THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

THE THERMAL DEGRADATION OF POLYCHLOROPRENE.

by

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Summary of Thesis for the Degree of Doctor of Philosophy.

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The thermal degradation of polychloroprene has been examined by thermoanalytical techniques. These indicate that under temperature programmed conditions, degradation occurs in two main stages, namely dehydrochlorination with a rate maximum (at 10°/min.) of 370°C, and carbonisation with a rate maximum at 450°C. Since the two processes overlap and because scission reactions occur simultaneously with dehydrochlorination, the yield of hydrogen chloride is only 90% of the total contained in the polymer.

A small amount (less than 5%) of the hydrogen chloride is eliminated prior to the major dehydrochlorination reaction. The quantity lost in this early reaction varies from one polymer sample to another, and it appears that this reaction takes place at irregularities in the chain produced by abnormal polymerisation or by oxidation. This view is borne out by the fact that a polymer which had been prepared

under vacuum at -40°C showed very little of the early elimination reaction. Although this polymer was more stable at the start of the degradation, it gave an earlier maximum rate during the main dehydrochlorination than the others examined, suggesting that its greater regularity facilitated the elimination process.

The kinetics of dehydrochlorination were examined and a value of 39.6Kcal./mole was obtained for the activation energy for the elimination reaction.

An ultraviolet spectroscopic technique was developed to examine partially degraded polymer films and a number of polymers which decompose by an elimination process were studied. Polychloroprene was found to be different from the other polymers in that the structure produced by the elimination of only one molecule could be observed at the start of the reaction, whereas in the others, polymers were produced by consecutive elimination of a number of molecules.

Infrared analysis of degraded polychloroprene indicated that methyl groups are formed during the degradation and methane was identified as one of the major products of carbonisation. The amount of methyl group formation was much higher than in poly(vinyl chloride) and the reason for this may be the scission reactions which accompany dehydrochlorination.

The structure and degradation of some blends of polychloroprene with other polymers were studied and it was concluded that neither chlorine atoms nor other small mobile radicals were produced by degrading polychloroprene.

PREFACE.

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

I am indebted to the Science Research Council for the award of a Research Studentship, during the tenure of which this work was performed.

My thanks are also due to my colleagues in the Macromolecular group for useful assistance and discussion and to various members of the technical staff of the Chemistry Department, in particular to Mrs. F.Lawrie, Mr. R.G.Perrit, and Mr. A.Carson.

I am very grateful to my wife for typing the manuscript.

Finally, I wish to thank Dr. I.C.McNeill for his general supervision and constant encouragement throughout my work.

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CHAPTER I

INTRODUCTION

Polychloroprene

(a) Historical

Polychloroprene, otherwise known as neoprene, is a synthetic elastomer produced by polymerisation of 2-chloro-1,3-butadiene (chloroprene). The polymer was discovered in 1931 by Carothers[1] and was the first synthetic rubber to be produced commercially in the United States. Since then a large number of other synthetic rubbers have been produced, but the market for neoprene has shown continuous expansion.

(b) Properties and Applications

Western World plant capacity for the polymer in 1964 was 194,000 tons.[2] Although SBR rubber is cheaper for many applications especially in tyres and is therefore produced in much larger amounts, neoprene has better dynamic properties than most other synthetic rubbers.

The polymer is vulcanised by heat treatment, alone, or with the oxides of zinc and magnesium. In this state it has very good oil and solvent resistance and withstands oxidative aging reasonably well.

The vulcanizate is used in the manufacture of oil resistant gaskets, hoses and drive belts and for shoe soles and coatings for wires and cables. Some grades of neoprene with suitable crystallisation characteristics are used to make impact adhesives and the latex can be used for the treatment of paper and fabrics.

(c) Polymerisation

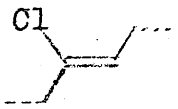
Emulsion polymerisation is normally employed, with molecular weight control by one of two methods.

In the first method, sulphur is added to the emulsion mixture and copolymerised into the chain in blocks of about six atoms every hundred or so monomer units.[3] At a subsequent stage some of the S - S bonds are broken by free radical attack of an agent such as tetraethylthiuram disulphide.

The second process involves the addition of a chain transfer agent, usually lauryl mercaptan, resulting in an increased rate of termination, by the growing polymer radical abstracting hydrogen from the mercaptan. The transfer gives rise to a mercaptyl radical which may initiate further polymerisation. The use of a mercaptan modifier produces polymer with a lighter colour and a lower sulphur content than the first process.

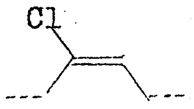
(d) Structure

The polychloroprene chain may contain different types of unit according to how the double bonds in the monomer take part in the polymerisation process. The four possible units are illustrated below, with typical analysis figures[4] for a polychloroprene made at 40°C.



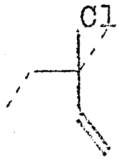
1,4 trans

86%



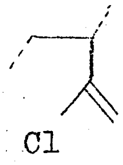
1,4 cis

10%



1,2

1.6%



3,4

1.0%

1,4 addition especially to form a trans double bond is the preferred mode of polymerisation, while 1,2 and 3,4 additions may be regarded as side reactions which produce minor irregularities in the chain. A further complicating factor is the possibilty of head to head or tail to tail structures which amount to 10 - 15%.[5] As the polymerisation temperature is reduced the number of irregularities of all types decreases[4] with the result that the crystallinity increases and elastomeric properties are lost.

Polymer Degradation

Because of the economic importance of synthetic materials a great deal of effort is devoted to studying the manner in which they lose their desirable properties under the influence of physical agencies such as heat, ultraviolet light, radiation, ultrasonics and mechanical stress. This research is directed towards stabilising existing polymers against these effects and devising new polymers and copolymers to resist a particular degradative influence.

As well as being technically important the chemistry of polymer degradation is academically interesting because the macromolecular environment of a reactive intermediate may have a profound effect on the course the reaction takes. In addition to the preventive aspect of polymer degradation studies, there is a growing interest in the carbonisation process and in the electrical, mechanical and absorption properties of residues produced from controlled degradation. Results from investigations in this field are applied for instance in the design of ablative heat shields for spacecraft re-entry and in the production of carbon fibres.

Experimentally, thermal degradation is one of the easiest to study, since all that is required is a source of heat and an accurate measurement of the temperature of the polymer. Despite this fact, the mechanism by which most polymers degrade thermally is still not fully understood.

In an atmosphere containing oxygen, supply of energy from any of the sources mentioned may have a similar effect to attack by ozone, and the formation of hydroperoxides frequently leads to more rapid degradation. Polymer degradation has therefore often been studied in an oxygen free atmosphere in order to remove complicating oxidative effects. This is especially true of thermal degradation where most pyrolysis experiments are conducted in vacuum or under a stream of inert gas so that the degradation products are rapidly removed from the hot zone and secondary reactions are not important.

(a) Types of Thermal Degradation

Thermal degradation processes maybe divided into scission reactions and substituent reactions. Scission of the polymer main chain, either in the middle or at labile ends, may result in depolymerisation to monomer as in poly(methyl methacrylate) and poly(α-methyl styrene), or in the production of a wide range of fragments of different masses as in polyethylene. Reaction in the substituents of the polymer chain can either result in the combination of side groups or in the elimination of the substituent group altogether. The formation of anhydride units during the degradation of poly(methacrylic acid)[6] is an example of a combination reaction and the production of iso-butene from poly(tert-butyl methacrylate)[7] is an elimination reaction.

(b) Polydienes

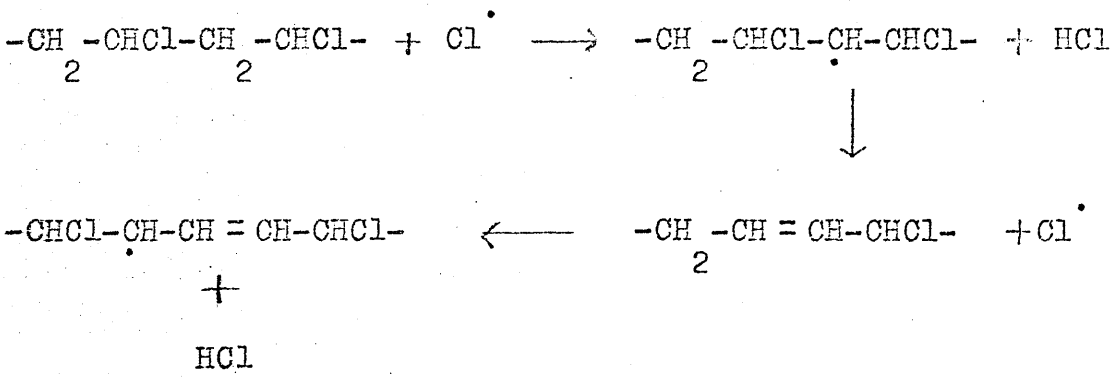
Polydiene elastomers like polyisoprene and polybutadiene degrade by rupture of the interunit C – C single bond with the formation of an allylic radical. The products of degradation are mainly high boiling point tars but a significant amount of monomer and dimer are formed. The yield of isoprene from rubber has been studied by a number of workers and the figure given ranges between 3.4% and 44%.[8] It appears that high temperature and high heating rates favour monomer production.

(c) Poly(Vinyl Chloride)

In general, chlorine containing polymers eliminate hydrogen chloride as the first stage in degradation. The most studied polymer in this class is poly(vinyl chloride) (PVC) since commercially it is a very important material. The elimination reaction in this polymer produces long sequences of double bonds which confer coloration to the polymer very early in the degradation. The colour in the polymer makes it unacceptable for many applications before its physical properties are adversely affected.

Dehydrochlorination of PVC exhibits autocatalysis by evolved hydrogen chloride,[9,10] and is accompanied by cross-linking[11] and by the formation of a small amount of benzene from polyene cyclisation at temperatures above 200°C.[12,13,14]

The mechanism by which the elimination occurs is thought to be radical in nature,[13,15,16,17] though unimolecular[18,19] and ionic[20] mechanisms have also been proposed. In the radical process the chain reaction is propagated by a chlorine atom as shown below.



$$-CH_2-CHCl-CH_2-CHCl- + Cl^{\bullet} \longrightarrow -CH_2-CHCl-\dot{C}H-CHCl- + HCl$$

$$-CH_2-CHCl-\dot{C}H-CHCl- \longrightarrow -CH_2-CH{=}CH-CHCl- + Cl^{\bullet}$$

$$-CH_2-CH{=}CH-CHCl- + Cl^{\bullet} \longrightarrow -CHCl-\dot{C}H-CH{=}CH-CHCl- + HCl$$

The initiation and termination steps are the subject of considerable discussion.

End groups,[11,21] free radical initiators,[10,11,22] peroxides either added or formed on the chain,[23] branch points[19,22] and comonomers which build into the chain like branch points,[24] have all been shown to affect the initiation process.

Termination reactions which have been suggested, include combination of polymer radicals or chlorine atoms in pairs. Evidence has been presented that the degradation follows 3/2 order kinetics, which is explicable by a scheme where termination occurs only by combination of chlorine atoms.[13]

No chlorine however has yet been detected in the products and 3/2 order kinetics are not always followed.[22] Polymer radical combination produces cross-linking, but in solution cross-linking and dehydrochlorination seem to be unrelated reactions.[25]

The usual test for a free radical reaction is inhibition by a radical acceptor but little is known about materials which have a strong affinity for chlorine atoms at 200 °C. Some highly unsaturated substances have been shown to act as stabilisers for PVC,[26] but common inhibitors for oxidation reactions either have no effect or in fact accelerate the reaction.[22]

Results obtained by McNeill and Neil[16,27] suggest that the chlorine atom can be absorbed by another polymer intimately blended with the PVC. The removal of the chlorine atom has the effect of stabilising the PVC and may also result in a change in the degradative behaviour of the other component in the blend.

Polychloroprene Degradation

Polychloroprene eliminates hydrogen chloride during degradation and thus behaves more like PVC than polyisoprene to which it is structurally analogous. Compared with the extensive literature on PVC degradation however, the number of papers on the break down of polychloroprene is very small.

The unstabilised polymer readily degrades through addition of oxygen to the double bond so that in normal use the purely thermal degradation is not a significant problem. For this reason the non-oxidative pyrolysis of this polymer has nearly always been studied with a view to identifying polychloroprene in an unknown polymer sample.

The literature on the degradation of polychloroprene in both oxidative and non-oxidative atmospheres is reviewed below.

(a) Oxidative Degradation

The oxidative degradation of polychloroprene has been studied at temperatures up to 150°C. Hydrogen chloride is eliminated during the oxidation at a rate which is closely related to the rate of oxygen uptake.[28,29] The activation energy for hydrogen chloride loss is reported to be 9.2,[30] 12[31] and 15.8[29] Kcal./mole. The reaction has a short induction period and is autocatalytic.[28,29,31]

Preliminary measurements have been reported for the loss of hydrogen chloride from polychloroprene in a nitrogen atmosphere at the same temperatures as used to study oxidation. In two cases the rate of the thermal reaction was found to be insignificant,[28,29] but Dvorak and Matyska[31] found that a small amount of hydrogen chloride was rapidly evolved before the rate fell to a very low level. The maximum amount given off in the rapid evolution was 5% and this stage of break down was attributed to the 1,2 irregular structures in the chain. Their polymer seems to have been very unstable to have degraded without oxygen at 90°C. It may be that some prior oxidation had taken place, although all precautions to avoid this were observed. Bailey[29] showed that oxidation produced a polymer which lost hydrogen chloride under nitrogen. The rate of evolution of hydrogen chloride decreased by a first order law as the labile structures from oxidation were removed.

Oxidised polymer was found to contain peroxides which could be estimated by titration[29] and a variety of C = 0 and C – 0 chromophores appeared in the infrared spectrum.[28,29,32,33]

During oxidation, the molecular weight may either increase through cross-linking or decrease by chain scission. The latter appears to be more important in accelerated oxidation at raised temperatures[29,34] but at ambient temperature both processes take place.[34] The cross-links are most likely to be peroxide bonds since they are broken easily by ultrasound,[35] or even on a precipitation chromatography column.[36]

The crystallisation of polychloroprene aged in air at temperatures between 65 and 100 C° was studied by X-ray crystallographic techniques by Kossler and Svob.[30] They found that the limiting degree of crystallisation was reduced because the new chemical structure could not fit the polymer crystallisation pattern. The rate of crystallisation however was very little affected, suggesting that cross-linking at these temperatures was not important.

(b) Degradation by Ultraviolet Light

After exposure to ultraviolet light the polymer became insoluble. X-ray diffraction photography of films stretched after irradiation, indicated that the crystallites in the polymer were to some extent prevented from becoming oriented in the direction of stretch.[37] Both phenomena are evidence of cross-linking.

Irradiation in solution produced a decrease in molecular weight but the effect was less than in solutions of natural rubber.[38]

(c) Thermal Degradation

In an early study of the pyrolysis of elastomers in air and nitrogen, Skinner and McNeal[39] used a differential thermal analysis (DTA) technique combined with a method of measuring fume intensity. On heating at roughly 35°C/min. to 500°C all elastomers evolved fumes in an exothermic reaction, neoprene having a particularly sharp exotherm. The evolution of hydrogen chloride was also measured and the rate maximum was found to correspond to the peak in the exotherm at about 450°C. Vulcanisation and compounding agents were found not to remove the exotherm and no phosgene was detected when the polymer was heated in air. More recently the DTA curve was recorded at a heating rate of 10°C/min. and the exotherm peak was observed at 377°C.[40]

Torii et al.[41] showed that at a heating rate of 200°C/hour the degradation took place in two stages - elimination of hydrogen chloride followed by decomposition of the residue. Their thermogram shows a small amount of weight loss in the 200 - 300°C region but the main reaction took place between 300 and 450°C. They established that hydrogen chloride did not accelerate the dehydrochlorination.

Neoprene degradation products have been examined by mass spectroscopy. In Wall's experiments[42] the polymer was heated for 20 minutes at 400°C and this treatment removed 68% of the chlorine as hydrogen chloride and yielded 2% monomer. With the belief that very rapid heating rates simplified the product distribution, Zeemany[43] heated polymers on an electrical filament to 1700°C in 5 seconds. The major product from neoprene was found to be chloroprene monomer. It is of interest that the corresponding treatment of PVC yielded hydrogen chloride and benzene, not vinyl chloride.

Chemical methods were devised to test for the pyrolysis products of polychloroprene by Burchfeld,[44] but Feuerberg[45] considered them unreliable and recommended quantitative chlorine analysis of the polymer sample as the best method of identification and estimation of polychloroprene.

Infrared spectroscopy was used by Harms,[46] and Hummel[47] to examine the pyrolysis products. The liquid fraction spectrum indicated the presence of methyl groups and aromatic rings, and the gaseous fraction contained monomer.

Gas chromatographic analysis of the pyrolysis products is also reported. Using a flash pyrolysis temperature of 550°C attained in 7 seconds, and a di-n-decylphthalate column, Voigt found four peaks,[48] the second of which was identified as hydrogen chloride. Sung[49] used a pyrolysis temperature of 450°C and a combination of silica gel and tetra-methyleneglycol dimethyl ether columns, and he observed a complete range of hydrocarbons from C_1 to at least C_4. In neither case were peaks assigned to monomer.

The information in the literature on the degradation of polychloroprene may be summarised thus:-

1. Dehydrochlorination takes place less readily than in PVC unless oxygen is present.
2. Small chain fragments may be produced especially at high heating rates.

3. The residue from dehydrochlorination degrades at higher temperatures just as in the case of PVC.

Purpose of This Work

The study of the thermal degradation of polychloroprene was undertaken in order to attempt to find out more about how the elimination reaction in this polymer proceeded. Because the reactions in PVC are better understood, this superficially analogous polymer was borne in mind throughout the work on polychloroprene in order to determine if the degradations had any common features.

CHAPTER 2

EXPERIMENTAL

Polymer Preparation

(a) Purification of Commercial Polymer

The polychloroprene most used in this work was Butachlor MC30, a gift from the Distillers Company Ltd. This polymer had been prepared in an emulsion system with a mercaptan chain transfer agent. Before use the polymer was purified from stabilisers, soap residues and inorganic fillers by reprecipitation.

Benzene or toluene was used as solvent and the polymer solution allowed to stand so that it could be decanted from the small amount of sediment at the bottom of the flask. The polymer was precipitated and redissolved under nitrogen and 0.01% phenyl β-naphthylamine antioxidant added before filtration. The filtrate was reprecipitated under nitrogen from dilute solution and the resulting white elastic polychloroprene was dried under vacuum for several days during which time it was progressively cut into smaller pieces.

When stored under vacuum in the dark the amount of yellowing which occurred in the polymer was very slight, but when exposed to air it became yellow within hours and gradually darkened to a deep brown. In order to minimise oxidation effects, fresh polymer was purified before starting any set of experiments.

The number average molecular weight (M_n) of the purified polymer was determined to be 156,000 by osmometry (Mechrolab High Speed Membrane Osmometer).

Solutions of polychloroprene containing no antioxidant rapidly became yellow unless the air above the solution was displaced with nitrogen. Toluene solutions of polymer were stored under refrigeration.

(b) Low Temperature Polymerisation

Polychloroprene (PC-40) was prepared at -40°C to determine the effect of structural irregularities on the degradation. The emulsion recipe used was based on that of Johnson and Bebb[50] and employed by Maynard and Mochel[4] in their studies of the effect of polymerisation temperature on the structure of polychloroprene.

Polymerisation was carried out in a 90ml. bulb sealed under vacuum. The ingredients of the polymerisation mixture are shown in Table 1.

Chloroprene was distilled under vacuum from a 50/50 mixture of chloroprene/p-xylene obtained from the Distillers Company Ltd. A second distillation gave a middle cut (20°C at 150mm.) which was shown to be pure by gas-liquid chromatography.

Table 1

Recipe for Emulsion Polymerisation of Chloroprene at -40 C.

Component	Weight (g.)	Volume (ml.)
Chloroprene	20.35	21.3
Water	23.10	23.1
Glycerol	54.30	43.0
Potassium oleate	1.03	
Lissapol NDB(i)	0.72	
Benzoyl peroxide	0.10	
Sodium pyrophosphate (decahydrate)	0.12	
Ferrous ammonium sulphate (hexahydrate)	0.12	
Sorbose	0.12	
Butane thiol	0.04	

(i) A detergent prepared by Imperial Chemical Industries Ltd.

Potassium oleate and benzoyl peroxide were recrystallised from ethanol.

Glycerol was used as an antifreeze but if the experiment were to be repeated, methanol or a methanol / glycerol mixture would be more satisfactory since the high viscosity of pure glycerol led to difficulties in degassing and in emulsification.

Butane thiol was used as a transfer agent in place of the dodecyl mercaptan employed by Johnson and Bebb.

Sorbose, potassium oleate, glycerol and Lissapol were added to the bulb which was then warmed and shaken to assist dissolution. The bulb was attached to the vacuum line and the contents degassed. (The temperature of the liquid had to be raised to about 80 C in order to reduce the viscosity sufficiently for the gas to escape.) The required amount of degassed water was then distilled in from a reservoir and the mixture was thawed and degassed again. Addition of the water reduced the viscosity of the mixture and thus facilitated this process, provided that foaming was kept in control.

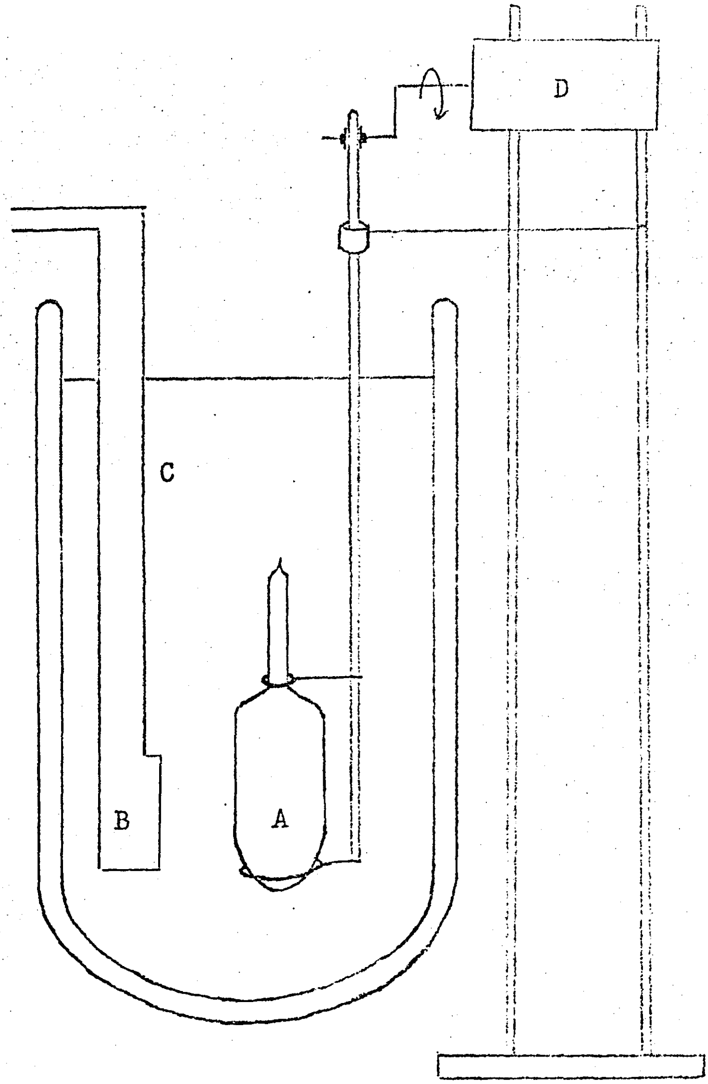
Following complete degassing, the mixture was frozen and the bulb removed from the vacuum line. The remaining components of the initiator system were then quickly added and the bulb returned to the vacuum line. After evacuation, the mixture was thawed in order to let these solids sink into the mass of the glycerol mixture, where some but not all of them dissolved. The required amounts of butane thiol and chloroprene were then distilled in and the stem of the bulb sealed.

The bulb was placed on the arm of a reciprocating shaker inside a thermostat bath at -40°C (Townson and Mercer "Minus Seventy") as shown in fig. 1. The locus described by the bulb three times per second was an oval 1½ inches in the vertical direction and 2½ inches horizontally.

After 48 hours the viscous phase took on a whitish appearance and after 68 hours the bulb was opened and the polymer precipitated in methanol under nitrogen. The precipitate was filtered off and washed with distilled water to remove any residues which might not be soluble in methanol. The polymer was then shaken with benzene under nitrogen and after filtration of the solution, it was reprecipitated in methanol under nitrogen. The precipitate was dried in vacuum at room temperature for 10 days, at the end of which time a Pirani gauge no longer recorded solvent volatilising.

The yield of polymer was 4.3g. (21.5%) and its molecular weight (M_n) was 79,700.

Fig. 1. Apparatus for emulsion polymerisation at -40°C.



A. Bulb containing polymerisation mixture.

B. Heat exchanger of thermostat.

C. Methanol at -40°C.

D. Electric Motor.

(c) Other Polychloroprenes

Chloroprene reacts with atmospheric oxygen to form a labile peroxide which distils with the monomer.[51] No additional initiator is therefore necessary for polymerisation in air or under vacuum, though the rate of spontaneous polymerisation is rather low. Polymers prepared in air and under vacuum and those obtained from other sources are described below.

PC1 was prepared by allowing 40ml. of chloroprene sealed in a 50ml. bottle to stand at room temperature in the dark for 10 days. The polymer was insoluble, but swelled in benzene which was used to remove unreacted monomer.

PC3 was prepared in bulk in air in a dilatometer at 30°C. Before being immersed in the thermostat, the vessel was sealed with a rubber cap which enclosed monomer and air in the volume ratio of 3:1. After 10% polymerisation the polymer was precipitated in methanol, dissolved in benzene and reprecipitated. This polymer was particularly unstable with respect to yellowing.

PC4M resulted from keeping unstabilised monomer in air at 5°C for four months. This polymer was just soluble in benzene and was reprecipitated in methanol.

PC2 was prepared under vacuum without added initiator in a dilatometer at 30°C. Polymerisation was taken to

2% after 3 days and the polymer was reprecipitated as before.

PC4 was prepared under vacuum at 50°C again without initiator. Polymerisation was stopped after 38 hours when 13% conversion had been reached. The polymer was isolated and purified using the benzene methanol system. The molecular weight (M_n) of this polymer was 214,000.

MC30 Fractions 1 and 2.

50g. of purified MC30 were dissolved in 2 litres of benzene at 22°C. 500ml. of methanol were added slowly with stirring and a precipitate formed. This redissolved on heating the solution to 28°C and reprecipitated on cooling again to 22°C. The precipitate (Fraction 1) was filtered off and another 200ml. of methanol added. The precipitate thus formed (Fraction 2) was not redissolved by standing overnight at 30°C and was filtered off. Further addition of methanol to the solution caused the formation of colloidal polymer but no more precipitate could be isolated.

The molecular weight (M_n) of fractions 1 and 2 were 190,000 and 98,500 respectively.

SC20 was another sample from the Distillers Company Ltd. It was a polymer which had been made using the sulphur method of controlling molecular weight.

Neoprene DP was a sample from the Du Pont Company's plant in Northern Ireland. The history of the sample was unknown, but its white colour suggested that it was a mercaptan modified polychloroprene.

Analysis of Configuration by Infrared Spectroscopy

The amounts of each type of unit present in commercial polymer (MC30) and in polychloroprene prepared at -40°C (PC-40) were estimated by the infrared method devised by Maynard and Mochel.[4]

(a) Experimental

Purified MC30 and PC-40 were dissolved in carbon disulphide and carbon tetrachloride to make solutions of accurately known concentration of about 100mg./ml. Carbon tetrachloride was used as solvent above 1000cm^{-1} and carbon disulphide for the region 500-1000cm^{-1}. The whole spectrum 500-4000cm^{-1} was recorded on a Perkin Elmer 225 Grating Infrared Spectrophotometer and the regions 1600-1700cm^{-1} and 750-1000cm^{-1} were rerun on a Unicam SP100 Infrared Spectrophotometer with SP130 Grating in order to make the absorption measurement. Before the spectra were recorded, the wavelength scale of the SP100 was calibrated in the upper regions using the 1696cm^{-1} band of ammonia. The calibration for the lower region was taken from existing tables.

(b) 1:2 and 3:4 Units

The infrared spectra of both polymers in the region

750-1000cm^{-1} are shown in fig. 2. The band at 826cm^{-1} is a measure of total 1:4 polymerisation, the band at 928 and shoulder at 982cm^{-1} are due to the olefinic group in 1:2 units, and the band at 882cm^{-1} to the chlorovinyl group in 3:4 units.

It is evident from fig. 2 that PC-40 has less structural irregularities than MC30. The absorption coefficients determined by Maynard and Mochel for the peaks at 923 and 882cm^{-1} were 11.5 and 18.4 moles/litre/mm. respectively. These figures were used to calculate the percentage of each irregularity in the two polymers.

(c) Cis/Trans Ratio

Since the absorptions of the cis and trans double bonds in polychloroprene overlap, the peak at 1660cm^{-1} contains contributions from both isomers. If the absorptions are assumed to be additive, then the following formulae hold.

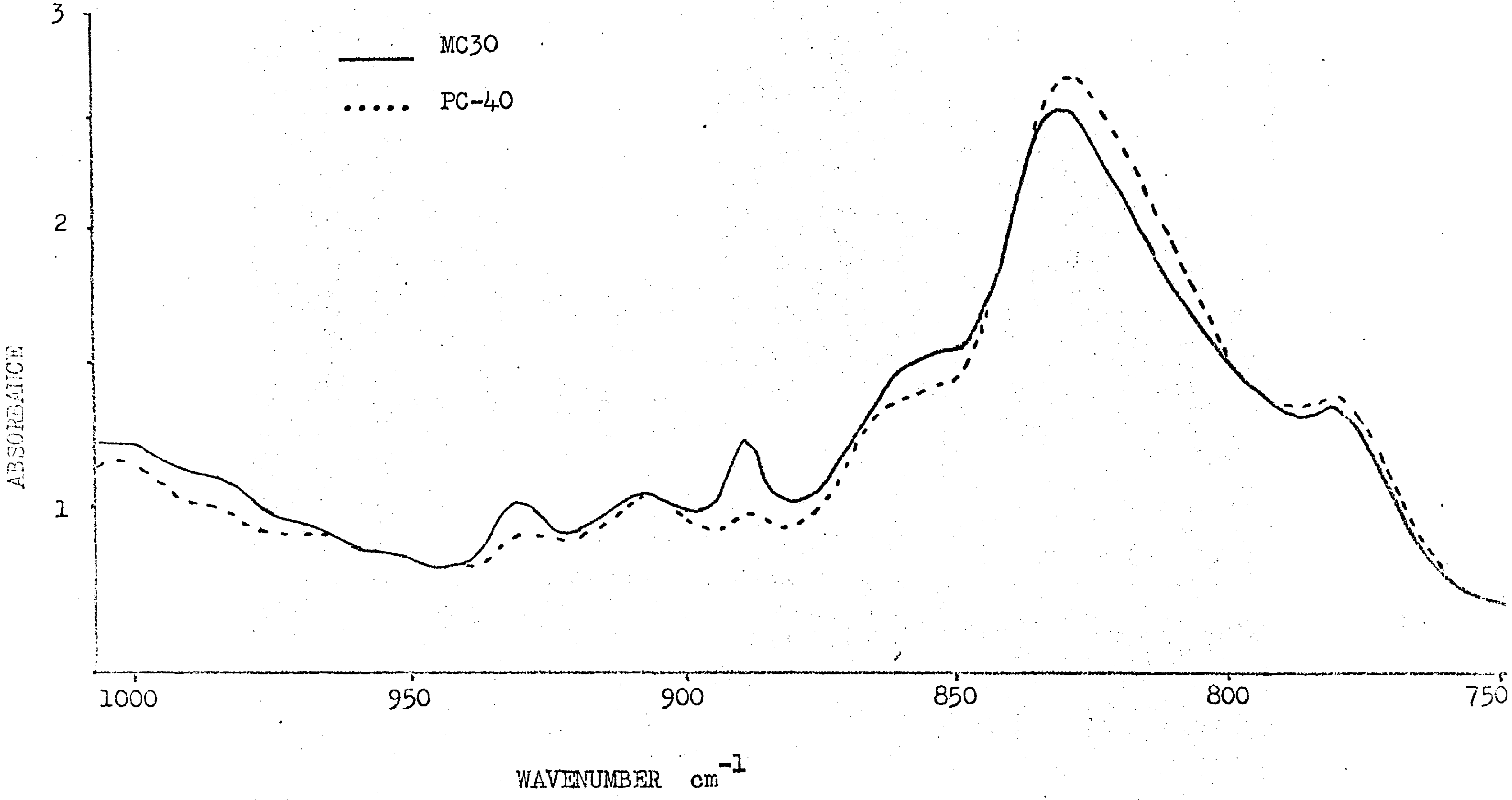
$$A_t/d = \alpha_t^t[T] + \alpha_t^c[C]$$

$$A_c/d = \alpha_c^t[T] + \alpha_c^c[C]$$

thus

$$[T]d = \frac{A_t\alpha_c^c - A_c\alpha_t^c}{\alpha_t^t\alpha_c^c - \alpha_t^c\alpha_c^t}$$

Fig. 2. Infrared spectra of Polychloroprenes in CCl_4 solution.



and

$$[C]d = \frac{A_c\alpha_t^t - A_t\alpha_c^t}{\alpha_t^t\alpha_c^c - \alpha_t^c\alpha_c^t}$$

where

[T] is molar concentration of the trans isomer,

[C] is molar concentration of the cis isomer,

d is cell length (mm.),

A_t is absorption at maximum for the trans isomer i.e. 1660cm^{-1},

A_c is absorption at maximum for the cis isomer i.e. 1652cm^{-1},

α is absorption coefficient.

Superscript indicates the isomer.

Subscript indicates at which wavelength it applies i.e. t, the maximum for trans, 1660cm^{-1} and c, the maximum for cis, 1652cm^{-1}.

The original set of values for α were obtained by Maynard and Mochel for model compounds, but were improved by Ferguson[52] following the discovery of a stereospecific synthesis of cis polychloroprene.[53] Ferguson's values, shown in Table 2, were used to determine the amount of cis and trans isomers in each polymer.

Table 2

Wavenumber	α^t	α^c
t 1660cm^{-1}	2.65	1.63
c 1652cm^{-1}	1.35	2.39

The overall analysis of the polymer, showing the amount of each type of unit determined from the infrared spectrum, is given in Table 3. The figures for cis and trans percentages were normalised so that when added to the figures for 1:2 and 3:4 units, the total came to 100%.

Table 3

Microstructure of Polychloroprenes Determined by Infrared Spectroscopy.

Unit	Percentage			
	MC30		PC-40	
	Determined	Normalised	Determined	Normalised
1:2	1.1	1.1	0.5	0.5
3:4	1.2	1.2	0.4	0.4
1:4 trans	78.6	82.4	104.5	94.2
1:4 cis	14.6	15.3	5.5	4.9

Thermal Volatilisation Analysis (TVA)

(a) Principle

TVA was used as the primary means of characterising the degradation. The technique has been described by McNeill elsewhere,[54,55] but for convenience a brief account is given here.

The sample is heated in a continuously evacuated tube at a linear rate of temperature rise. Pirani gauges are situated between the sample tube and the cold traps of the vacuum system and these respond to the increase in pressure when degradation products are distilling from the hot zone. The Pirani output, which is recorded as a function of temperature, is related to the rate of degradation on a non-linear scale which varies from one product to another. A TVA curve is thus an empirical measure of the rate of degradation as a function of temperature.

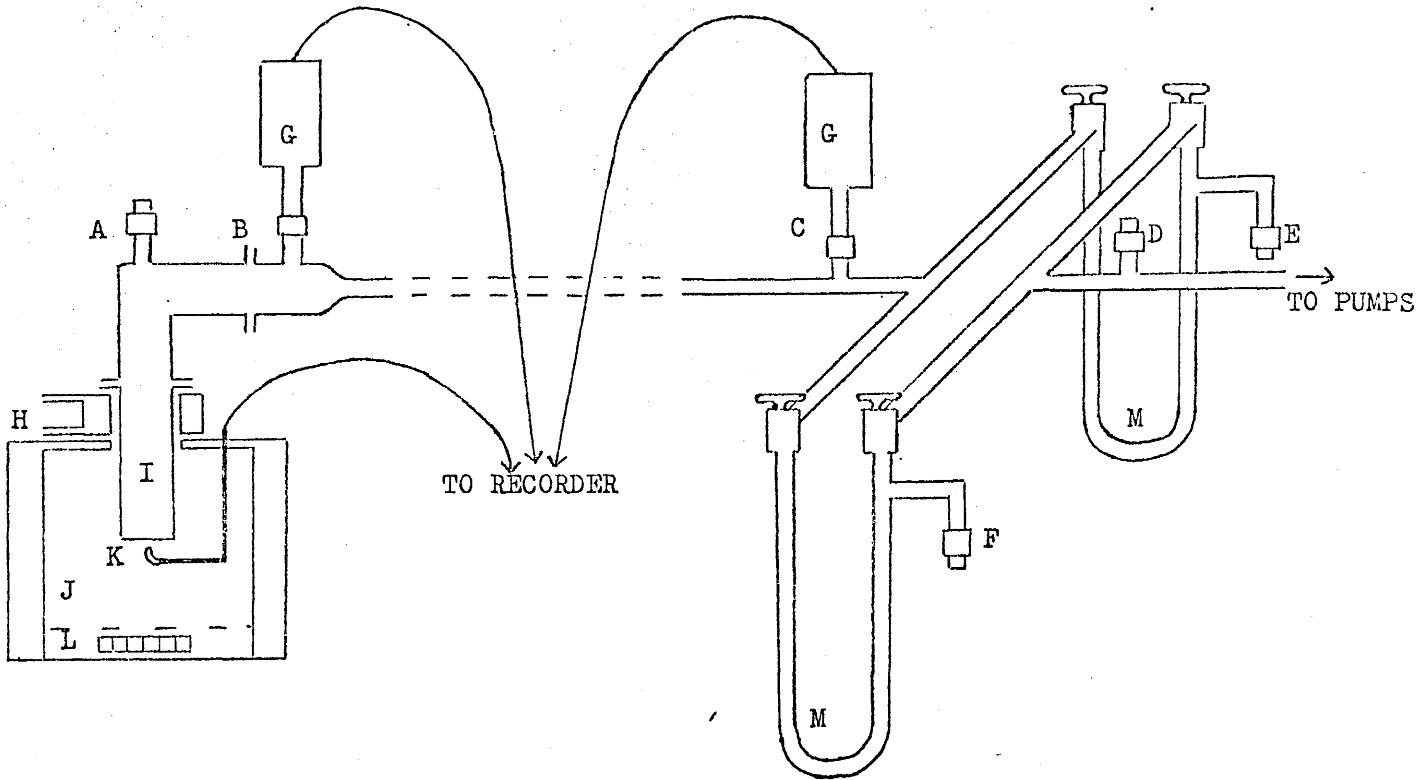
(b) Apparatus

The apparatus used is shown in fig. 3. Pirani gauges at B and C responded to all the volatile products, but if one of the gauges was repositioned at D, behind the cold trap, then a response was obtained for only those products which were not condensed in liquid nitrogen.

The alternative route trap system was designed to allow a portion of the products to be collected in one trap, which could then be closed off and the other trap used, so that the conditions of degradation were very little disturbed. Products could be distilled out of the trap through arms E or F to another vessel.

The oven was a Perkin Elmer F11 Precision oven with

Fig. 3. TVA Apparatus



A	Thermocouple inlet				
B,C,D	Positions for Pirani gauges				
E,F	Attachment Points for Collector vessels				
G	Pirani Gauge	H	Water Cooled Ring	I	Degradation Tube
J	Oven	K	Oven Thermocouple	L	Oven Fan
M	Cold Trap				

Linear Temperature Programmer. The gauges and control unit were Edwards High Vacuum model 8/2. A Leeds and Northrup Speedomax H 12 channel multipoint recorder was used to record the emf from the thermocouple and the Pirani gauges. The chart speed was normally 12 inches/hour though a speed of 30 inches/hour was available.

(c) Temperature Calibration

The recorder was operated with a 10mV. range card and a 2.5/1 potential divider on the temperature channel. The reading obtained on the chart by applying known potentials through the potential divider to the recorder was determined and thus the chart reading could be related to temperature by the use of chromel alumel thermocouple tables.

The temperature reading obtained during degradation was measured by the oven thermocouple. Since it was the sample temperature which was of interest, and this was different due to the thermal gradient across the base of the degradation tube, it was necessary to calibrate the tube for the temperature lag at the various heating rates used in this work.

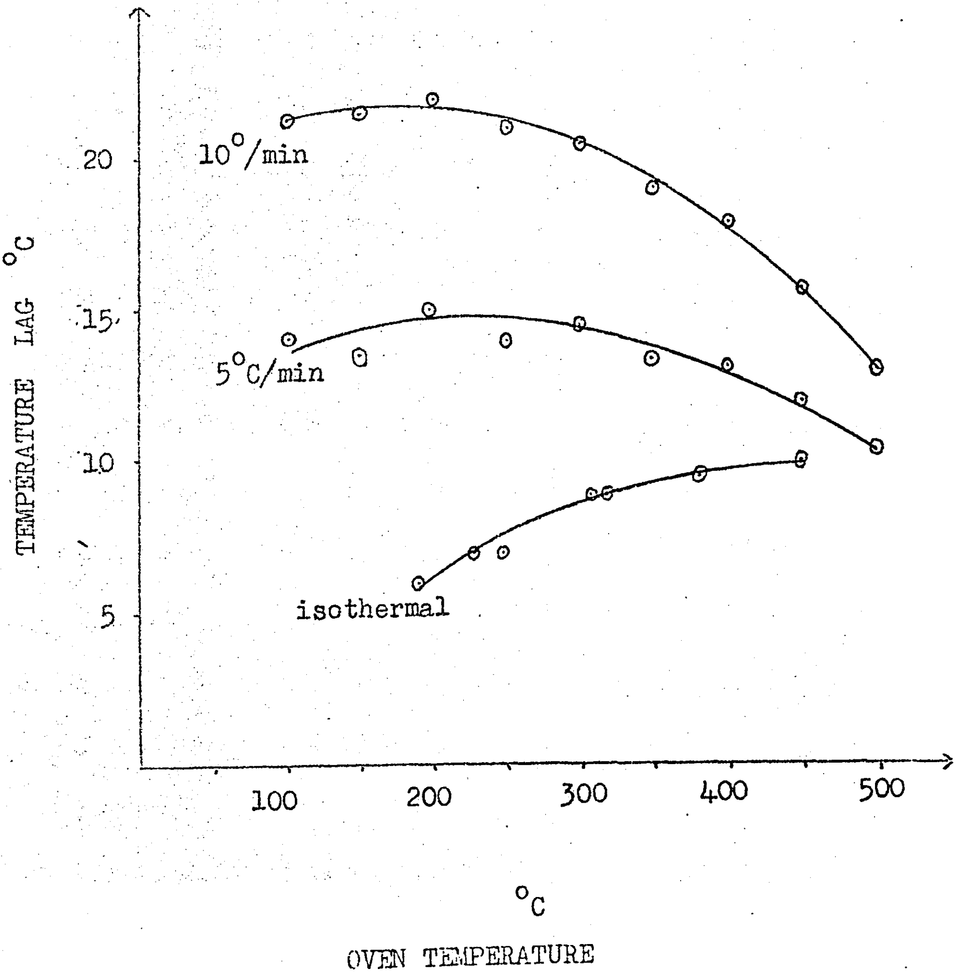
An internal thermocouple was introduced through the socket A in fig. 3 and the junction pressed against the tube base which was covered in a thin film of Apiezon L grease to improve thermal contact and simulate sample conditions. The internal and external temperatures were measured on the recorder by discarding the potential divider and replacing the 10mV. range card with one made specially for chromel alumel thermocouples in the range 0 - 600°C. No reference junctions were required, since this range card embodied an internal compensator. The chart paper was changed for a type which read temperature directly when used in conjunction with the special range card.

The difference between internal and oven temperatures was measured from the chart paper every 50°C. Fig. 4 shows the mean results from 7 calibration runs at 10°/min. and 5 runs at 5°/min., together with the isothermal lag at various temperatures.

(d) Calibration of the Pirani Gauges to Hydrogen Chloride

In order to obtain quantitative results from the TVA system it was necessary to calibrate the Pirani gauges to the flow of hydrogen chloride. This was prepared by allowing Analar hydrochloric acid to drip on to concentrated sulphuric acid. The gas was passed through sulphuric acid to remove any remaining traces of water, and collected by freezing at liquid nitrogen temperatures. The material thus collected was degassed by successive warming to -110°C in melting ethanol and pumping out while frozen in liquid

Fig. 4. Temperature lag vs Oven Temperature (Pyrex Tube)



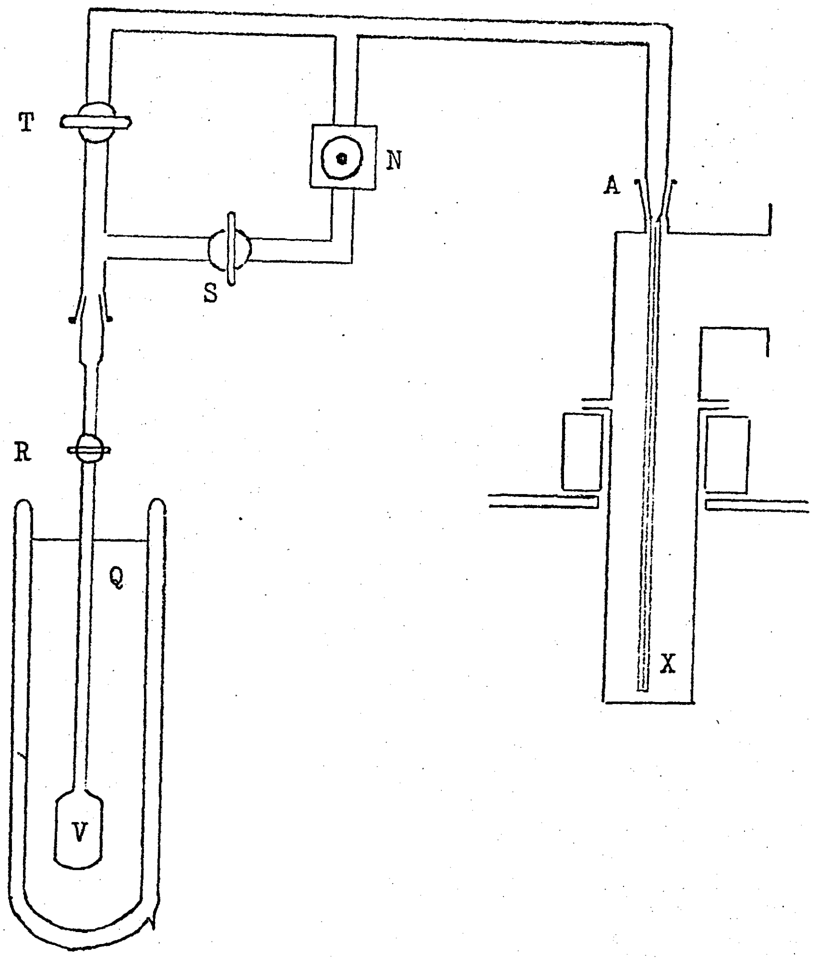
nitrogen. Hydrogen chloride was then distilled at -110°C to the long stemmed vessel V shown in fig. 5, in which it could be kept at liquid nitrogen temperatures until required for a calibration.

