5089

OPERATOR
DATE 28-4-73.

REF. NO.

related compounds and that the chain fragments are closely related to the initial polymer. It seems also that the Si-C bond is remaining intact since there is no indication of the production of methane.

F. The "Sealed Tube" Degradation Technique.

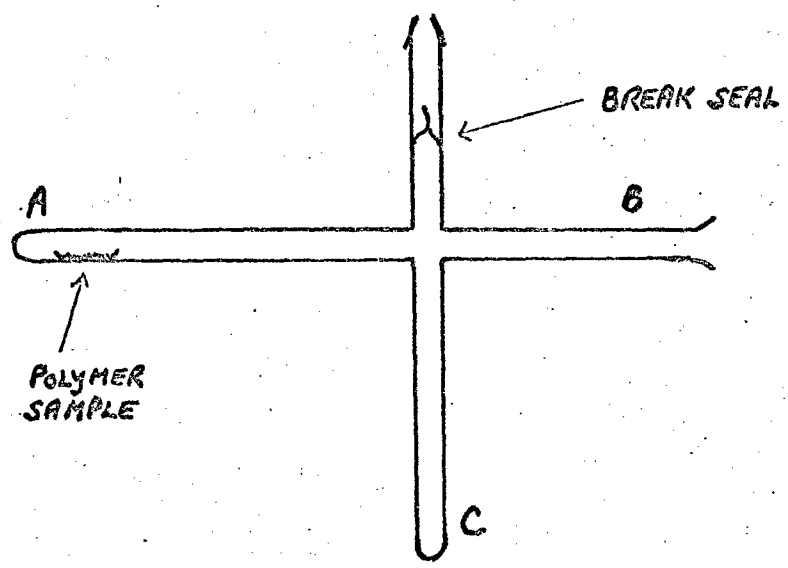
Having completed all the preliminary investigations described in earlier sections of this chapter it is now appropriate to make a more systematic and detailed study of the thermal degradation of poly(dimethyl siloxane). It is proposed to use the "sealed tube" technique which has been successfully applied in the past to similar investigations.[22,23] The equipment necessary is being constructed and assembled. The "sealed tube" is represented in figure 42.

A sample of polymer ($\simeq$50-100 mg) is placed in an aluminium boat, inserted at B and pushed along to point A. The apparatus is then evacuated and sealed off at B. Tube A is inserted into a thermostatted furnace and C immersed in liquid nitrogen. After a predetermined reaction time the volatile degradation products may be examined by attaching D to a vacuum system, breaking the break seal and collecting the products in a manner consistent with the method of analysis contemplated, i.r., g.l.c., etc.

Less volatile large chain fragments (the "cold ring" fraction) accumulate in A just outside the furnace and may be recovered by breaking the tube at an appropriate point and washing out with solvent. Residual polymer is also available for inspection.

Fig. 42.

THE "SEALED TUBE".



G. Conclusions.

Progress in studying the thermal degradation of poly (dimethyl siloxane) may thus be summarised as follows:

a. Satisfactory methods for the preparation of suitable samples have been established and samples prepared.

b. Suitable methods and conditions for the measurement of molecular weight have been determined.

c. The main features of the degradation process as revealed by two thermal analysis methods, namely TVA and TGA, have been established.

d. Thus the reaction starts around 350°C. Tetramer and trimer are the main products of degradation in vacuum. Oxygen has a profound effect on the reaction.

e. Gas-liquid chromatographic methods have been devised for the separation and analysis of products.

f. It has been established that neither residual catalyst nor the molecular weight of the starting polymer have a significant influence on the threshold degradation temperature or the general characteristics of the thermal degradation reaction. End blocking by 1,1,1,3,3,3-hexamethyldisilazane surprisingly leads to a lower degradation temperature threshold although the subsequent build up in degradation rate is slower.