The experimental arrangement (fig. 5) was similar to that used by Neil[56,57] in calibrating for common liquids arising from polymer degradation. In the case of hydrogen chloride however the amount of material which had passed through the system was estimated at the trap, rather than at the reservoir.

With V in liquid nitrogen all taps were opened and the system pumped out. The by-pass tap T was then shut and the liquid nitrogen round V replaced with ethanol at -110°C. The needle valve N was adjusted so that the required Pirani output was recorded. When the response was steady, the "U" traps were switched and the hydrogen chloride was collected for a suitable time (15 min. - 3 hours depending on the rate). During the calibration the liquid nitrogen round the "U" trap had to be kept topped up and the needle valve constantly adjusted to keep the rate steady, while the ethanol bath slowly warmed up.

At the end of the calibration, the taps on the "U" trap were closed and the hydrogen chloride distilled on to the surface of 5ml. of frozen distilled water which was contained in a 50ml. flask attached to the side arm of the trap.

Fig. 5. Apparatus for calibration of Pirani Gauges to HCl.



A.	Socket in TVA system as in fig. 3.
N.	Needle Valve.
Q.	Melting ethanol.
R,S,T.	Stopcocks.
V.	Container for HCl.
X.	Capillary inlet.

When thawed the solution was titrated against 0.1M sodium hydroxide using phenolphthalein indicator.

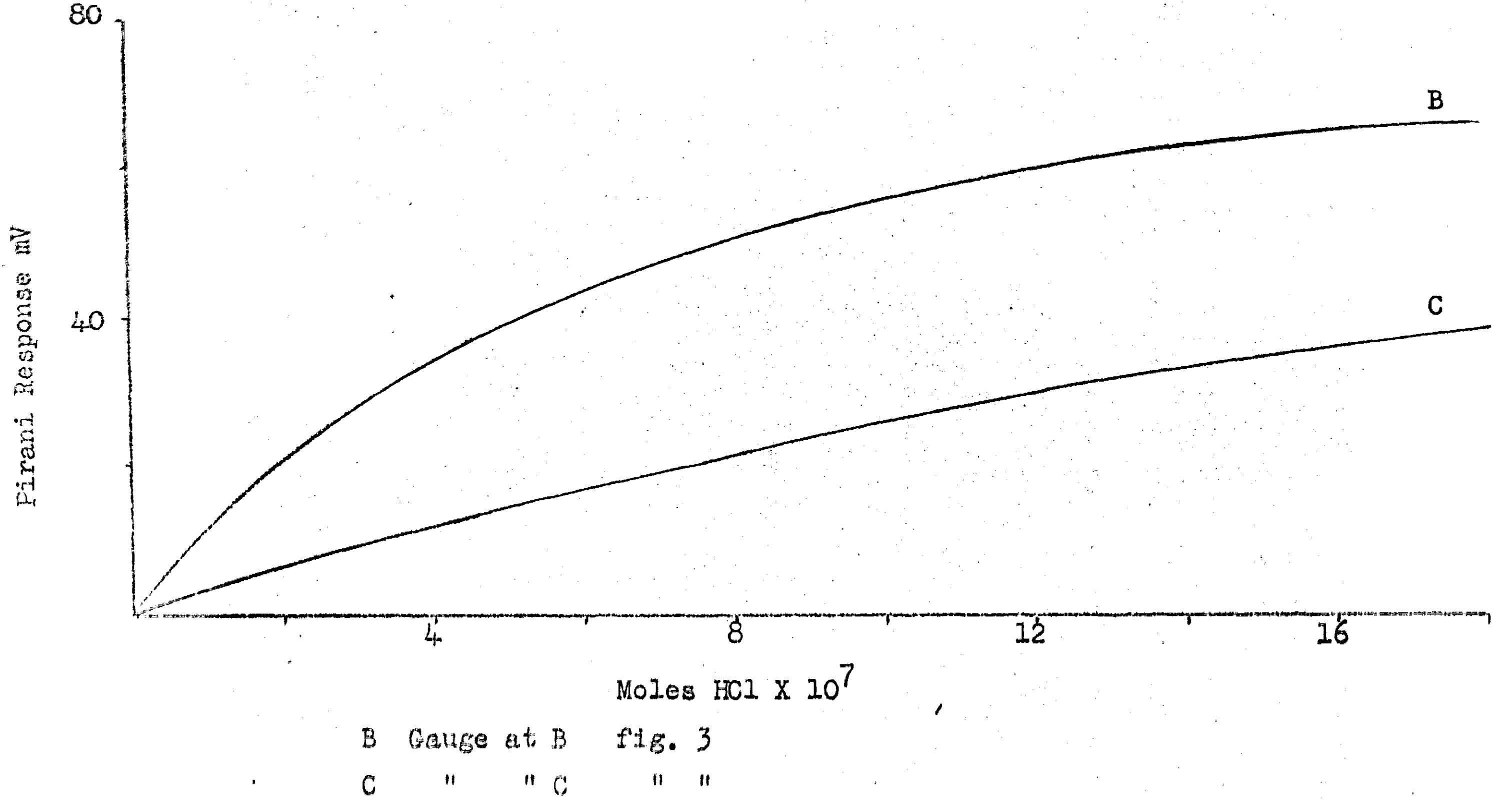
The average Pirani response within each ½ inch (2½ min.) division on the chart was estimated and the figure used to calculate the mean response during the run. In any run the maximum deviation of a division average from the mean value for the run was less than 0.2mV. and in most runs the deviation was kept below 0.1mV. The results of 42 experiments were plotted on a graph of Pirani response versus flow rate of hydrogen chloride (fig. 6). The shape of the graph is the same as the calibration curves determined by Neil for other substances. The values of the Pirani response for a given flow rate for hydrogen chloride and for water are of the same order.

It must be emphasized however that the calibration data are only strictly applicable to the TVA system on which they were obtained. Not only does each Pirani gauge head respond slightly differently under the same conditions, but also any changes in the dimensions of the system or of the positions of the gauges can cause a different pressure to be experienced. The apparatus used in this work was very similar in construction to that used by Neil.

(e) Differential Condensation (DC) TVA

In the simple TVA apparatus described above, products

Fig. 6. Pirani Response vs Flow Rate of HCl



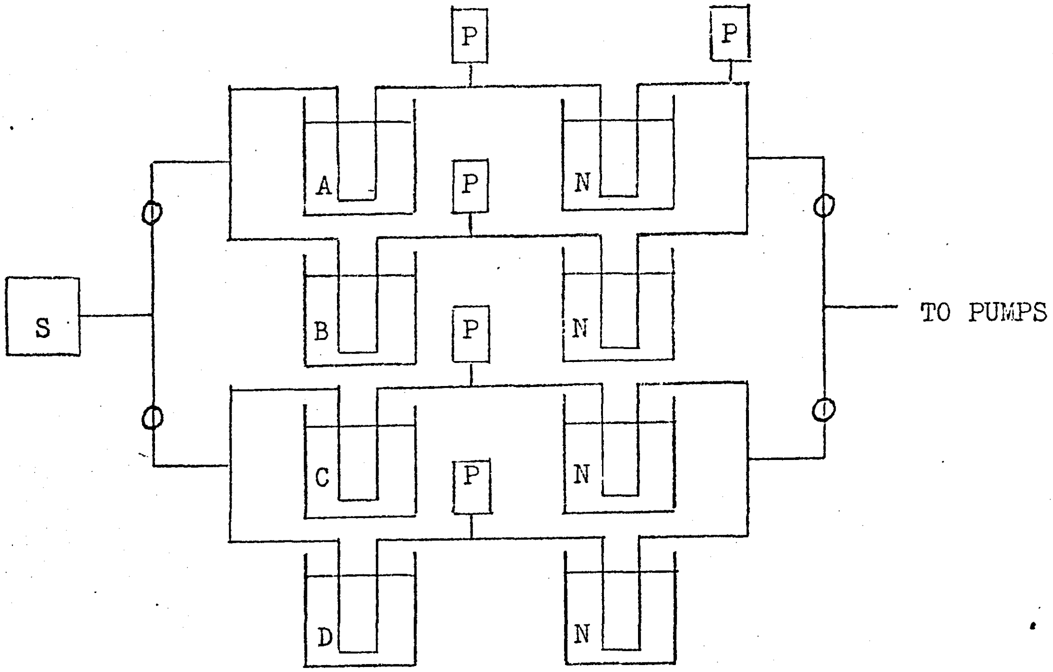
may be classified by whether or not they are condensable in liquid nitrogen. This principle of differential condensability may be extended by the use of other traps at different temperatures as described recently by McNeill.[58,59]

A schematic diagram of the apparatus is shown in fig. 7. The vacuum system between the hot zone and the pumps is split into four parallel lines, each of which consists of two "U" traps with a Pirani gauge to record the pressure in the short line between them. The trap nearer the sample is maintained at 0, -45, -75, or -100°C, and the second trap is kept at -196°C using liquid nitrogen. A fifth gauge is situated after one of the -196°C traps.

The gauges are connected to the control unit and recorder through variable potentiometers which are adjusted so that the responses from the gauges are as close as possible throughout the pressure range when a completely non-condensable gas is passed through the system.

The Pirani gauges respond to any material which is not completely condensed in the preceding trap. Substances which are not condensed at all, produce a normal TVA curve, but if partial condensation occurs, the material distills from the trap at a constant rate which is related to its vapour pressure at the trap temperature and the dimensions of the apparatus.

Fig. 7. Differential condensation TVA apparatus.



S.	Heated Sample.
ϕ	Stopcock.
P.	Pirani Gauge.
A.	Trap at 0°C. (ice)
B.	" " -45°C. (EtOH)
C.	" " -75°C. (EtOH/CO_2)
D.	" " -100°C.(EtOH)
N.	" " -196°C.(liq. N_2)

This behaviour is known as the "Limiting Rate Effect" and characteristic "limiting rates" enable some degradation products to be identified from the DC-TVA curves.

If the flow rate of the partially condensable material is too low to register a Pirani response equal to the limiting rate, then no limiting rate effect is observed since the trap never reaches saturation conditions.

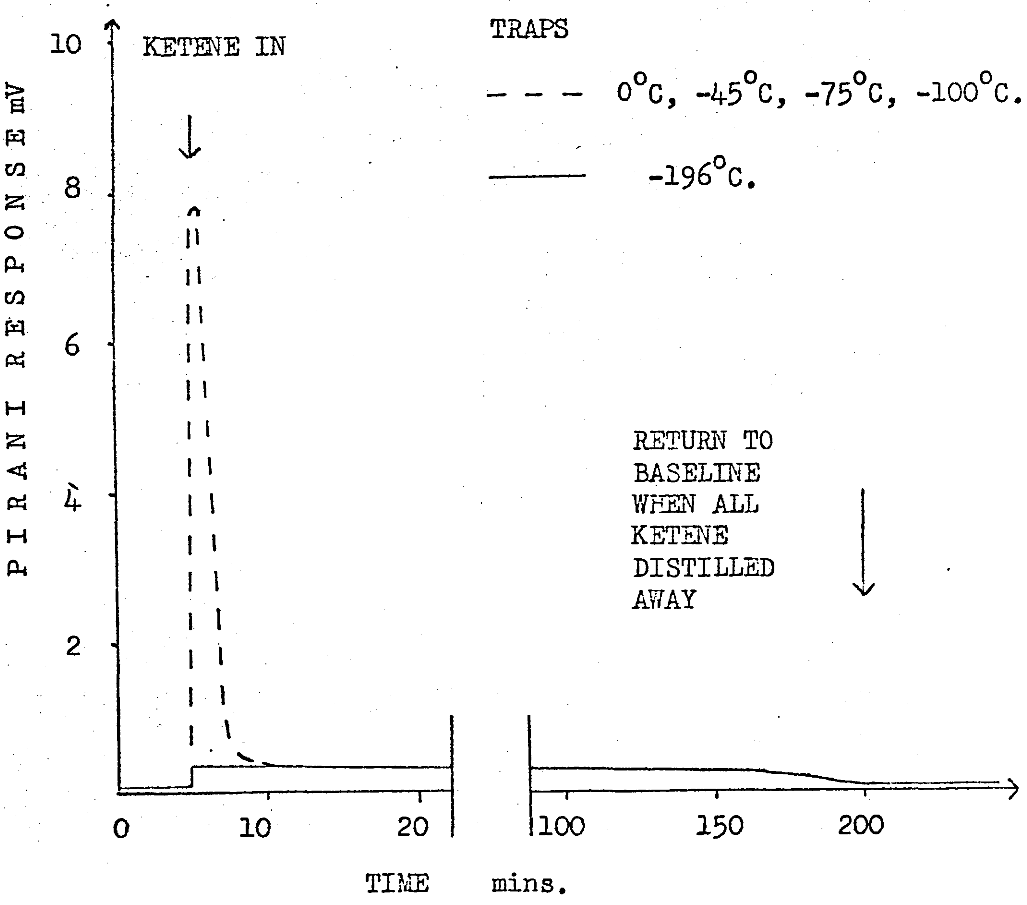
(f) Condensibility of Ketene in the Apparatus

The behaviour of many common polymer degradation products has already been recorded.[58,59] During this work ketene was added to the list of such substances.

A reservoir containing a small amount of ketene was fitted to the DC-TVA apparatus through a similar system to that used for hydrogen chloride calibration (fig. 5) so that the gas passed over the tube base and then through the traps. The Pirani traces obtained in the experiment are shown in fig. 8.

Too little material was present to maintain steady flow conditions but the Pirani responses when the needle valve was opened briefly, showed that ketene was non-condensable at all temperatures except -196°C. The gas was almost completely condensed at this temperature, but did exhibit a very small (0.3mV.) limiting rate. Distillation from the -196°C trap created a back pressure at the other Piranis

Fig. 8. Pirani Traces obtained on introduction of Ketene into DC-TVA apparatus.



equal to the limiting rate.

Dimerisation or decomposition would be expected to produce changes in the pattern of Pirani response but none was observed when the gas was passed over the degradation tube base at about 400°C.

To date ketene is the only substance which has been shown to have a limiting rate in the DC-TVA apparatus at -196°C.

Thermogravimetry (TG)

TG is a well established thermal analysis technique in which the weight of a sample is continuously recorded while the temperature is raised linearly. TG curves quickly provide a measure of the total extent of degradation, but require to be differentiated to obtain rates of reaction. The temperatures at which rate maxima occur are much less accurately measured than in TVA.

TG curves were obtained from a Du Pont 900 Differential Thermal Analyser with accessory 950 TG module. The thermobalance was of the null deflection type employing a photoelectric system to detect and compensate for movements of the quartz beam from which the platinum sample pan was suspended. The heat was supplied by a programmed furnace into which the silica tube enclosing the balance beam, sample pan and thermocouple slid horizontally. 10 - 20mg. samples were degraded in an atmosphere of nitrogen flowing at 50ml./min.

TG had the advantage that it could be used to study degradation in the region 500 - 1000°C which was inaccessible by other techniques.

Differential Thermal Analysis (DTA)

DTA is a well known thermal analysis technique in which the temperature difference between the sample and an inert reference material in the same thermal environment, is measured as the temperature is raised (or lowered) linearly. All types of exo- or endothermic processes are recorded in DTA. The heat energy involved may be associated with chemical reactions such as oxidation or degradation, or with physical changes such as melting, glass transition, etc.

DTA curves were obtained from the Du Pont 900 Differential Thermal Analyser. 10 - 20mg. of polymer were packed into a small glass tube and a thermocouple forced down so that the junction pierced the polymer mass. The reference thermocouple was positioned in a similar tube containing small glass beads. Sample and reference tubes fitted into a programmed heating block contained in a glass dome through which nitrogen passed at 1 litre/min.

Gas Product Analysis

(a) Infrared Spectroscopy

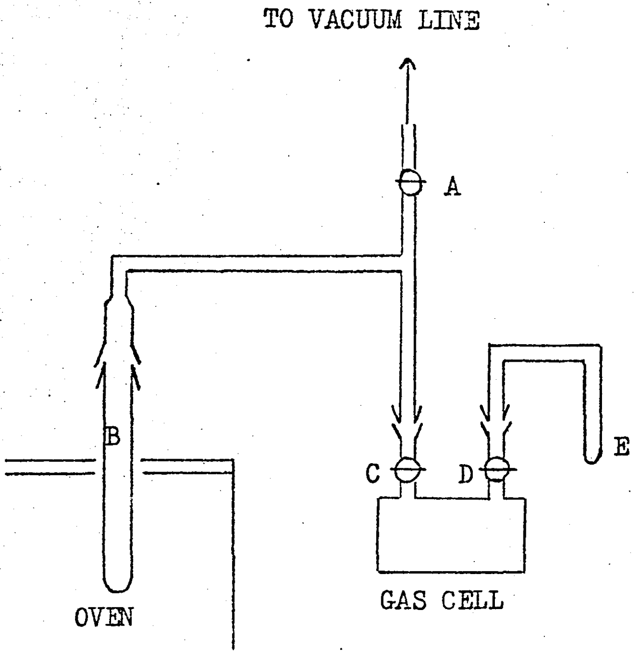
The gases were collected in a 10cm. gas cell and the spectrum recorded on a Perkin Elmer 257 Spectrophotometer. The experimental arrangement is shown in fig. 9. 200mg. of polymer were weighed in the tube B and the whole system was evacuated through tap A. The small finger trap E was surrounded by liquid nitrogen and the sample was heated at 5°/min. By suitable manipulation of taps A and C the gas products from a selected temperature range could either be collected or pumped off. After degradation, tap C was closed, E was warmed to room temperature, then D was closed and the cell removed to the spectrophotometer.

(b) Gas Chromatography

A much modified form of the Gallenkamp Junior Gas Chromatograph with a thermal conductivity detector was employed. The apparatus is shown diagramatically in fig. 10.

The sample was weighed in the tube Z and the pyrolysis vessel was evacuated through tap X. The vessel was then removed to the oven and heated at 5°/min. to a selected temperature and then cooled rapidly. During the degradation the trap Y was immersed in liquid nitrogen. The pyrolysis vessel was fitted to the chromatograph and Y was warmed to -110°C by immersion in a bath of melting ethanol. At this

Fig. 9. Apparatus for collection of products in infrared gas cell.

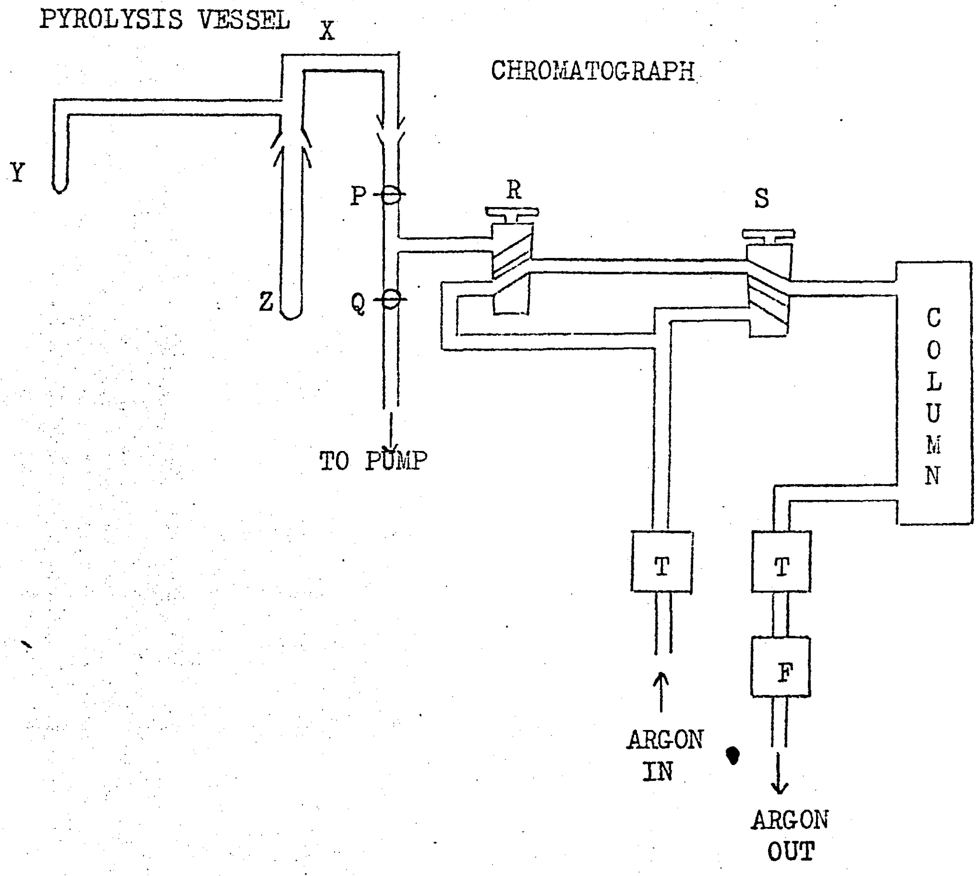


A,C,D. stopcocks

B. sample tube

E. finger trap

Fig. 10. Apparatus for Gas Chromatography.



T.	Thyristor.
F.	Flow Meter.
R,S.	Three way taps.
P,Q,X.	Stopcocks.
Y.	Finger Trap.
Z.	Degradation tube.

temperature hydrogen chloride was condensed and there was no risk of flowing out the stopcocks or the ground glass joints in the system.

The space from Q through R to S and between P and X was evacuated and then Q was closed. Tap X was opened and the sample expanded into the chromatograph inlet system up to S. The sample was introduced into the carrier gas flow by turning R and S simultaneously so that the stream was diverted to the upper route through R and S. For the second sample injection P was closed and R and S rotated so that when Q was opened the space QPS was evacuated. When Q was again closed, P was opened and the sample expanded as before.

A 16 feet silica gel column at room temperature with an argon carrier gas flow rate of 24ml./min. was used. Under these conditions retention times were found to be 6 minutes for hydrogen and 9 minutes for methane.

A series of degradations with programmed heating at 5^{o}/min. up to different temperatures was carried out. For each sample three injections were used and the mean taken, for although about 3% of the sample was lost at every injection the rise in the temperature of the trap round Y tended to counteract this trend. The method of paper cut outs was used to find the integrated peak area. The weight of the paper enclosed by the peak and the base line was determined and multiplied by the recorder attenuation factor to give an arbitrary measure of the area under the peak. The greatest error in this process was in the estimation of the base line especially if this was sloping due to changes in room temperature.

In order to relate the peak area to the amount of gas present, the pyrolysis vessel was filled to known pressures with hydrogen or methane from a cylinder. The pressures, which were measured on a mercury manometer at 20°C were 12, 16, 22mm. for hydrogen and 76, 152, 185mm. for methane. The vessel was attached to the chromatograph with limb Y at -110°C and the gas sampled three times as before.

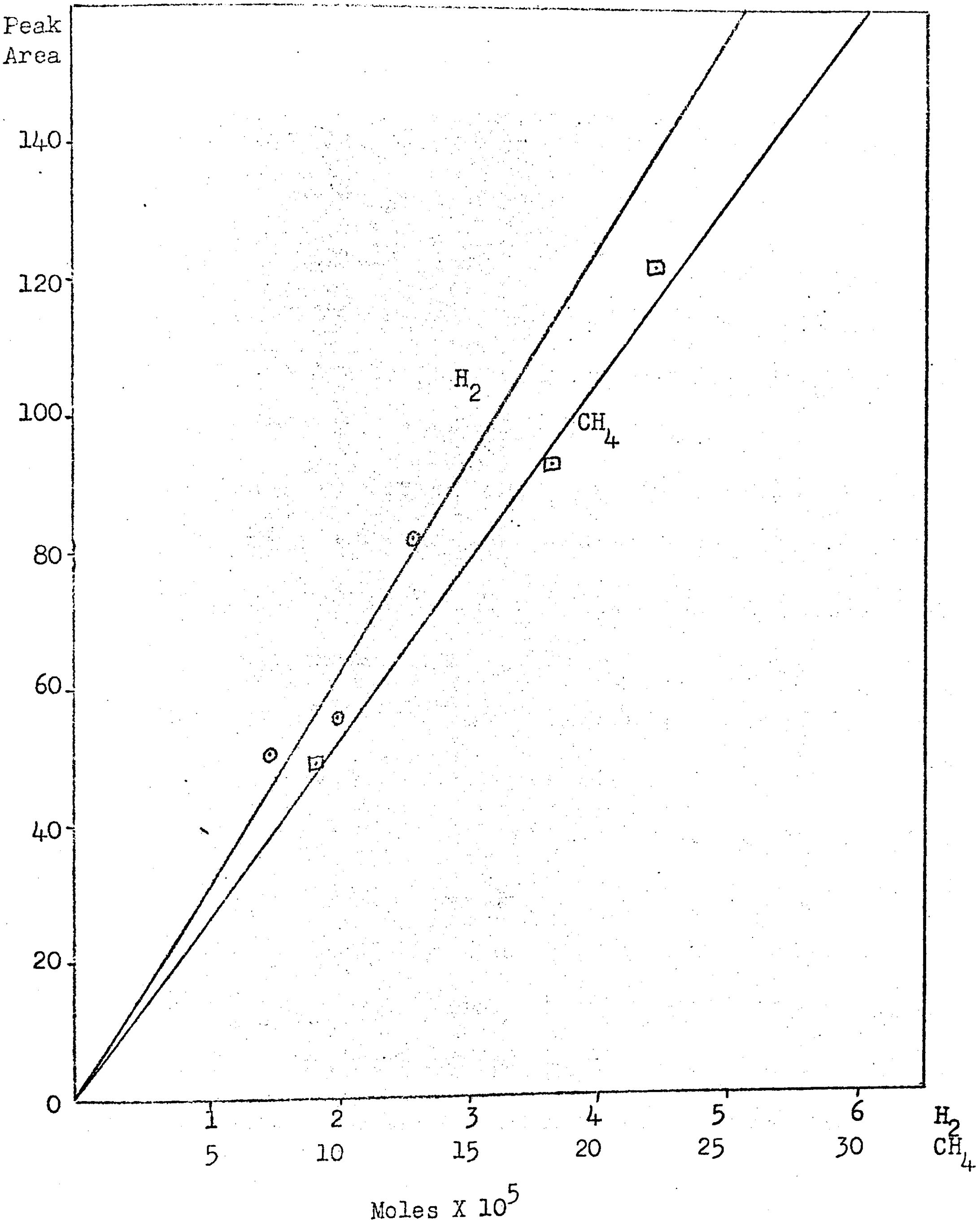
The volume of the pyrolysis vessel was determined as 22ml. by measuring the gain in weight when filled with water.

Fig. 11 shows the results of the calibration.

Collection of Liquid Products

A number of methods were employed to collect the volatile liquid products of polychloroprene degradation. All appeared to give one major component when examined by thin layer chromatography (tlc). The yield of this product was so small that a large amount of polymer had to be degraded to an advanced extent of reaction in order to obtain a significant quantity of liquid.

Fig. 11. Chromatograph Calibration for H_2 & CH_4.



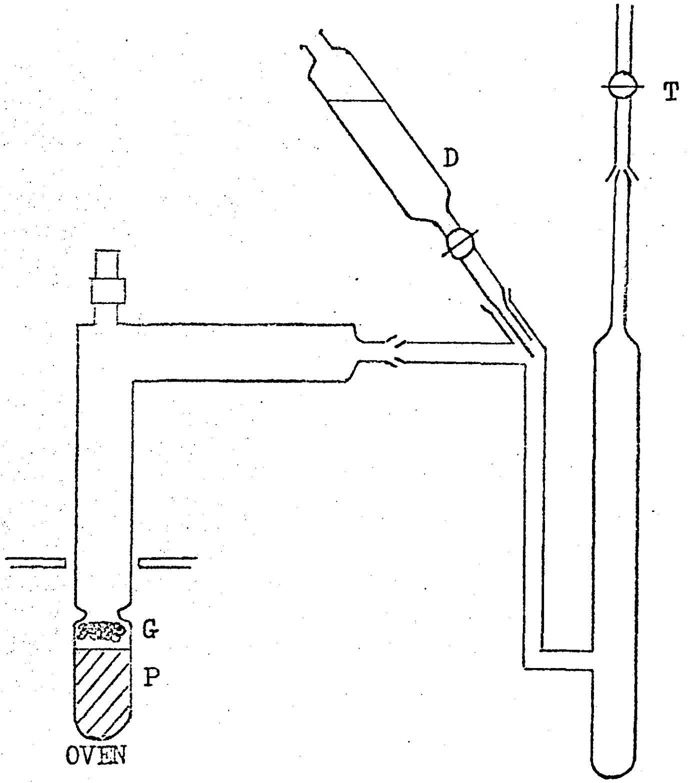
It was found that when a large mass of polymer was heated above 300°C a very violent degradation occurred. This "flash" pyrolysis was presumably due to the heat of reaction not being lost and thus causing the sample temperature to rise very quickly.

Another problem was that the hydrogen chloride produced in the degradation reacted quite readily with the liquid to form a red viscous gum. A product separation trap at -100°C was tried but the best method appeared to be to collect all the products at liquid nitrogen temperatures and neutralise the acid with sodium carbonate solution.

The apparatus used for collecting and neutralising the products is shown in fig. 12.

10g. of MC30 was cut into small lumps and placed in the degradation tube followed by a plug of glass wool used to prevent the polymer from rising above the constriction if "flash" pyrolysis occurred. The system was continuously evacuated through tap T while the sample was heated at 5°/min. to 300°C, then at 1°/min. to 380°C and then again at 5°/min. to 410°C. When the sample had cooled T was closed, and immediately the liquid nitrogen around the trap had been removed, warm concentrated sodium carbonate solution was added from the dropping funnel. The solution froze on contacting the cold glass, but as it melted it reacted with

Fig. 12. Apparatus for collection of liquid products.



T.	Tap on vacuum line.
D.	Dropping funnel.
G.	Glass wool plug.
P.	Polymer (small lumps).

the hydrogen chloride.

When the carbon dioxide pressure had built up to nearly atmospheric the trap was released from the vacuum line and after the effervescence had ceased, the solution was poured out into a separating funnel. The trap was washed with water and then several times with ether, all the washings being collected in the separating funnel. The aqueous layer was run off and extracted several times with ether, which was combined with the original layer. This ethereal solution was then extracted once with dilute sodium carbonate and then several times with distilled water. The solution was then run into a flask and dried over magnesium sulphate. On evaporation of this solution about 400mg. of a brown-yellow oil were obtained.

Some of the oil could be distilled on a vacuum line and then purified by tlc or it could be chromatographed directly, the distillation serving only to remove the brown products which did not move from the base line of the tlc plate.

A sticky green cold ring fraction collected at the top of the degradation tube and a brown tar collected below this. The tube was broken at the division between these two fractions and the upper one was dissolved out in ether or toluene while the lower part, including the residue was extracted with chloroform from which a brown pitch was recovered on evaporation.

Spectroscopy of the Residue

The chemical changes which degradation produced in the polymer were qualitatively examined by infrared and ultra-violet spectroscopy. The polymer was degraded in the TVA apparatus at 5°/min. and when a predetermined point in the thermogram was reached the oven was rapidly cooled. Points throughout the temperature range were selected in order to give as complete a picture as possible of the changes occurring.

(a) Infrared

A Perkin Elmer 257 Infrared Spectrophotometer was used to record the spectrum of the sample in the form of a film or of a finely ground powder in a potassium bromide matrix. Apart from a small range of overlap, the sample form was dictated by the fact that residues below 390°C were impossible to grind, and above 410°C films started to break up.

Powder samples were obtained from the degradation of small lumps of polymer. Film samples were prepared by the evaporation of about 0.5ml. of 50mg./ml. polymer solution in toluene on 9mm. diameter sodium chloride discs. Before degradation the spectrum of the film was recorded to check that the film thickness was comparable with the others of the series. The disc was heated in the TVA tube with the polymer surface uppermost. The extra temperature lag caused by the 4mm. layer of rock salt between the polymer and the tube base was determined to be about 19°C by comparison of the TVA curves from the degradation of film on discs and cast on the tube base directly.

(b) Ultraviolet

Because of the insolubility of the degraded polymer and because unsupported films of suitable thickness were found extremely difficult to handle, the ultraviolet spectra investigated were of films degraded on a silica glass support.

TVA degradation tubes with overall length 115mm. were constructed in silica glass to fit the sample cavity of the Unicam SP800 Spectrophotometer used in this work. The light loss due to absorption and reflection by the 2mm. thick silica window forming the base of the tube was found to be only 10% and to be entirely compensated by an identical tube placed in the reference beam of the instrument.

The temperature lag was found to be about 6°C greater for the shorter tubes by comparison of the TVA curves obtained using silica and Pyrex degradation tubes.

Films were cast on the tube base (10sq. cm. in area) by evaporating 1ml. of a solution of polychloroprene in toluene in a vacuum oven at room temperature. 20mg. films were used to study the early part of the degradation process and 2mg. films for the later stages.

A variety of other polymers were also examined by this technique for comparison purposes. These films were made from 100mg. or 20mg. of polymer dissolved in a suitable solvent.

The spectrophotometer directly recorded absorbances up to a value of 2. When the intensity of absorption increased beyond this value a filter with an absorbance value of 1 was placed in the reference beam and this conveniently extended the range of the instrument to a value of 3. For absorption higher than this, the zero control of the machine was reset and the intense part of the spectrum recorded again with sufficient overlap to enable the strong absorption to be superimposed on the spectrum at the correct level.

Above an absorbance value of about 3, the detectors in the instrument received too little light for accurate photometry. The noise level increased and the definition was drastically reduced. Spectra with maxima above 3 were therefore only included because they completed the series and were expected to be more or less featureless.

CHAPTER 3

THERMAL ANALYSIS

Thermal Volatilization Analysis

(a) MC30

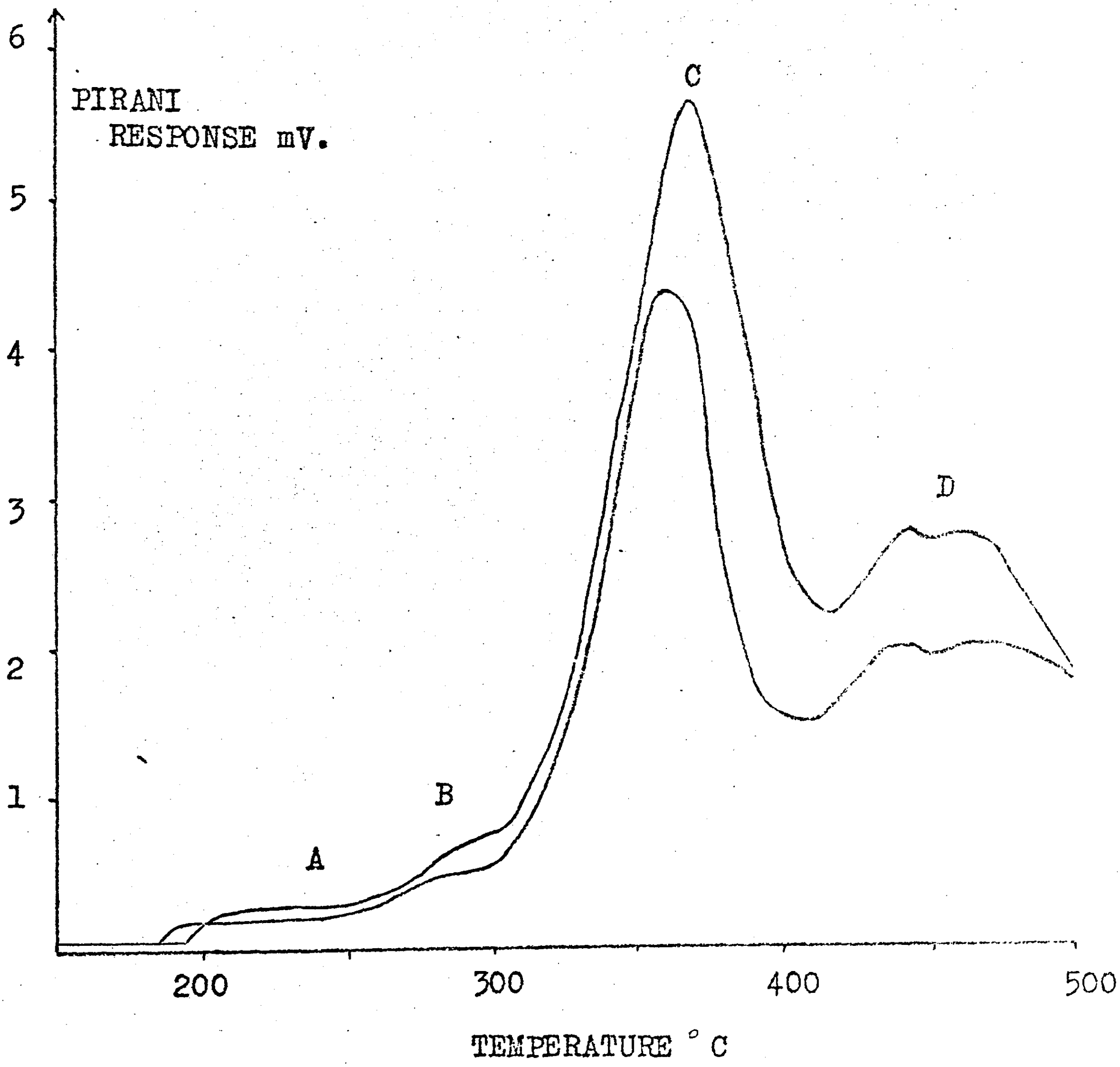
The TVA curves at heating rates of 5 °/min. and 10 °/min. for purified MC30 are shown in fig. 13. The lower heating rate gives peaks at reduced temperatures with smaller maximum rates. The main peak C is for the dehydrochlorination reaction and the secondary decomposition of the residue causes peak D. A small amount of degradation takes place below 300 °C, occurring in two stages indicated A and B in the diagram.

Sample form caused some changes in the TVA curves. Films showed a smooth peak for the secondary decomposition reaction D (fig. 14) whereas lumps gave an irregular plateau after an initial smooth rise (fig. 13). Films gave a slightly broader peak C, with a lower maximum rate, but the position of the maximum was not significantly affected.

The residue at the end of the TVA degradation was a black carbon coke. It appeared that melting did not occur until about 450 °C because if the degradation was interrupted before this point, the sample form had not changed. Lump samples also showed a break in peak D about

Fig. 13

TVA curves for MC30 at different heating rates, 30mg. samples as small lumps.



Upper curve 10°/min.

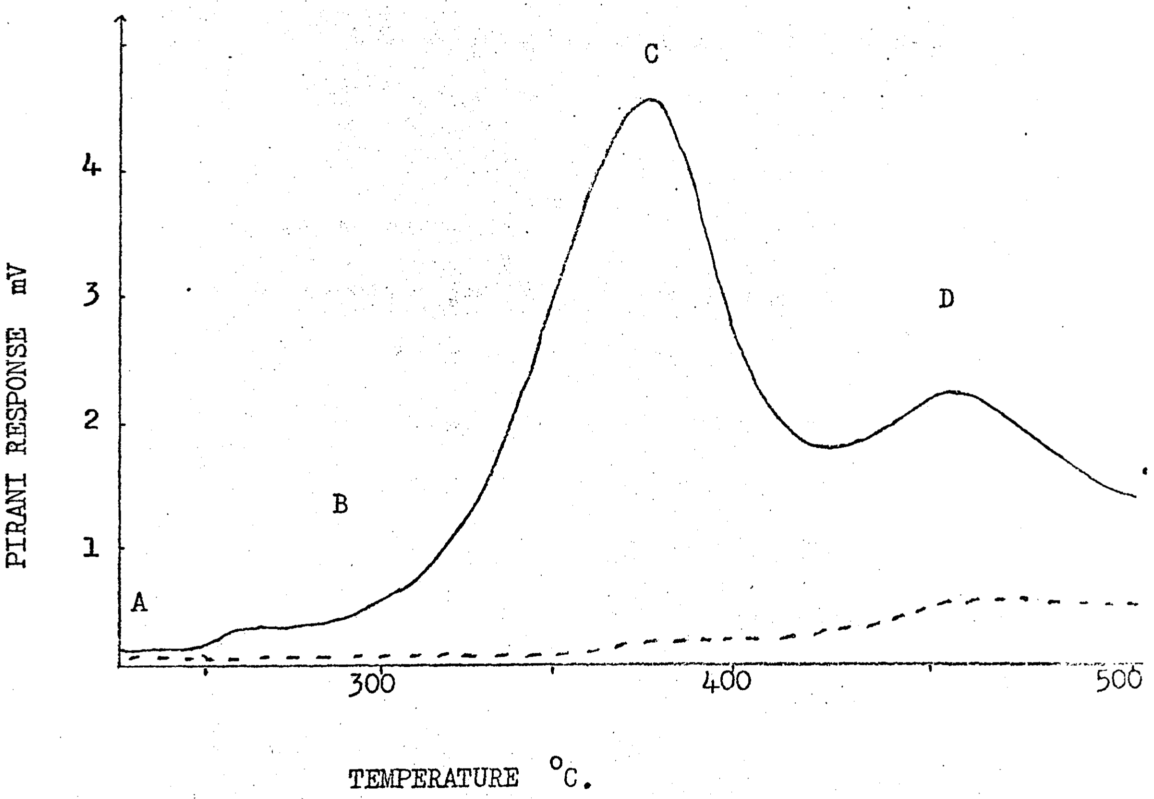
Lower curve 5°/min.

A, B, C, D explained in text.

Fig. 14. TVA of Polychloroprene (MC30) film.

20 mg film.

10°/min.



this point.

A yellow-brown "cold ring fraction" was left on the walls at the top of the tube after TVA. Interrupted TVA and also the use of a glass instead of a metal cooling ring, showed that the highly coloured deposit did not form until 425°C. Below this temperature an oil was formed, starting below the peak C maximum as a mist of clear droplets, and progressing as the temperature rose, to a film of light yellow or greenish gum.

The TVA curves in fig. 14 indicate that non-condensable products are evolved in small amounts during the later stages of reaction C. The trace for non-condensables increases during the secondary reaction. More information on this aspect of the degradation can be obtained from the DC-TVA (discussed later) in which the Pirani gauges are in nearly equivalent positions and are electrically balanced.

(b) Different Polychloroprenes

Other polychloroprenes examined all behaved similarly to MC30 in respect of degradation above 300°C but differences were noted in the amount of degradation taking place below this temperature. Samples prepared in vacuum had a very much reduced stage B volatilization but no clear relationship between the conditions of polymerisation and the amounts of reactions A and B was evident. The characteristics of the TVA curves for all the polymers are given in Table 4.

PC-40 was prepared in order to determine whether A and B could be completely eliminated by minimising irregularities and oxidation structures in the polymer. Fig. 15 shows that although the early degradation is much less in this polymer it is not entirely absent. Although more stable initially, PC-40 has an earlier rate maximum for stage C, than MC30 or any of the other polymers.

(c) Oxidised Polychloroprene

A few experiments were performed to examine the effect of oxidation on the thermal stability of the polymer. 30mg. polymer films were cast from benzene solution on the base of the TVA tube by blowing nitrogen over the surface of the solution. The tube was then evacuated on the TVA apparatus at room temperature until all the solvent was removed. After isolating the tube from the pumps the stopper at A (fig. 3) was removed and the oven heated isothermally for the required time. Fig. 16 illustrates the effect on the TVA curve of progressive amounts of oxidation of the polymer films.

The first effect of oxidation is to increase the amount of low temperature degradation which takes place. The temperature at which degradation starts, drops from 190°C to 150°C in the least oxidised film and to 110°C in the more

Table 4 (Overleaf)

Comparison of TVA Curves of Polychloroprenes.

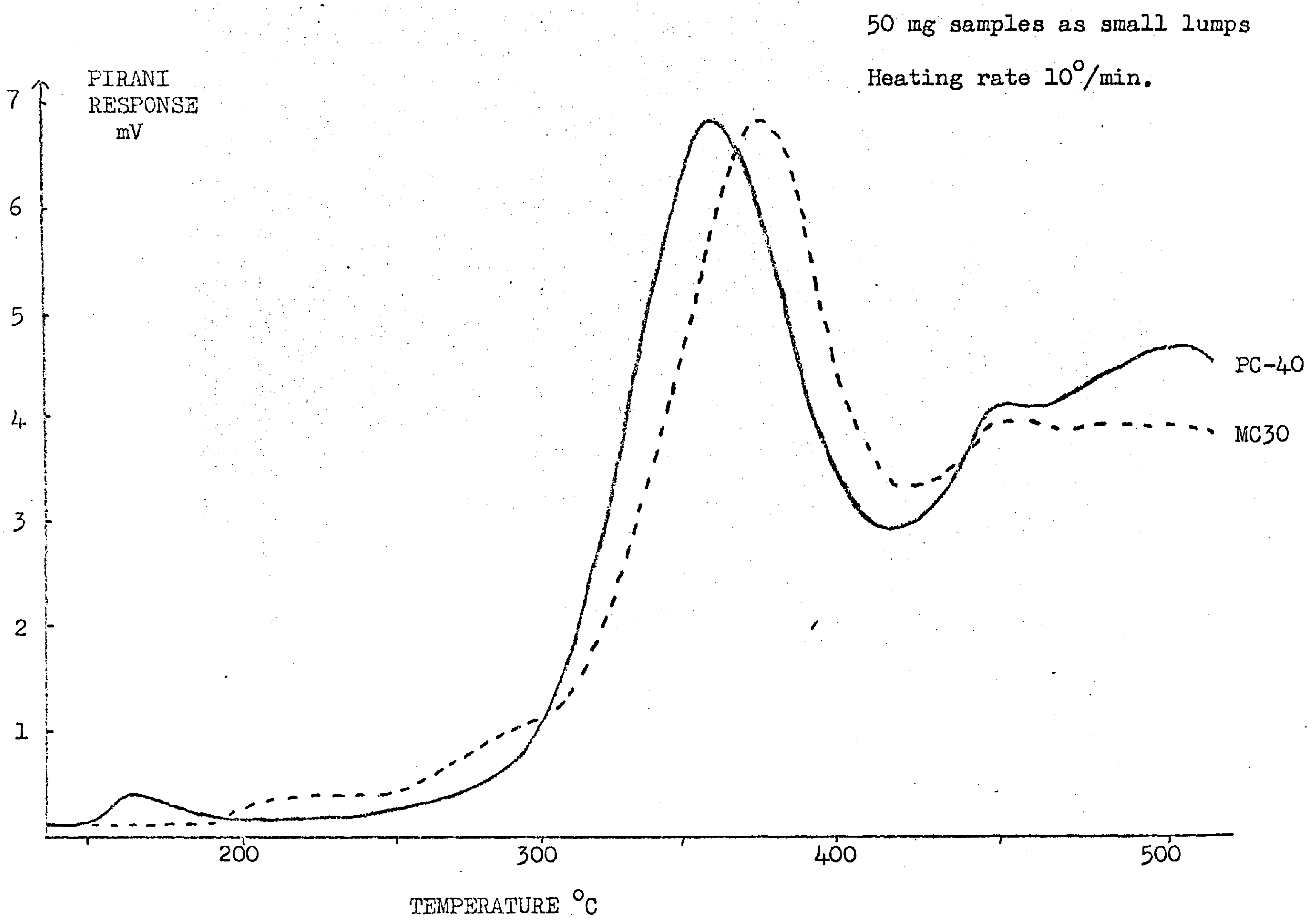
Table 4

Polymer	Notes on Polymerisation	Peak C T_{max} °C 10 °/min.
MC30 unpurified	emulsion (mercaptan)	369
SC20 unpurified	emulsion (sulphur)	371
Neoprene D.P.		373
MC30 purified	M_n 156,000	368
MC30 Fraction 1	M_n 190,000	369
MC30 Fraction 2	M_n 98,500	372
PC1	Bulk in air, room temperature, cross-linked.	367
PC3	Bulk in air, 30°C.	367
PC4M	Bulk in air, 30°C, partially cross-linked.	372
PC2	Bulk in vacuum, 30°C.	364
PC4	Bulk in air, 50°C.	370
PC-40	Emulsion in vacuum, -40°C.	356

Table 4 cont.

Remarks
A plateau 200 - 250°C, B shoulder 305°C.
A and B originally similar to MC30 but after being stored for 2.5 years, A plateau 140 - 220°C, B plateau 245 - 290°C.
A plateau starts at 180°C and a peak at 240°C, B similar shoulder to MC30.
No difference from the unpurified.
A and B the same as for MC30, C peak is slightly sharper.
A and B are the same as for MC30.
Plateau of volatilization from 100 - 240°C - may include trapped solvent and monomer evaporating, may obscure A. B as for MC30.
A similar to MC30, B twice as high with plateau 270 - 300°C.
A and B slightly smaller than for MC30.
A starts at 170°C and plateau is slightly lower than for MC30, B hardly evident. D peak during charring at 440°C is much higher than in any of the other polymers.
A starts at 165°C, plateau slightly lower than for MC30, low maximum at 200°C. B is absent.
A starts at 150°C, a small peak at 161°C followed by very low plateau. B is absent.

Fig. 15. TVA of PC-40 and MC30



50 mg samples as small lumps

Heating rate 10°/min.

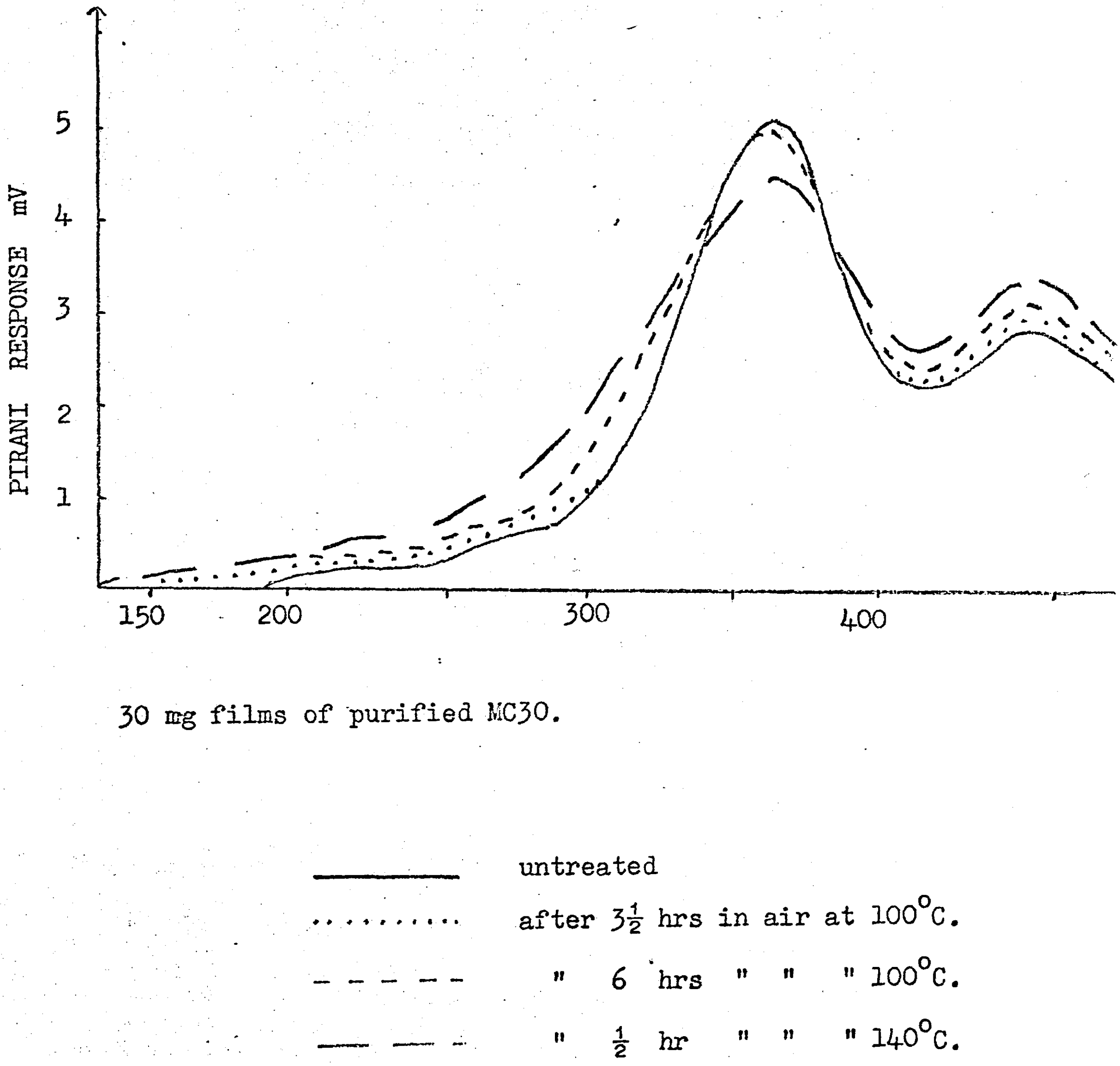
oxidised films.

In the most oxidised film it is impossible to distinguish A and B stages in the TVA curve. It may be that the stage A reactions are increased thus obscuring stage B, but this seems unlikely in the absence of a definite peak between 200 and 250°C. Probably this oxidation reaction is unconnected with stages A and B but it must be borne in mind that accelerated oxidative aging may have a different effect from aging at ambient temperature.

The oxidation reduces the height of peak C as is expected if the total amount of hydrogen chloride evolved is not to be changed. Peak D increases with the amount of oxidation so that it may eventually be higher than the diminished C peak. This effect was seen in the degradation of a 22mg. film which had been heated for 2 hours at 100°C and 0.5 hour at 120°C. The slightly yellow polymer gave a C peak shifted from 370 to 360°C because of the increase in the low temperature degradation, but the D peak although now higher than the C peak, still gave a maximum at 450°C.

The increase in height of the peak for carbonisation in oxidised polychloroprene may be related to results obtained by Gilbert, Kipling and McEnaney[60,61] for the pyrolysis of the residue obtained by heating PVC in air at 250°C until dehydrochlorination was complete. Compared to the residue from PVC dehydrochlorinated under nitrogen, this substance

Fig. 16. TVA of Oxidised films of Polychloroprene.



30 mg films of purified MC30.

gave an increased carbon yield at higher temperatures and also a larger evolution of gaseous products between 400° and 800°C. It was suggested that oxygen increases the number of cross-links formed in the first stage and thus hinders decomposition to tar sized fragments. More material is thus left to undergo complete carbonisation by the loss of hydrogen and other small molecules, and also oxygen is lost from the residue in the form of oxides of carbon.

The effect in oxidised polychloroprene could be attributed to similar causes but TG and gas product analysis would be required before firm conclusions could be drawn.

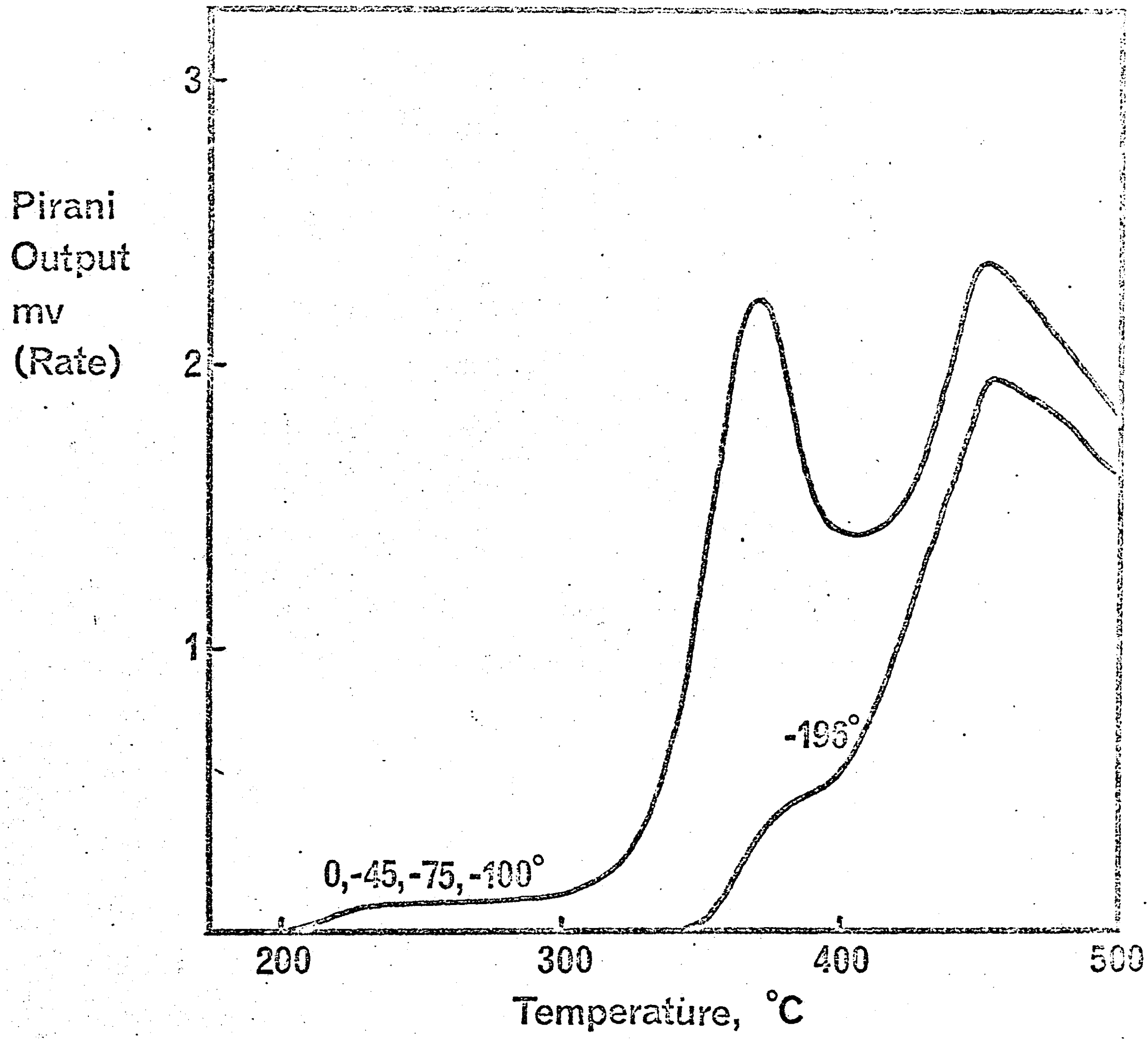
Differential Condensation (DC) TVA

The nature of the degradation products from polychloroprene was examined by DC-TVA, the curves obtained being shown in fig. 17. The most striking difference between these curves and those described previously is that the D peak has become greater than the C peak.

DC-TVA shows that most of the first peak is non-condensable at -100°C and condensable at -196°C just as is expected for hydrogen chloride. Products which are non condensable at -196°C are also evolved, and in the D peak these account for almost all the volatile products detected by the Pirani gauges.

Fig. 17. DC-TVA of 50 mg. film of polychloroprene.

10°/min.



The DC-TVA apparatus appears to be more sensitive than the simple system to the non-condensable products. The reason for this is not clear, but might be due to the pumps not being able to evacuate the large volume of the trap system so quickly in this apparatus.

Thermogravimetry

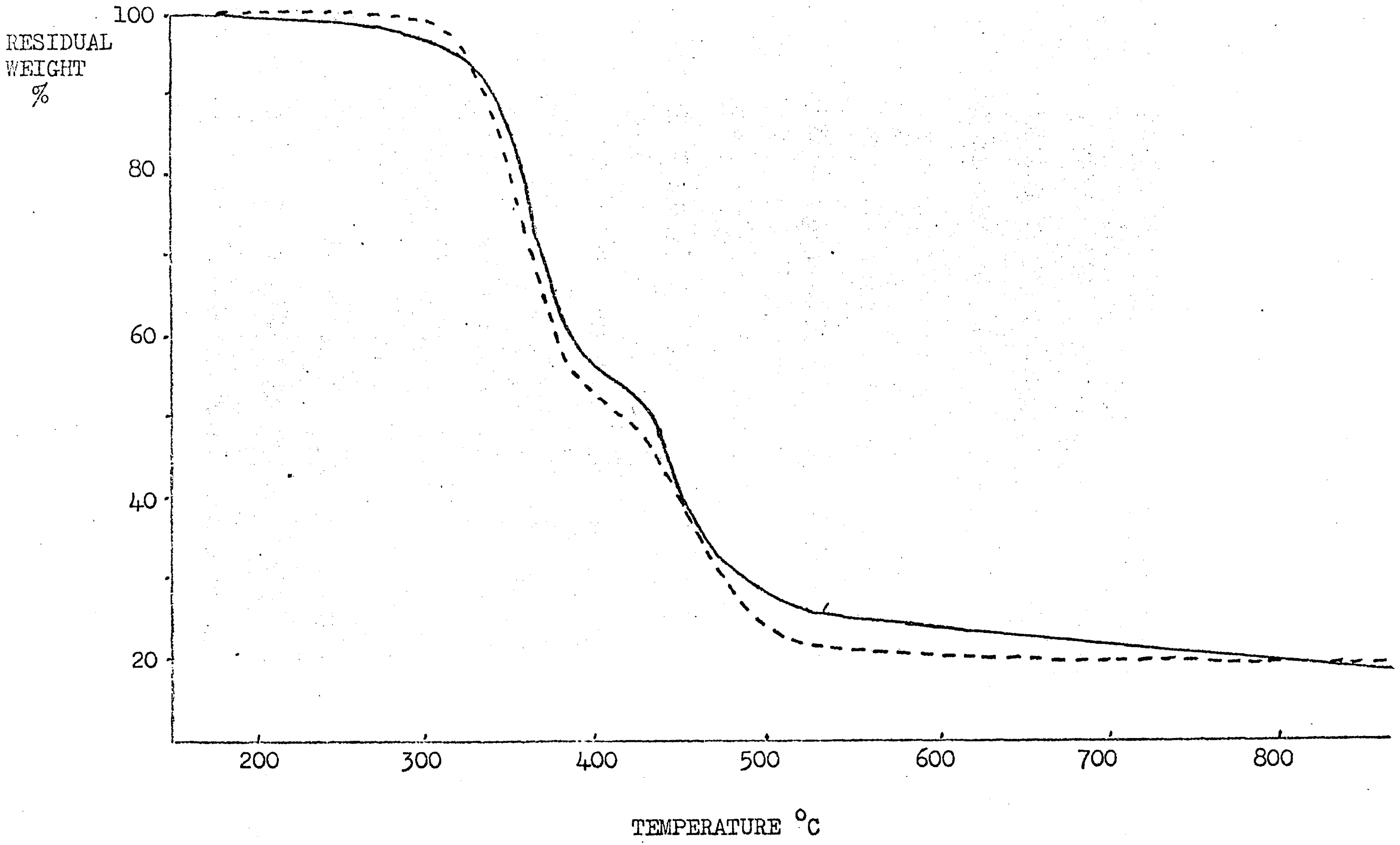
The 10°/min. TG curves for MC30 and PC-40 are shown on fig. 18. They indicate that a two stage weight loss occurs to give a residue of about 20%. As shown by TVA, PC-40 is more stable below 300°C than MC30, but has an earlier rate maximum in the first stage of degradation.

The maximum rate of weight loss in the primary decomposition is at 365°C for MC30 and at 357°C for PC-40. The point of inflection between the two stages is at 406°C in MC30 and at 410°C in PC-40 with corresponding weight losses of 44.5% and 49% up to that point. Since the total hydrogen chloride content of polychloroprene only accounts for 41.2% of the weight, it is evident that side reactions accompany dehydrochlorination in both polymers.

The second stage of degradation occurs fairly smoothly in PC-40 and is almost complete by 550°C when 21% residue is left. In MC30, the secondary decomposition curve is not smooth and at 550°C, with 23% residue, weight is still

Fig. 18. TG curves for MC30 (full line) and PC-40 (dashed line)

Heating rate 10°/min



being lost. Both polymers show virtually linear weight loss from 550°C to the upper limit of the TG apparatus (about 960°C). At this point 17% residue is left from MC30 and 19% from PC-40.

The TG curves show that the more regular polymer loses weight in better defined stages, with a slightly higher weight loss in the first step. The residue produced after secondary decomposition is more stable in the case of the regular polymer so that although less coke is left from PC-40 pyrolysis up to 550°C, more remains at 1000°C than for MC30.

Differential Thermal Analysis

The DTA curves for MC30 and PC-40 are shown on fig. 19. To try to minimise sample form effects which are very important in DTA, both samples were packed hard into the bottom of the DTA tube. Two important features may be seen in the range 0 - 500°C. The first is the endothermic melting of the crystalline regions of the polymer. This takes place at 36°C in MC30 and at 54°C in PC-40. The reason for this difference and for the large difference in the size of the peaks, is that the more regular structure of PC-40 permits a much greater degree of crystallinity.

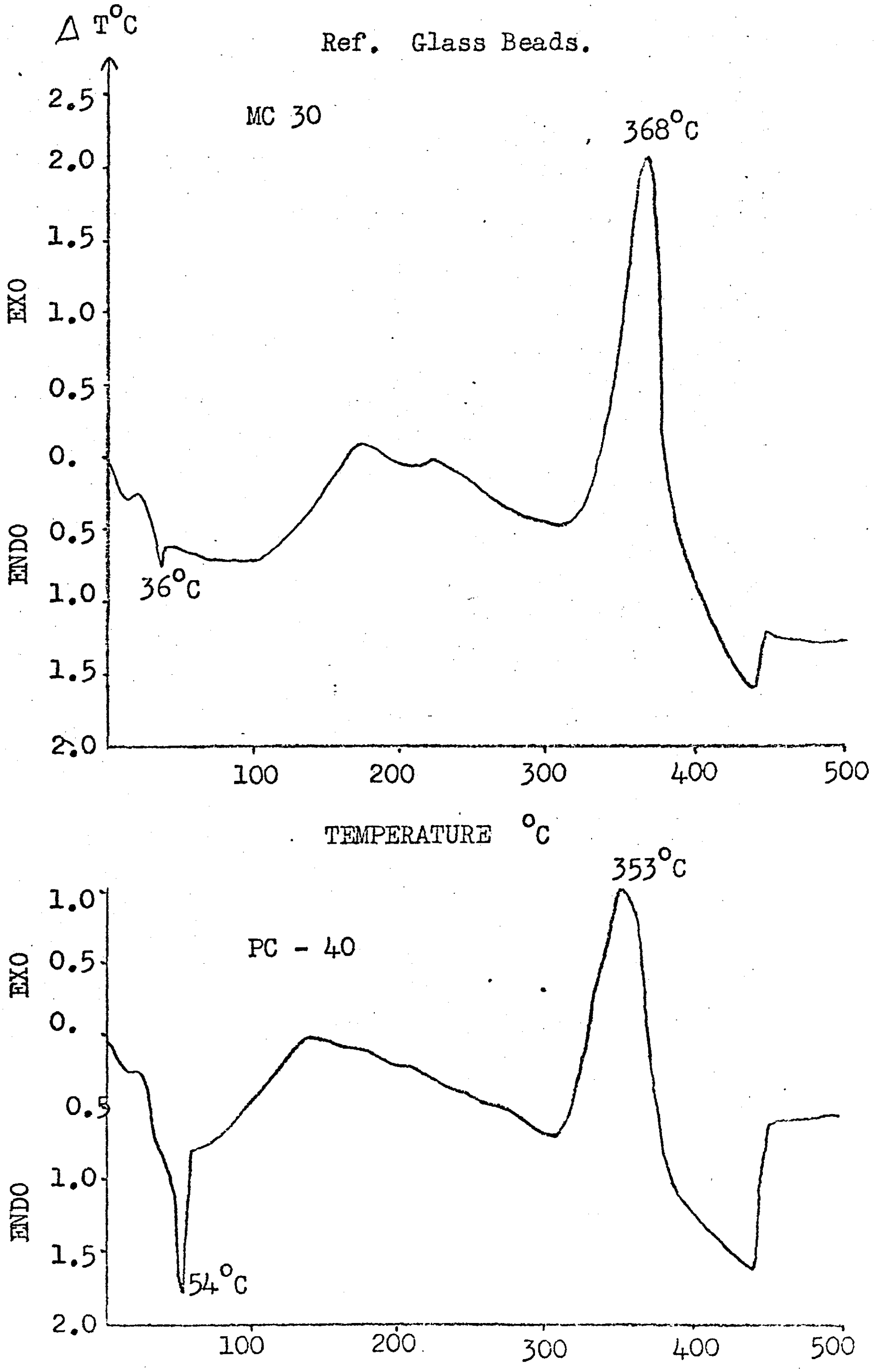
The second characteristic is an exotherm which peaks at

Fig. 19. Differential Thermal Analysis of Polychloroprenes.

20 mg Samples 10°/min.

Nitrogen Atmosphere.

Ref. Glass Beads.



368°C in the case of MC30 and at 353°C for PC-40. The exotherm is due to degradation and the DTA curves confirm the TVA and TG results which show PC-40 to have an earlier maximum than MC30. Although the reproducibility of the magnitude of the features of the DTA curves is not very good, PC-40 gives a consistently lower exotherm than MC30. Because of the increased width of the PC-40 peak the area under the peaks in both polymers is approximately equal.

The sharp break at 450°C occurs when the polymer forms a coke and bubbles up the sample tube. At the end of this process very little material is left at the position of the thermocouple junction, most of it being found round the thermocouple sheath in the upper part of the tube. It is likely that the change in heat capacity of the system, rather than any thermal change in the polymer, is responsible for this feature.

Similarly the endothermic drift between 150°C and 450°C is probably due to an imbalance of the thermal capacities of the sample and reference since it does not appear in DTA curves of polychloroprene already reported. The DTA curve obtained by Schwenker and Beck[40] showed exothermic drift and the peak maximum for degradation at 10°/min. was determined to be 377°C. A DTA curve for neoprene in the range -100° to +350°C appears in the manual for the Du Pont[62] instrument used. This shows a melting point of 44°C and little base line slope from there until degradation starts.

A 15mg. sample of powdered PVC (Geon 101), which is an equivalent molar quantity to 20mg. of polychloroprene gave a 3°C endotherm at 275°C on the Du Pont apparatus. There was also a slight exotherm between 350° and 430°C and a small endotherm at 450°C. There is some disagreement in the literature about the DTA of PVC. Dollimore and Heal[63] reported that the dehydrochlorination was initially exothermic before becoming endothermic. Two earlier references[64,65] describe an endothermic elimination but the largest feature of these DTA curves is an exotherm at a temperature above that required for elimination. The results of Murphy and coworkers[64] were obtained in an atmosphere of 3mm. of air which might cause the exotherm which was observed to have a maximum at 580°C (heating rate unspecified). Morita and Rice[65] however used an atmosphere of pure nitrogen and they also recorded a large exotherm this time between 310° and 400°C at a heating rate of 10°/min.

Evolution of Hydrogen Chloride

The amount of hydrogen chloride liberated by the polymer during programmed degradation was investigated using the product collection system of the TVA apparatus. A reservoir containing frozen distilled water was connected to the "U" trap and at some known point in the TVA curve the taps at the top of the trap were closed and the products distilled into the reservoir. The hydrogen chloride was estimated by titration with 0.1M sodium hydroxide solution using phenolphthalein as indicator.

A sample of PVC (Breon 113) was also degraded to the end of the dehydrochlorination stage in order to check the efficiency of the hydrogen chloride collection system. It is reported[66] that at least 95% of the chlorine in PVC is eliminated as hydrogen chloride. In view of the fact that the TVA showed that the PVC was not entirely free from trapped volatiles, the figure of 96.5% collected hydrogen chloride seems satisfactory. The results for polychloroprene and PVC are shown in Table 5.

About 90% of the chlorine in polychloroprene is lost as hydrogen chloride mostly between 300° and 400°C. Increasing the heating rate caused a small decrease in the amount of hydrogen chloride produced, but the fastest heating rate available on the oven was only a nominal 40°/min. Using this programme a temperature of 450°C was reached in 15min., by which time most of the dehydrochlorination was complete. 10 min. later a temperature of 510°C was reached and this was maintained for 20 mins. These conditions do not approach the flash pyrolysis conditions under which the polymer was reported to give predominantly monomer,[43] but the results do show a trend in this direction.

Fig. 20 illustrates the correlation between the total weight loss as determined by TG and the weight loss due to dehydrochlorination. The divergence of the curves shows that hydrogen chloride does not entirely account for the weight loss in the first stage of degradation. Since the first and second stages are not well separated a small amount of the second reaction goes on before the first stage is complete. This explanation is supported by the fact that TVA shows a small amount of non-condensables being evolved during the dehydrochlorination. In addition a small quantity of liquid products was formed during the degradation. The amount was too small to be detected on the DC-TVA but showed as a light condensate on the cold ring, and a few drops of a pleasant smelling oil floating on top of the solution in the titration flask.

Table 5

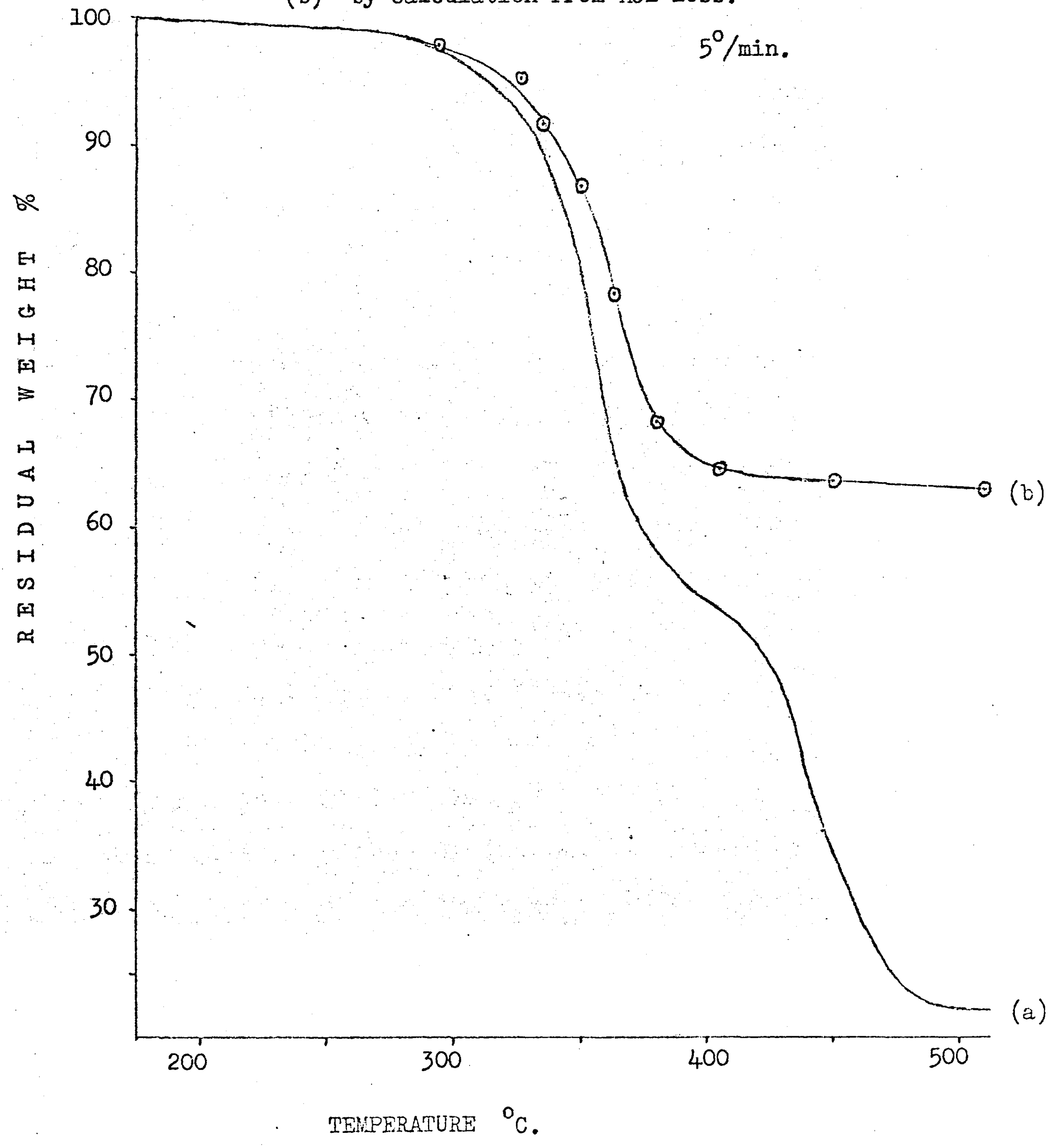
Amount of Hydrogen Chloride Evolved During Programmed Degradation up to Temperature Shown.

Temperature (°C)	Heating Rate (°C/min.)	Weight of Sample (small lumps) (mg.)	Volume of 0.1M NaOH (ml.)	HCl as % Polymer Chlorine
510	5	130.0	13.10	89.4
510	5	128.0	12.98	90.0
510	10	128.5	12.78	88.2
510	40	127.9	12.35	85.7
450	5	126.1	12.67	88.9
405	5	129.8	12.58	86.0
380	5	122.5	10.35	74.9
380	5	122.6	10.70	77.5
380	5	132.2	11.50	77.2
362	5	132.4	7.92	53.0
362	5	127.4	7.55	52.4
350	5	123.0	4.55	32.0
338	5	130.1	3.05	20.7
338	5	132.0	3.07	20.6
326	5	128.7	1.62	11.2
326	5	137.0	1.92	12.0
295	5	131.4	0.80	5.4
PVC				
405	5	92.8	14.27	96.5

Fig. 20. Residual Weight % vs Temperature.

(a) by T.G.

(b) by calculation from HCl loss.



CHAPTER 4

ANALYSIS OF VOLATILE PRODUCTS

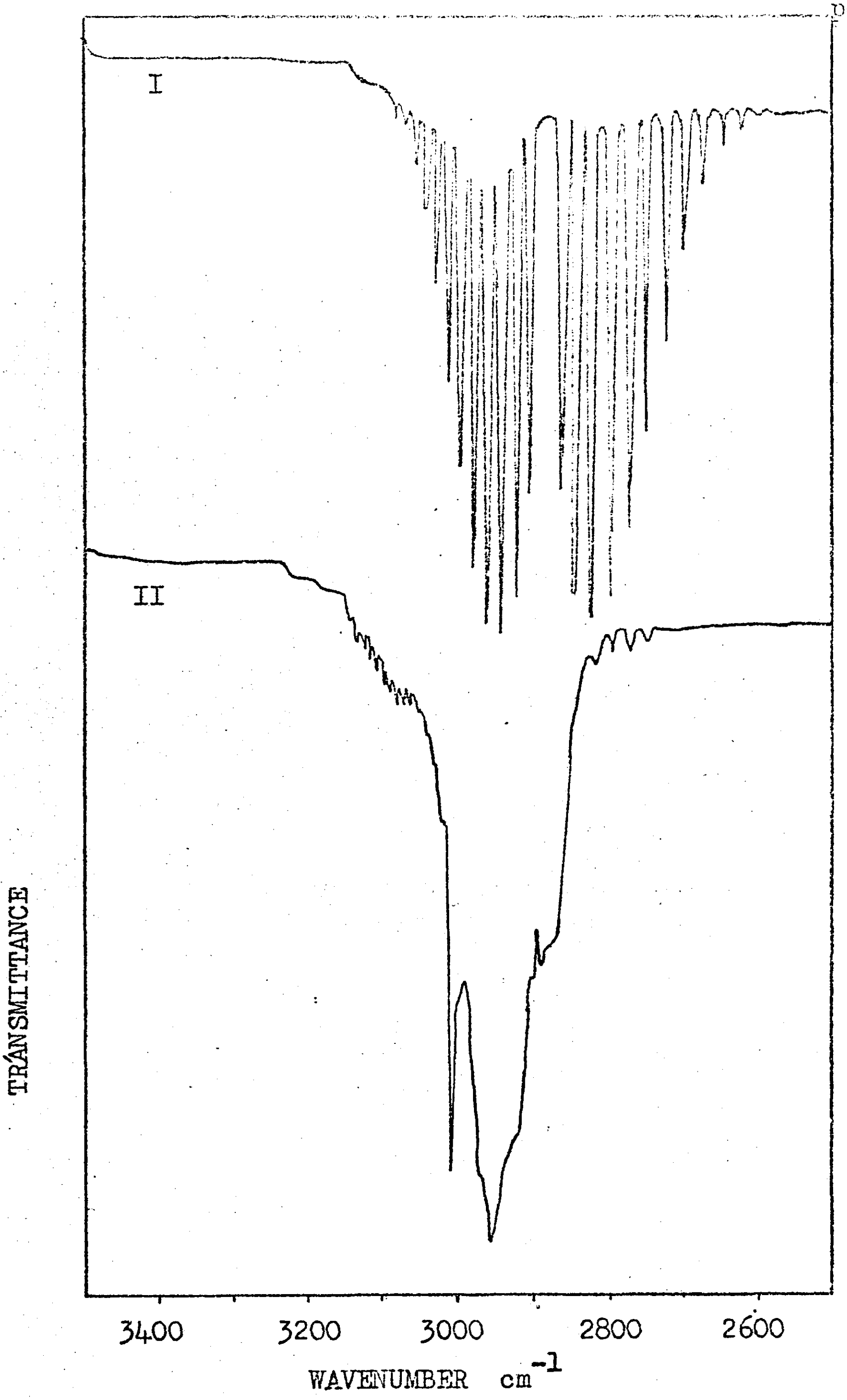
Infrared Analysis of Gaseous Products

Figs. 21 and 22 illustrate the spectra of the gases evolved by polychloroprene (MC30) heated at 5°/min. Spectrum I is of the products given off between 170° and 400°C corresponding to the first peak in the TVA, and spectrum II is of the products from degradation at higher temperature.

I is essentially a spectrum of hydrogen chloride with a characteristic band pattern between 3100 and 2600cm^{-1}. It also contains a peak at 950cm^{-1} due to ethylene and two small peaks at 920 and 875cm^{-1} for chloroprene monomer. There is also a small peak at 670cm^{-1} which appears as a doublet in I and a singlet in II. Carbon dioxide impurity might be responsible for one of the double peaks.

The most diagnostic peaks in II are at 1305 and 3020cm^{-1}. Both have associated fine structure but this is partially obscured in the case of the 3020cm^{-1} peak by other C - H absorptions and also confused with the spectrum of the small amount of hydrogen chloride present. The two absorptions at 1305 and 3020cm^{-1} are characteristic of methane. More ethylene is present than in I since the

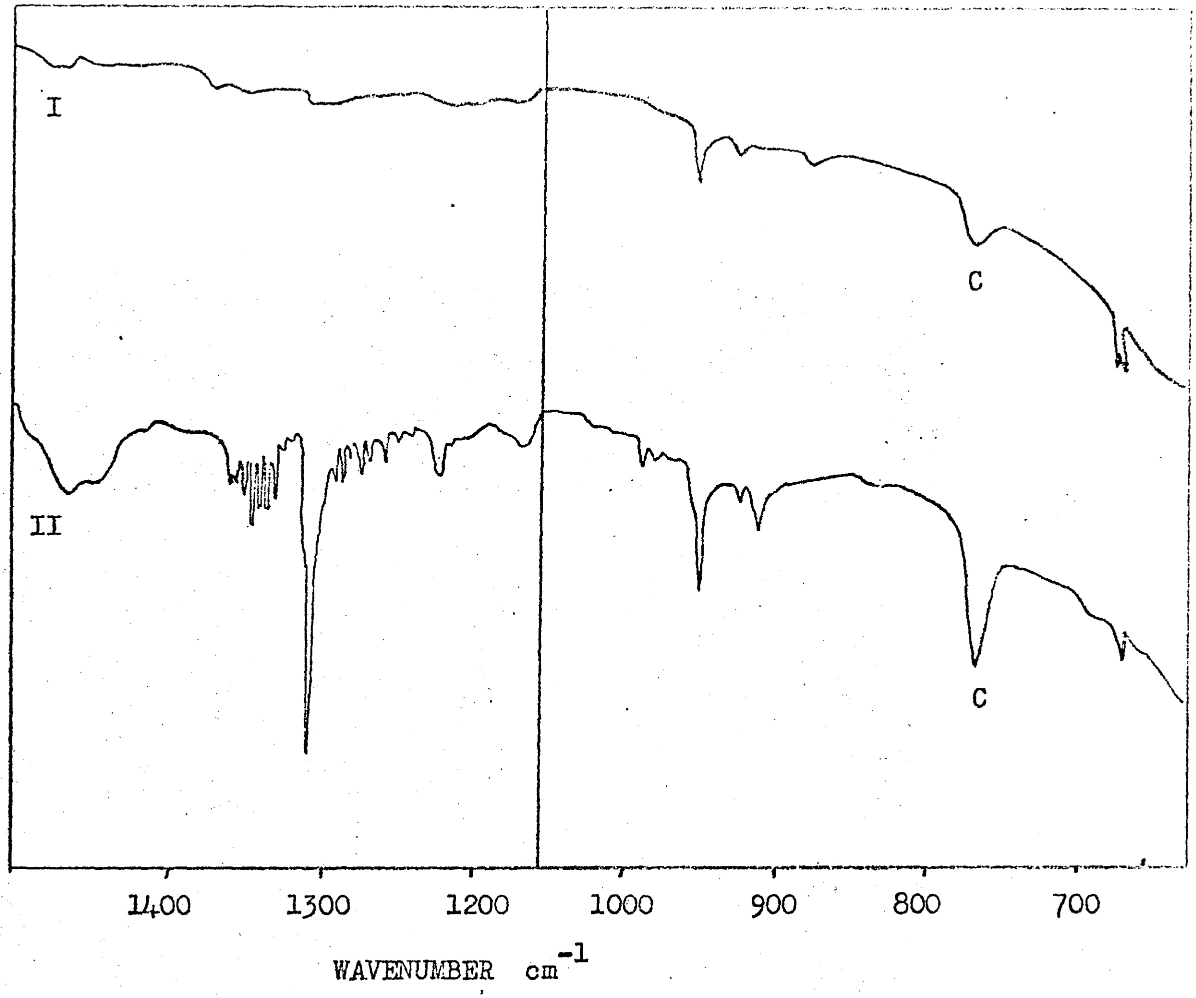
Fig. 21. Infrared spectrum (3,500 - 2,500 cm^{-1}) of volatiles from polychloroprene.



HEATING RATE 5°/min.

I. 170 - 400°C. II. 400 - 510°C.

Fig. 22. Infrared spectrum (1,500 - 625 cm^{-1}) of volatiles from polychloropre



I & II as Fig. 21.

C is a peak for Chloroform used to clean the cell.

band at 950cm^{-1} is increased and a broad peak at about 1450cm^{-1} appears. The small peaks at 912 and 990cm^{-1} may be due to propene reinforcing the ethylene absorptions at these figures and the 920cm^{-1} peak may be due to monomer although the 875cm^{-1} peak is absent.

The spectra described above were obtained by the degradation of 200mg. samples in the apparatus shown in fig. 9. Several attempts were made to increase the sample size to between 2 and 10g. in order to magnify the small peaks from the minor components. In every case uncontrolled "flash" degradation took place above 300°C as described on page 37. The spectra obtained from these degradations show the same peaks as described before with better defined structure in the 1000 to 850cm^{-1} region and also peaks at 1590 and 1580cm^{-1} for monomer. Traces of carbon monoxide and carbon dioxide can be detected in the gas products of the largest samples indicating the breakdown of oxygenated structures in the polymer.

Gas Chromatography

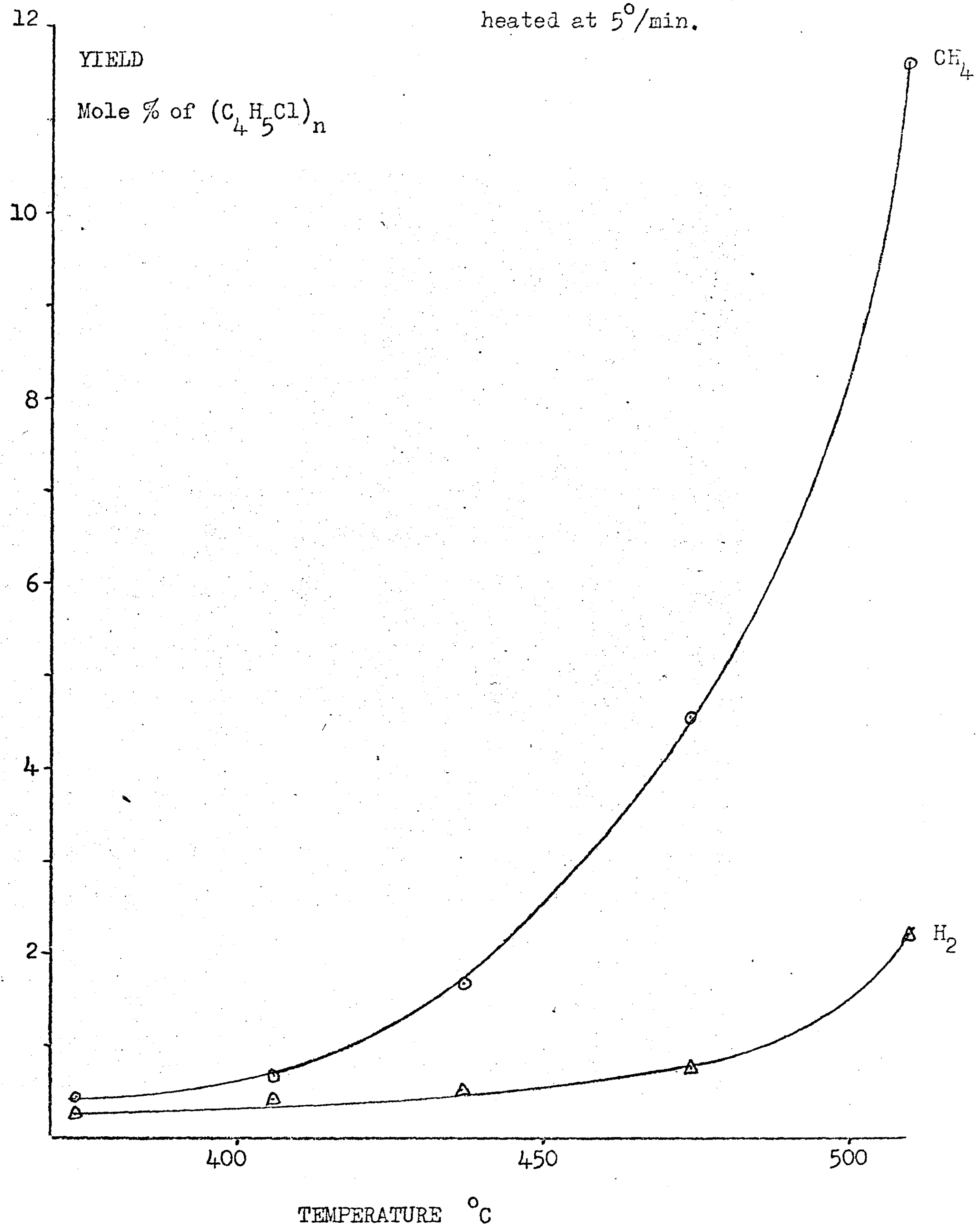
This technique was used to detect and estimate hydrogen and methane in the pyrolysis products of polychloroprene. A series of degradations programmed at 5°/min. up to temperatures of 374, 400, 437, 474 and 510°C was carried out using the pyrolysis vessel shown in fig. 10. 200mg. samples of small lumps of purified MC30 were used for the three highest temperatures and 300mg. and 400mg. samples for the 400°C and the 374°C degradations respectively. The results of the gas chromatographic analyses of the products of these degradations are displayed graphically in fig. 23.

Both hydrogen and methane are given off in small amounts below 400°C. At this temperature the rate of evolution of methane starts to increase and continues to do so up to 510°C. The rate of hydrogen evolution increases slightly after 450°C but the total amount of hydrogen produced is much less than the amount of methane. Unfortunately only the initial stages of the carbonisation reaction could be observed since the oven was not designed for use above 510°C.

The quantity of methane liberated during the pyrolysis is much larger than expected by analogy with PVC. Both Stromberg and coworkers[13] and Gilbert and Kipling[60] have examined the products of the secondary decomposition of PVC by heating the polymer until the elimination reaction was virtually complete and then degrading the residue at a higher temperature.

Stromberg[13] used a mass spectrometer to analyse the

Fig. 23. Cumulative yield of H_2 and CH_4 from Polychloroprene heated at 5°/min.



products from heating dehydrochlorinated PVC at 400°C for 30 minutes. He reported that the yields of hydrogen and methane were less than 0.1%.

Gas chromatography was used by Gilbert and Kipling[60] to examine the gases liberated from PVC residue heated in steps of 100°C between 400°C and 900°C. At each stage the temperature was held constant until gas evolution had dropped to a very low level. Their results, recalculated on a molar basis, are shown in Table 6. They found significant amounts of the gases being formed even at 400°C.

For a more direct comparison of the two polymers, and in order to resolve the conflicting results described above, 300mg. samples of PVC (Breon 113) were degraded at 5°/min. to temperatures of 437 and 510°C and the gases were analysed in the same way as for polychloroprene. The results are shown in Table 7 along with the equivalent figures for polychloroprene reduced to the same C_2 monomer unit as in PVC.

Measurable amounts of hydrogen and methane were obtained from PVC degradation to 437°C suggesting that Stromberg underestimated the amount of these products.

The results in Table 7 indicate that the methane yield from polychloroprene is about twice that from PVC. It is difficult to make a direct comparison between Gilbert

Table 6

Gas Yields from PVC Heated in Stages of 100°C.
(Calculated from results by Gilbert and Kipling.)[60]

Temperature °C	400	500	600	700	800	900
Gas	Cumulative yield mole % of $(CH=CH)_n$					
Hydrogen	0.6	3.2	7.5	12.2	14.7	16.3
Methane	2.2	4.3	4.8			4.9

Table 7

Gas Yields from PVC and Polychloroprene Heated at 5 °/min.