Using the "sealed tube" technique described in section F of this chapter and appropriate analytical methods, a systematic study of the thermal degradation of poly(dimethyl siloxane) may now be undertaken with a view to establishing the detailed mechanism of degradation and the structural features upon which

stability depends. The following topics seem to be relevant.

a. Further studies of thermal analysis using TGA and TVA.

b. Molecular weight changes during degradation.

c. Detailed analysis of volatile products.

d. Changes in the involatile residue.

e. Influence of molecular weight of the starting material.

f. Effect of end-stopping stabilisers.

g. Effect of polymer preparation - temperature, initiator, etc.

It is anticipated that these studies could later be extended to other polysiloxanes, for example, poly(diphenylsiloxane) and appropriate copolymers.

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Department of Chemistry University of Glasgow, Glasgow G12 8QQ, Scotland	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Degradation Reactions in Polymers

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Scientific 70 Feb 01 - 73 Jun 30

5. AUTHOR(S) *(First name, middle initial, last name)*

Norman Grassie, Roy Jenkins, John Cunningham and Ian G. MacFarlane

6. REPORT DATE 73 August 31	7a. TOTAL NO. OF PAGES 111	7b. NO. OF REFS 23
8a. CONTRACT OR GRANT NO. F61052-69-C-0026 b. PROJECT NO. 7342 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) None 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* None	

10. DISTRIBUTION STATEMENT

11. SUPPLEMENTARY NOTES Tech., Other	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio 45433

13. ABSTRACT

This report is concerned with three distinct aspects of polymer degradation and stability with the general aim of the production of materials of improved stability through a more complete understanding of their degradation mechanism and its relationship to chemical structure.

The photothermal degradation of copolymers of methyl methacrylate and n-butyl acrylate covering the whole composition range has been studied at 165°C. The gaseous and liquid products, which consist of hydrogen, carbon monoxide, methane, methyl methacrylate, n-butyl acrylate, n-butanol and n-butyraldehyde were analysed quantitatively using a gas chromatographic technique and the yields related to copolymer composition. Zip lengths, calculated from molecular weight and volatilisation data, decrease with increasing acrylate content of the copolymer but are higher than those observed during thermal degradation. Infra-red spectral changes in the residue are attributed to lactone formation and associated with the formation of butanol. The "cold-ring" or chain fragment fraction of the products becomes increasingly more abundant as the acrylate content of the copolymer is increased and spectral differences from the original polymer have been accounted for. All the products and principal features of the reaction are explained in terms of a radical process initiated by scission of pendant acrylate units and propagated

DD FORM 1 NOV 65 1473

Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Degradation of Polymers						
Photothermal Degradation						
Thermal Degradation						
Stability of Polymers						
Copolymers, Degradation of Methyl Methacrylate						
n-Butyl Acrylate						
Gas-Liquid Chromatography						
T.G.A.						
T.V.A.						
Products of Degradation of Polymers						
Friedel-Crafts Polymers						
Poly(Dimethyl Siloxanes)						
Infra-Red Spectroscopy						
Pyrolysis of Polymers						
Mechanism of Degradation of Polymers						
Thermal Analysis						

Security Classification

Abstract (cont'd)

by a combination of depropagation, intra and intermolecular transfer processes the relative importance of which depends upon copolymer composition. Differences from the thermal reaction and the corresponding reaction in copolymers of methyl methacrylate and methyl acrylate are discussed.

It is shown that a number of aromatic compounds, both carbocyclic and heterocyclic, may be copolymerized with dimethoxy-p-xylene with stannic chloride as catalyst. Purification of materials and preparations of copolymers are described.

The preparations of a number of poly(dimethyl siloxanes) are described. Thermal analysis using TGA and TVA have shown that thermal decomposition starts at approximately 360°C but this is depressed somewhat by reprecipitation. Neither heating to 130°C to destroy residual catalyst nor the molecular weight of the starting polymer have any significant influence on the threshold degradation temperature or the general characteristics of the thermal degradation reaction. End-blocking lowers the degradation temperature threshold although the subsequent build up in degradation rate is slower. The principal products of degradation are cyclic trimer and tetramer and g.l.c. and infra-red methods are being devised for their analysis.