Temperature °C	437		510	
Gas	Hydrogen	Methane	Hydrogen	Methane
Polymer	Cumulative gas yield mole % of $(CH=CH)_n$			
PVC	0.7	0.4	1.1	2.8
Polychloroprene	0.3	0.8	1.1	5.8

and Kipling's figures and those obtained here for PVC, but it appears that prolonged heating at 400°C causes the evolution of a considerable amount of methane whereas programmed heating to 437°C produces very little. A related observation is the fact that a methyl group peak was recorded in the infrared spectrum of the residue of prolonged heating at 400°C whereas none appeared in PVC heated at 5°/min. to 405°C. (Chapter 6). The total amount of methane liberated by PVC when heated in stages up to 900°C is less than the amount produced from polychloroprene when subjected to programmed heating up to only 510°C. This confirms the evidence that polychloroprene yields much more methane than PVC on carbonisation of the residue from dehydrochlorination.

It is unfortunate that the silica gel chromatograph column did not permit the passage of larger molecules than methane since it would have been interesting to follow the production of ethylene at the same time as the other gases.

Liquid Products

(a) Oil

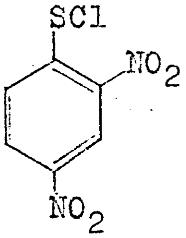
About 80mg. of a light yellow fruity smelling oil were recovered from the main band of the thin layer chromatography (tlc) plate of the products from the degradation of 10g. of polymer. The infrared, proton magnetic resonance (pmr) and mass spectra of the oil were obtained and it became evident that several components were present. Ions were present in the mass spectrum which could only reasonably be accounted for by empirical formulae containing oxygen and in fact it had been noted that an extra band appeared in the tlc of the products when these had been stored for a day or two. It appears that the polymer degradation produces a variety of similar compounds, some of which are susceptible to oxidation.

Gas-liquid chromatographic analysis on a Carbowax column initially at 70°C gave at least six overlapping bands in the first 40 minutes after injection but one peak was about ten times larger than the others. Programming the chromatograph oven at 5°/min. after the first peaks were over, resulted in the appearance of another series of overlapping peaks when the column temperature was about 120°C.

It was thought that if some of the compounds could be converted to derivatives, then separation by crystallisation and chromatography might be possible. The infrared spectrum of the oil showed that a double bond was present amd reagents were therefore chosen which would add to unsaturated compounds.

The first modification tried was bromination by reaction of the oil with bromine in carbon tetrachloride solution followed by removal of excess reagent by extraction with sodium carbonate. A reaction took place - the oil turned brown and lost its characteristic smell but no crystals could be isolated.

Hopes were high for the success of the second reagent, 2,4-dinitrobenzenesulphenyl chloride (i) which readily



(i)

forms stable crystalline adducts with olefinic compounds.[67] A useful property of these adducts is that the base peak in the mass spectrum, which is far larger than the other peaks, occurs at m/e = (molecular weight of olefin - 1) or occasionally at m/e = (molecular weight of olefin).[68]

The oil was treated with this reagent in acetic acid and after a few hours the solution was diluted with ice and extracted with ethyl acetate. The extracts were washed with brine, sodium bicarbonate and then dried over magnesium sulphate. After clarification of the resulting solution with charcoal, separation was attempted by tlc. Comparative tlc with samples of the adducts of cyclohexene and cyclooctene had shown that one of the products had the same polarity as these adducts. However, when this compound was isolated, it proved impossible to crystallise although the oil obtained on evaporation of the solvent, partially solidified on standing. The mass spectrum of this solid was obtained but there was no outstanding peak and it appeared that the "adduct" was in fact a complex mixture.

Because of the separation difficulties involved, the examination of the oil was not carried any further, and only a limited amount of information can be gained from the evidence collected up to this point.

The last peak of any size in the mass spectrum is at m/e 194 but small peaks continue up to 232. The oil therefore consists of compounds which have a molecular weight around that of the dimers of chloroprene. The molecule $C_8H_{10}Cl_2$ should give peaks in the mass spectrum at m/e 176, 178 and 180 in the ratio 9:6:1. These peaks are present, but the ratio is 13:10:5. Peaks however do occur at 141 and 143 in the ratio of 3:1 corresponding to the loss of one chlorine atom and in fact m/e 141 is the base peak of the spectrum.

The infrared and pmr spectra are shown in figs. 24 and 25. The absorption in the infrared at 885cm^{-1} is characteristic of a disubstituted vinyl group and the fact that

Fig. 24. Infrared Spectrum of oil produced by degradation of polychloroprene.

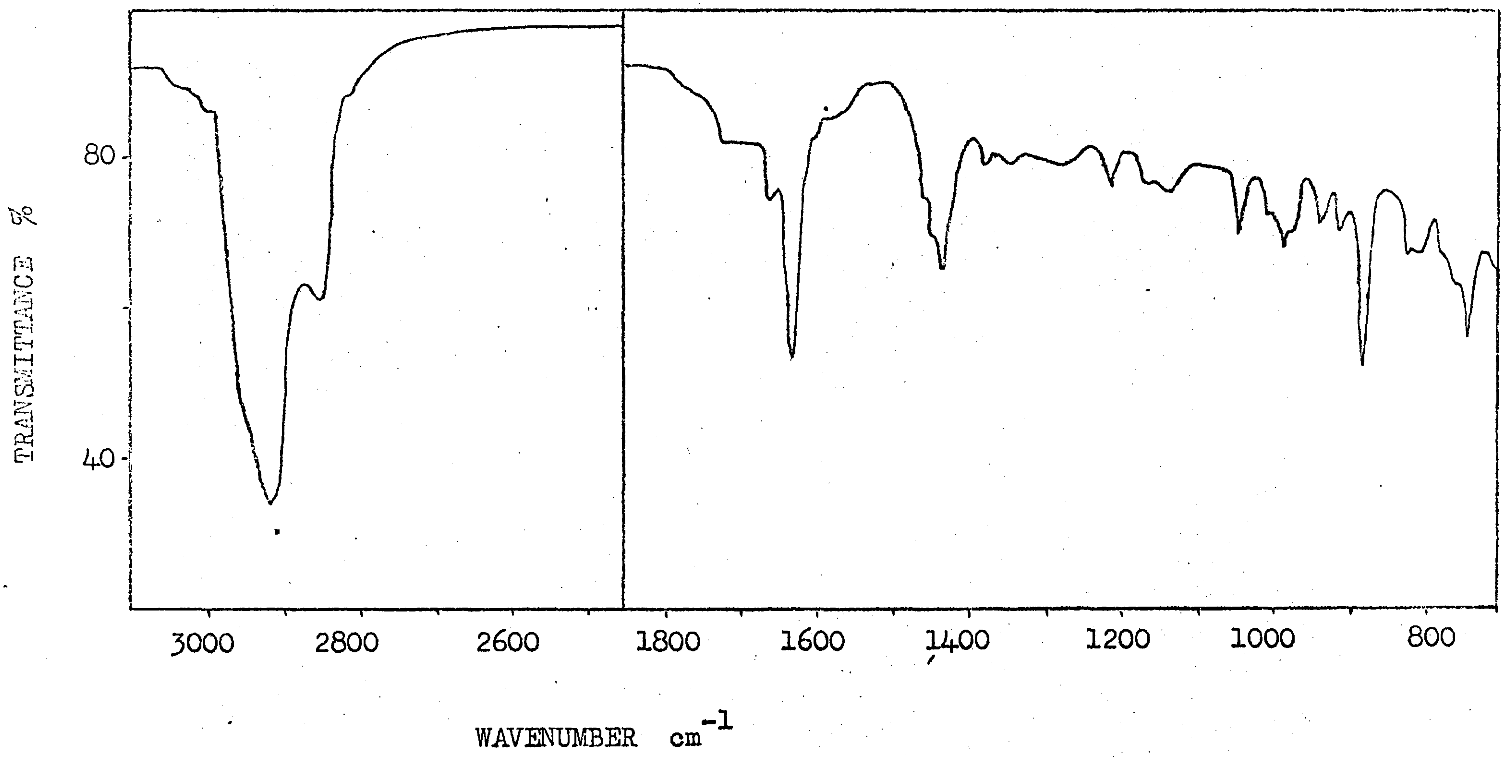
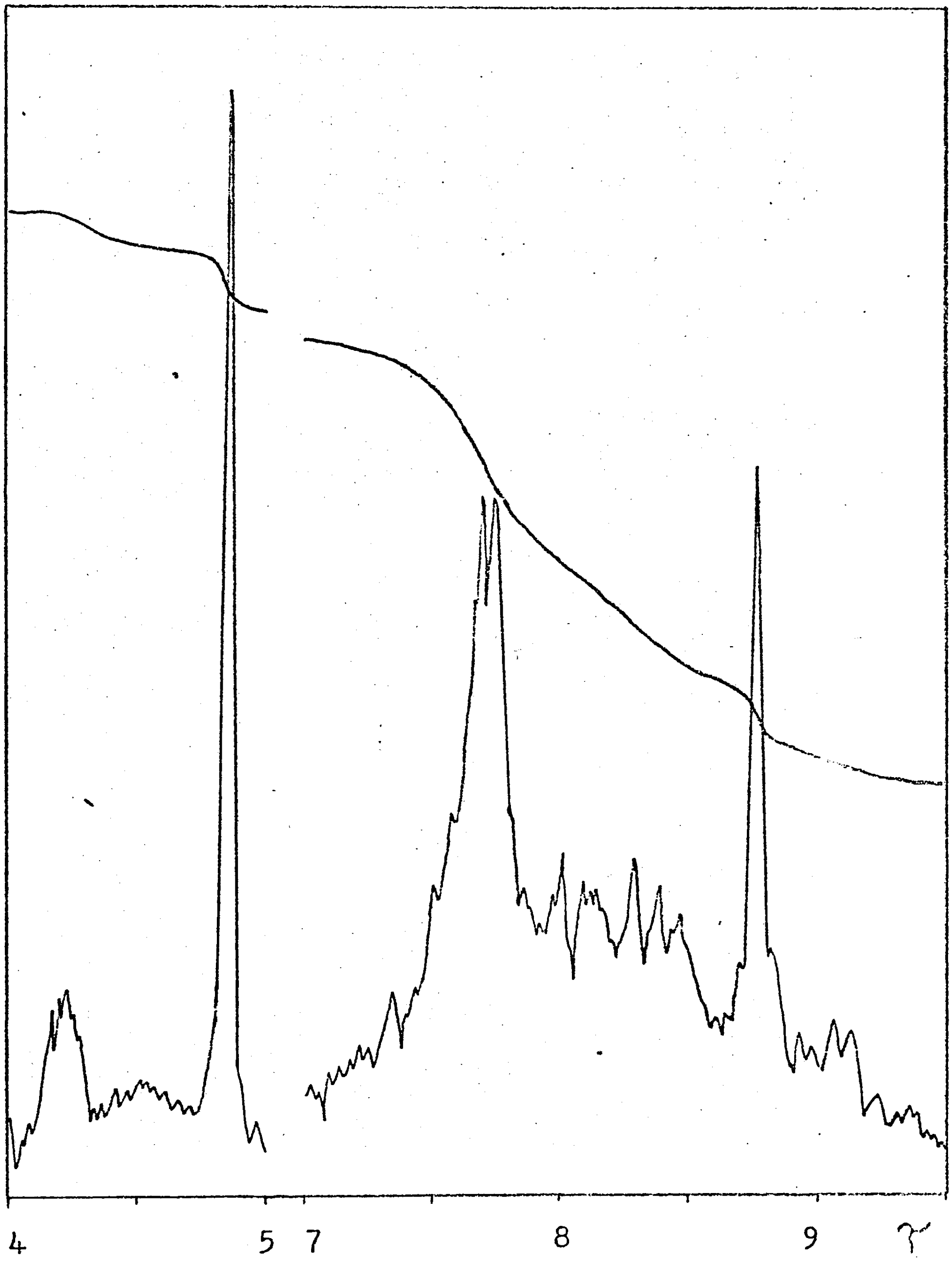


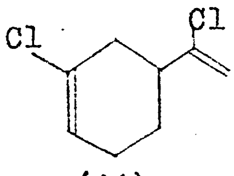
Fig. 25. NMR spectrum of oil produced by degradation of polychloroprene

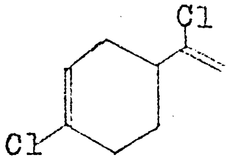


the corresponding pmr signal appears at 4.82τ instead of 5.35τ indicates that a chlorovinyl group is present. The absence of any splitting in the 4.82τ signal is also proof that there is no hydrogen on the carbon adjacent to the methylene group producing the signal.

The other indications of double bonds are the peaks at 1630 and 1660cm^{-1} in the infrared spectrum which were found to vary in relative size from sample to sample as the composition of the mixture changed. The peak in the pmr spectrum at 4.2τ is also olefinic, being caused by a proton attached to a double bond which is either chlorine substituted or inside a ring or both. Although there is no indication of conjugated double bonds in the infrared spectrum, the ultraviolet spectrum of a solution of the oil in hexane gave a peak at 203mμ possibly for the chlorovinyl group, and a shoulder at 225mμ which might be caused by diene impurities.

Chloroprene forms a range of dimeric products[69 - 74] and although some of the spectral properties of the oil correlate with structures of types (ii) and (iii), the sample is too impure to make positive identification.


(ii)


(iii)

(b) Green Cold Ring Fraction

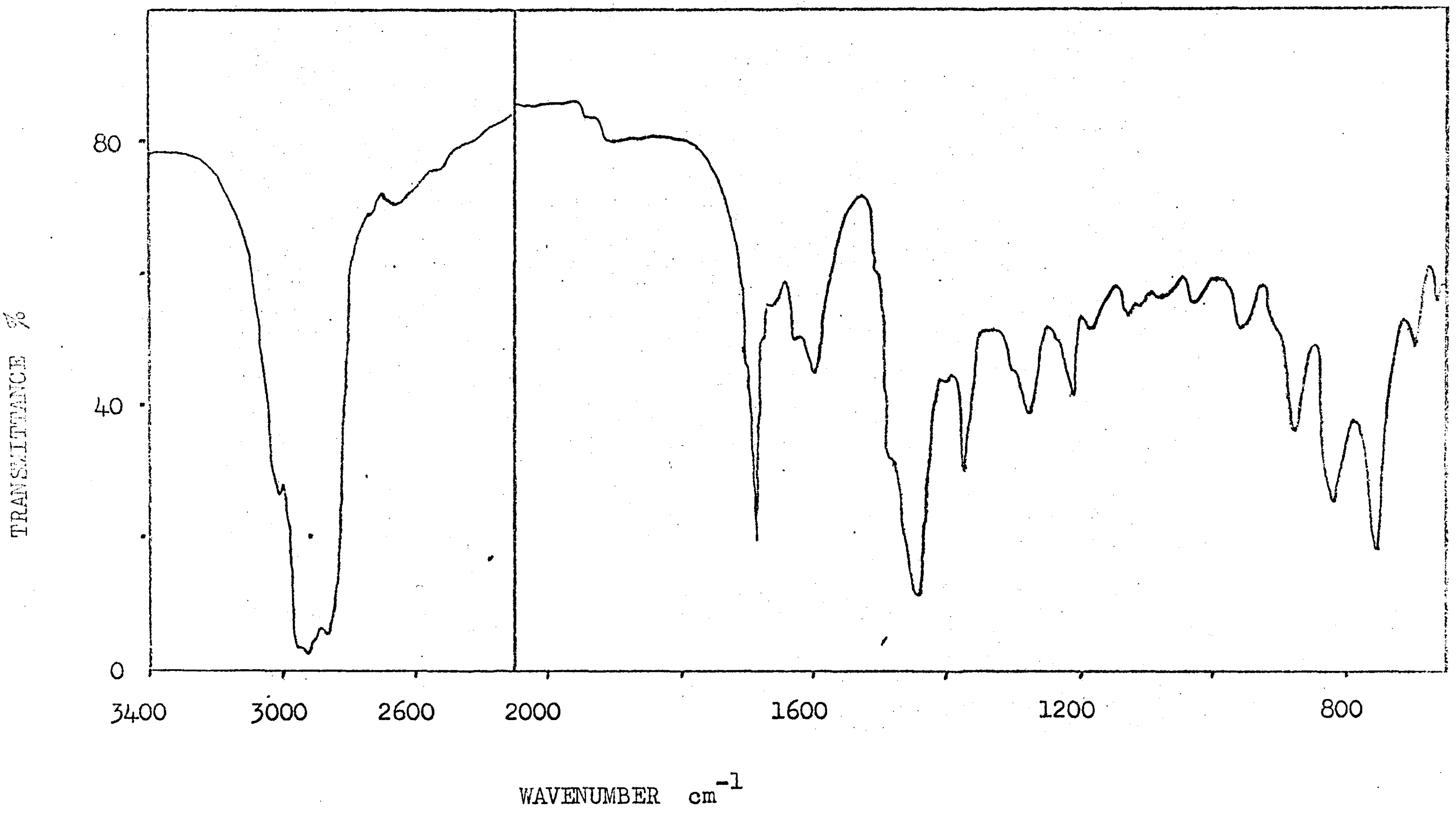
This was found to have an infrared spectrum similar to the oil. Its molecular weight was determined at about 340 using a Hewlett Packard 301A Vapour Pressure Osmometer.

(c) Pitch Fraction

The infrared spectrum of this fraction which is shown in fig. 26, is similar to the spectrum of the liquid products obtained by Harms and Hummel.[46,47] The bands in the 650 - 1000cm^{-1} region indicate that a diversity of aromatic groups are present. There is also a strong absorption at 1215cm^{-1} in the aromatic C - H in plane deformation region. Taking this together with the strongest peak in the lower region at 750cm^{-1} leads to the conclusion that a high proportion of the aromatic rings are 1:2 disubstituted. Peaks associated with C = C bonds occur at 1660 and 1640cm^{-1} while there are also peaks at 3000 and 1600cm^{-1} which could be assigned to double bonds or aromatics. The small shoulder at 1490cm^{-1} is an aromatic absorption.

Aliphatic structures are also present as the peaks at 2900, 1450 and 1380cm^{-1} show. The last mentioned of these serves to identify methyl groups in the tar fraction. One strong band which has not yet been discussed is that at 1690cm^{-1} which would only seem to fit a carbonyl group conjugated with a double bond or an aromatic ring. Oxidation

Fig. 26. Infrared spectrum of pitch fraction from polychloroprene degradation.



after pyrolysis is the most likely explanation.

The spectrum shows strong similarities with the spectrum of the residue at an advanced state of degradation (Chapter 6) and also with the spectrum of the tar obtained by the pyrolysis of PVC.[75]

CHAPTER 5

KINETICS OF DEHYDROCHLORINATION

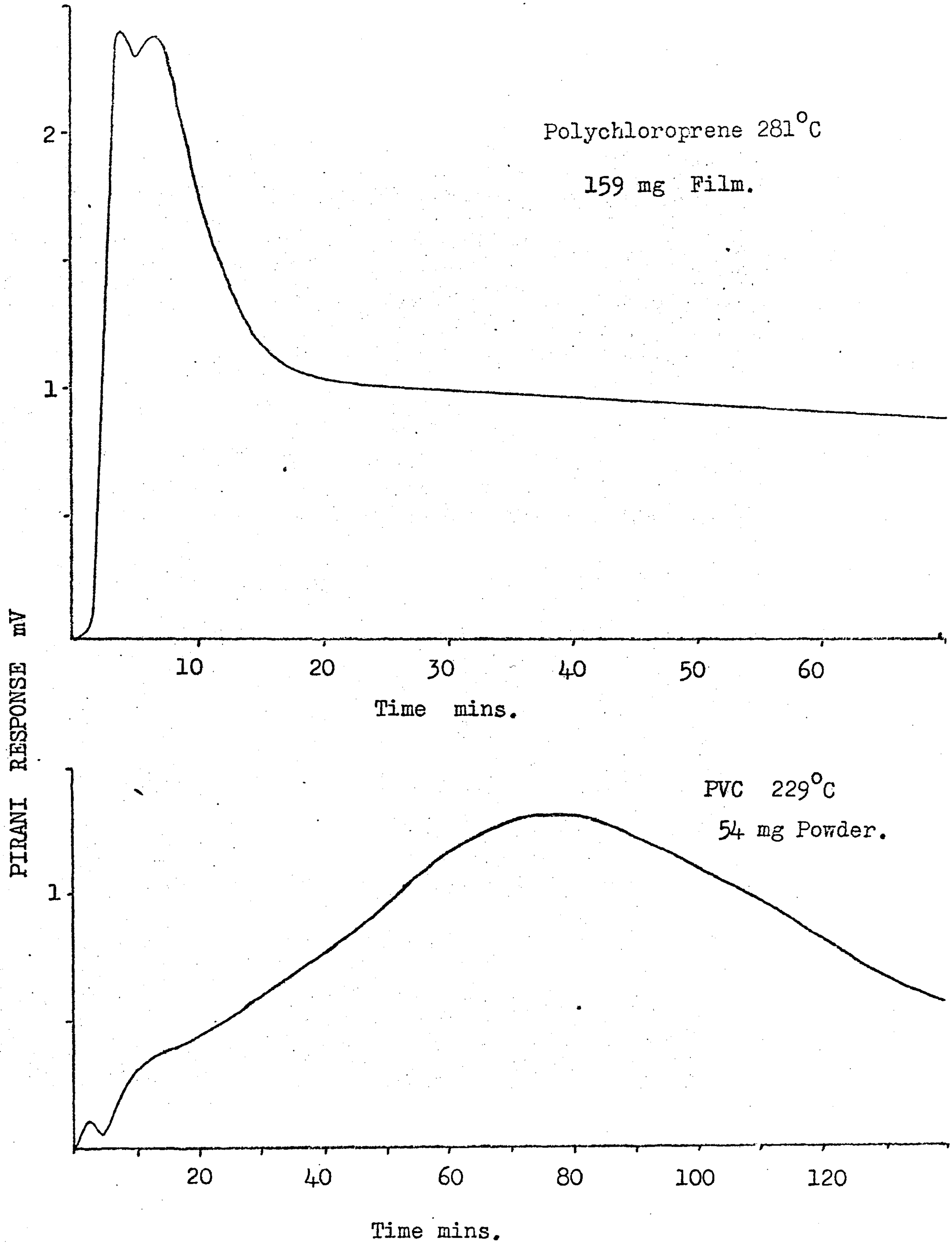
Isothermal TVA

(a) Shape of the Curve

The rate of dehydrochlorination of polychloroprene was examined using the TVA apparatus isothermally. A 159mg. film was cast on the base of the tube by evaporation under nitrogen of a benzene solution of purified MC30 and when free from solvent it was degraded at a temperature between 260 and 290°C for 5 to 6 hours while the flow rate of the hydrogen chloride evolved was continuously recorded by the Pirani gauge. The oven in the TVA system takes about 30 minutes to reach isothermal conditions, which means that the first part of the record cannot be used for kinetic measurements.

A typical trace obtained during an isothermal degradation of polychloroprene is shown in fig. 27 with a trace for PVC for comparison. The polychloroprene trace shows two peaks initially for stages A and B followed by a gradual decrease in the rate during stage C. The PVC curve has a maximum some time after temperature equilibrium has been attained which is caused by the autocatalytic effect of the hydrogen chloride produced. Film and powder PVC samples

Fig. 27. Isothermal Degradation of Polychloroprene and PVC in the TVA apparatus.



of about 50mg. gave the same form of degradation curve but thin films, which have been shown[27] to have increased stability under programmed conditions of TVA, were not examined isothermally here. The effect of hindered hydrogen chloride diffusion during the isothermal degradation of PVC has been discussed by Geddes.[76]

Polychloroprene gave the same shape of curve for both lump and film samples. A 1mg. film was examined using a 1mV. range card in the recorder and the trace again had the same appearance as for the larger samples but it was not possible to make any rate measurements. There is thus no evidence for any diffusion effects in polychloroprene degradation which might complicate the kinetics.

(b) Treatment of Results

At the end of an isothermal degradation the hydrogen chloride in the trap was distilled into a bulb containing distilled water and estimated by titration against 0.1M sodium hydroxide using phenolphthalein indicator. The result of the titration was used to calculate the percentage degradation at the conclusion of the experiment. The values of the Pirani responses were converted to flow rates of hydrogen chloride at suitable time intervals depending on the slope and curvature of the trace, and the area under the curve in each interval was determined in mole units of hydrogen chloride.

The total area under the curve was found to exceed the titration value by about 13%, either because some substance other than hydrogen chloride was also produced or because the temperature at which the hydrogen chloride was evolved affected the Pirani response. The percentage degradation at points along the curve was evaluated using the expression below :-

$$\% \text{ degradation at any point} = \text{total } \% \text{ degradation} \times \frac{\text{area up to point}}{\text{total area}}$$

Apart from the initial 30 minute period which is complicated by oven warm up, and A and B type decomposition, the rate of degradation and the rate/% undegraded both decrease continuously. In order to obtain kinetic parameters from the results a graph was made of log(rate) versus log(% undegraded). If the kinetics can be expressed in the form

$$\frac{-dF}{dt} = kF^n$$

where $F = C/C_o$

C = hydrogen chloride content of polymer

C_o = initial hydrogen chloride content of polymer

t = time (secs.)

k = rate constant ($sec.^{-1}$)

n = order of reaction

then

$$\log -\frac{dC}{dt} = n \log F + \log k + \log Co$$

$$\left\{ \frac{dF}{dt} = \frac{1}{Co}\frac{dC}{dt} \right.$$

therefore

$$\log -\frac{dF}{dt} = \log -\frac{dC}{dt} - \log Co = \log k + n \log F$$

which rearranges to the expression above.}

Since $-\frac{dC}{dt}$ is the rate measured by the Pirani, the graph of log(rate) versus log(% undegraded) has a gradient of n and an intercept at 100% undegraded, i.e. log(% undegraded) = 2, of log k.Co.

The points measured in five isothermal degradations are shown on fig. 28 with the lines obtained by treating the points by the least squares method of linear fit drawn in. Isothermal degradations at temperatures above 290°C give an increased curvature in the graph possibly because more side reactions are taking place. Analysis is also complicated by the fact that 20% of the reaction is finished before the temperature is stabilised.

The values obtained for the order of reaction and the rate constant are given in Table 8. It appears from the table that the order of reaction is close to 1.5 and a test

Fig. 28. log(rate) vs log (% undegraded) for Polychloroprene Isothermal Degradations.

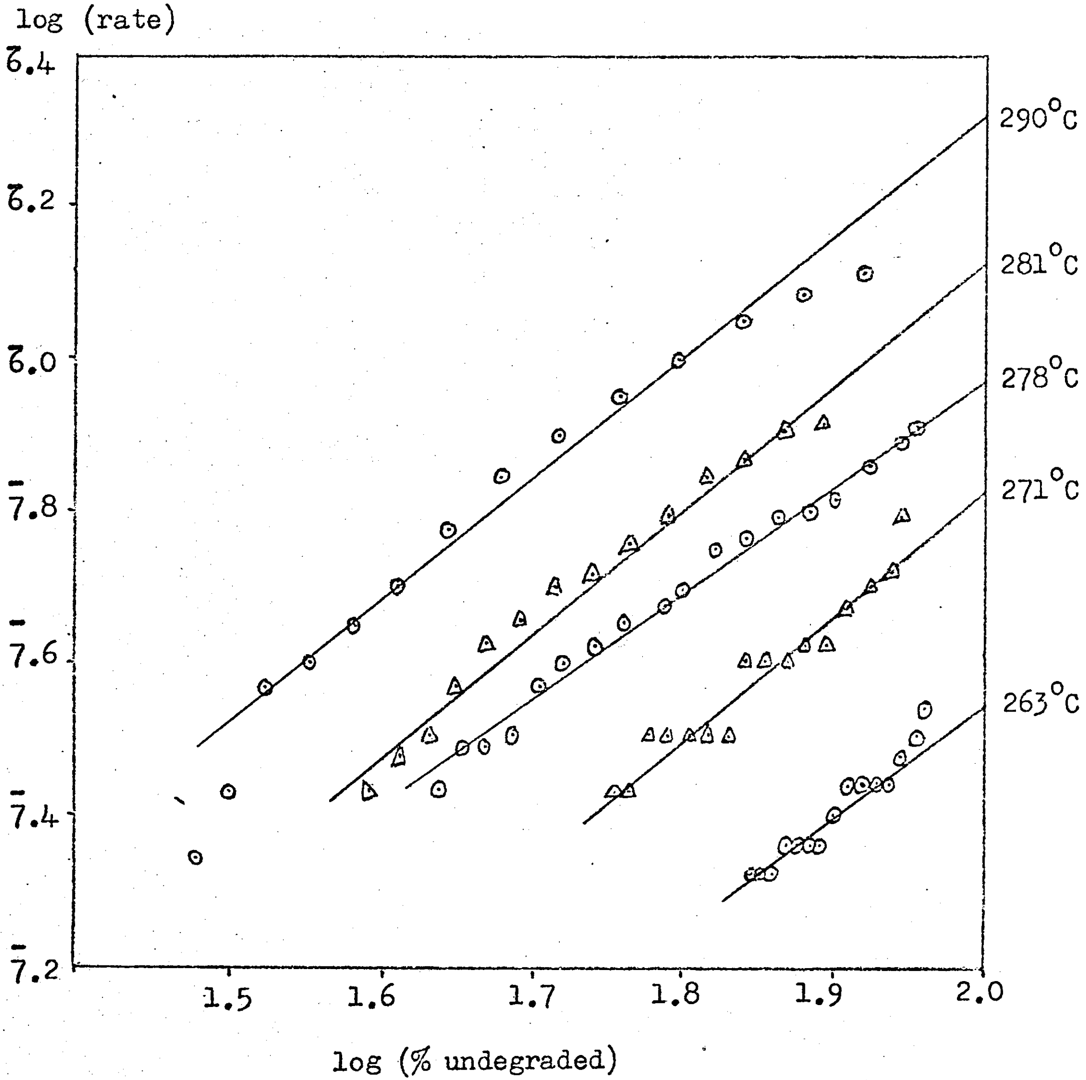


Table 8

Order of reaction (n) and Rate Constant (k) for Isothermal Degradations.

Temperature °C	n	k (sec.$^{-1}$)
263	1.46	1.95×10^{-4}
271	1.61	3.70×10^{-4}
278	1.42	5.26×10^{-4}
281	1.62	7.43×10^{-4}
290	1.66	1.167×10^{-3}

for 1.5 order was made by plotting (% undegraded)$^{-0.5}$ versus time of degradation for the 278°C run. The graph is quite a good straight line as fig. 29 shows, indicating that 1.5 order kinetics do hold.

The activation energy (E) and pre-exponential factor (A) were determined by applying the Arrhenius equation

$$k = Ae^{-E/RT}$$

to the log(rate) intercepts at 0% degradation (fig. 28). A graph was made of log k.Co versus the reciprocal absolute temperature as in fig. 30, and the equation of the line and the standard deviation of the gradient and intercept were calculated by the least squares method. The gradient of the line was taken as -E/2.3R and the intercept as log A.Co giving the values below.

$$E = 39.6 \pm 2.0 \text{ Kcal./mole.}$$

$$\log A(\text{sec.}^{-1}) = 12.4 \pm 0.8$$

Kinetic Parameters from TVA Curves

(a) Assuming Zero Order Reaction

In the early stages of the reaction the amount of material lost is very small and the quantity of polymer degrading can be considered to be the same as the initial amount throughout. This means that in the equation

Fig. 29

Test for 1.5 order in 278°C isothermal degradation of polychloroprene.

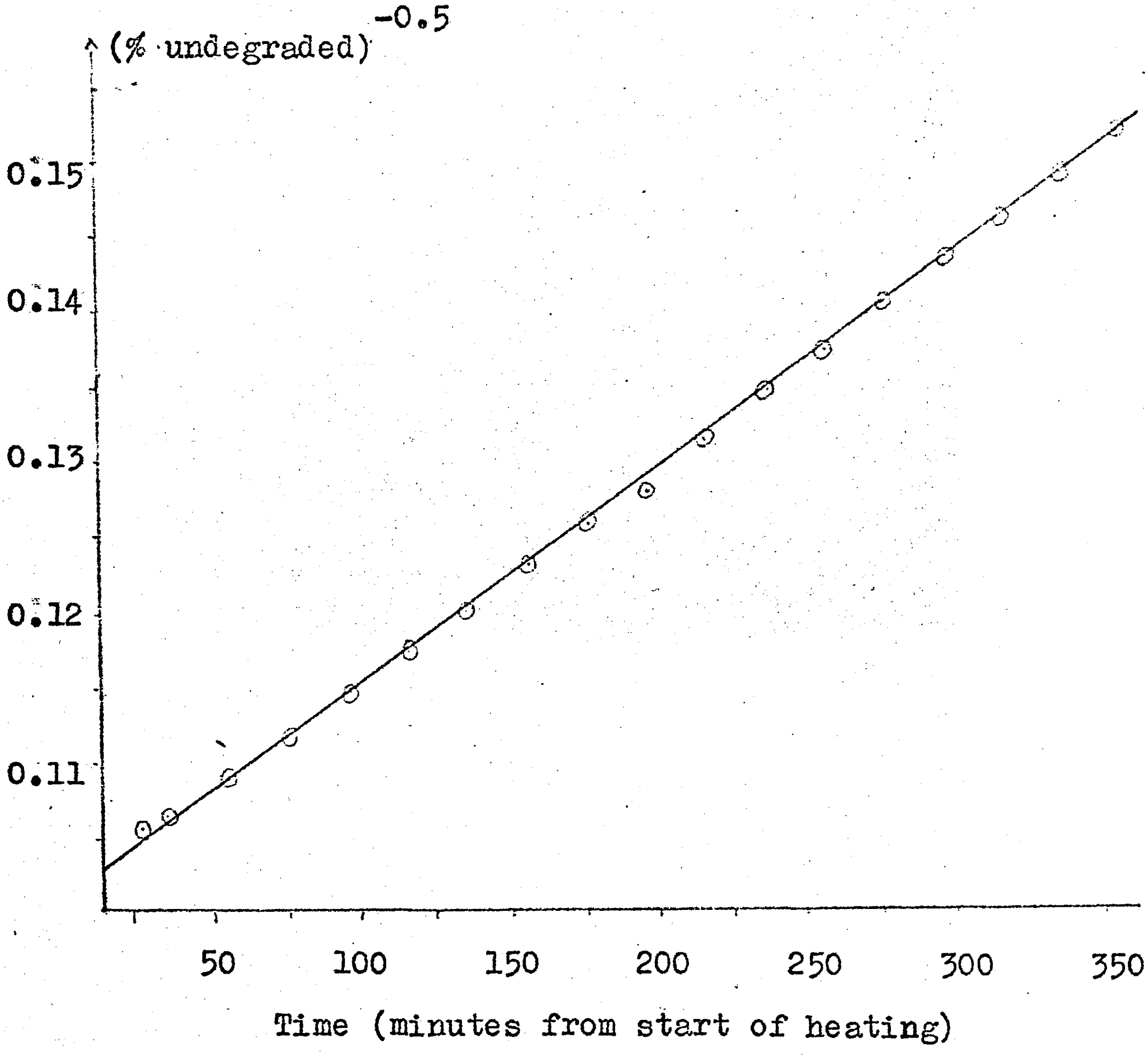
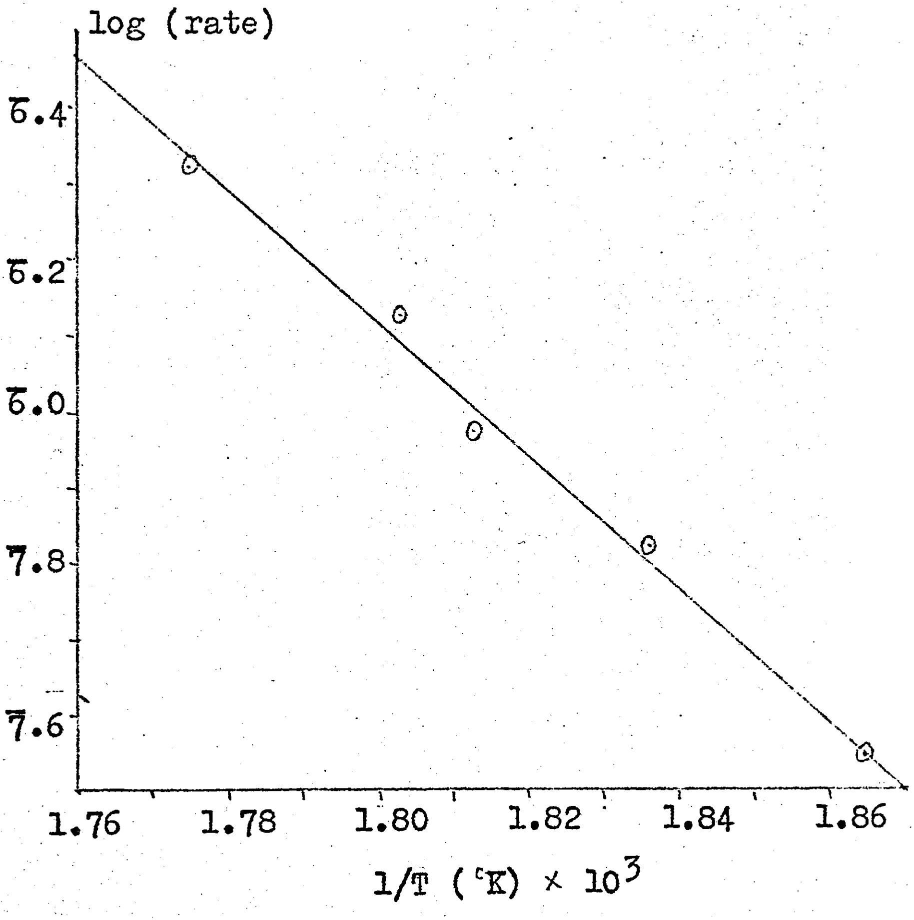


Fig. 30

log (rate) at 0% conversion vs. 1/T for polychloroprene isothermal degradations.



$$\log -\frac{dC}{dt} = n\log F + \log k + \log Co,$$

given in the previous section,

then $F = 1$ and $n\log F = 0$.

In effect this is equivalent to assuming that the rate is independent of the degree of conversion i.e. the reaction is zero order.

Substituting the Arrhenius expression for k in the above equation, it follows that

$$\log -\frac{dC}{dt} = -E/2.3RT + \log A + \log Co.$$

A plot of $\log -\frac{dC}{dt}$ against $1/T$ therefore has gradient $-E/2.3R$ and an intercept of $\log A.Co$.

The method was applied to TVA curves of lump samples of PC4 heated at 5°/min. and 10°/min. and to the TVA curve of a film of purified MC30 heated at 10°/min. The reason for choosing PC4 was that no stage B reaction was present to complicate the first part of the degradation. Points between 320 and 350°C were selected and the flow rate of hydrogen chloride at each point determined from the Pirani calibration curve. The graphs obtained are shown in figs. 31, 32 and 33 with the best fitting straight lines drawn in as calculated by the least squares method. E and A values given by the gradients and the intercepts of the lines are tabulated overleaf.

Fig. 31

log (rate) vs. 1/T for 19.4mg. PC4, 10 °/min.

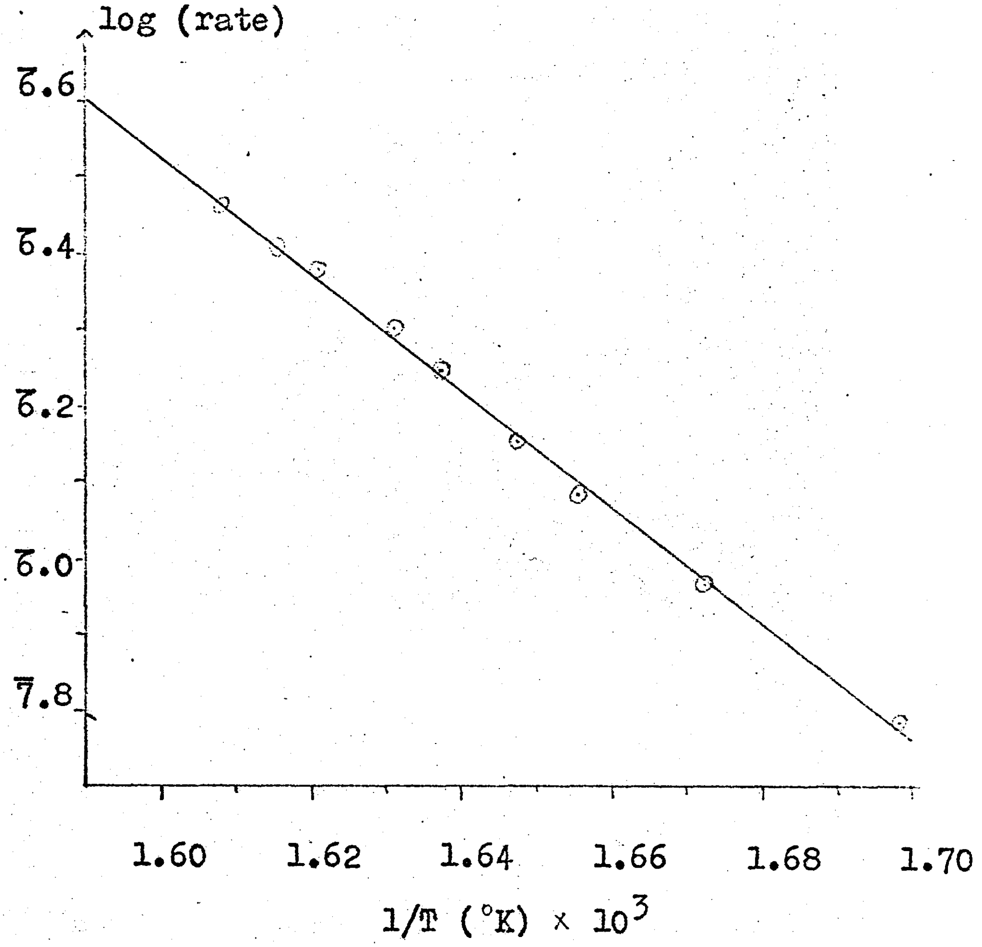


Fig. 32
log (rate) vs. 1/T for 19.7mg. PC4, 5 °/min.

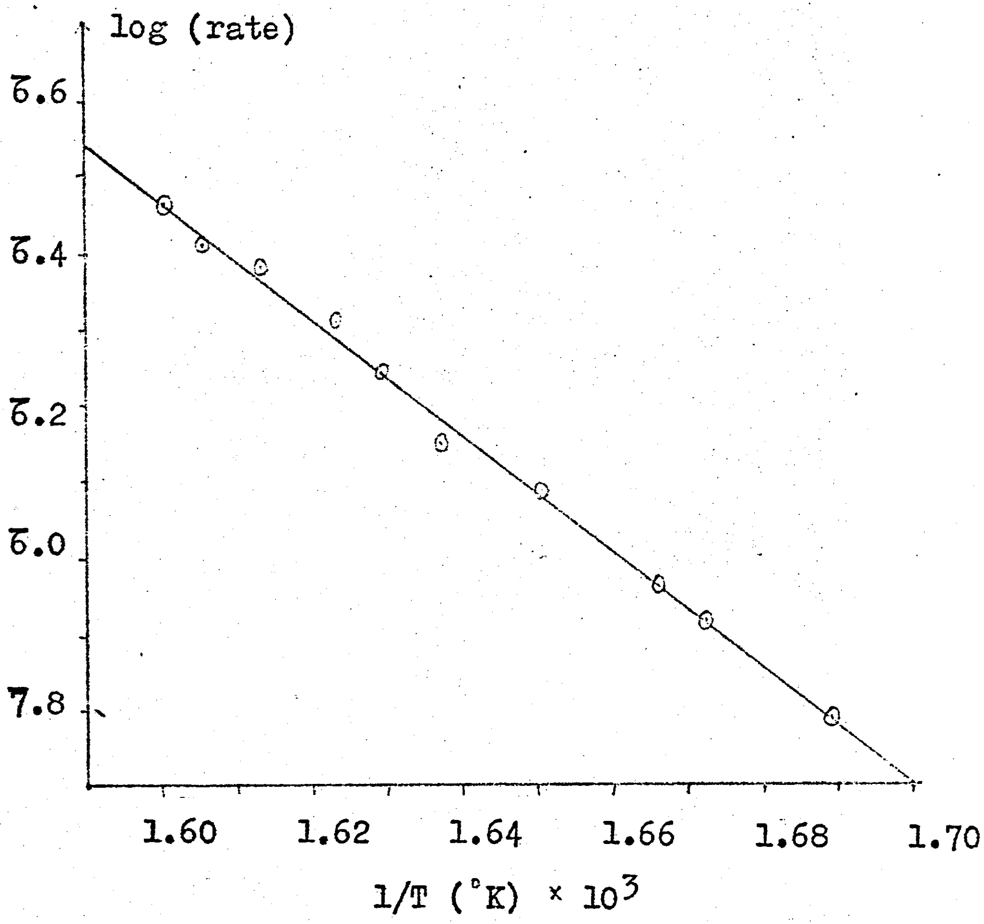


Fig. 33

log (rate) vs. 1/T for 20mg. MC30 film, 10°/min.

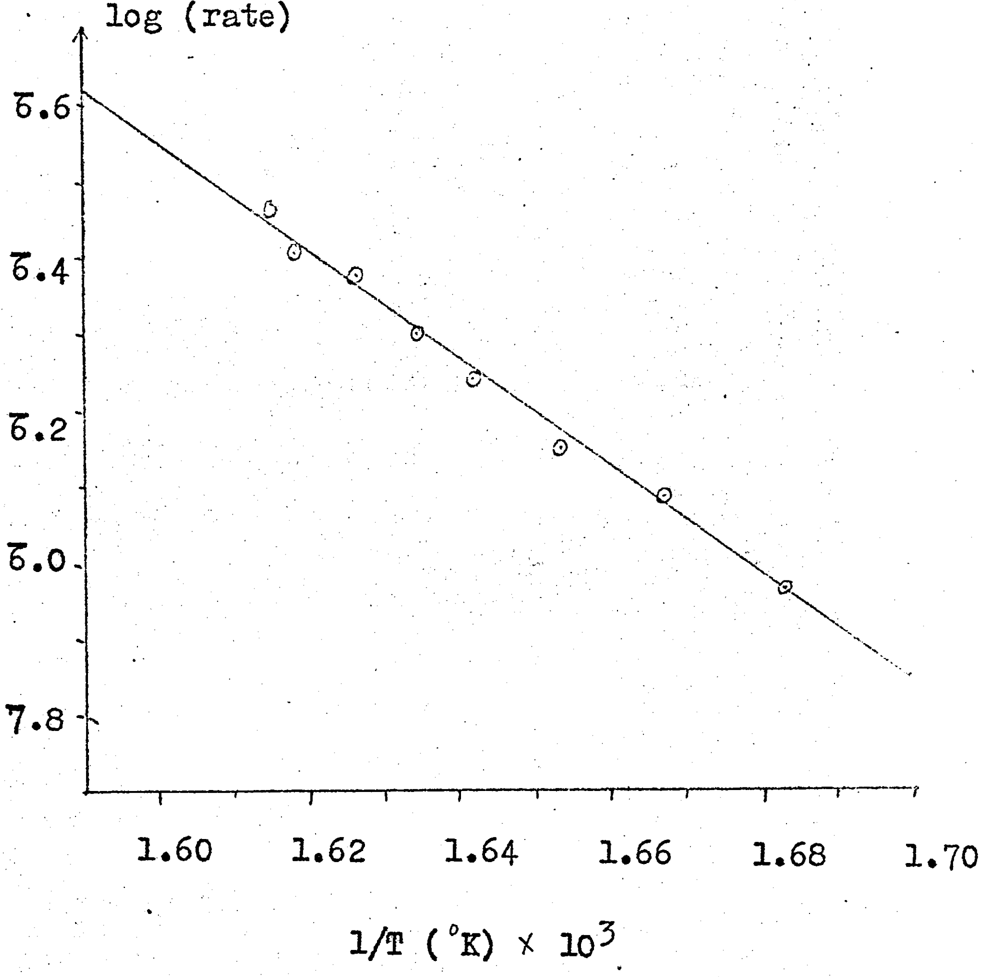


Table 9

E and A from Log(rate) versus 1/T Plots for TVA Curves.

TVA Curve	E (Kcal./mole)	Log A ($sec.^{-1}$)
PC4 10 °/min.	34.9	10.4
PC4 5 °/min.	34.6	10.2
MC30 10 °/min.	32.9	9.7

Although the graphs seem to be fairly linear, it has been shown by Neil[56] that the effect of neglecting the term in F is to produce curvature towards a lower gradient as the reaction proceeds. The results for E and A from this method are therefore probably rather less than the true values.

(b) Kissinger Method

TVA is a very good technique for determining the temperature at which the maximum rate of degradation occurs (T_{max}). This quantity can be used to calculate the activation energy for the process and for this the Kissinger method[77] is especially useful since no rate measurements are required.

The formula used is derived here for a first order reaction but holds approximately for all values of n. All the symbols have the same significance as before and the heating rate is denoted by β,

$$\text{i.e.} \quad \beta = \frac{dT}{dt}.$$

For a first order reaction,

$$-\frac{dF}{dt} = kF, \quad \text{therefore} \quad -\frac{dF}{dT} = \frac{k}{\beta} F.$$

Using the Arrhenius expression for k, it follows that,

$$-\frac{dF}{dT} = \frac{A}{\beta} e^{-E/RT} F.$$

The condition for a maximum is that

$$-\frac{d^2F}{dT^2} = 0,$$

$$\text{i.e.} \quad \frac{A}{\beta} \left\{ \frac{E}{RT^2} e^{-E/RT} F + e^{-E/RT} \frac{dF}{dT} \right\} = 0,$$

$$\text{i.e.} \quad \frac{E}{RT^2} e^{-E/RT} F = e^{-E/RT} \frac{A}{\beta} e^{-E/RT} F,$$

$$\text{therefore} \quad \frac{E}{RT^2_{max}} = \frac{A}{\beta} e^{-E/RT}.$$

On taking logarithms and rearranging this becomes

$$\log \beta - 2 \log T_{max} = -\frac{E}{2.3R} \frac{1}{T_{max}} - \log \frac{E}{RA}.$$

Thus a graph of $(\log \beta - 2\log T_{max})$ has gradient $-\frac{E}{2.3R}$

and intercept $-\log \frac{E}{RA}$.

Kissinger's method thus requires T_{max} measurements for a range of heating rates. The TVA apparatus used here however had only been calibrated for heating rates of 5 and 10 °/min., therefore only two points were used and no graph was drawn. The T_{max} values were taken from the TVA curves of PC4 used in the previous calculation. T_{max} was 362°C at 5.85 °/min. and 371°C at 10.57 °/min., and application of the Kissinger method to these figures gave results of 43.7Kcal./mole for E and log A $(\mathrm{sec.}^{-1})$ = 11.5. Little confidence can be placed in these results, however, without further measurements of T_{max} at widely different heating rates.

Activation Energy from a TG Curve

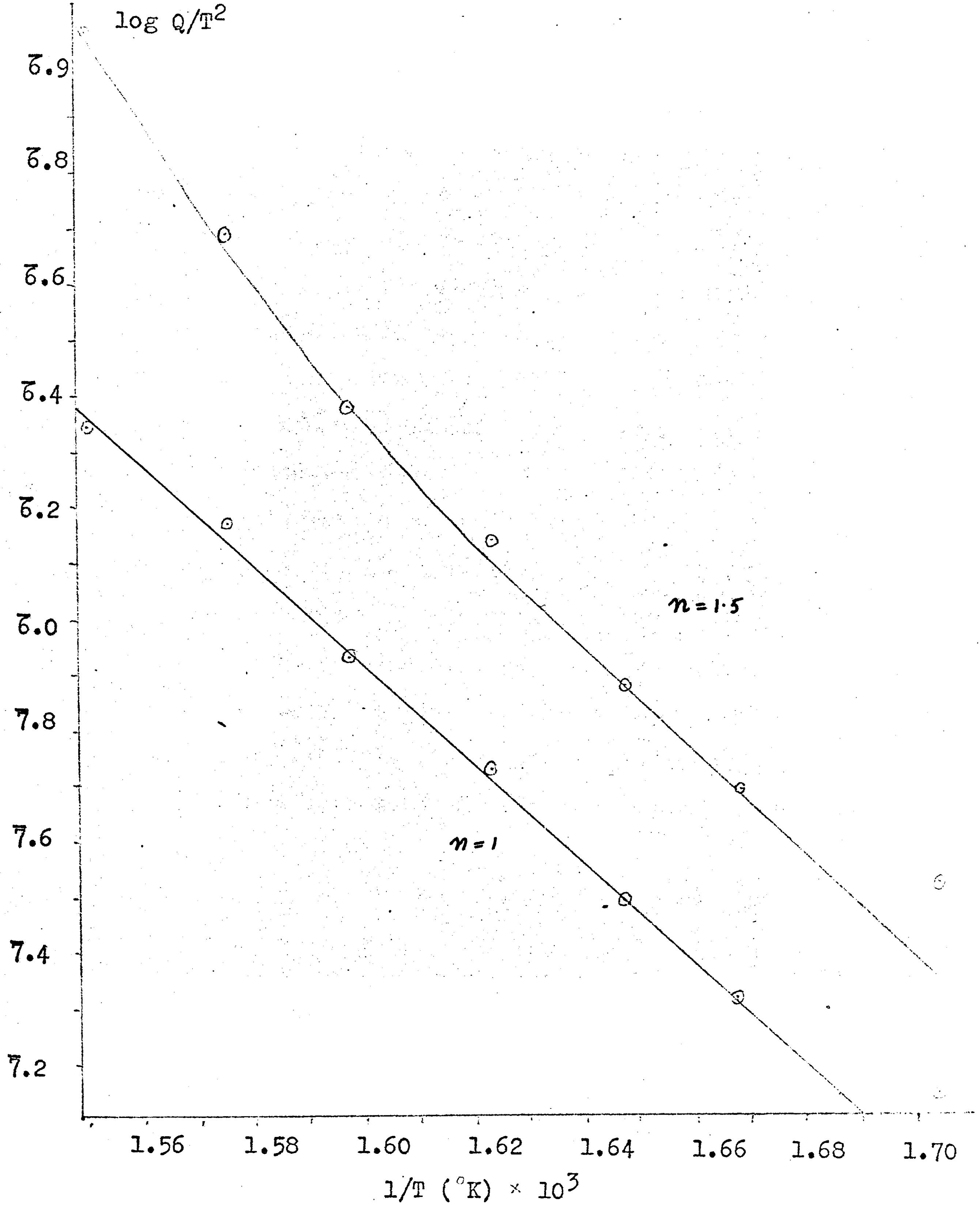
Several ways of obtaining kinetic parameters from TG curves have been devised and the various methods have been discussed and compared in a number of reviews.[78,79,80] One of the procedures which gives an accurate result,[80] holds true for reactions of any order, and is fairly simple to apply, is the Coats and Redfern method. This involves plotting log Q/T^2 versus $1/T$ where $Q = \frac{1-F^{(1-n)}}{1-n}$, unless $n = 1$ when $Q = -\log F$. The best straight line is found by varying n and this line has gradient $-E/2.3R$. A full derivation of the equations which lead to this conclusion may be found in reference 31.

One difficulty in applying this method to polychloroprene degradation is the overlap of the two stages of the TG curve. An overall activation energy, taking into account the side reactions occurring simultaneously with dehydrochlorination could be found, if it was clear at what point the first stage ended. Unfortunately this is not the case and the point of inflection in the curve between the two stages is therefore estimated as the end of the first reaction A 5°/min. TG curve of MC30 was recorded on an expanded scale and the point of inflection was determined as 395°C at 43.2% weight loss, in fair agreement with the first stage weight loss quoted in chapter 3 for the 10°/min. TG curve.

The functions log Q/T_2 with $n = 1.5$ and $n = 1$ were calculated at temperatures of 314, 327, 334, 343, 353, 362 and 372°C and the graphs obtained are shown in fig. 34. It is evident that $n = 1.5$ produces curvature whereas $n = 1$ gives a straight line apart from the point at 314°C which might reasonably be expected to be in error because of the effects of the early A and B type features of polychloroprene degradation. The equation of the best straight line through the other six points was calculated and from the gradient the value of E was 40.9Kcal./mole.

Fig. 34

$\log Q/T^2$ vs. $1/T$ for a 5°/min. MC30 TG curve.



Activation Energy from Hydrogen Chloride Evolution Data

Coats and Redfern's method was applied to the dehydrochlorination reaction of polychloroprene using the data in Table 5. The value of F was taken as (1 - fraction of polymer chlorine lost as hydrogen chloride), an expression which would be valid for the dehydrochlorination even in the presence of side reactions provided they did not remove chlorine. Only 90% of the polymer chlorine is however removed as hydrogen chloride and therefore a slight error is introduced.

The calculation was performed for the mean results at temperatures of 326, 338, 350, 362 and 380°C for $n = 1.5$ and $n = 1$. There is too much scatter in the results (fig. 35) to decide which value of n produces the lesser curvature and accordingly the equations of the best fitting straight lines were calculated for both sets of points. The gradients of the lines were used to determine the activation energy which was found to be

$$E = 33.6\text{Kcal./mole if } n = 1$$

$$\text{and } E = 38.6\text{Kcal./mole if } n = 1.5.$$

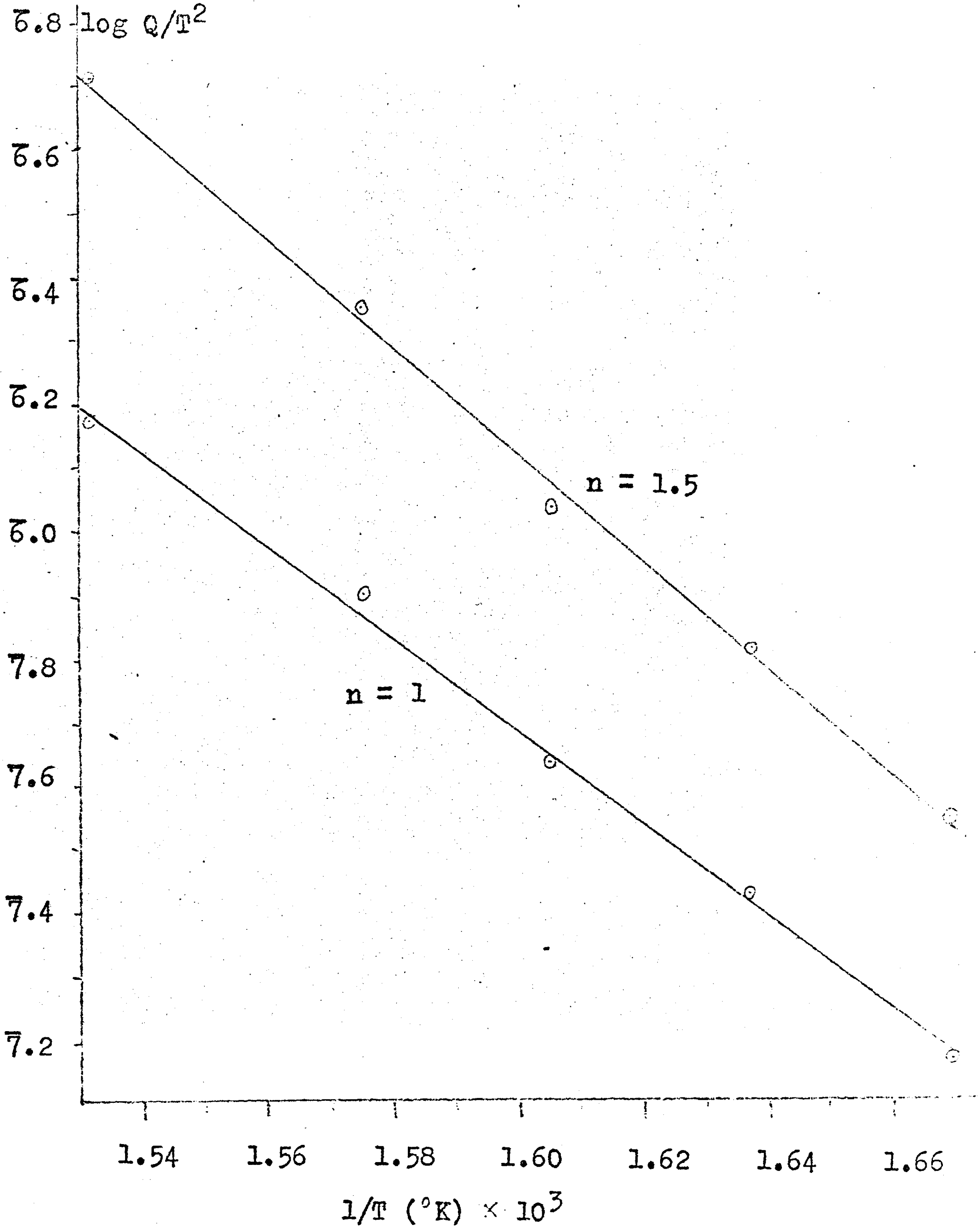
Summary

Isothermal degradations give values of

$\log A\ (\text{sec.}^{-1}) = 12.4$ and $E = 39.6$Kcal./mole.

Fig. 35

log Q/T^2 vs. $1/T$ for data from Table 5.



Treatment of the results from programmed experiments by a variety of methods gives values in the range shown below, where the lower figure is known to be too low.

$$\log A\ (\text{sec.}^{-1}) = 9.7 \text{ to } 11.5$$

$$E = 32.9 \text{ to } 43.7\text{kcal./mole.}$$

The isothermal results are thus confirmed to a fair degree.

Values of $n = 1.5$ and $n = 1$ were both found to fit some of the data.

These results are further discussed in Chapter 9.

CHAPTER 6

SPECTROSCOPIC EXAMINATION OF THE RESIDUE

Infrared Spectroscopy

(a) Changes in the Spectrum with Increasing Degradation

Typical spectra of the polymer heated to different temperatures are displayed in fig. 36. The undegraded film occasionally has a small carbonyl peak or shoulder at 1720cm^{-1} due to oxidation (as in the spectrum in fig. 36). This peak disappears when the polymer was heated to 300°C but the only other changes showing in this spectrum (not illustrated) are the disappearance of the peak at 925cm^{-1} due to 1:2 units, and the appearance of barely distinguishable peaks at 1600 and 960cm^{-1}.

The residue from degradation to 344°C shows more differences from the undegraded polymer. The unconjugated C = C stretching vibration at 1660cm^{-1} and its overtone at 3300cm^{-1} decrease and a broad peak at 1600cm^{-1} for conjugated C = C appears. The C - H out of plane deformation band at 960cm^{-1} for trans disubstituted double bonds also becomes more evident. The double bonds in the original polymer have two alkyl and one chlorine substituent and and give an absorption at 826cm^{-1} which becomes less intense as hydrogen chloride is eliminated. The C - H

Fig. 36 (Overleaf)

Infrared Spectra of Degraded Polychloroprene.

Fig. 36. Infrared Spectra of Polychloroprene heated at 5°/min to Temperature shown.

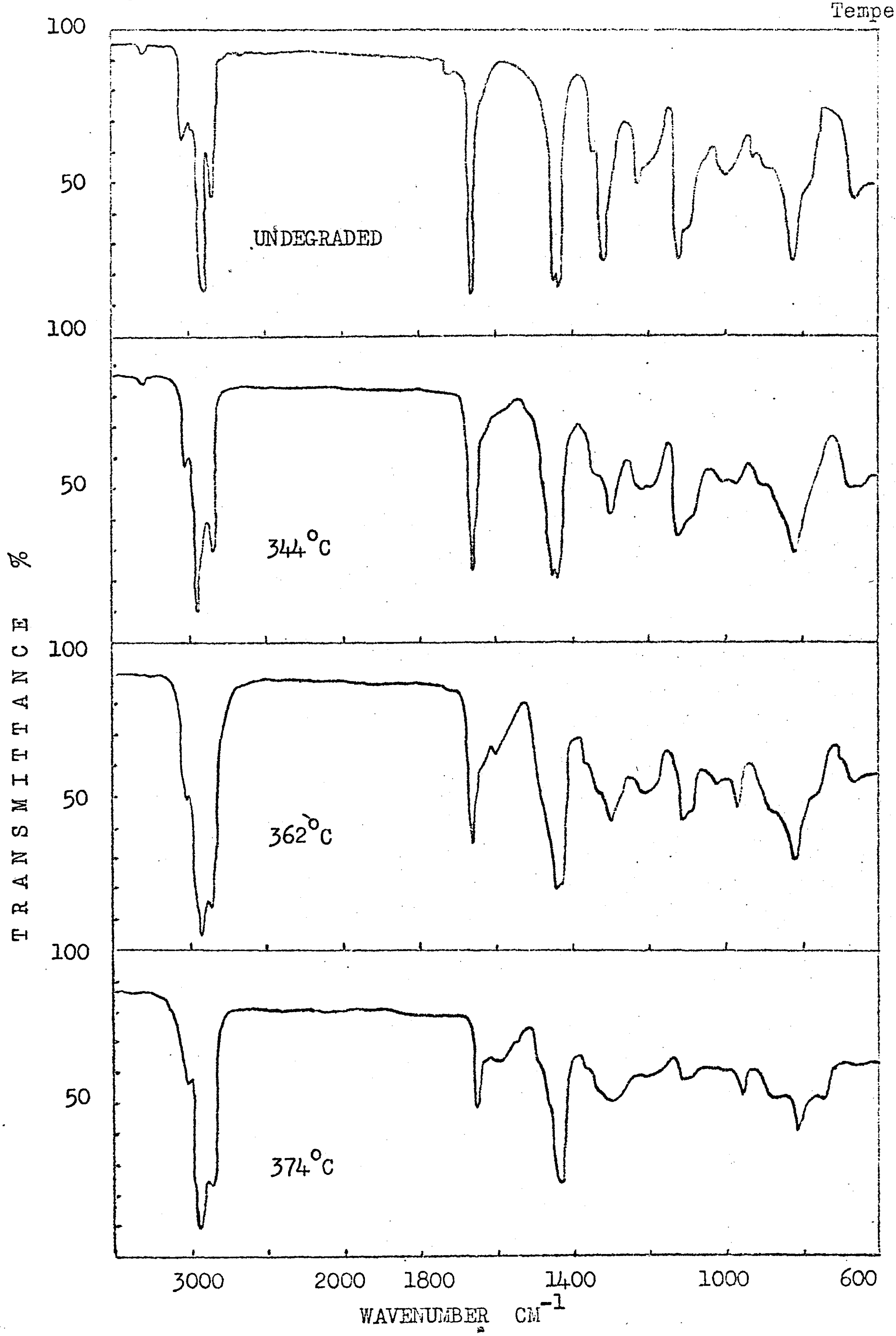
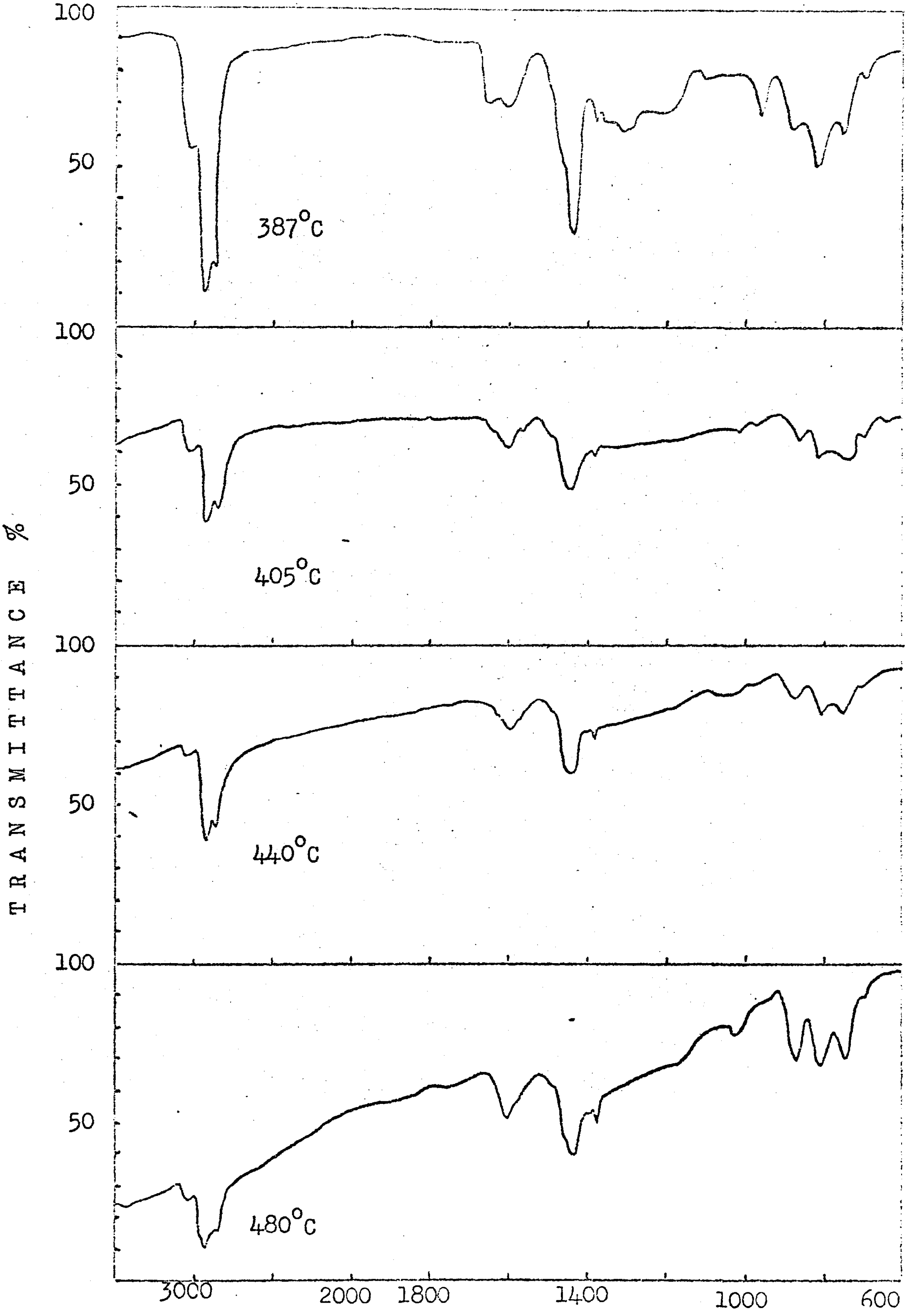


Fig. 36. Continued.



deformation peaks of the methylene groups of the polymer at 1442, 1430, 1300 and 790cm^{-1} and the other peaks in the spectrum of the undegraded polymer become smaller, but the largest one present, the C - H stretching band at 2910cm^{-1} shows little change.

In the spectra of the residue at 362 and 374°C the changes described above become more pronounced, and in addition a peak at 1375cm^{-1} appears. This frequency corresponds to the symmetrical deformation of the C - H bonds in a methyl group. Changes also occur in the region below 900cm^{-1} where the maximum in the 820cm^{-1} peak shifts to 815cm^{-1} and peaks at 870 and 850cm^{-1} appear. These absorptions indicate the formation of aromatic structures within the residue.

The spectrum at 387°C displays an increase both in the double bond vibrations at 1600 and 960cm^{-1} and in the aromatic bands. A new peak at 695cm^{-1} becomes evident in the aromatic region.

The spectra at 405°C and at higher temperatures were recorded in potassium bromide disc form. They show the disappearance of the 960cm^{-1} band due to cyclisation and the concommittant increase in the aromatic vibrations. The methyl group peak at 1375cm^{-1} persists throughout the temperature range and a new absorption appears at 1020cm^{-1}.

A spectrum was also recorded of the residue at 510°C.

It contained the same strong aromatic peaks as the 480°C residue but the others were reduced in intensity and in definition.

(b) Absorptions not Present

Elimination in polychloroprene might produce an alkyne or allene structure. Unfortunately because a change in dipole moment is a prerequisite for an absorption in the infrared, the $C\equiv C$ stretch produces only a weak absorption in unsymmetrically substituted alkynes and no absorption at all in symmetrical ones. There is no evidence for alkyne absorption in the region 2260 - 2190cm^{-1} but the triple bond produced within a polymer chain would be in an almost symmetrical environment. Allenes have infrared active frequencies at 1970 - 1950cm^{-1} and at about 1060cm^{-1} but neither of these appears in the spectra.

(c) Aromatic Substitution

In order to investigate the aromatic substitution pattern an extremely finely ground residue from degradation to 455°C was compacted into a potassium bromide disc and the spectrum recorded on a Perkin Elmer 225 Grating Spectrophotometer. The result was similar to the 440°C spectrum in fig. 36 but some extra detail could be distinguished in the aromatic C - H out of plane deformation region. Peaks were visible at 870, 810, 750, 695 and 665cm^{-1}.

The absorption at 750cm^{-1} can only be due to mono-, 1:2 or 1:3 disubstitution. Since the peak at 695cm^{-1} is not very large, mono substitution is not prevalent. The presence of strong peaks at 870 and 810cm^{-1} could indicate a variety of substitution patterns which contain only 1, 2 or 3 adjacent C - H bonds on the aromatic nucleus.[82]

(d) PVC

The spectrum of degraded PVC is of interest at this stage for comparison. PVC heated to 405°C gives a spectrum rather similar to that of the equivalent polychloroprene residue. The aliphatic C - H stretching vibration at 2900cm^{-1} is smaller and the peak for C = C stretch at 1580cm^{-1} is about 10cm^{-1} lower than in polychloroprene. The 1440cm^{-1} peak is present as in polychloroprene but the 1380cm^{-1} band for methyl groups is missing. There is a much stronger absorption at 960cm^{-1} for double bonds and the largest aromatic peak is at 750cm^{-1}. The other aromatic frequencies in order of decreasing intensity are 810, 695, 870 and a small shoulder at 670cm^{-1}.

These observations are in agreement with the results of Gilbert and Kipling[83] except that they observed a small methyl group peak after prolonged heating of the residue at 400°C. The amount of methyl group formation however, is not nearly so great in PVC as in polychloroprene. The predominance of the 750cm^{-1} band in pyrolysed PVC indicates the formation of mono- and disubstituted aromatics. In polychloroprene, although the 810cm^{-1} aromatic peak is the largest, the difference between the intensities of the 870, 810 and 750cm^{-1} absorptions is not very great, which probably indicates that the substitution pattern may take more diverse forms.

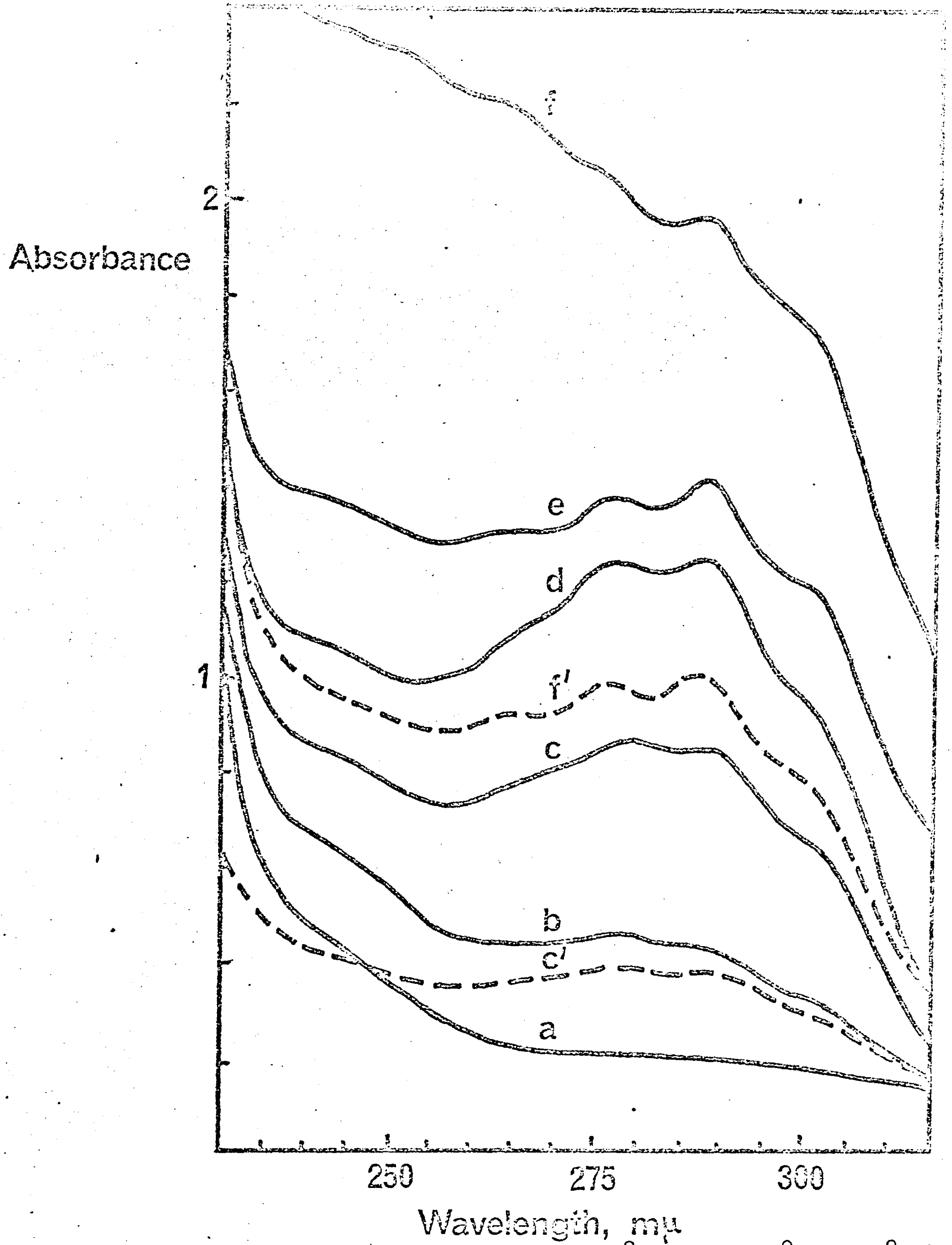
Ultraviolet Spectroscopy

The ultraviolet (UV) spectra of degraded films of polychloroprene MC30 are shown on figs. 37 and 38. They show how a distinct four peak pattern arises early in the degradation to be obscured later by a featureless absorption which extends from low wavelengths to 550mμ.

The spectrum with the highest absorption intensity in fig.37 was recorded from a film heated to 295°C, i.e. just past stage B, (page 42) which seems to be the point at which the details of the spectrum become indistinct. Isothermal heating at 210°C furnishes a similar set of spectra to those on fig. 37. Only 10 minutes are required to produce a spectrum like the one from programmed heating to 278°C and a 295°C type spectrum results after 100 minutes.

Films of PC-40 were also examined, and two typical spectra appear on fig. 37. There is no change in the

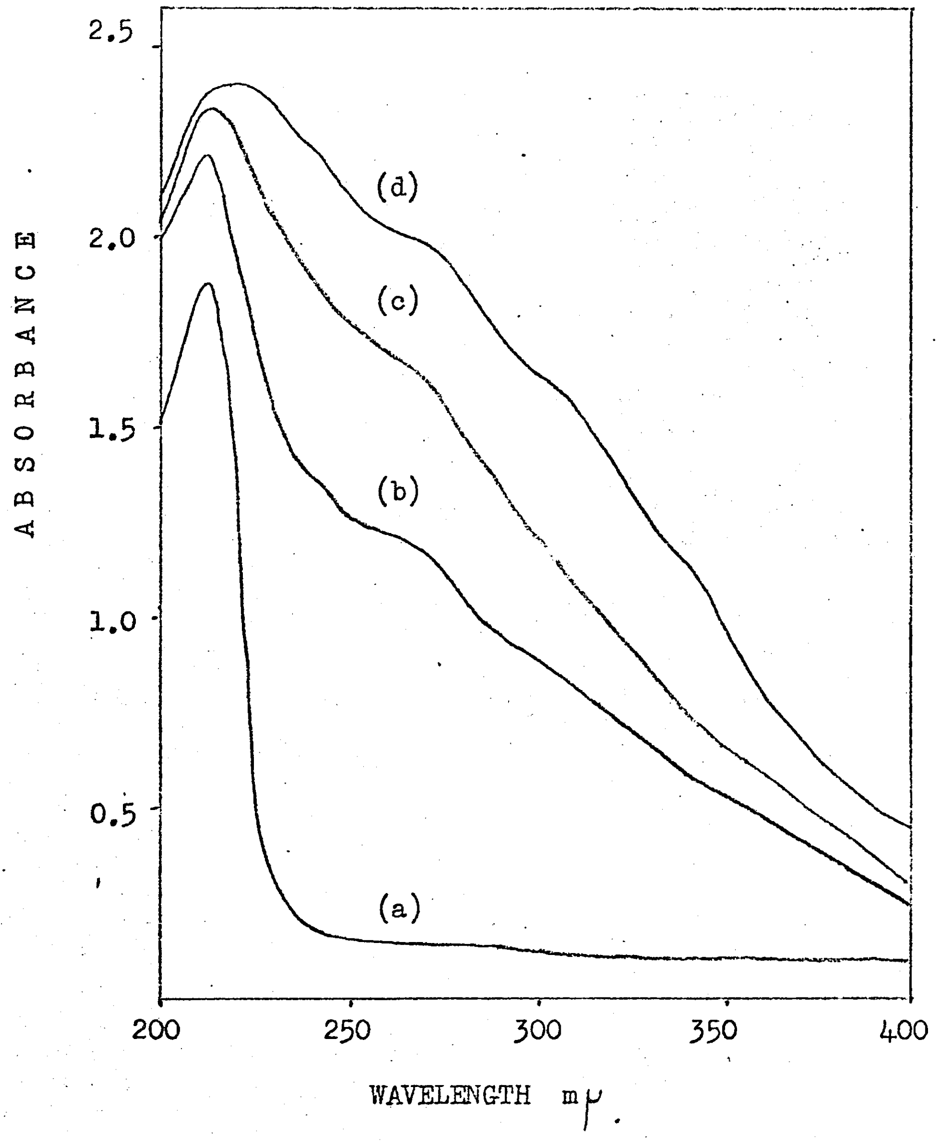
Fig. 37. UV Spectra of 20 mg. films of polychloroprene.



Full line MC30 undegraded (a) and heated at 5°/min to 185°(b) 210°(c) 233°(d) 278°(e) 295°(f)

Dashed line PC-40 heated to 233°(c') and 295°(f')

Fig. 38. UV spectra of 2mg Films of Polychloroprene.

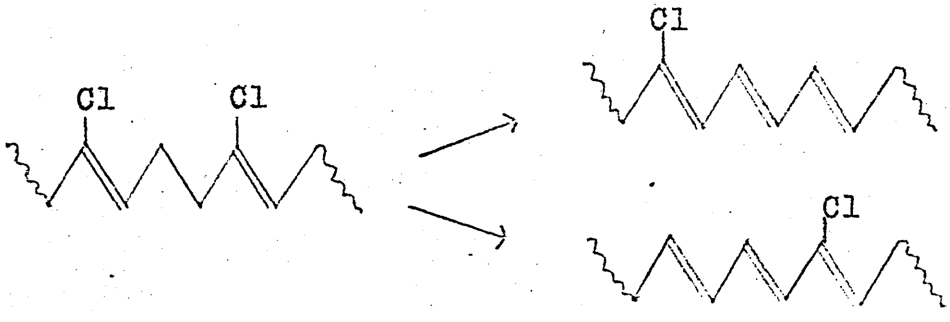


undegraded (a) and

heated at 5°/min to 356°C (b), 381°C (c) 418°C (d).

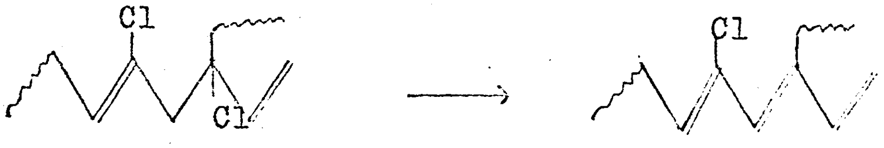
positions of absorptions but the intensity is greatly reduced, thus demonstrating that the features in the UV spectrum are linked to the amount of dehydrochlorination which takes place at an early stage in the reaction. This polymer does not show stage B reaction so that most of the dehydrochlorination for the 295°C spectrum has come from reaction C. At 320°C the spectrum is similar to 295°C spectrum of MC30.

The two maxima in the spectra occur at 277 and 288mμ and the inflections at 265 and 300mμ. Interpretation of the spectra however presents rather a problem in the absence of sufficient data on the UV spectral properties of chlorotrienes. The result of dehydrochlorination at a 1:4 unit is probably either a 1-chloro- or a 2-chloro-1,6-dialkylhexatriene, (i) and (ii), while a 2-chloro-1,4-dialkylhexatriene (iii) may be formed from a 1:2 unit.



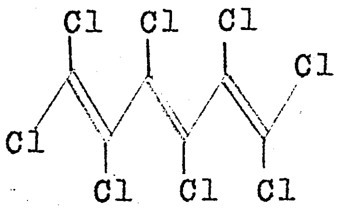
(i)

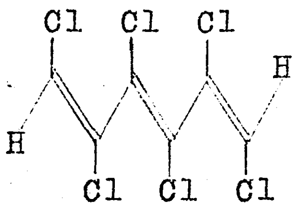
(ii)

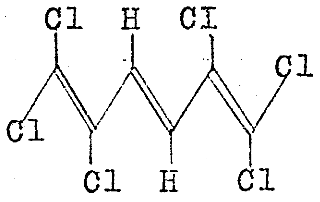


(iii)

Reference spectra of these monochlorotrienes could not be found in the literature although more highly chlorinated compounds have been examined. The spectra of perchlorohexatriene (iv) and 1,6-dihydro-hexachlorohexatriene-1,3,5 (v) are similar[84,85] and show a maximum at 266$m\mu$ and a shoulder between 250 and 300$m\mu$ (in iso-octane).


(iv)


(v)


(vi)

3,4-Dihydro-hexachlorohexatriene (vi) gives a different spectrum[85] because conjugation is not impaired by the steric strain involved by the chlorine atoms in adjacent 2, 3, 4 and 5 positions. It gives peaks at 320, 300 and 290$m\mu$ and further fine structure at shorter wavelengths (in iso-octane).

Chlorine substitution to pre-existing chromophores has been shown to produce a bathochromic shift of about 10mμ[86] so that one might expect to see the spectrum of a 1,6-dialkylhexatriene (vii) moved to longer wavelength by

(vii)

this amount. It is shown in a later section on vinyl acetate polymers that this chromophore gives peaks at 261, 272 and 283mμ when present in a polymer film. The wavelengths of the absorptions in degraded polychloroprene are 16mμ higher and there is an additional fine structure peak at 265mμ.

It is of course possible that the absorption is the sum of two or more different series of peaks, for instance 265, 277 and 288mμ and 277, 288 and 300mμ. Different structures such as (i), (ii) and (iii) or cis/trans isomerism could be responsible, but whether the spectrum is that of a pure chromophore or a mixture of similar chromophores, it seems likely that chlorotriene structures are present although positive identification must await the spectroscopic examination of model compounds.

The spectra in fig. 38 are not very informative. It appears that before very much of the dehydrochlorination has taken place, longer polyene sequences are produced and such a variety of chromophores is present that the band structure is lost. Although absorption does extend to 550mμ there is little beyond 450mμ, corresponding to about 12 double bonds in conjugation.[87] The colour of films degraded beyond the initial stages is yellow unlike PVC films examined in the same way which appear red even at the start of the degradation. The UV spectra of degraded PVC and other polymers is described in the next chapter.

CHAPTER 7

ELIMINATION REACTIONS IN OTHER POLYMERS

Reasons for Investigation

A number of vinyl polymers degrade by elimination reactions leaving a main chain unsaturation structure. It was decided to investigate some of those by the UV spectroscopic technique used for polychloroprene as well as by other methods as seemed appropriate.

PVC was examined for a comparison with polychloroprene of the dehydrochlorination reaction in the two polymers and also to ensure that the results obtained by the UV method agreed with those of previous workers. Polychloroprene and PVC were found to behave entirely differently with respect to the initial length of polyene conjugation produced and it was considered of interest to find out if either of these was typical of elimination reactions in general.

Poly(Vinyl Chloride) (PVC)

The polymer examined was Breon 113, an additive free polymer produced by British Geon. Cyclohexanone was used to make solutions from which films were cast by vacuum evaporation of 1ml. of solution.

(a) DC - TVA

The curves for a 50mg. powder sample are shown in fig. 39. Dehydrochlorination takes place at lower temperature than in polychloroprene and the carbonisation reaction is well separated from the elimination. TGA shows that PVC dehydrochlorinates quantitatively in programmed degradation and it is therefore not surprising to find almost no non-condensables being evolved during the first peak. The dehydrochlorination reaction is apparently a much cleaner one than in polychloroprene. The peak for secondary decomposition has a maximum at about the same temperature as in polychloroprene.

(b) UV Spectra

Typical spectra are reproduced in fig. 40. Maxima and inflections occur at 235, 267, 279, 290, 312, 327, 342, 366, 390, 414, 440, 464 and 484mμ in agreement with previous observations.[88,89] Absorption extends to 650mμ even in the very early stages of degradation and as the reaction proceeds the intensity increases with the short wavelength peaks growing most rapidly.

PVC thus contrasts with polychloroprene by producing at the first stage in the reaction, very long polyenes. (According to Geddes[89] absorption above 500mμ implies the presence of over 20 conjugated double bonds.) The term

Fig. 39. DC-TVA of PVC. 50 mg. Powder. 10°/min.

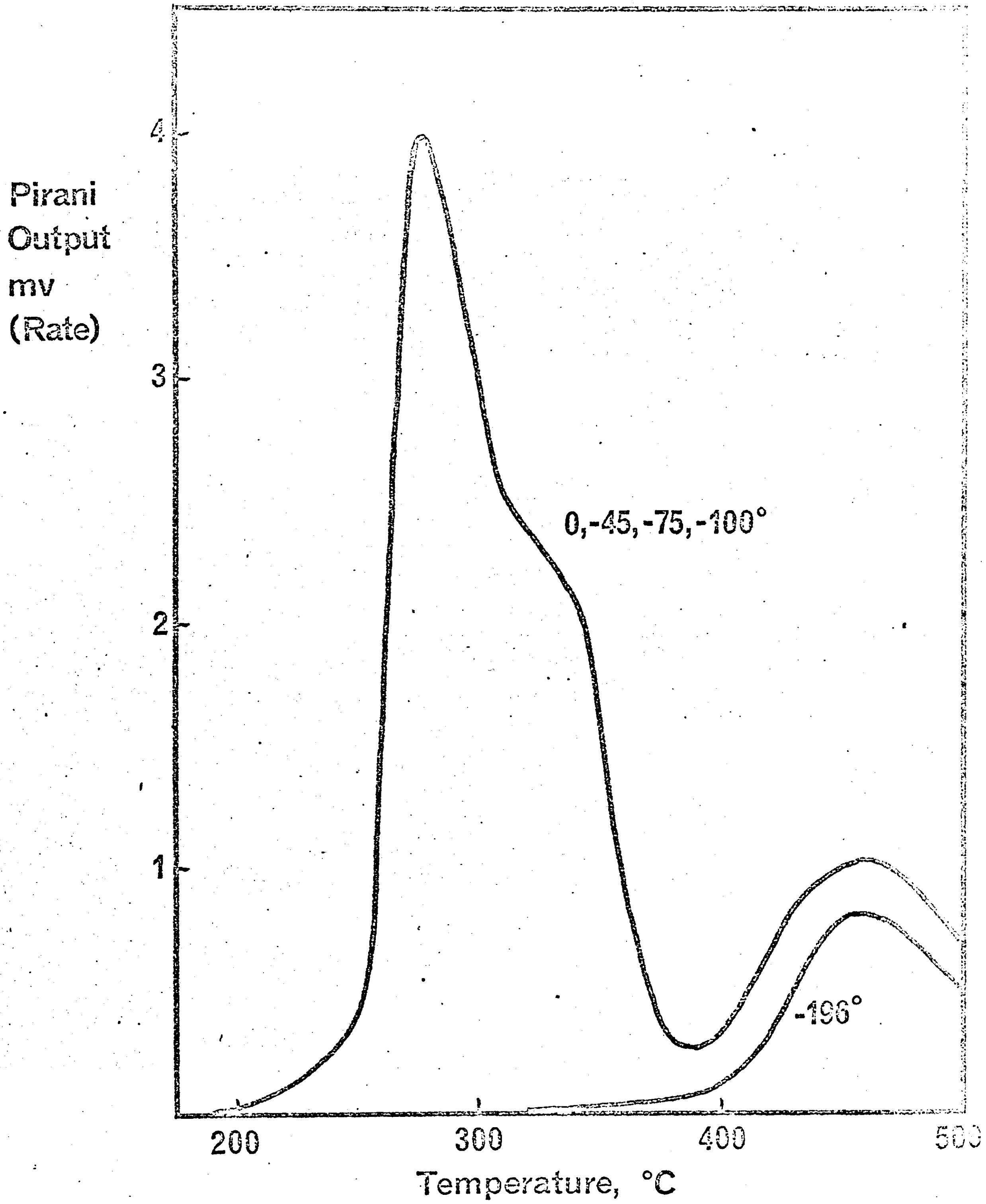
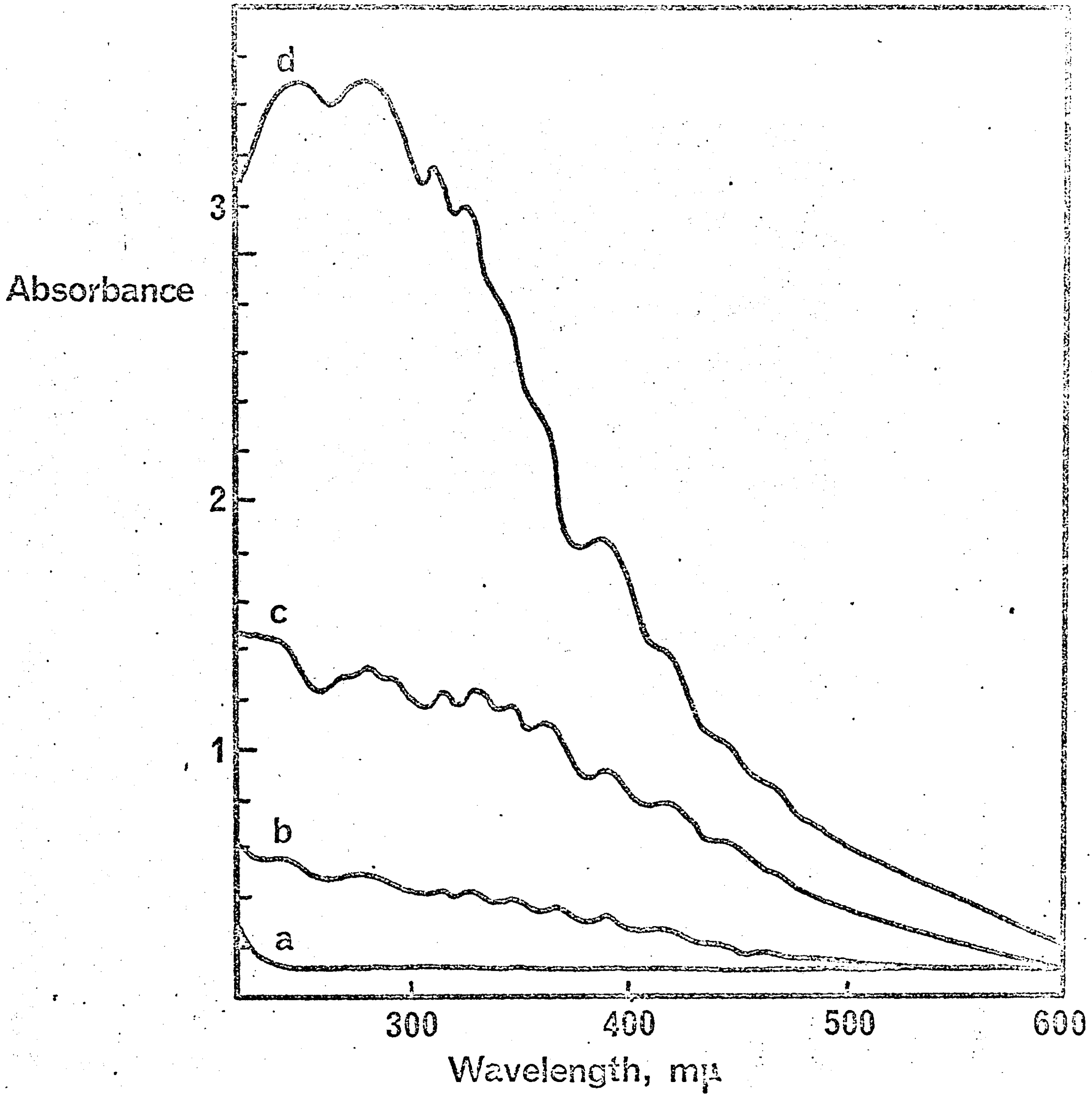


Fig. 40. UV Spectra of 100 mg. films of PVC.



undegraded (a) and heated at 5°/min to 215°(b) 227°(c) 259°(d) "zipper reaction" has been used to describe the elimination process which runs down the chain removing hydrogen chloride until a termination step takes place.

Poly(Vinyl Acetate) (PVA)

(a) Previous Work

PVA has been shown to degrade by acetic acid elimination. In Grassie's reaction scheme[90] the degradation is initiated at chain ends and proceeds through the molecule by allylic activation of adjacent units for a non-radical chain reaction process which is not terminated until a chain end is reached.

Servotte and Desreux[91] have shown that a cross-linking process co-exists with the deacetylation. They found oxygen in the residue despite the fact that quantitative elimination took place and suggested that it was bound up in ester groups within the cross-linked structure and not adsorbed after degradation. This seems doubtful in view of the fact that Gilbert and Kipling[60] had shown earlier that many polymer residues, including that from PVA degradation, adsorb atmospheric oxygen.

Besides acetic acid, Grassie identified ketene and carbon dioxide in the products and attributed these to decomposition of acetic acid. Servotte and Desreux used gas-liquid chromatography to examine the products and failed to find either carbon dioxide or ketone but did note the presence of water as well as acetic acid and two unidentified components, one of which was probably benzene.

The infrared spectrum of the residue was examined by the Belgian authors who were unable to make a positive identification of polyenes. These authors themselves however state that the spectrum resembles that of degraded PVC and do not make it clear which frequencies they would regard as characteristic of double bonds in extended conjugation. The only evidence offered by either Grassie or Servotte and Desreux that polyacetylenes are formed, is the fact that the polymer colours on heating.

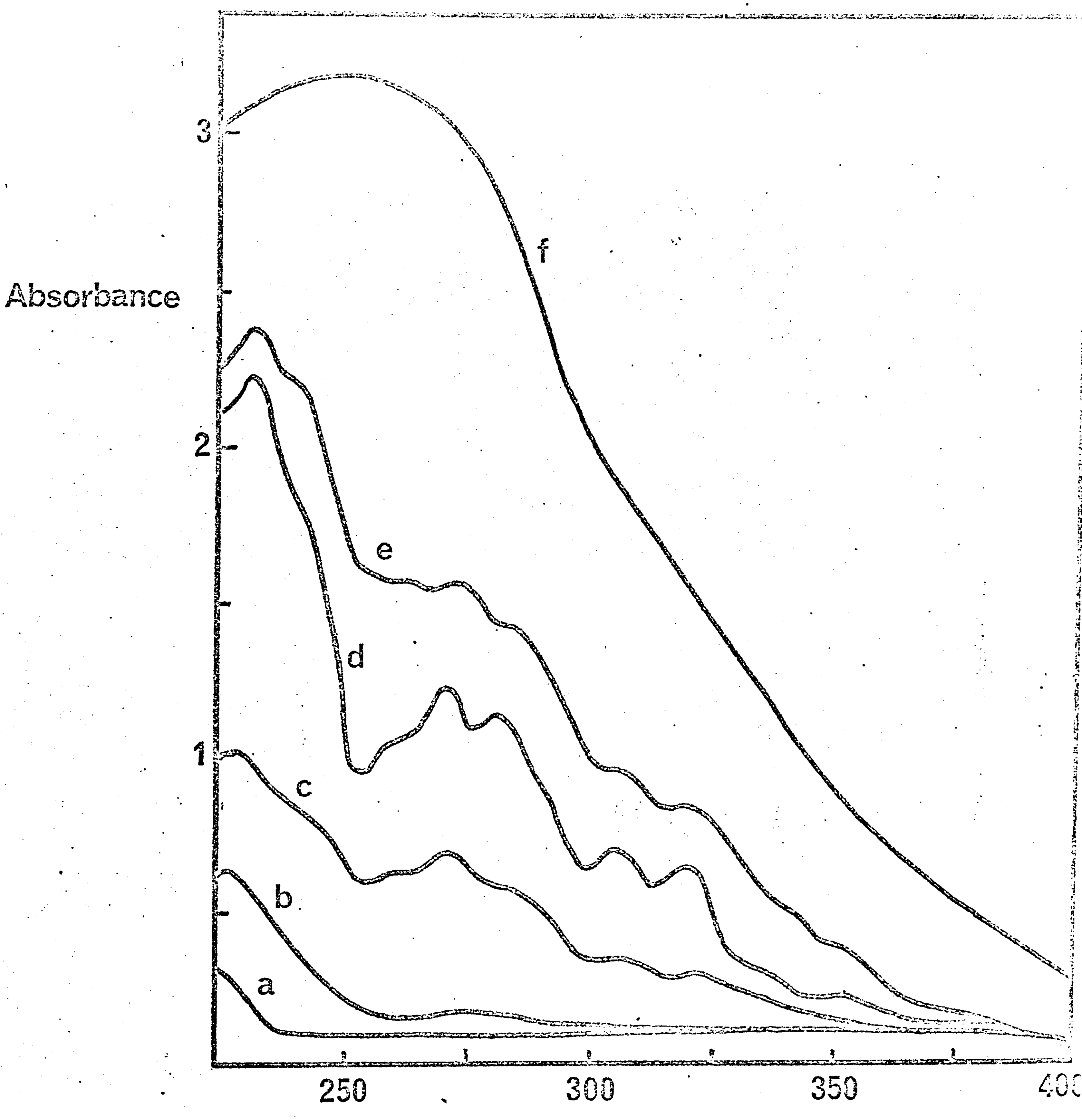
(b) Polymer

The polymer was used as supplied by B. D. H. Ltd. without purification. Polymers of different molecular weight from the B. D. H. polymer, were made by bulk polymerisation at 50°C using azo-bis-isobutyronitrile and benzoyl peroxide and were found to give identical TVA curves. Films were cast from 1ml. of toluene solution by vacuum evaporation.

(c) UV Spectra

UV spectra of degraded PVA films (fig. 41) show the growth of polyenes of much shorter length than in PVC. Absorption does not extend beyond 500mμ and again the short wavelength absorptions give the greatest increase

Fig. 41. UV Spectra of 20 mg. films of PVA.



undegraded (a) and heated at 5°/min to 289°(b) 301°(c) 313°(d) 332°(e) 381°(f) with further degradation. Peaks occur at 233, 261, 272, 283, 305, 335, 350 and 380mμ. The triad centred on 272mμ is due to the 2,4,6 octatriene chromophore, which has maxima at 252, 263 and 274.5mμ in solution in hexane and 260, 270 and 279mμ in chloroform.[87] This peak assignment is discussed further in the section on copolymers of vinyl acetate with ethylene. The more polar solvent reproduces the polymer film conditions better and other peaks correspond to maxima in the absorption spectra in chloroform solutions of dimethyl polyenes with up to six double bonds in conjugation. Trace quantities of longer polyenes are present, extending the absorption to 500mμ.

The UV results for PVA conclusively prove the existence of polyenes in thermally degraded polymer. The sequence length of the polyenes is shorter than in PVC as would be predicted from the appearance of the degraded films. PVA films degrade to a yellow colour, the intensity depending on the extent of degradation, whereas degraded PVC films are consistently a red colour of varying intensity.

(d) Volatile Products

Infrared analysis of the products volatile at -75°C revealed carbon dioxide, carbon monoxide, methane and ketene. The spectrum of ketene has already been described,[92,93,94] but in order that there should be no doubt about its presence a sample was prepared so that the spectrum could be recorded on the same instrument as that used to examine the degradation products.

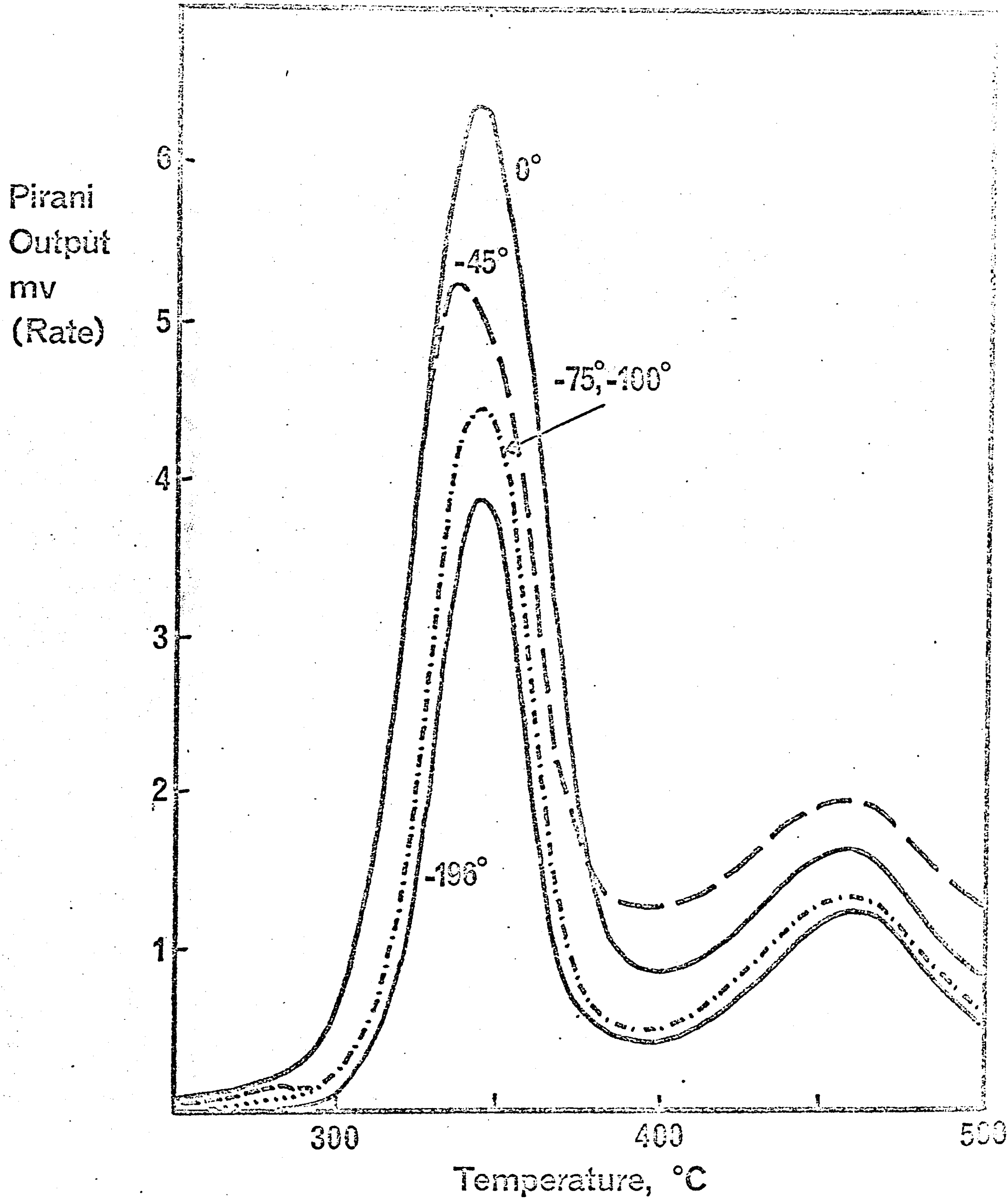
Ketene was prepared by pyrolysing acetone on porcelain beads at 600°C. The gas condensed in a liquid nitrogen trap while the methane also formed in the reaction passed through the trap without condensing. The ketene was distilled twice at -100°C before being examined in the infrared gas cell and on the DC - TVA apparatus (chapter 2).

An absorption with P Q R branches at 2160, 2150 and 2135cm^{-1} was characteristic of ketene. In the absence of other substances the gas was fairly stable and the size of the peak in the infrared spectrum was only diminished to one half of its original absorbance value after 3 days. An attempt was made to measure the kinetics of dimerisation using the infrared peak as a measure of concentration but no simple kinetic law was observed throughout the whole period of 8 days.

(e) DC - TVA

The DC - TVA curves are shown in fig. 42 and again two peaks are formed, one for elimination and the other for secondary breakdown. The gauge following the -196°C trap responds only to the non-condensable gases, carbon monoxide and methane. The difference between this curve and the

Fig. 42. DC-TVA of PVA. 50 mg. Powder. 10°/min.



-75 and -100°C traces is due to the trapping of carbon dioxide and ketene. Acetic acid is completely trapped at the three lowest temperatures, but at -45°C it condenses and distils over to the liquid nitrogen trap at a steady rate, causing the -45°C trace to stay at a constant height above the -75 and -100°C responses.

The initial separation between the -75 and -100°C traces shows the presence of water, which distils from the -75°C trap at a very small but characteristic rate. Because of the non-linearity of the Pirani responses, the separation disappears at higher pressures.

The use of a silica degradation tube in place of a Pyrex one has no effect on the TVA curve, and if the polymer is covered by a thin layer of copper powder the amount of non-condensable products evolved in the elimination reaction is unchanged.[95] These observations seem to indicate that the catalytic decomposition of acetic acid is not responsible for the formation of the minor products.

(f) Conclusion

A wider variety of products has been found than in previous work and polyenes with restricted length of conjugation have been shown to be formed. The results of McNeill and Neil on PVA/poly(methyl methacrylate) blends suggest that PVA degradation may be a radical reaction like

PVC.[27] Minor products could be formed by side reactions of acetyl radicals and decomposition of the chain propagating radical would have a limiting effect on the length of conjugation. As in PVC, interchain transfer of radical activity or radical combination cross-linking could also restrict the number of double bonds formed consecutively. Clearly PVA degradation is worthy of further study using all the modern techniques which have been developed since the original work was done.

Vinyl Acetate/Ethylene Copolymers

(a) Polymers

"Alathon" polymers 3185 and 3130 made by Du Pont Ltd. and stated to contain 33% and 12% vinyl acetate were reprecipitated from warm toluene solution into petroleum spirit (40 - 60°C). The purification was done by Mr J. McClune (a 4th year student) who also obtained the TVA and infrared data. Films were prepared by vacuum evaporation of warm toluene solutions but were opaque due to precipitation occurring before evaporation. Film quality however improved on heating the polymer.

(b) Sequence Length

The length of the sequences in the blocks in the copolymer was calculated using the "run number" method described by Harwood and Ritchey,[98] The run number, R, is defined as the average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units.

In the arguement below, E denotes an ethylene unit, A, a vinyl acetate unit and (A) and (E) are the percentages of A and E in the copolymer. The polymer is considered to be infinite or cyclic and vector signs are used to note a distinction between the units on the left and on the right.

Since there are as many A runs as E runs in the copolymer the percentage of $\overrightarrow{AE}$ links is R/2. Each A must be joined in the direction of the arrow to either an A or an E and therefore the percentage of $\overrightarrow{AA}$ linkages is (A) - R/2. The probability that a given unit is part of any specified type of link is simply the percentage of those links divided by the percentage of the unit in the copolymer. (Trivial exception — the probability for any A in a $\overrightarrow{EE}$ link is zero.)

Thus the probability of a given A being in an $\overrightarrow{EA}$ link is

$$P_{\overrightarrow{EA}} = R/2(A).$$

Since there are as many $\overrightarrow{AE}$ links as $\overrightarrow{EA}$ links

$$P_{\overrightarrow{EA}} = P_{\overrightarrow{AE}} = R/2(A),$$

also

$$P_{\overrightarrow{AA}} = \frac{(A) - R/2}{(A)}.$$

The overall probability that A is in any particular sequence of links is the product of the probabilities for the individual links times the number of positions for A. Therefore,

$$P_{EAE} = P_{\overrightarrow{EA}}\, P_{\overrightarrow{AE}} = (P_{\overrightarrow{EA}})^2 = R^2/4(A)^2,$$

$$P_{EAAE} = 2\, P_{\overrightarrow{EA}}\, P_{\overrightarrow{AA}}\, P_{\overrightarrow{AE}} = (P_{\overrightarrow{EA}})^2\, P_{\overrightarrow{AA}}$$

$$= \frac{R^2}{4(A)^2} \cdot \frac{(A) - R/2}{(A)},$$

$$P_{EAAAE} = 3\, (P_{\overrightarrow{EA}})^2\, (P_{\overrightarrow{AA}})^2$$

$$= \frac{R^2}{4(A)^2} \cdot \left[\frac{(A) - R/2}{(A)}\right]^2,$$

etc.

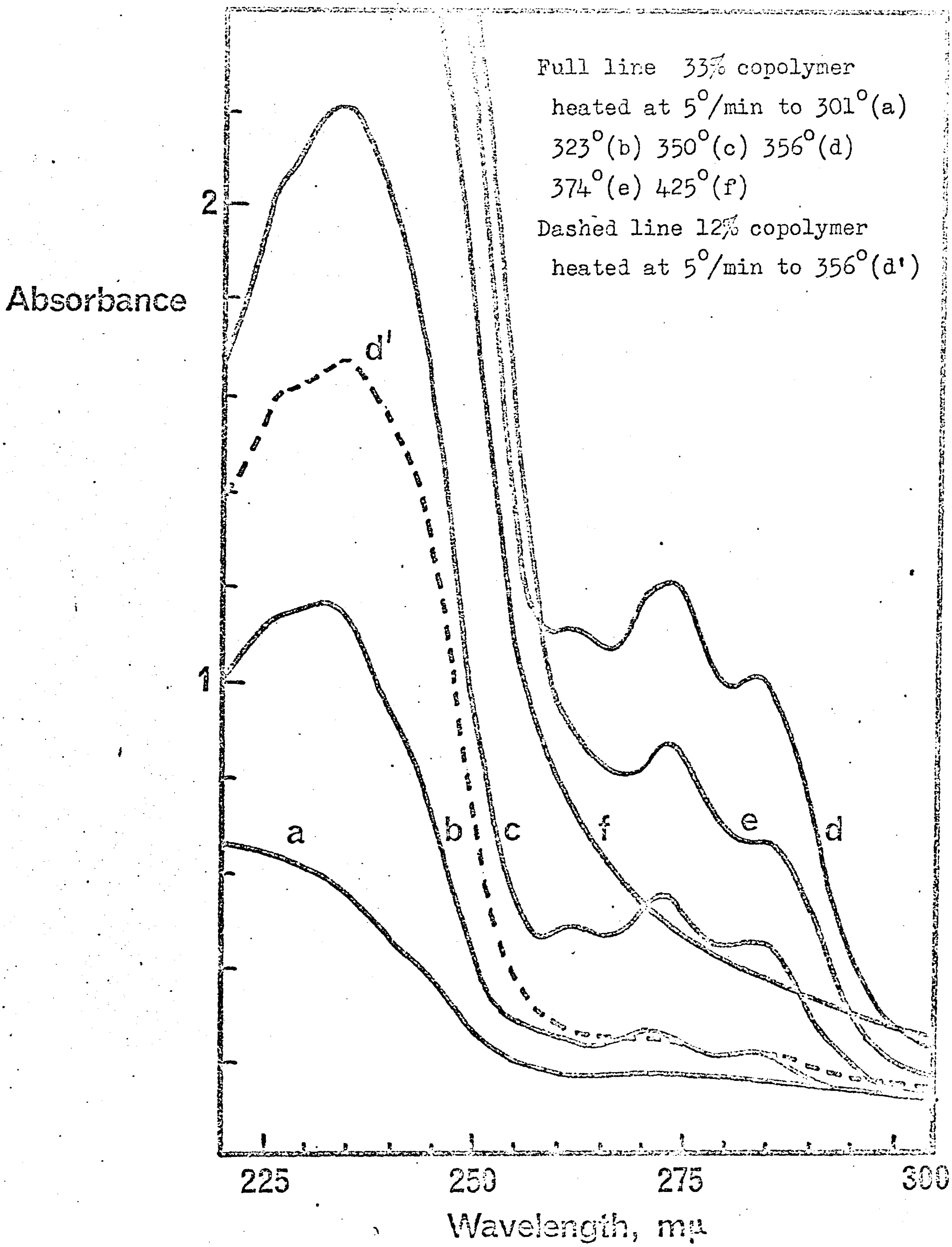
Using the above relations the percentage of A in bounded blocks can be easily calculated once R has been determined. Vinyl acetate forms an ideal copolymer system with ethylene[97] so that the vinyl acetate builds into the polyethylene chain entirely at random and the copolymer has the same composition as the monomer feed. The run number for such a system is given by

$$R = (E)\,(A)/50.$$

(c) UV Spectra

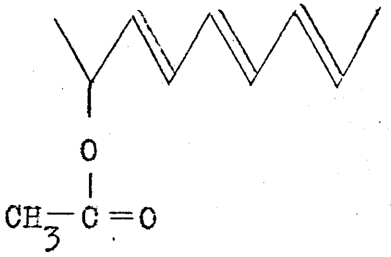
Representative spectra are illustrated on fig. 43. The polymer with 12% vinyl acetate contains 18.6% of the acetate groups in blocks of two but only 3.7% in blocks

Fig. 43. UV Spectra of 20 mg. films of Vinyl Acetate/Ethylene Copolymers.



of three or more. Absorption is therefore confined to the diene region centred on 235mμ.

The 33% vinyl acetate copolymer contains 29.6% of the acetate groups in blocks of two, 14.7% in blocks of three, and 10.9% in larger blocks. Thus absorption beyond the triene region is almost absent. The peaks for the triene occur at 261, 272 and 283mμ in the copolymer, exactly as in PVA, demonstrating that the wavelength of the absorption is not affected by whether the polyene is terminated by an acetate group (i) or by a methylene group (ii).



(i)

(ii)

p-toluenesulphonic acid has been used to produce colour in PVA dissolved in methanol.[98] Longer conjugated sequences were observed than in this work and maxima were recorded for polyenes with up to twelve double bonds. The conclusion was reached that the acetate group at the end of the polyene extended conjugation by an amount equivalent to half a C = C unit. The results with vinyl acetate/ethylene copolymers indicate that this is not the case in polymer films.

(d) DC - TVA

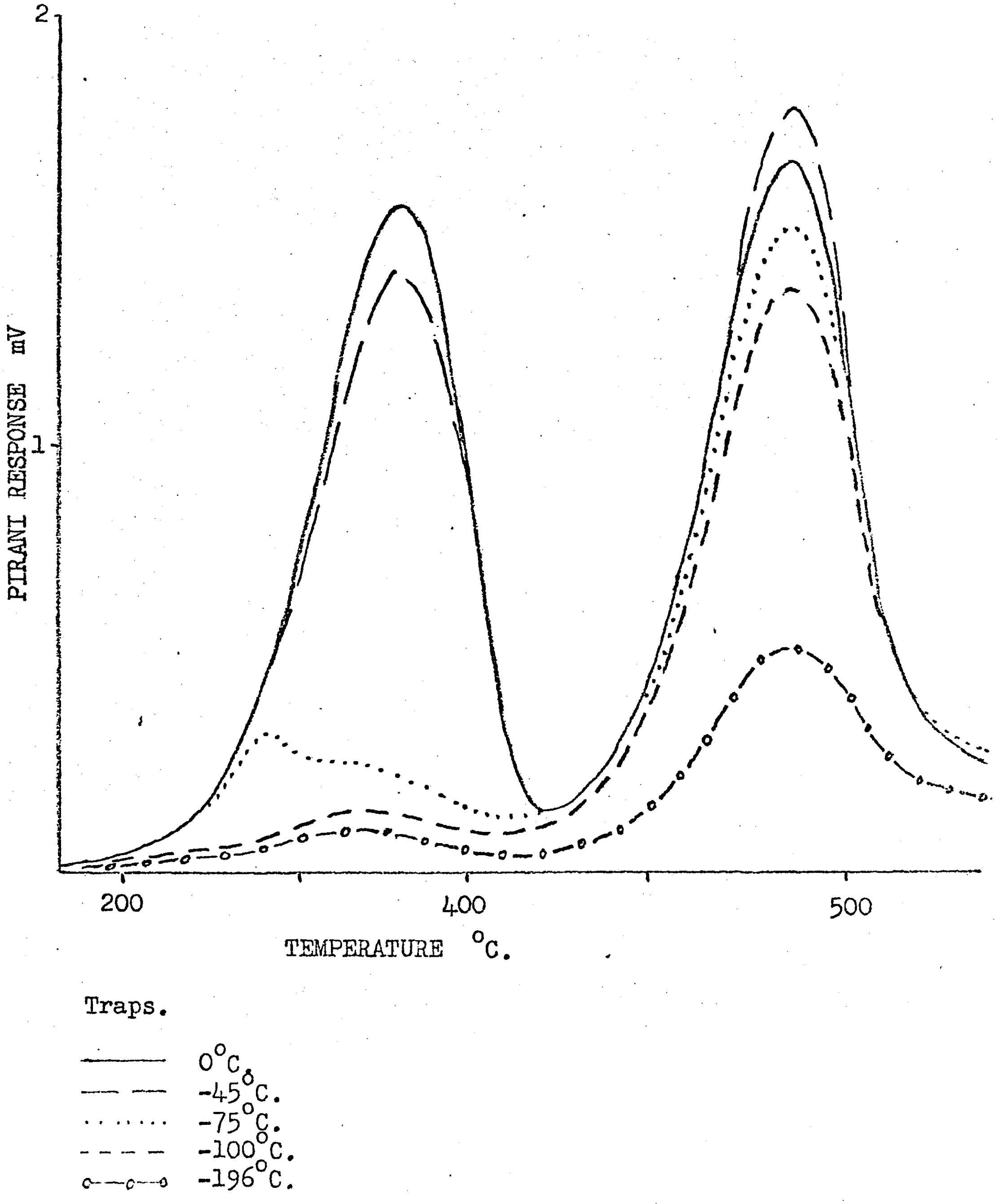
The TVA curves of the 12% vinyl acetate copolymer are shown in fig. 44. There are two peaks with maxima at 374 and 480°C, the latter corresponding to the TVA maximum for polyethylene. The 33% copolymer gives peaks at the same positions but the first peak for acetate decomposition is much larger. Degradation starts at about 290°C as in PVA but the maximum occurs 28°C later. The stabilisation is presumably due to the fact that each short sequence of vinyl acetate units in the polymer requires its own initiation step.

The triene peaks in the 33% copolymer (fig. 43) grow to a maximum intensity at 356°C just after the TVA maximum at 5°/min. The rate of break up of the polyene structures must overtake their rate of formation above this temperature but because of the long segments of saturated chain present, little backbone disintegration occurs until the C - C bonds break. Infrared analysis of the chain fragments which collect on the cold ring at the top of the tube indicates the absence of acetate groups.

(e) Volatile Products

Infrared spectroscopy was used to show that the volatile products condensable at -75°C consist mainly of acetic

Fig. 44. DC-TVA of 12% Vinyl Acetate/Ethylene copolymer.



acid while those not condensed at this temperature are ethylene, methane, carbon dioxide, carbon monoxide and ketene. The DC - TVA suggests that these by-products of acetic acid elimination are formed to a lesser extent in the copolymers with ethylene than in PVA itself, but the non-linearity of the Pirani gauge makes it difficult to reach a definite conclusion about this.

(f) Comparison with Vinyl Acetate/Styrene and Vinyl Acetate/Methyl Methacrylate Copolymers

Because of the stability of the polyethylene chain, the copolymers of vinyl acetate with ethylene provide excellent materials for studying the reactions of short sections of PVA chain.

Vinyl acetate/styrene and vinyl acetate/methyl methacrylate copolymers were studied as part of research projects by fourth year students, Mr J. McClune and Mr D. Tosh. Unfavourable reactivity ratios[99] made it difficult to produce copolymers with a vinyl acetate content above 20% in the case of the styrene copolymer and 40% in the case of the methyl methacrylate copolymer.

The TVA curves of both sets of copolymers exhibit only one maximum indicating that degradation occurs simultaneously in both types of unit in the copolymer. Increasing amounts of vinyl acetate in styrene copolymers progressively shift the maximum from 410°C for polystyrene towards the maximum for PVA at 346°C. A similar effect was observed in methyl methacrylate copolymers containing over 10% vinyl acetate, but when only small amounts of the comonomer were present an increase in thermal stability took place. The reason for this is that the macroradical with a vinyl acetate end group is very unreactive with the result that most of the polymer molecules have terminal acetate units. Because of this there can be no labile unsaturated end groups as present in poly(methyl methacrylate) and therefore the degradation of the copolymer is hindered. When more vinyl acetate units are present they cause instability in the chain just as in the case of the copolymers with polystyrene.

The change in stability of these copolymers throughout the composition range examined, is in strong contrast to the behaviour of copolymers of vinyl acetate with ethylene, where two separate reactions occur at temperatures which are independent of the composition.

Acetate groups were found in the cold ring fraction from both copolymers confirming that chain scission reactions occur before elimination is complete. The products from the acetate groups in the copolymers were similar to those from PVA but the styrene copolymers gave little carbon monoxide and no ketone.

It is apparent that the copolymers of vinyl acetate with styrene or methyl methacrylate present much more complex systems than the copolymers with ethylene because reaction in both component units of the copolymer occurs at the same time.

Poly(Vinyl Formate)

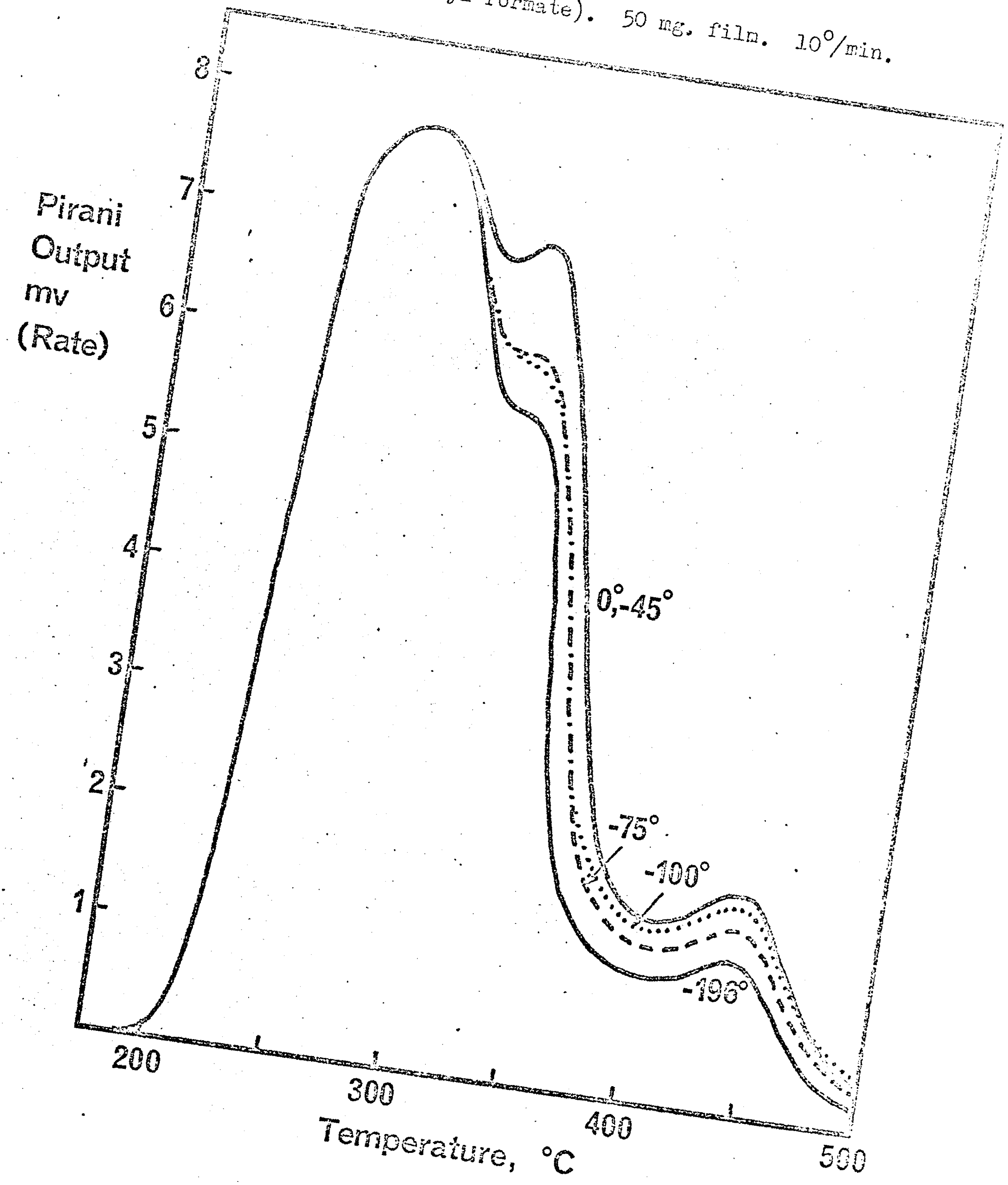
The polymers were prepared and the degradation examined by Mr A. Jamieson (fourth year student).

Vinyl formate was polymerised in bulk using azo-bis-isobutyronitrile as initiator either at 60°C or at 0°C in the presence of UV light. Films were cast from solution in acetone by evaporation in the atmosphere at room temperature. The samples ranged in molecular weight (M_w) from 23,000 to 170,000 (from viscosity measurements of acetone solutions at 30°C), but all gave similar TVA curves.

On degradation this polymer produces UV spectra which are indistinguishable from those from PVA. Poly(vinyl formate) is however less thermally stable and the DC - TVA curves are quite different, fig. 45. The elimination reaction peak, with a maximum at 271°C (10 °/min.) is entirely non-condensable at first and later has a shoulder at 330°C which is partly composed of condensable material.

By analogy with PVA, the expected degradation product

Fig. 45. DC-TVA of poly(vinyl formate). 50 mg. film. 10°/min.



is formic acid, and infrared analysis shows that this is indeed the major product of degradation along with quantities of carbon monoxide, carbon dioxide and methane. TG indicates a 64% weight loss in the first stage of degradation ending at 375°C which corresponds to quantitative elimination of formic acid. However when this substance is passed into the DC - TVA apparatus it is fully condensed at -75°C and lower temperatures but not condensed at all at 0 or -45°C. Formic acid dissociates at 160°C to form carbon dioxide and hydrogen but not apparently under TVA conditions because no change in the pattern of condensability was found when the tube was heated to 350°C while the vapour was flowing into it.

There is evidence for formic acid condensing in the latter part of the TVA peak but the largest Pirani response is for material non-condensable at -196°C i.e. hydrogen, carbon monoxide or methane. It is very difficult to explain the fact that the first part of the peak appears entirely non-condensable or to account for the presence of methane in the products. Obviously a more detailed study is required including in particular measurements of the amount of hydrogen evolved.

Poly(Vinyl Alcohol)

The polymer used was Gelvatol 060G (manufactured by the Shawinigan Chemical Co.) which had been reprecipitated by addition of the aqueous polymer solution to methanol. According to the manufacturers the polymer had a very low residual acetate content and certainly no carbonyl absorption was present in the infrared spectrum of the polymer film. For the UV examination films were prepared by evaporation of 1ml. of aqueous solution under vacuum.

The thermal degradation of poly(vinyl alcohol) has been studied by several workers[100,101,102] and the main products of degradation have been shown to be water from elimination, and acetaldehyde from depolymerisation.

Four peaks are present in the DC - TVA curve for the polymer (fig. 46). The first low broad peak has a maximum at 121°C and the limiting rate in the -75°C trace proves that water is being evolved. Because water is used as a solvent for this polymer it is difficult to distinguish between trapped solvent volatilising and water being chemically eliminated. Degradative dehydration of poly (vinyl alcohol) has been reported at this temperature leading to the loss of a variable amount of water. Inter- as well as intramolecular elimination has been suggested.[103]

The second peak has a maximum at 255°C and some of the products are trapped at -75°C, some at -100°C and a small amount is non-condensable at -196°C. The rate

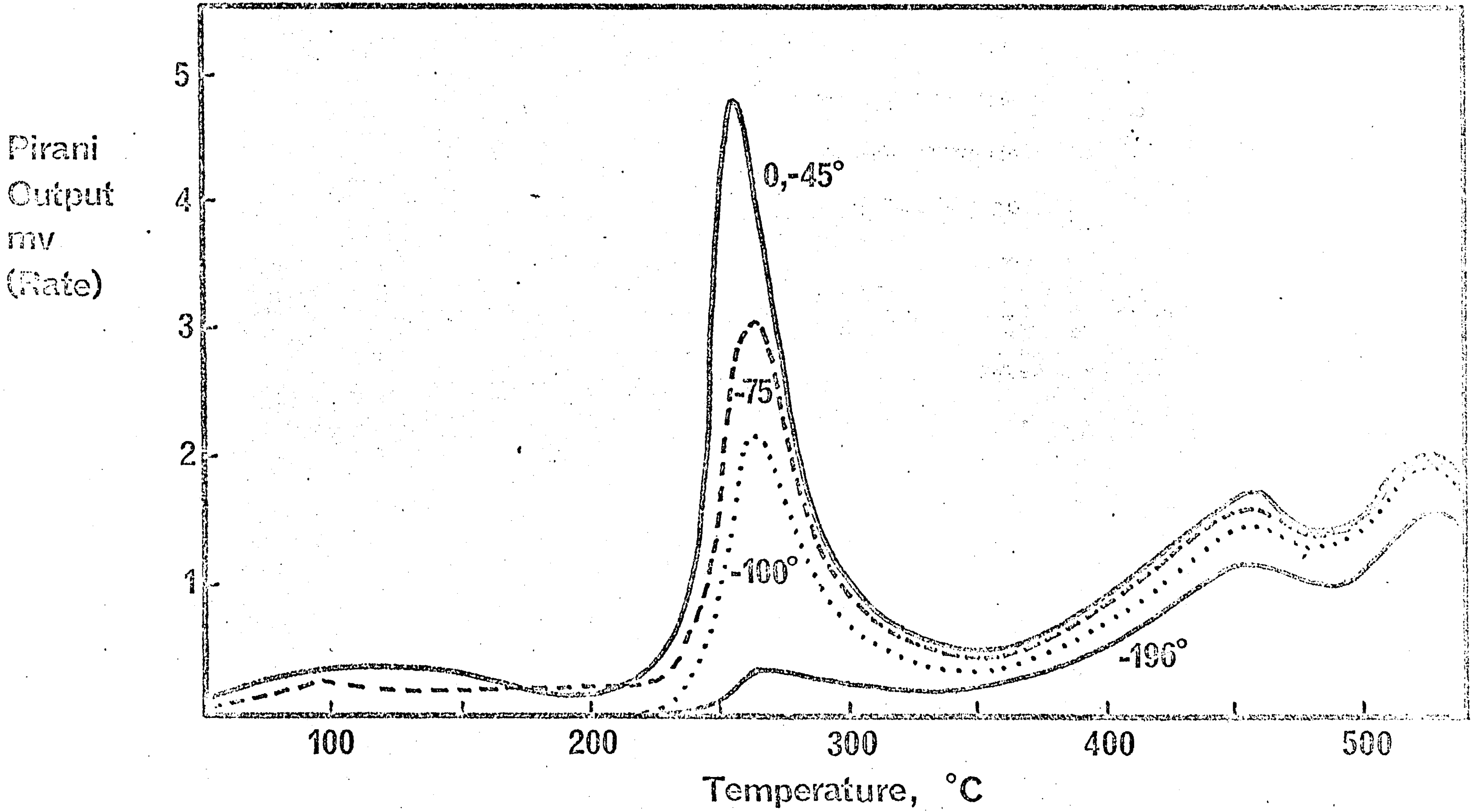


Fig. 46. DC-TVA of poly(vinyl alcohol). 50 mg. powder. 10°/min.

maximum in the curves for traps at temperatures lower than -45°C occurs at 264°C indicating that the product composition changes during this stage of reaction. The Pirani responses during this TVA peak can not be explained on the basis of water and acetaldehyde alone, and possibly formaldehyde and hydrogen which have also been reported to be formed during the degradation,[101,60] account for the responses of the -100°C and -196°C Piranis.

The remaining two peaks are mainly composed of non-condensables and have maxima at 459 and 523°C.

The UV spectrum of poly(vinyl alcohol) frequently contains a peak at 280mμ which is caused by the dienone chromophore.[104] Gelvatol 060G had no such absorption, and when degraded gave maxima at 235, 263, 273, 283, 307, 322, 335 and 352mμ, (fig. 47). In the early stages of degradation the first four were not as strong as the absorptions at longer wavelengths, but later the pattern became similar to PVA.

Conclusions

Examination of the UV spectra of the partially degraded films indicates that polychloroprene behaves differently from the polymers discussed in this chapter in that the first unsaturated structure is produced by the elimination

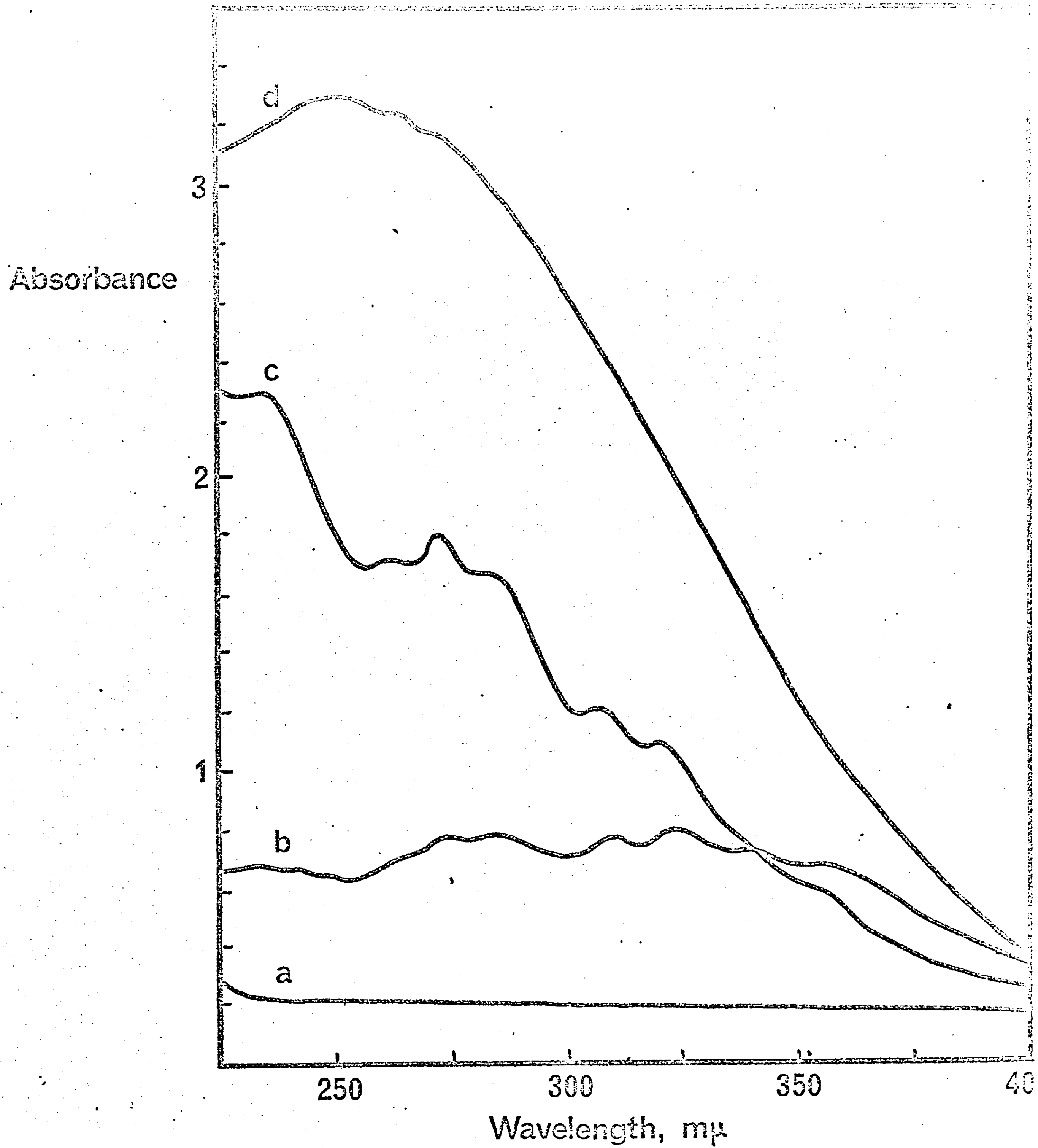


Fig. 47. UV Spectra of 100 mg. films of poly(vinyl alcohol) undegraded (a) and heated at 5°/min to 221°(b) 265°(c) 290°(d)

of only one molecule. Conversely in the other polymers zipper reactions occur causing the formation of various lengths of conjugated chain by the elimination of several molecules.

The zip length is highest in PVC, next comes poly(vinyl alcohol) and then PVA and poly(vinyl formate). Progressive degradation in these polymer films does not cause more absorption to take place at longer wavelengths as might be expected as the conjugation length increased. In fact the greatest growth occurs in the short wavelength absorptions probably because cross-linking reduces the effective length of conjugation by decreasing chain mobility and preventing the formation of the planar configuration of the polyene. An alternative explanation is that the long polyene sequences tend to cyclise to aromatic structures with increasing temperature. A shift to shorter wavelength as the degradation temperature rises has already been observed[88] for PVC films and solutions in the temperature range 150 to 220°C.

TVA appears to be a very sensitive technique for detecting the evolution of degradation products of lower molecular weight than those expected from elimination in the PVA type of polymer. Future investigations to determine the origin of these minor products should provide more information about the nature of the elimination process.

CHAPTER 8

POLYMER BLENDS

Incompatibility

In a solution of two polymers, the molecules of each type tend to aggregate so that above a certain concentration, a phase separation occurs and two layers are formed in the solution.[105,106] Evaporation of binary mixtures of polymers in solution usually produces an opaque film which contains micelles of one polymer in a matrix of the other.

The phenomenon manifested by the absence of random mixing of the polymers is known as "polymer incompatibility" and has been explained in terms of the thermodynamic properties of polymer solutions.[107,108] Polymer blends, especially rubber or synthetic elastomer reinforced styrene resins, are very important technically and their morphology has received some attention. The subject has been reviewed by Fettes[109] who reported that the size of the micelles is often between 1 and 15μ. An examination of the structure of blended films is described in a later section of this chapter.

Degradation of Blends

In spite of the heterogeneity of the mixed polymer system, interactions may occur between the polymers during thermal degradation. Thus Richards and Salter[99] observed that admixture of poly(α-methyl styrene) with polystyrene increased the yield of styrene monomer during degradation. Poly(α-methyl styrene) depolymerises by a radical chain reaction at a lower temperature than is required to degrade polystyrene, and the radicals produced can initiate degradation in polystyrene.

Before McNeill and Neil's recent papers[16,27] describing effects in the degradation of blends of PVC or poly(vinyl acetate) with some other polymers, interactions had also been reported between polypropylene and several vinyl polymers,[111] between polyacrylonitrile and acetyl cellulose,[112] and between poly(methyl methacrylate) (PMMA) and PVC.[113]

Degradation of Mixtures of PVC and PMMA

The PVC/PMMA system was extensively studied by McNeill and Neil[16,27] who found that PVC initiated degradation in PMMA. Examination by DC - TVA indicated that hydrogen chloride evolution from PVC was slightly retarded and considerably more methyl methacrylate was lost at an early stage in the degradation. The peak maximum temperature for methyl methacrylate production was delayed and a small amount of non-condensable products was evolved in the later part of the degradation.

The theory put forward to explain these changes was that chlorine atoms from degrading PVC diffuse into the PMMA regions in the blend and initiate a depolymerisation reaction. The PVC degradation is retarded by the loss of some of the chain propagating chlorine atoms. A second type of interaction also takes place, in which the hydrogen chloride produced by the PVC reacts with PMMA to form anhydride units which stabilise the PMMA. At higher temperatures the anhydride rings break down to give non-condensable products.

If the above theory is correct, and the evidence in its favour is very convincing, then it seems possible to use the earlier production of monomer from PMMA in a blend with another polymer, as a criterion for the presence of small radicals during the thermal degradation of the other polymer.

The degradation of blends of polychloroprene (PC) with PMMA was therefore studied to see if radicals could be detected in the breakdown of polychloroprene.

Degradation of Mixtures of Polychloroprene with PMMA

(a) Evidence from DC - TVA

The polymer blends were examined in the form of films cast on the base of small crucibles, four of which could stand side by side at the bottom of a normal sized TVA degradation tube. For comparison with the results for blends, a film of pure PMMA was cast in two of the crucibles and pure polychloroprene in the other two and the four placed in the TVA tube and degraded simultaneously. Each crucible contained 10mg. of polymer from the vacuum evaporation of 1ml. of toluene solution.

The extra temperature lag arising from the use of the crucibles inside the degradation tube was easily determined from the TVA curves of the unblended films since the peak maximum temperature for both polymers was already known.

PMMA degrades completely to monomer by two possible reactions.[114] In the first, depolymerisation is initiated at unsaturated chain ends, and in the second, the depolymerisation reaction proceeds after the random scission of one of the backbone C - C bonds. Thus PMMA prepared by a free radical process shows two peaks in the TVA.[115] The lower temperature peak is due to the first reaction and the peak size is proportional to the number of unsaturated chain ends which the polymer contains. Very high molecular weight PMMA shows no peak for chain end initiation. No unsaturated chain ends are produced in the anionic polymerisation of methyl methacrylate and therefore this polymer also has only one TVA peak. Anionic PMMA (prepared by D. Neil) was used in this investigation.

In the DC - TVA the methyl methacrylate from PMMA degradation is trapped at -75°C but not fully condensed, since it distils away at a constant limiting rate. Monomer is completely condensed at temperatures of -100°C or lower.

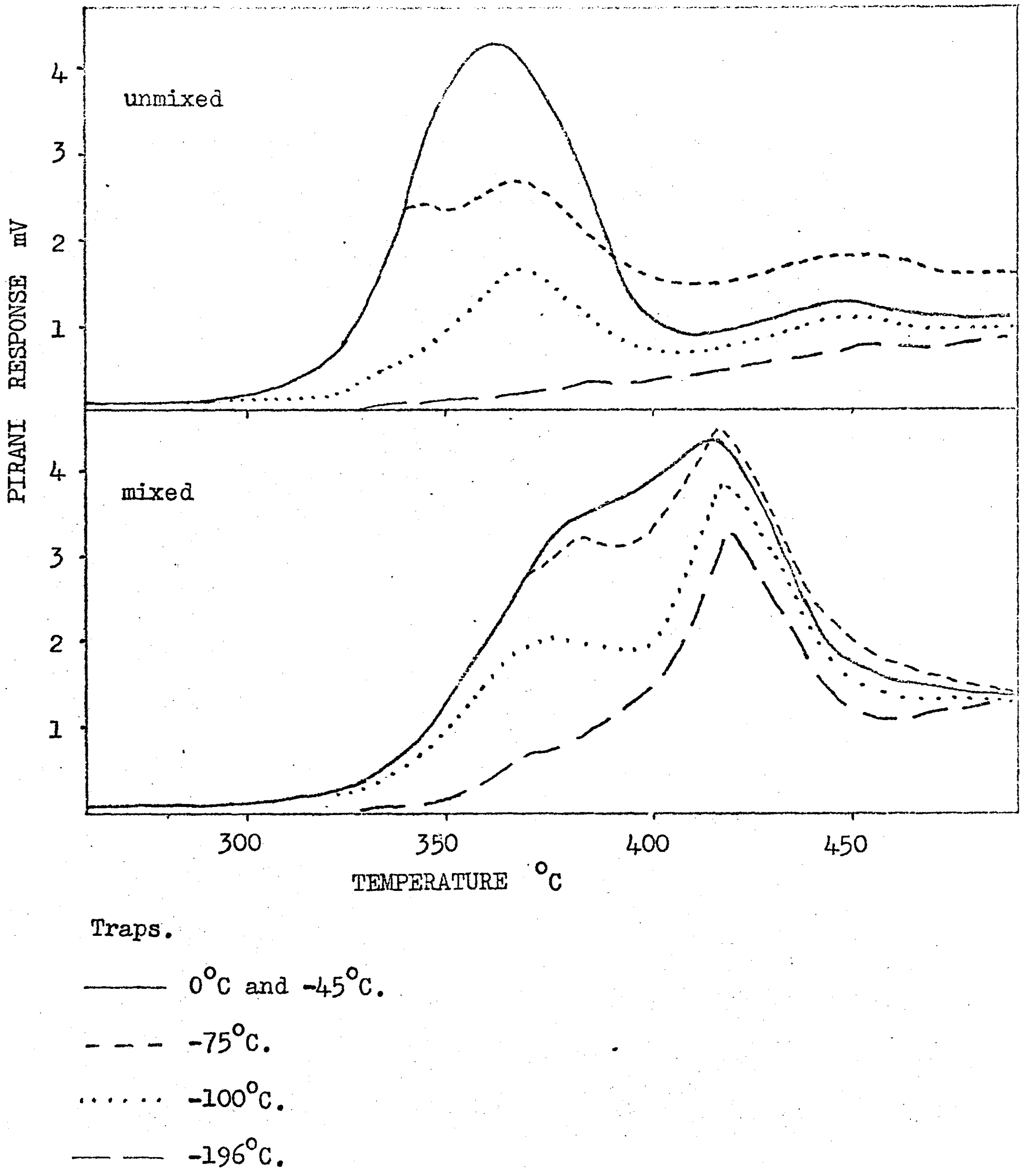
The DC - TVA curves for polychloroprene have already been described, (Chapter 3).

The curves for the 1/1 blend are shown in fig. 48 together with the curves obtained from simultaneous degradation of equal amounts of unmixed polymer.

It is clear that no early PMMA breakdown takes place but the evolution of volatile products is delayed to higher temperature. Analysis of the different Pirani responses in detail, gives more information about the interaction which the two degrading polymers have on one another.

The -196°C trace for the unmixed sample is as expected from the degradation of polychloroprene alone. Degradation of the blend gives an entirely new peak of non-condensable material with a maximum at 417°C.

Fig. 48. PC/PMMA DC-TVA 10°/min.
20 mg each polymer.

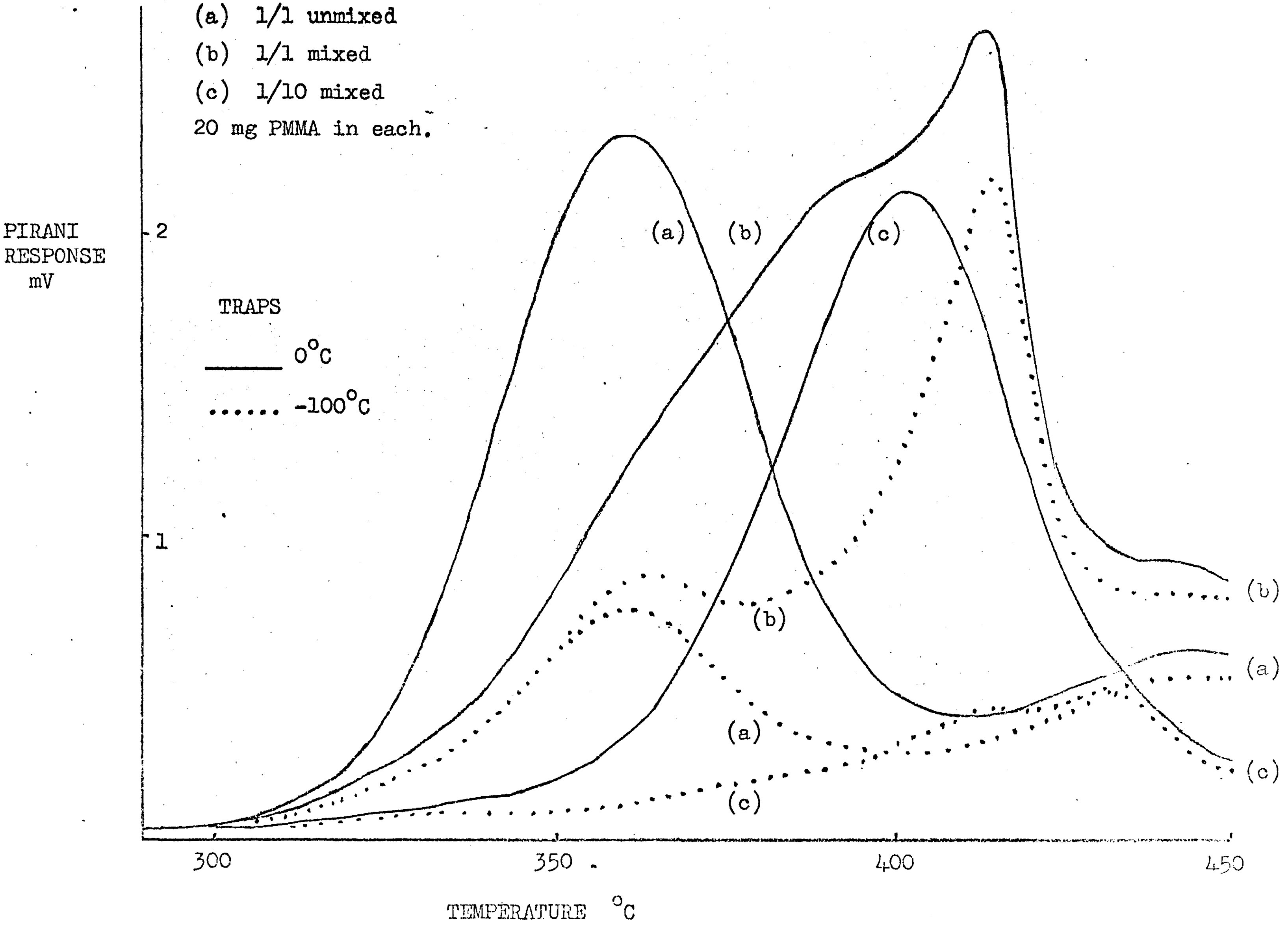


The -100°C trace responds to hydrogen chloride as well as the non-condensables, but not to methyl methacrylate. The maximum at 370°C in this trace is only shifted very slightly to higher temperatures. Since the earlier part of this curve is unaffected, the shift is probably due to the rising pressure of non-condensables rather than to a chemical effect on the hydrogen chloride evolution.

In the unmixed polymers the -75°C trace clearly shows the limiting rate effect by remaining at a constant level above the -100°C trace. This also happens in the mixed system, but the separation becomes smaller at the top of the second peak due to the non-linear response of the Pirani gauge. Monomer production starts earlier in the unmixed films and the -75°C trap is still losing monomer at the end of the heating programme (500°C), but in the mixed polymer system the limiting rate distillation is finished by the end of the run. Thus TVA indicates that less monomer is produced in the degradation of the mixed polymers.

The effect on the 5°/min. TVA degradation of a small amount of polychloroprene blended with PMMA, is illustrated in fig. 49. 10% by weight of polychloroprene in PMMA produces a clear film, TVA of which shows the peak for PMMA degradation shifted to higher temperature. In place of the large non-condensable peak produced in the 1/1 blend

Fig. 49. PC/PMMA DC - TVA 5°/min



only a slight shoulder appears.

The TVA evidence may be summarised in four points.

1) There is no increase in PMMA degradation early in the degradation.

2) Hydrogen chloride evolution from polychloroprene is not affected.

3) Monomer production in PMMA is inhibited, taking place at a higher temperature and to a smaller extent. Only a small amount of polychloroprene in the blend is required to produce this effect.

4) A new peak of non-condensable material appears at 417°C (10 /min.) the size of the peak depending on the amount of polychloroprene in the blend.

The effects described in (3) and (4) were observed in PVC/PMMA degradation by McNeill and Neil[16,27] but the extent to which (4) took place was a good deal smaller. The explanation was found in the reaction of hydrogen chloride with PMMA causing the formation of anhydride units in the chain. The anhydride rings stabilise the PMMA by acting as blocking agents through which the unzipping chain reaction cannot pass. Only a few units are necessary to cause significant enhancement of stability because of the chain nature of the reaction.

(b) Anhydro-poly(methacrylic acid)

Six membered ring anhydrides are formed when poly (methacrylic acid) is heated.[6] The resulting polymer is known as anhydro-poly(methacrylic acid) and it is an obvious model for the structures produced in PMMA by the action of hydrogen chloride. Anhydro-poly(methacrylic acid) degrades by break up of the rings to give carbon monoxide, carbon dioxide and methane.[27] The TVA maximum for this reaction occurs at 452°C at a heating rate of 10°/min.

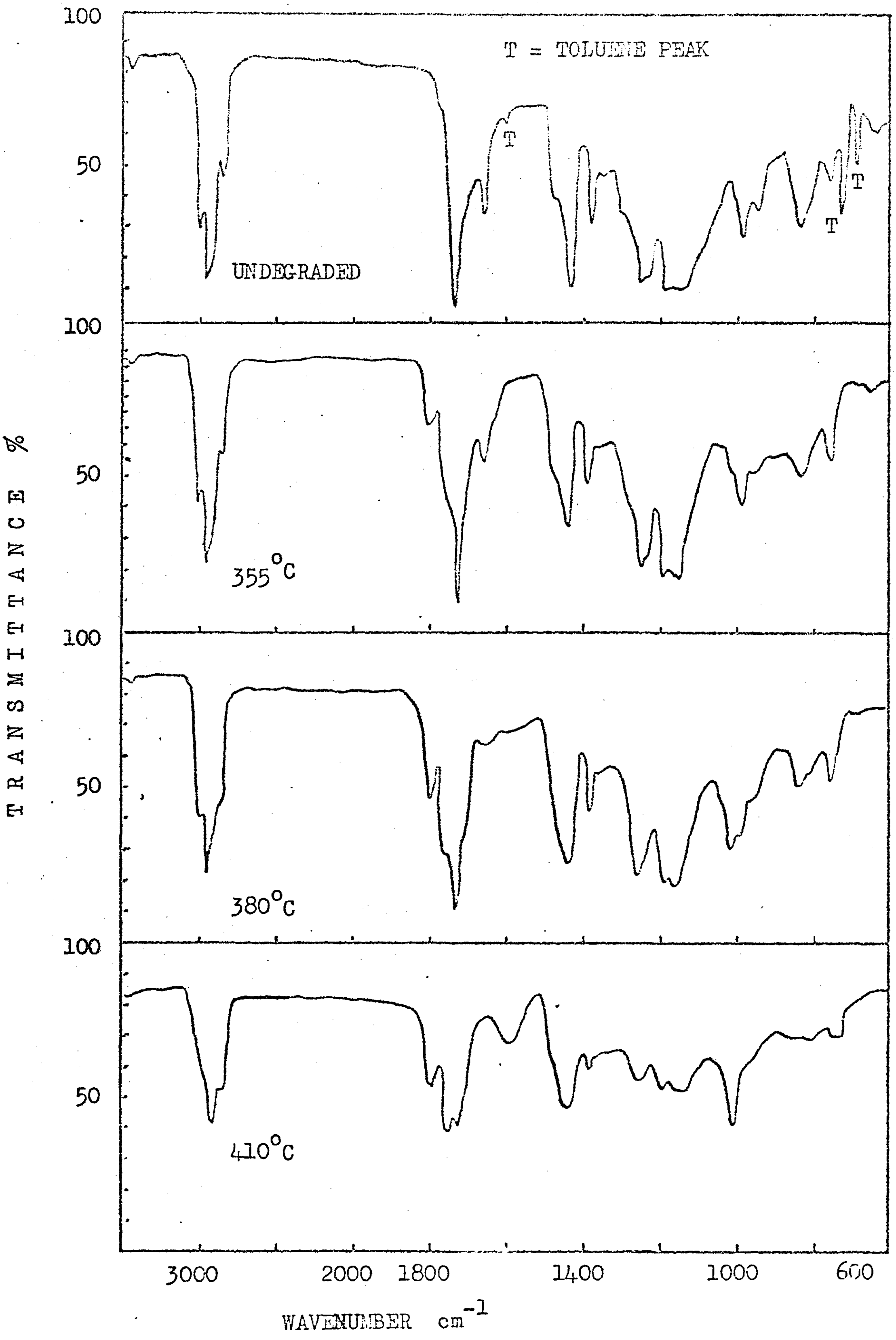
The infrared spectrum of the polymer was examined by Grant and Grassie[6] who observed bands at 1795, 1750 and 1022cm^{-1}, characteristic of six membered anhydride rings. McNeill and Neil extracted PMMA from a partially degraded PVC/PMMA blend and showed that the infrared spectrum of this polymer contained small peaks at 1800 and 1020cm^{-1} due to anhydrides.[27]

(c) Infrared Analysis of Residue

The salt disc technique employed to examine films of degraded polychloroprene was also used to investigate the chemical structures within degraded 1/1 PC/PMMA blends.

The spectra obtained are shown in fig. 50. There is no doubt about the presence of twin carbonyl peaks at 1800 and 1760cm^{-1} and a C - O stretch at 1015cm^{-1}, all of which are typical of six membered ring anhydrides. The

Fig. 50. Infrared spectra of PC/PMMA blend films heated at 5°/min to Temperature shown.



features appear more clearly in these spectra than in those obtained in the investigation of PVC/PMMA residues. Spectra from films tend to have better definition than those from pressed discs as used to examine polymer extracted from PVC/PMMA blends, but more importantly, detection is made easier by the fact that the concentration of anhydrides in PC/PMMA blends is much higher.

The spectra show the growth of anhydride peaks as ester groups in the polymer react with hydrogen chloride. In the last spectrum most of the PMMA has been removed and only anhydride units are left with the polychloroprene residue. In a further spectrum (not shown) of the residue from degrading the blend to 410°C all the anhydride absorptions have gone and all that remains is a spectrum of the residue from polychloroprene degradation with a little extra absorption in the 1660 - 1770cm^{-1} region.

(d) Volatile Products

Besides methyl methacrylate and hydrogen chloride, carbon dioxide and methyl chloride were identified in the degradation products of PVC/PMMA blends. The amount of carbon dioxide was sufficient for detection by infrared analysis of the products in a gas cell but methyl chloride was only detected by mass spectral analysis. Substances not condensable at -196°C were not collected for analysis by either method.

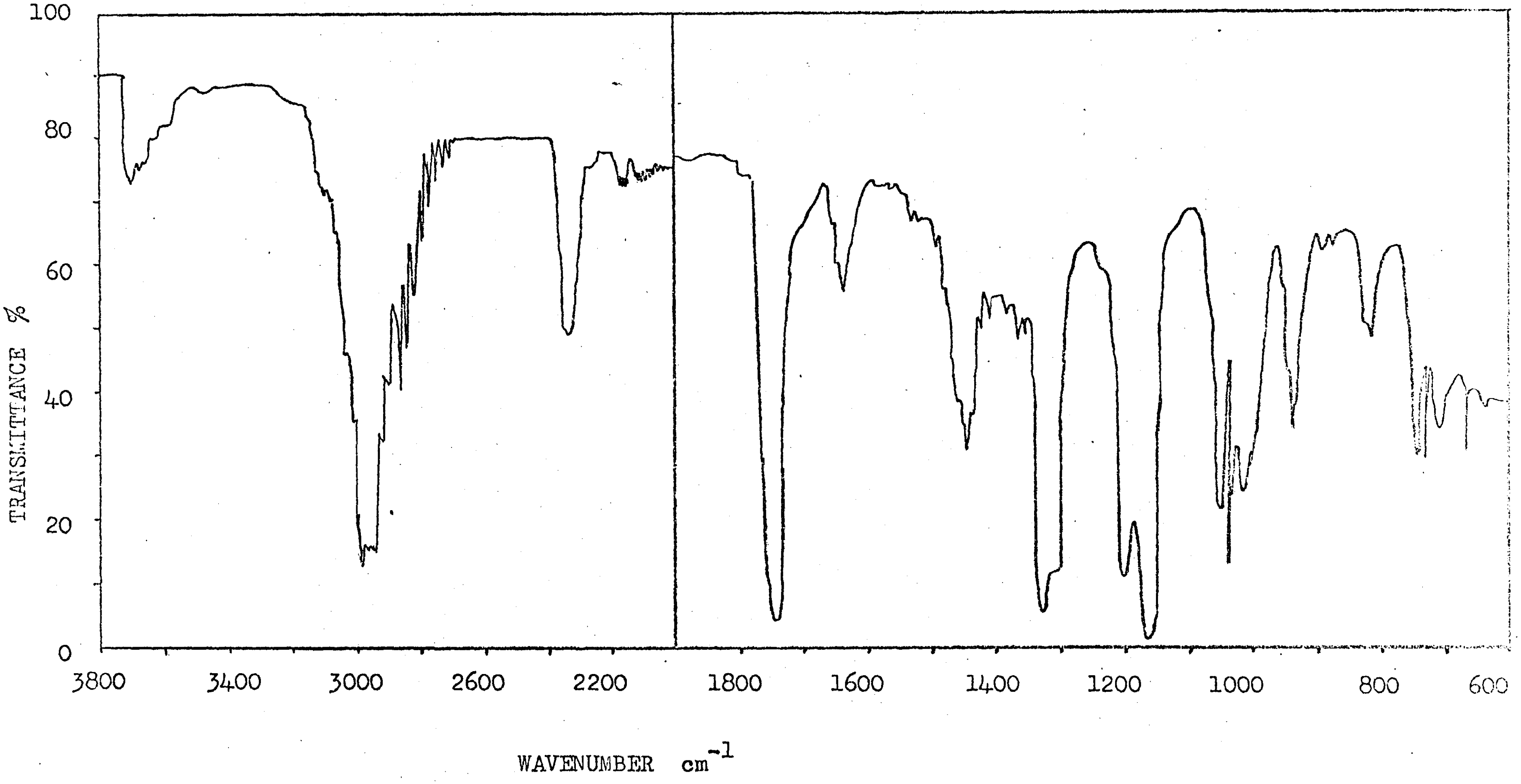
The products from PC/PMMA blends were collected in a gas cell using the arrangement shown in fig. 9 with the modification that two small degradation tubes were connected to the system in place of the one shown (B). The use of two tubes permitted a larger sample size to be used without increasing the film thickness and also it made it possible to degrade two polymers simultaneously without mixing them. Degradation was at 5°/min. and the products were collected in the temperature range 200 to 450°C, this being chosen to exclude solvent and also methane from the latter stages of polychloroprene residue degradation.

The spectrum of the gases from degradation of 160mg. of a 1/1 PC/PMMA blend is shown in fig. 51. By also degrading the same amount of the polymers in separate tubes it was easy to determine which peaks arose from the products of interaction.

The bands at 2340, 3700 and 670cm^{-1} indicate carbon dioxide while the twin peaks with fine structure at 2180 and 2120cm^{-1} are evidence for carbon monoxide.

By analogy with anhydro-poly(methacrylic acid) methane is predicted as a product, but its spectrum is almost entirely obscured by other absorptions. The strongest peak in the spectrum of methane is at 3020cm^{-1} but the unmixed

Fig. 51. Infrared spectrum of volatiles from PC/PMMA blend.



polymer products also give a band in this position from the hydrogen chloride evolved. The size of the peak increases in the blend degradation products and some additional fine structure is seen between 3050 and 3100cm^{-1}. Since the other absorption of methane at 1305cm^{-1} is completely overlapped by the spectrum of methyl methacrylate this fine structure is the only evidence for methane which the spectrum shows.

Methyl chloride is also present in the mixture, though only a part of the spectrum is free from interference by other absorptions. Methyl chloride gives three bands between 700 and 750cm^{-1} which are clear in the spectrum of the products from the blend. It also gives fine structure in the region 1000 - 1100cm^{-1} but this is obscured by an absorption of a different kind not present in the products of degradation of the unmixed sample.

The other part of the methyl chloride spectrum which can be identified is the fine structure between 1350 and 1450cm^{-1} which is superimposed on the methyl methacrylate absorptions in this region. In the products of the unmixed sample the largest absorption in the 3000cm^{-1} region occurs at 2960cm^{-1}, but in the blend it is at 2980cm^{-1} with another less sharp but almost as intense peak at 2950 - 2960cm^{-1}. Methyl chloride has two strong bands at 2980 and 2950cm^{-1}

which are probably responsible for the changes observed in this region.

The three peaks at 1020, 1030 and 1050cm^{-1} are caused by methanol which also gives a small O - H stretching vibration between 3600 and 3700cm^{-1}.

(e) Action of Anhydrous Hydrogen Chloride on PMMA

McNeill and Neil[27] proposed a mechanism for the formation of anhydrides in PMMA by the action of hydrogen chloride. This mechanism required both methanol and methyl chloride to be produced in equimolar amounts and was thus open to doubt since methanol could not be detected.

The fact that methanol has now been observed in the products of the PC/PMMA blend proves that the proposed mechanism is essentially correct as far as the products of reaction are concerned, but there is no evidence for any of the intermediates. It is possible that an acid chloride group might be formed transiently before reacting to give an anhydride. The mechanism suggested by McNeill and Neil is shown in fig. 52.

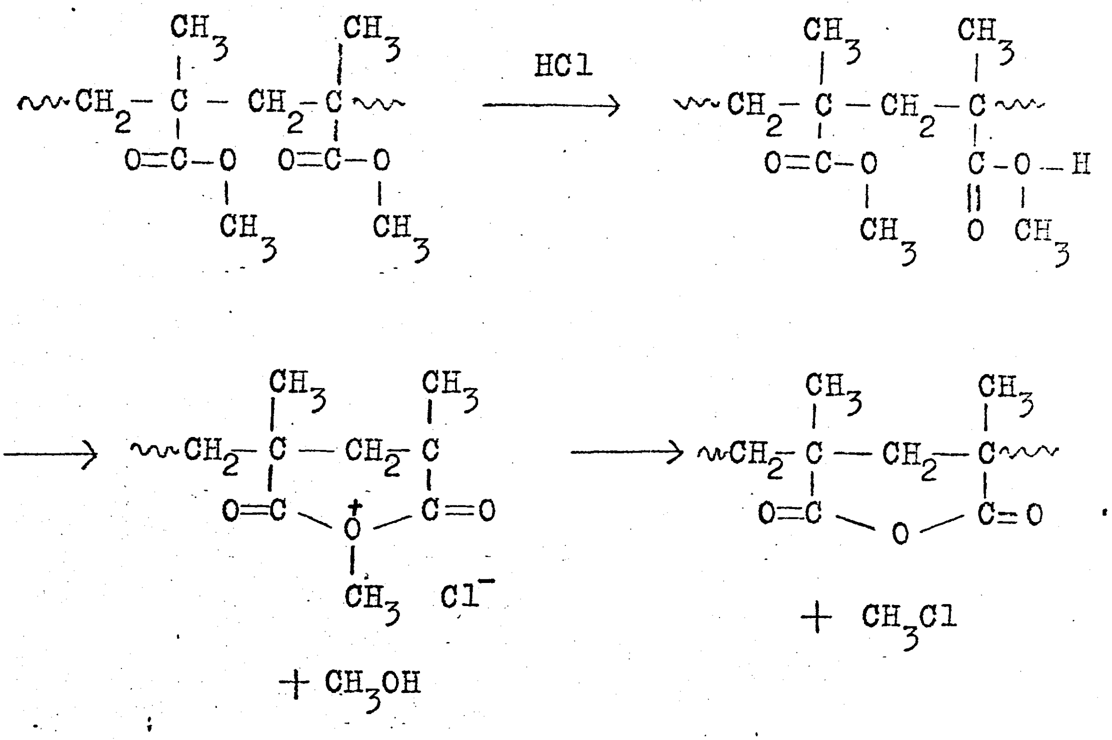
(f) Reasons for the Different Behaviour of PC and PVC in Blends with PMMA

From the results presented above, it is possible to derive two conclusions.

1) PC/PMMA blends do not show any interaction of the type

Fig. 52

The possible effect of Hydrogen Chloride on PMMA (from reference 27).



which in PVC/PMMA blends causes early degradation of the PMMA.

2) PMMA reacts with the hydrogen chloride produced by polychloroprene in the same way as in PVC/PMMA blends, but to a much greater extent.

The first factor which must be considered in seeking an explanation for the differences is the different temperature range in which the reactions take place. Polychloroprene degradation in the main takes place above 300°C, about 80°C higher than PVC. The PMMA probably reacts more readily with hydrogen chloride at this increased temperature. If this is so, then the stabilising effect of the hydrogen chloride would reduce the amount of monomer which could be produced by depolymerisation initiated by diffusing radicals. Even so one would still expect to observe some early depolymerisation.

Moreover it was shown that as little as 10% PVC in PMMA could initiate depolymerisation. Since the polychloroprene used in the blend was the type MC30, which degrades to a small extent (about 5%) below 300°C it might be thought that this would be sufficient to initiate PMMA depolymerisation unless the early dehydrochlorination reaction in polychloroprene is not a radical process.

Another factor to be taken into account, is the form of the sample. PVC and PMMA both soften during the degradation whereas polychloroprene is still solid during the dehydrochlorination stage of the degradation. It might therefore be more difficult for radicals to diffuse across the phase boundaries.

The size of the micelles too, might have an effect, since the larger they are the less likely it is that diffusion across phase boundaries can take place. It is shown in a later section of this chapter that the micelles of polychloroprene in PMMA are much larger than in the PVC/PMMA blend. However, small micelles as well as large ones are formed and the 10% blend contains micelles comparable in size to those in the PVC/PMMA blend, and yet early depolymerisation of PMMA is completely absent.

Although some other explanations have been discussed in the preceding paragraphs, the simplest and most convincing interpretation of the results of the experiments on PC/PMMA blends is that no small radicals are produced in degrading polychloroprene.

Degradation of Blends of Polychloroprene and Polystyrene

When blends of polychloroprene and polystyrene (PS) are examined, polychloroprene is found to cause the same effect on polystyrene as PVC. Dehydrochlorination of PVC is retarded by blending with it another polymer which has hydrogen atoms which are susceptible to abstraction by chlorine atoms.[27] The degradation of the other polymer may or may not be affected by this interaction. In PVC/PS blends the degradation of the PS is delayed, probably because chlorine atoms from PVC cause cross-linking or chain scission in the polystyrene and increase its thermal stability.

(a) DC - TVA

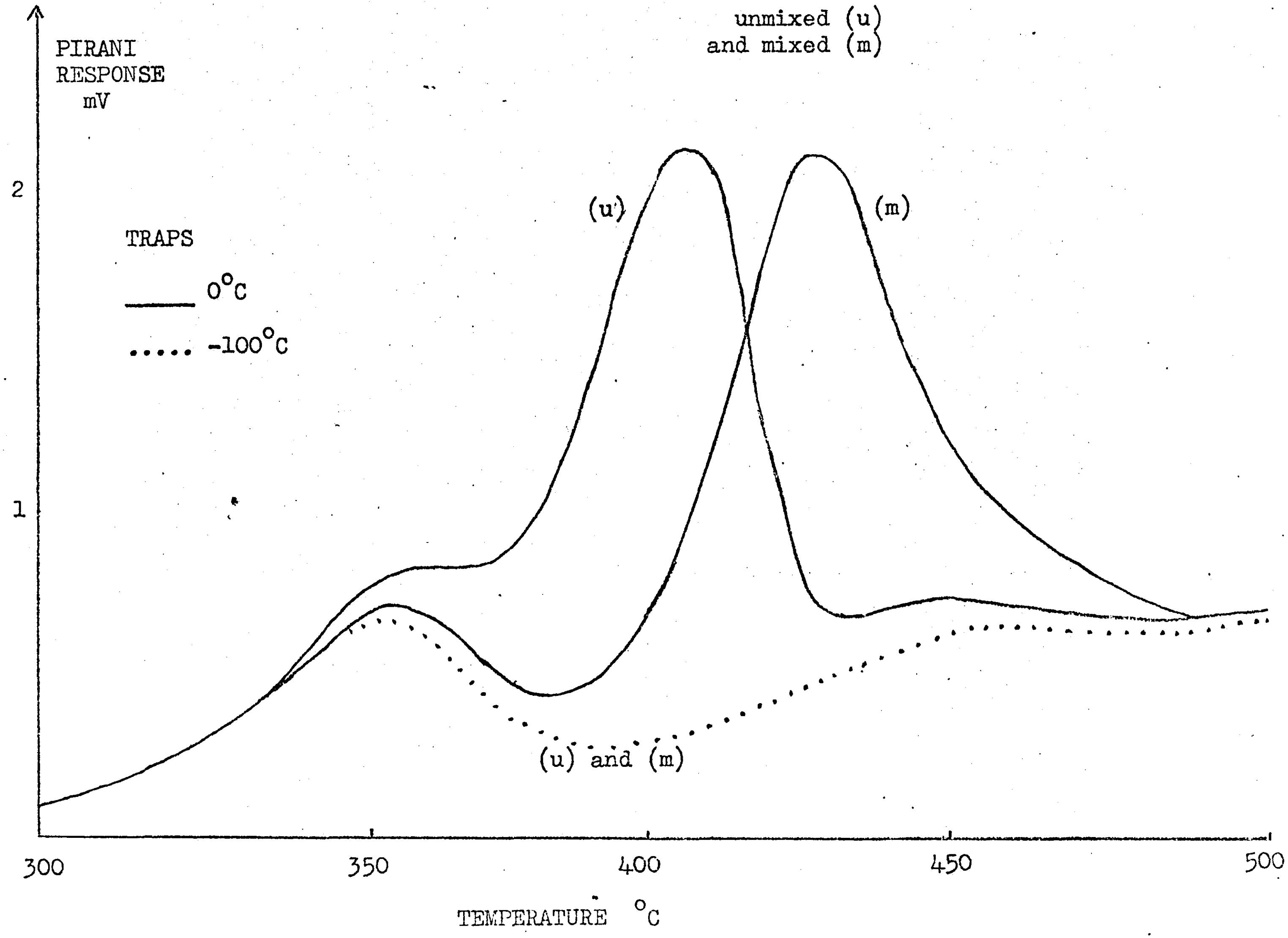
20mg. each of polychloroprene and polystyrene were degraded as mixed and unmixed films in two crucibles inside the degradation tube of the DC - TVA apparatus.

Comparison of the TVA curves from mixed and unmixed samples (fig. 53) indicates that the peak maximum for polystyrene degradation is changed from 407°C to 427°C (5°/min.). Styrene is the main product of degradation of polystyrene and gives a low limiting rate in the -75°C trap.[58,59] The -100°C trace is due to the degradation products from polychloroprene and it is evident that no change in this takes place.

(b) Effect of Hydrogen Chloride on Polystyrene

Although it was difficult to imagine how hydrogen chloride could react with polystyrene to give a polymer with increased stability, two experiments were performed

Fig. 53. PC/PS DC - TVA 5°/min 20 mg each polymer
unmixed (u)
and mixed (m)



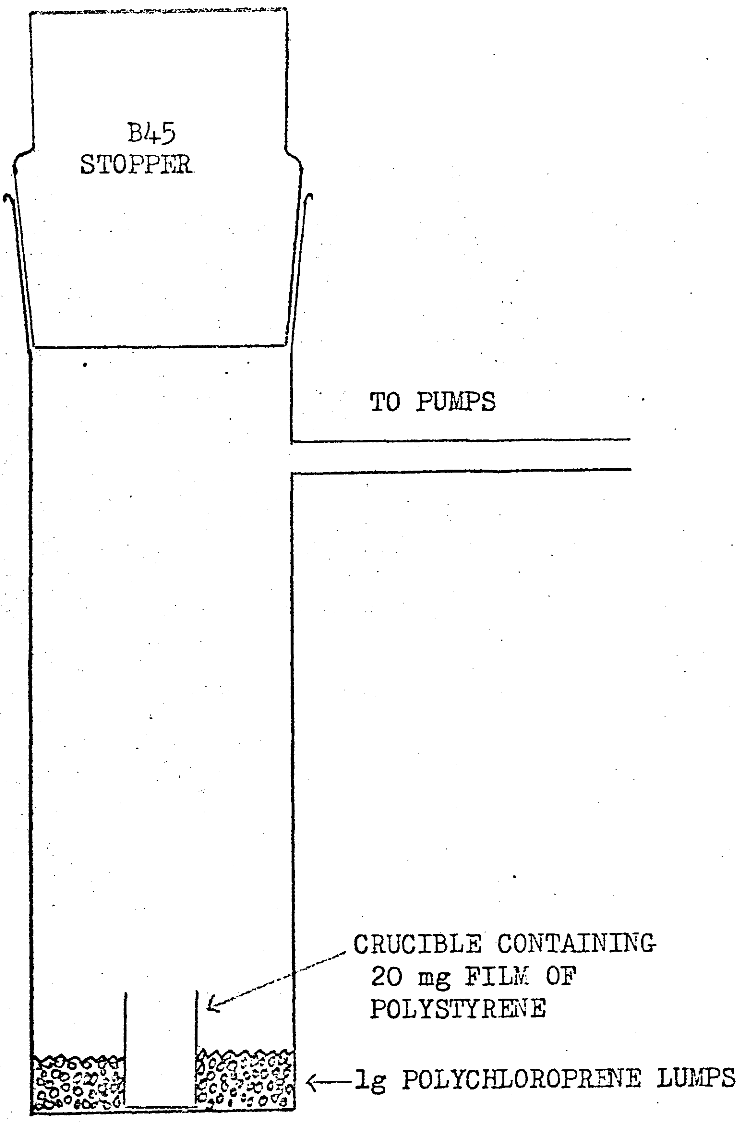
to determine whether this possibility could be discounted.

In the first experiment, 20mg. films of polychloroprene and of polystyrene were heated at 5°/min. in separate crucibles in the degradation tube just as when obtaining the traces for the unmixed films. After the solvent had been removed the taps isolating the degradation tube from the traps were closed. Degradation was stopped at a temperature equivalent to the minimum between the two peaks in the TVA curve of polychloroprene.

After cooling, the taps were opened and a TVA run of the remaining polymers. The polystyrene peak was found to be reduced in size by about one third and the peak maximum occurred at 413°C (c.f. 407°C for PS not treated in this way).

The effect of a higher pressure of hydrogen chloride on polystyrene was examined using the system shown in fig. 54. A crucible containing a 20mg. polystyrene film was surrounded by 1g. of small lumps of polychloroprene. The stopper at the top of the tube was taped down and heating started at 5°/min. After the solvent had been removed, the tube was sealed off at the side arm without interrupting the heating. The volume in which the hydrogen chloride from the degradation of polychloroprene was confined, was about 250ml. and the highest pressure reached was calculated to

Fig. 54. Apparatus used to examine effect of HCl on Polystyrene.



be about one atmosphere.

Heating was stopped at the same point as before and the stopper carefully removed when the tube was cool. Since some spots of the tars produced during polychloroprene degradation had settled on the polystyrene, the polymer was briefly washed with a little acetone (in which polystyrene is insoluble). The crucible was then placed in the degradation tube and the TVA curves obtained as before. These showed that just as in the previous experiment about one third of the sample had been lost in the first heating but now the reduced polystyrene peak had a maximum at 416°C.

Polystyrene which had been partially degraded in the TVA apparatus up to the same temperature as that used in the above experiments exhibited no change in the temperature of the peak maximum no matter whether an open or closed system was used. This confirmed the results of McNeill and Mohammed[116] who had already studied the effect of predegradation on polystyrene.

The above experiments demonstrate that heating polystyrene in hydrogen chloride up to a temperature at which some of it has degraded, does produce a small increase in the TVA peak maximum temperature of the remaining polymer. The increase in the stability of the polystyrene is not as great as when the polymer is heated in a blend with polychloroprene.

(c) Discussion of the Interaction

Hydrogen chloride produced within a polymer sample is naturally more likely to effect changes in the bulk of the polymer than when it has to diffuse in from the surface. The reason why there is little difference in the behaviour of the two samples subjected to greatly different pressures of hydrogen chloride may be that in both cases only the surface of the polymer was affected.

Nevertheless it is not easy to explain the effect of the hydrogen chloride on polystyrene. Addition to double bonds seems unlikely because most polymers containing chlorine eliminate hydrogen chloride to form a double bond at an early stage in degradation.

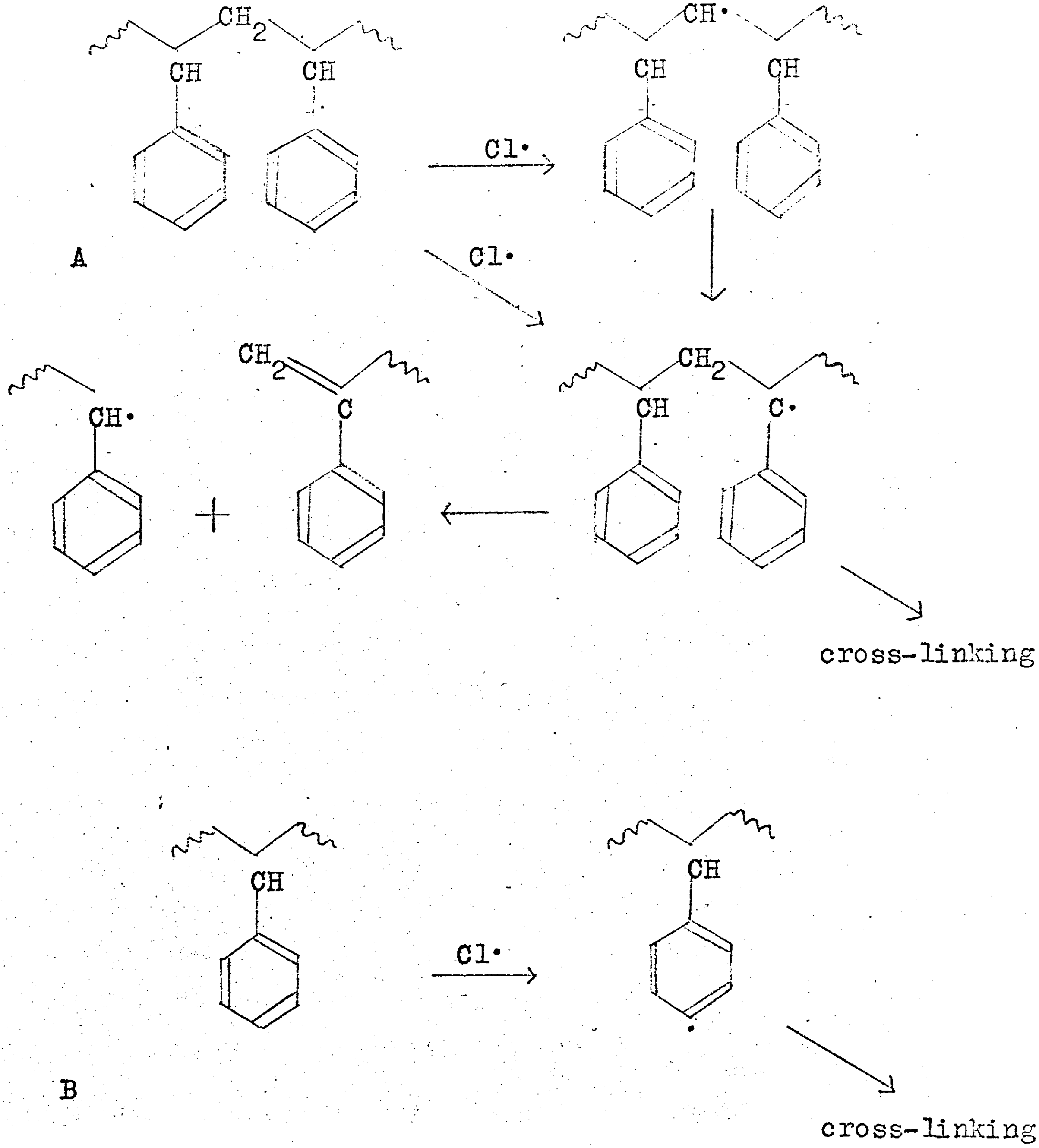
Homolytic scission of the hydrogen - chlorine bond might take place, especially in the presence of radicals from degrading polystyrene.

Chlorine atom formation from hydrogen chloride in the presence of alkyl radicals has been held responsible for the catalytic effect of hydrogen chloride during the pyrolysis of dimethyl ether[117] and neopentane[118] at temperatures of 450 - 480°C. The catalysis is due to the fact that a chlorine atom abstracts hydrogen a hundred times faster than a methyl radical.[117] Hydrogen chloride catalyses the decomposition of t-butyl peroxide in the range 90 - 185°C[119,120] and will not add to ethylene at 155°C unless a peroxide catalyst is present.[119] These results are taken as evidence that chlorine atoms can be formed at fairly low temperatures by reaction of a peroxide radical with hydrogen chloride. It is not known if chlorine atom formation from hydrogen chloride is responsible for the autocatalytic effect in PVC degradation.

A chlorine atom could react with polystyrene by abstraction of hydrogen to form a macroradical which could act as a centre for scission or cross-linking. Reaction with the vinyl polymer chain (fig. 55A) would be analogous to the normal mode of polystyrene degradation and thus it would seem unlikely that this causes an increase in thermal stability, although a small shift to higher temperature has been observed[116] in polystyrene degradation as the molecular weight is reduced. The chlorine atom could however combine with a hydrogen atom on a phenyl group to produce a radical not found in degrading polystyrene because none of the radicals in the degradation have the same hydrogen abstracting power as the chlorine atom. The most probable reaction of this radical (fig. 55B) is likely to be the formation of a cross-link by combination with another radical. Cross-linked polystyrene has been shown[121,122] to possess increased thermal stability over

Fig. 55

Proposed mechanism for the action of chlorine atoms on polystyrene.



linear polymer.

If a chlorine atom is responsible for the increase in stability of polystyrene in the blend, then the question arises whether it is produced directly in the polymer degradation or indirectly by the homolysis of hydrogen chloride. It seems clear that chlorine atoms are produced in PVC degradation and these are responsible for the effects in PVC/PS blends. In PC/PS blends hydrogen chloride is evolved at a higher temperature and the polystyrene is already degrading, thus a radical reaction between the hydrogen chloride and polystyryl radicals is more plausible. Despite the fact that no inhibition of dehydrochlorination was observed in PC/PS blends, the possibility that chlorine atoms are produced in polychloroprene degradation cannot be completely excluded, until it is shown that hydrogen chloride intimately mixed with degrading polystyrene causes an increase in stability equal to that in the PC/PS blend.

Degradation of Blends of Polychloroprene and PVC

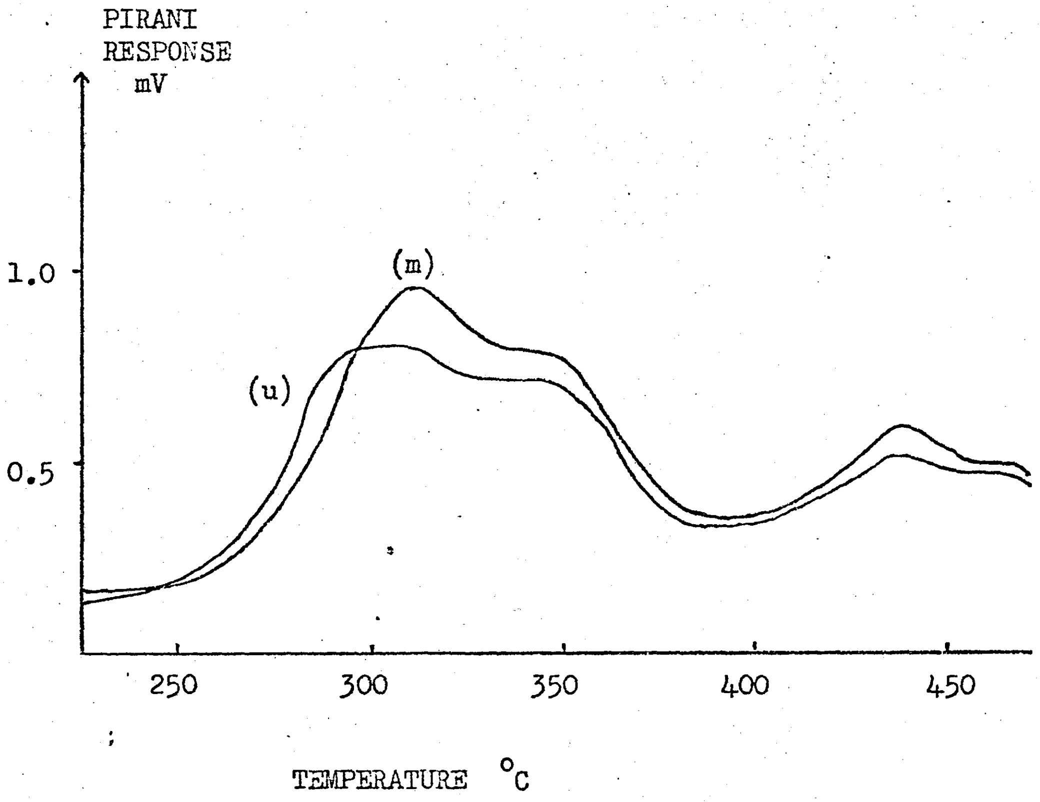
(With Mr I. Davidson, fourth year student)

Mixed and unmixed films of polychloroprene and PVC were heated at 5°/min. in a degradation tube which had two short limbs attached to the base, replacing the crucibles in the previous experiments. The TVA apparatus used was a two trap differential condensation system using temperatures of 0 C and -75°C. In this combination of polymers identical responses were obtained on both gauges since no products condensable at -75°C were evolved. The curves obtained are shown on fig. 56.

It is evident that the degradation of PVC is slightly retarded in this system just as in many other polymer blends. The increase in the height of the peaks in the mixed film is due to the increased overlap of the polychloroprene and PVC degradations. If the action of the chlorine radicals from PVC had an initiating effect on polychloroprene degradation then some of the hydrogen chloride from polychloroprene would be evolved at lower temperatures and the peak at 350°C would be reduced in size. However the TVA curves give no indication that this occurred though interpretation is hampered by the inability to distinguish between hydrogen chloride from one polymer or the other.

It is doubtful if more information can be obtained from this system without the use of labelled polymer, but the conclusion derived from the TVA results is that PVC is stabilised by polychloroprene, the degradation of which is not affected by the interaction with the PVC.

Fig. 56. PC/PVC 5°/min TVA



10 mg each polymer

unmixed (u)

and mixed (m)

Microscopy of Polymer Blends

(a) Previous Examinations of the Structures of Blends

The structures of the polymer blends discussed in this chapter were examined by optical and electron microscopy. Several such examinations of other polymer systems have already been reported, using a variety of techniques to contrast the polymers in the film.

Specimen preparation for phase contrast microscopy involving mounting, microtoming and staining has been described by Traylor[123] and his method has been used to study blends of styrene/acrylonitrile copolymers of various compositions.[124] The picture thus obtained for a just incompatible blend is similar to the appearance of the PVC/PMMA film examined under the microscope in this work.

Electron microscopy has also been employed to study polymer films.[eg. 125 - 133] Unsaturated elastomers can be stained with bromine[134] or osmium tetroxide,[135] and chrome shadowing or replicating techniques can be used to show surface features.

In this investigation unstained polymers were examined directly using an electron microscope and a simple optical microscope without phase contrast. Samples were prepared in the form of very thin films which meant that microtoming was not required. The chlorine atom in PVC or polychloroprene has a high enough electron density to act as a staining agent but the blend of these two polymers shows no contrast.

(b) Film Preparation and Microscopy

Solutions were made of 5mg./ml. and 1mg./ml. polymer in cyclohexanone (for blends containing PVC) or toluene. The solution of the blend was obtained by mixing 1ml. of each of the appropriate solutions.

For optical microscopy one drop of mixed solution was spread on a glass slide where it quickly evaporated. Dimensions of features in the film were estimated by comparison with a fine hair, the diameter of which had been accurately determined by a micrometer screw gauge.

For examination by the electron microscope (Siemens Elmiskop 1), one drop of mixed solution was allowed to spread freely over a water surface and solvent evaporation was virtually instantaneous. Part of the thin film was picked up on a small copper grid by lifting the grid from below the surface with a pair of forceps. Ideally the film would break round the edge of the grid but the failure rate for this operation was fairly high. The mounted film was inspected in the optical microscope before being placed in the sample chamber of the electron microscope.

Films containing polychloroprene had to be examined very shortly after preparation otherwise oxidation caused their complete disintegration. The energy of the electron beam soon burned holes in the film and the sample was kept moving between brief pauses for focussing and photography.

(c) Poly(methyl methacrylate) Blends with PVC and Polychloroprene

The 1/1 PVC/PMMA blend appeared as a mottled film when examined under the microscope. The micelles were estimated to be 1μ or less in size and this was confirmed by the photographs obtained using the electron microscope (Plates 1 and 2). The two photomicrographs show that the size of the micelles varies from one part of the film to another and that the phase boundaries are not clearly defined (especially in Plate 2). The dark lines in the photographs appear to be folds and the holes in the film are quite obvious.

The 1/1 PC/PMMA blend showed a much greater degree of incompatibility. Large irregularly shaped micelles were seen under the microscope and their size was estimated at about 2 - 20μ. Plate 3 was obtained by electron microscopy and shows that in addition to the large micelles, small ones also are formed. The phase boundaries of the large structures are very sharp but the small ones seem to blend more with the surrounding matrix. The dark regions are frequently puckered and occasionally contain areas of the

Plate 1

PVC/PMMA 1/1 Electron Microscope 3,200 X

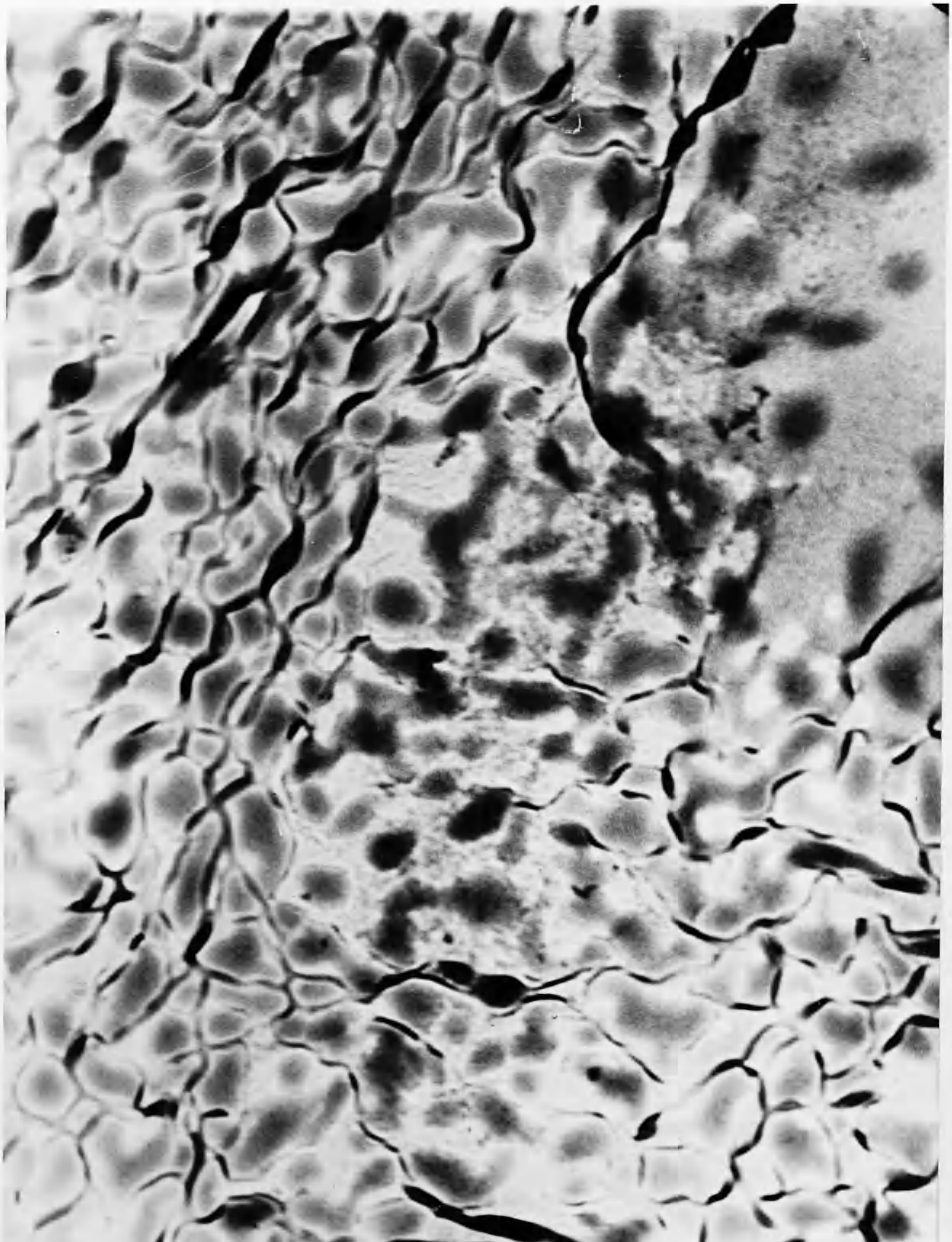


Plate 2

PVC/PMMA 1/1 Electron Microscope 3,200 X

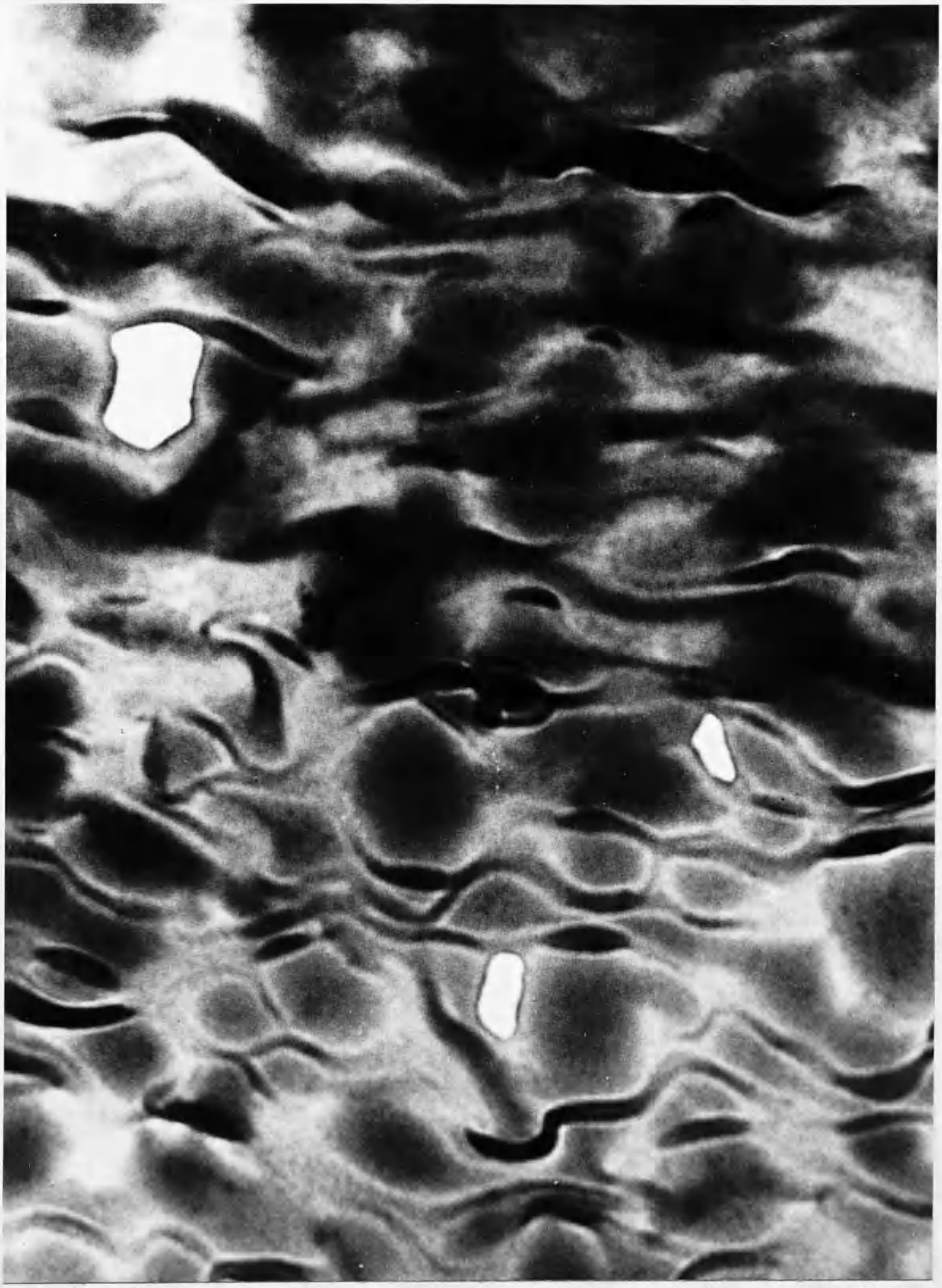


Plate 3

PC/PMMA 1/1 Electron Microscope 3,200 X

light coloured phase.

In order to determine which phase was polychloroprene, a 5/1 PC/PMMA blend was examined. This was predominantly a darker colour indicating that the dark phase was polychloroprene. Most of the film was composed of light spots on a grey background (Plate 4) but occasionally dark areas were formed on the same shade of grey (Plate 5). This suggests that the phase inversion occurs at about this ratio so that a small local concentration change may cause a different polymer to accumulate in the micelles.

A film of a 1/5 blend of PC/PMMA was also photographed (Plate 6). This shows that polychloroprene micelles become much smaller and the phase boundaries less distinct than in the 1/1 blend. The micelles are mainly smaller than those in the 1/1 PVC/PMMA blend and the contrast is about the same. A 1/10 PC/PMMA blend broke up too easily for mounting in the electron microscope and also gave too little contrast for successful examination optically. It is likely however that at this ratio the polymers are compatible or very nearly so, with extremely small regions of the dispersed phase. The amount of mixing in the 1/10 PC/PMMA blend therefore seems at least as good as in 1/1 PVC/PMMA which indicates that a sample form effect does not account for the absence of radical induced depolymer-

Plate 4

PC/PMMA 5/1 (major part) Electron Microscope 3,200 X

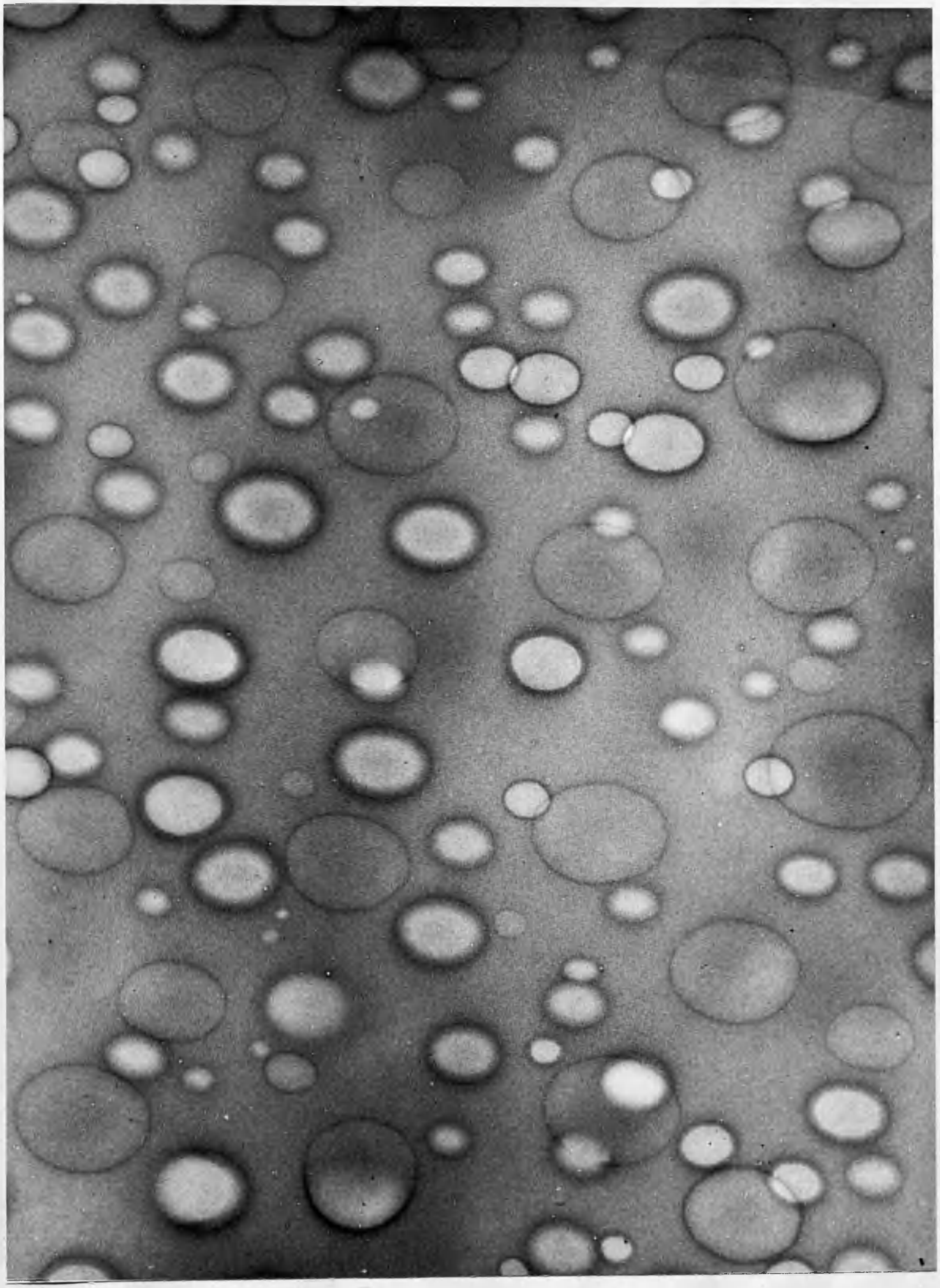


Plate 5

PC/PMMA 5/1 (minor part) Electron Microscope 3,200 X

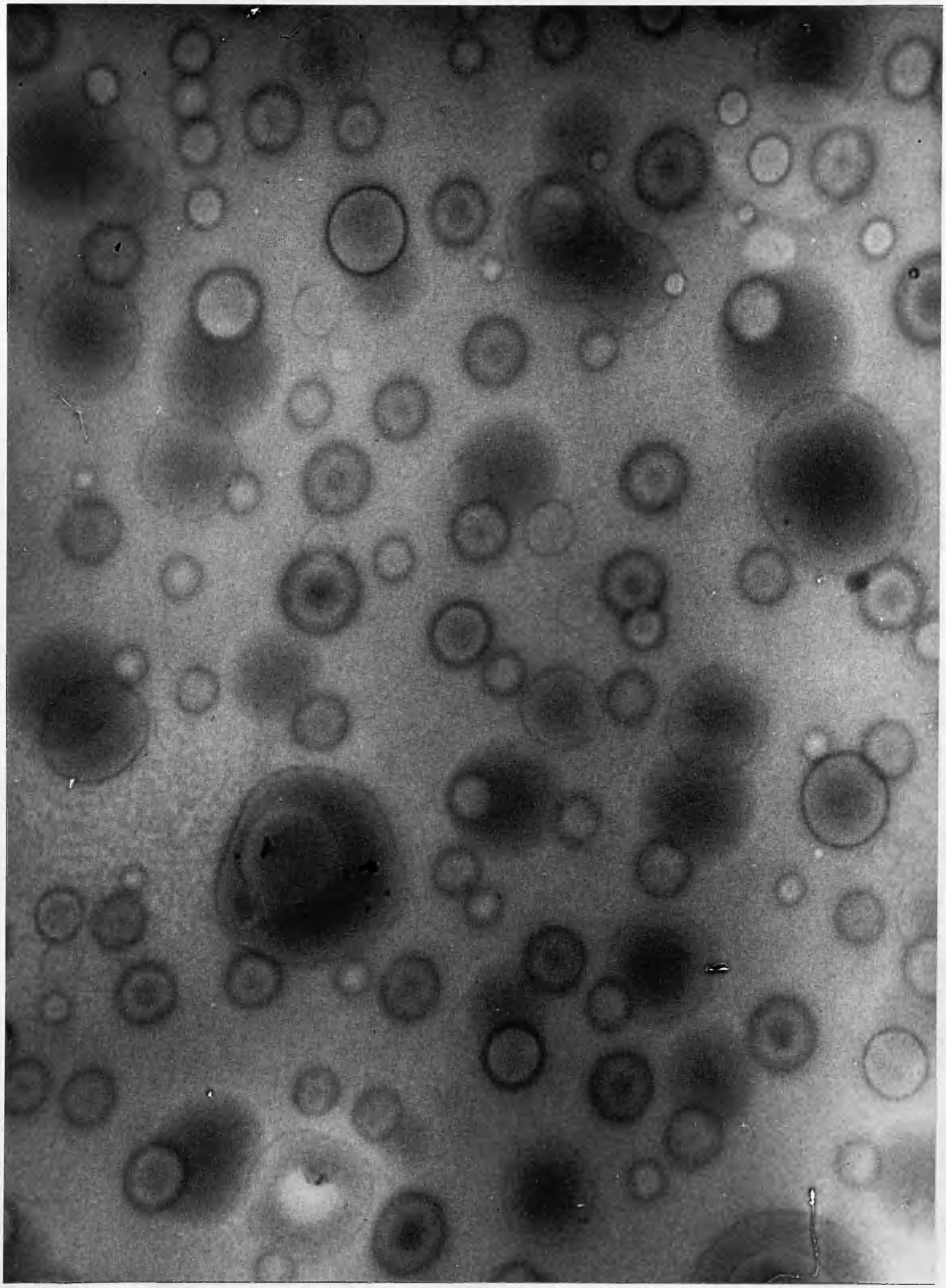
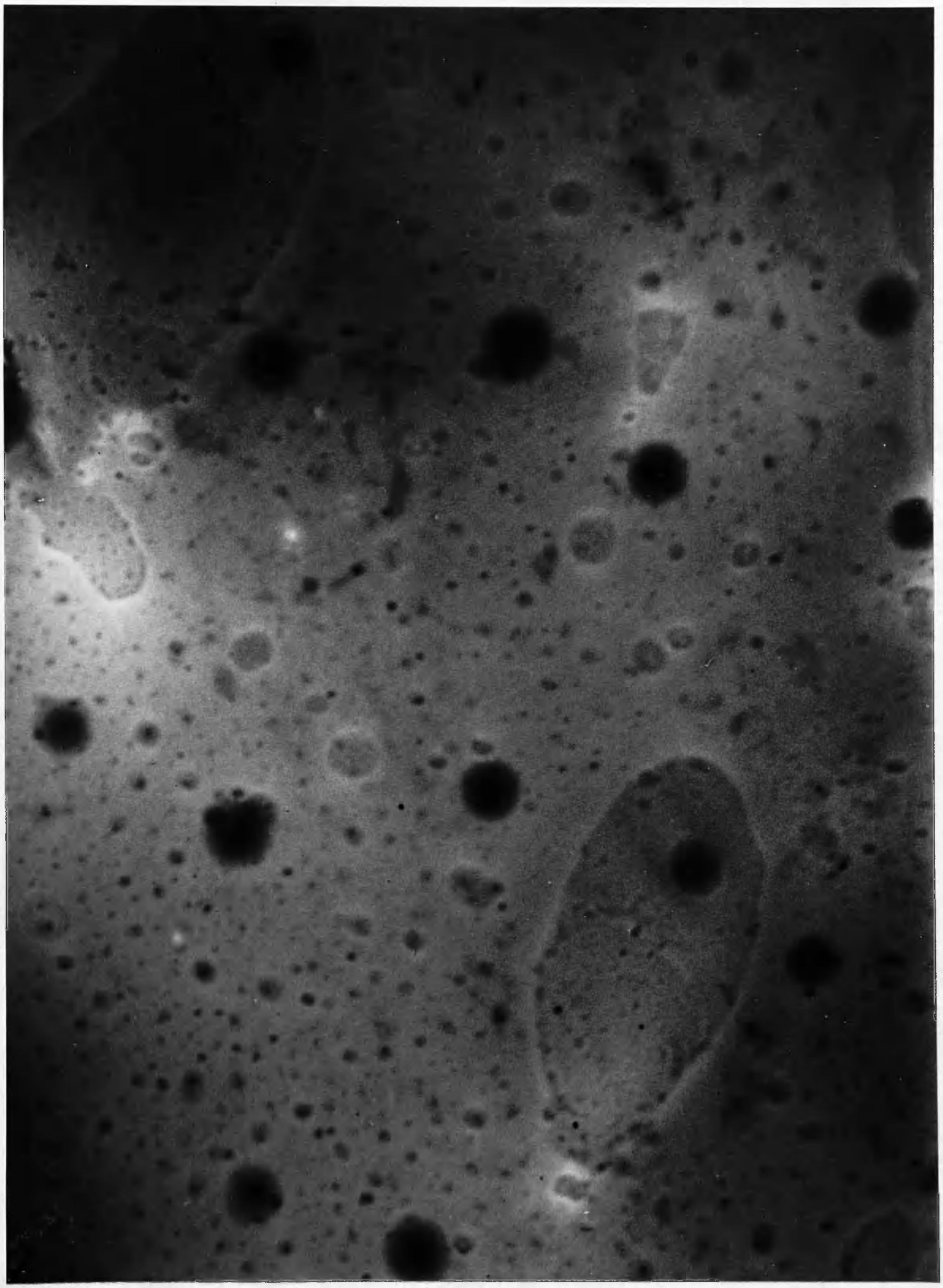


Plate 6

PC/PMMA 1/5 Electron Microscope 3,200 X



isation of poly(methyl methacrylate) in the blend with polychloroprene.

(d) Polystyrene Blends with PVC and Polychloroprene

The incompatibility of PVC with polystyrene in tetrahydrofuran solution has already been reported.[106]

The 1/1 PVC/PS blend showed poor contrast when examined optically but a picture was obtained from the electron microscope indicating that rounded micelles of polystyrene about 1μ in size were formed in a PVC matrix.

The 1/1 PC/PS blend cast as a film on a microscope slide, showed irregular regions of polychloroprene of between 2μ and 10μ in a matrix of polystyrene.

Despite the different microstructures of the blended films the effect on polystyrene degradation is the same in each case.

(e) Polystyrene/PVC Blend

No incompatibility could be detected by either type of microscopy but this was probably due to the lack of contrast in the two polymers. The method of staining with osmium tetroxide might be useful to examine this blend further

Summary

Blends of polychloroprene with PMMA show none of the early depolymerisation reaction which is one of the strongest pieces of evidence for the presence of small radicals during the degradation of PVC/PMMA blends. The hydrogen chloride produced by the degradation of both PVC or polychloroprene interacts with PMMA blended with them and causes the formation of six membered anhydride rings. Because of the higher temperature of degradation of the PC/PMMA system this reaction occurs to a much larger extent than in the PVC/PMMA system.

The TVA curves of PC/PVC blends shows that polychloroprene behaves like many other polymers in delaying the degradation of PVC. There is apparently no large effect on the degradative behaviour of polychloroprene, again suggesting that chlorine atoms are not involved in the dehydrochlorination of this polymer.

An increase in the temperature of degradation of polystyrene is observed in the TVA curves of PC/PS blends. This at first suggests that polychloroprene behaves like PVC and causes the stability increase by interaction of chlorine atoms with the polymer perhaps producing crosslinking. However other results indicate that hydrogen chloride alone can effect a small increase in the thermal stability of polystyrene. In view of this, and taking into consideration the fact that in the polymer blend the hydrogen chloride makes much better contact with the polystyrene, it is concluded that the experiments on polymer blends indicate that small radicals do not play an important part in polychloroprene degradation.

CHAPTER 9

DISCUSSION

Thermal analysis shows that the dehydrochlorination of polychloroprene is not a single stage process. A small amount of elimination occurs below 300°C (at 10°/min.) followed by the main dehydrochlorination reaction which is accompanied by side reactions. The early degradation is discussed first separately since it seems to be unconnected with the main reaction.

Although less than 5% of the hydrogen chloride content of the polymer is eliminated in the first stages, this early degradation can be detected by TG and TVA and it also shows up very well in the UV spectra of the partly degraded polymer. Comparison of the results obtained by these three techniques applied to samples of MC30 and PC-40 indicates a correspondence between the number of irregular structures in the polymer and the amount of low temperature degradation.

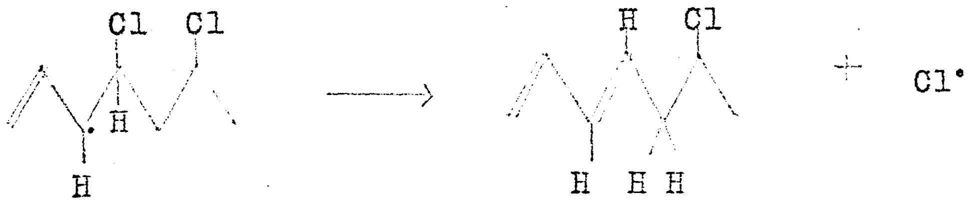
The tertiary allylic chlorine atom formed by 1,2 addition is known to be a source of instability towards hydrolysis[4] and reaction with amines.[136] Furthermore compounds containing a secondary chlorine in an allylic position have been shown[137] to be much less stable during gas phase pyrolysis than a model compound for the vinylic chlorine in the major part of the polychloroprene chain.

Dehydrochlorination at a 1,2 unit can easily result in a triene (page 81) and the UV results indicate that the formation of unsaturation in one unit does not initiate the production of long polyenes as in PVC.

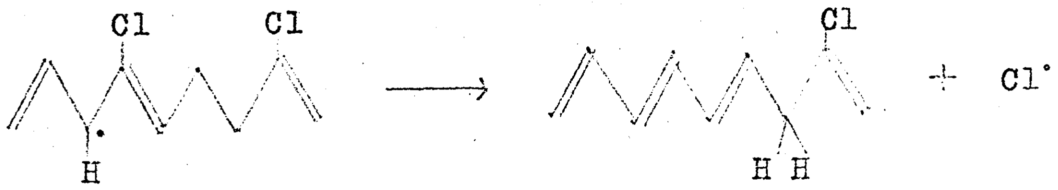
TVA showed that two stages of early dehydrochlorination could be distinguished (A and B, page 42). The polymers prepared in the absence of oxygen showed very little stage B reaction but all showed stage A to some extent. Possibly 1,2 units themselves cause the stage A degradation, and some structure produced by oxidation either of the labile 1,2 units or of the normal 1,4 units causes stage B. It was not found possible to produce a polymer with increased stage B degradation by accelerated oxidation at over 100°C (page 44) but the two polymers which did show stage B volatilisations were the polymer prepared in air at 30°C and the SC20 polymer after storage for 30 months.

The results described for the degradation of polychloroprene blends (chapter 8) suggest that the degradation of polychloroprene does not involve chlorine radicals. By analogy with PVC, the propagation step of a radical mechanism would take place as shown below, but this does not seem at all likely in view of the amount of rearrangement required.

PVC



Polychloroprene



Against the evidence from chapter 8 must be set the fact that a value of $n = 1.5$ appeared to fit some of the kinetic data. This value has been found for PVC and is typical of many radical chain reactions. However the kinetics were treated by separating the dehydrochlorination from the other reactions which may not be a valid approach to the problem and the value $n = 1$ obtained for the overall weight loss may be more useful.

Several authors[78,79,138,139] have warned against reading mechanistic significance into the kinetic results obtained from thermo-analytical techniques especially where overlapping reactions are concerned. The value of the activation energy can be used as an index of thermal stability, but must be carefully interpreted in the light of all the knowledge about a particular polymer degradation.

For instance, although the generally accepted value for the activation energy of PVC degradation is about 30Kcal./mole,[13,19,21,88,140] TG studies have given a value[141] of E = 72.5Kcal/mole. The reason for this is probably that the reaction does not follow simple n^{th} order kinetics because of the autocatalytic effect of the hydrogen chloride, although an alternative explanation has been offered.[142] When TVA results for PVC were treated by the method of assuming zero order (page 68) another high value of E = 42Kcal./mole was obtained.

The figure of 30Kcal./mole referred to above was obtained for isothermal experiments in which autocatalysis was not involved. By comparison with this result, the value of E = 39.6Kcal./mole for isothermal polychloroprene degradations is of the expected order of magnitude.

The mechanism of degradation of polychloroprene is rather problematical and there is little information to be gained from the few studies made of the pyrolysis of related compounds containing a vinylic chlorine. A model compound, 3-chloropent-2-ene has been shown[137] not to decompose below 400°C which indicates that a large destabilising effect can be attributed to the polymeric environment. The difficulty of eliminating hydrogen chloride from a vinylic group has also been noted[63,143] in the degradation of poly(vinylidene dichloride) $(CH_2CCl_2)_n$. Removal of one chlorine atom per unit in this polymer leaves a vinylic chlorine which hinders the elimination reaction, but eventually pure carbon is produced.

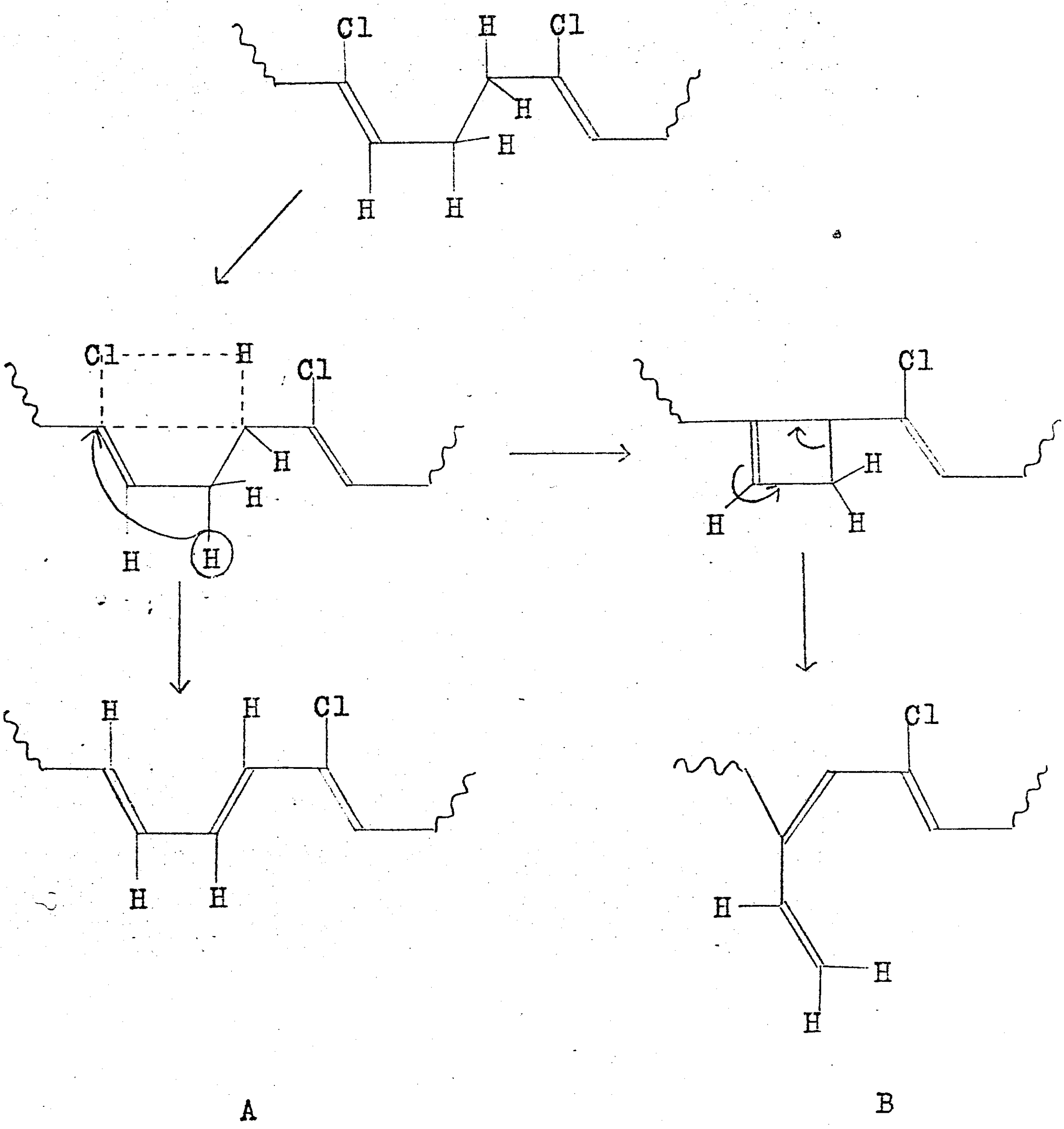
It has been proposed[144] that dehydrochlorination of polychloroprene by alkali metal in liquid ammonia takes place through an allene intermediate. A more likely first step in the heated polymer is the combination of the chlorine atom with the allylic hydrogen on C_1 in the next unit, to form a cyclobutene transition state. Migration of a proton from C_4 to C_2 with the simultaneous opening of the ring would form a conjugated triene as illustrated in fig. 57A.

The transition state can never approach a true cyclobutene or else another method of rearrangement could take place to form a pendant vinyl group (fig. 57B). Since the absorption for these vinyl groups occurs at 923cm^{-1} in the infrared and is one of the first to disappear from the spectrum of the degraded polymer, this transformation of the transition state must be discounted.

The mode of elimination illustrated in fig. 57A, is certainly not the only type of hydrogen chlorine link up which takes place in the degrading polymer but it seems to be one which could take place quite readily.

The apparent order of $n = 1.5$ means that the rate falls

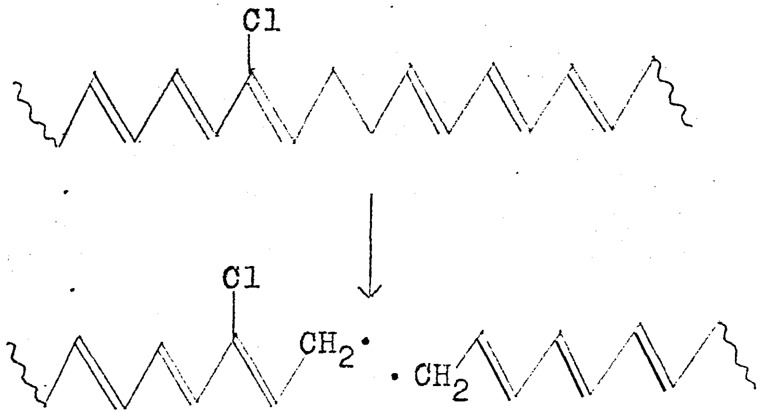
Fig. 57



off as the reaction proceeds, by a greater amount than a first order dependence on remaining chlorine. The ease with which a chlorine atom can be lost will depend on the configuration of the polymer chain in its neighbourhood and those chlorine atoms which are best situated for elimination will be lost first. As the reaction proceeds only chlorine atoms in sterically unfavourable positions will be left to be eliminated at progressively lower rates. Extremely accurate rate and composition measurements and the development of complex kinetic expressions for the dehydrochlorination would be required to test the validity of this view.

Qualitatively however the effect of the chain configuration can be observed in the lower thermal stability during the main part of dehydrochlorination of PC-40 compared to MC30 (chapter 3). In the more regular polymer, the chain arrangement required before elimination can take place is achieved more easily for a higher proportion of the chlorine atoms in the polymer.

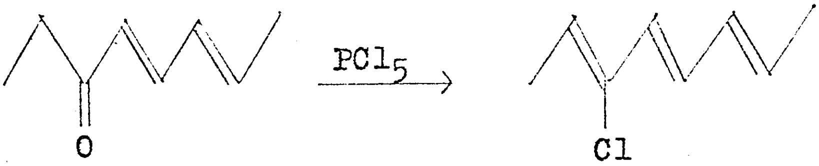
An interesting feature of the decomposition of polychloroprene is the number of methyl groups produced in the residue during degradation, and the amount of methane lost in high temperature pyrolysis. Many more methyl groups are produced than during PVC degradation and the explanation for this lies in the fact that the interunit bond in polychloroprene is liable to break. If some dehydrochlorination has already taken place, then depolymerisation of the radicals formed by the scission may be impossible, as for instance in the radical pair shown below.



Both of these conjugated radicals could transfer their radical centre to any point along the chain and might thus produce cross-linking, but it is also possible that a hydrogen could be abstracted so that a terminal methyl group was produced.

Some aspects of this investigation could be profitably pursued further. The technique whereby the changes in the UV spectrum of a polymer are examined while the course of the degradation is followed by TVA has already been applied to several polymers and others could be investigated in the same way provided that a satisfactory film could be cast in the silica degradation tube. An adaption of the UV method might be suitable for routine testing of polymers and especially for the comparison of the performance of stabilisers for polychloroprene.

It would be interesting to examine the UV spectra of model chlorotriene compounds, a possible synthetic route to which might be the action of phosphorus pentachloride on octa-4,6-diene-3-one as shown below.



One method of examining the mechanism of the dehydrochlorination reaction in polychloroprene in greater detail would be to use monomer labelled specifically with deuterium or tritium. The isotopic ratio of the hydrogen chloride evolved would be very informative and also some interesting effects might be seen in the infrared C - H absorptions of the residue, if a highly deuterated monomer were used.

Summary

The temperature programmed thermal degradation of polychloroprene occurs in three overlapping stages. The first is the loss of a small amount of hydrogen chloride from irregular structures formed either during the polymerisation or by subsequent oxidation.

The second type of decomposition is the loss of most of the polymer chlorine mainly as hydrogen chloride but also to a small extent as monomer and higher chain fragments. The dehydrochlorination reaction occurs at a higher temperature than in PVC and the activation energy for the process is about 39Kcal./mole compared to 30Kcal./mole in PVC. Another contrast with PVC is the different TVA behaviour of polychloroprene blends with poly(methyl methacrylate) where the absence of any early methyl methacrylate production suggests that chlorine atoms are not involved as radical chain carriers in the dehydrochlorination.

The third stage of degradation is the decomposition of the residue to a coke, along with the production of quantities of tar and non-condensable gases. Hydrogen and methane are present in the gas products while the infrared spectrum of the coke shows strong bands for aromatic structures formed by cyclisation of the double bonds left in the polymer after the elimination reaction.

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