THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF a-CHLOROACRYLONITRILE POLYMERS AND COPOLYMERS.

By

ERIC M. GRANT, B.Sc. (Glas.)

Supervisor: Dr. N. Grassie

Chemistry Department,
Glasgow University,
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PREFACE

The work described in this Thesis was carried out in the period October, 1960 to September, 1963, at the University of Glasgow in the Department of Physical Chemistry, which is under the supervision of Professor J.M. Robertson, F.R.S..

I am indebted to the Department of Scientific and Industrial Research for the award of a Research Scholarship, during the tenure of which this work was carried out.

My thanks are also due to various members of the technical staff of this department, in particular Messrs. I. Orr and R. Smith for general technical assistance and to Mrs. F. Lawrie and Miss P. Pellitt for obtaining the infra-red spectra.

I should also like to take this opportunity to thank other members of the Macromolecular Chemistry Section, in particular Dr. N.A. Weir and Mr.R.S. Roche for many interesting discussions on various aspects of this work.

Finally, I wish to thank Dr. N. Grassie for his general supervision of this work.

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CHAPTER 1

INTRODUCTION

The rapid advance of chemical knowledge combined with a corresponding increase in technological skills in the last thirty years, has led to the commercial development of a large number of man made polymers. These synthetic polymers now constitute the basis of the textile, paint, rubber, plastic and related industries. One important branch of chemical research on these compounds has been concerned with the understanding of the rapid deterioration which results on exposure to outside agents such as heat, light or oxygen. The increasing interest in this field has run closely parallel with the rapid development of the synthetic polymer industries. A more academic approach to this problem had to await a more detailed picture of polymer structure, hence it has only been in the last fifteen years that precise physical and chemical methods have been applied to the investigation of polymer degradation reactions, and a number of monographs on the subject have appeared[1-4].

Since the work described in this thesis has been confined to thermal degradation under high vacuum conditions, attention shall be focussed mainly on this aspect of the problem. The examples chosen in this introduction are a reflection of the materials and mechanisms studied in the experimental part of the thesis.

A comparison with model compounds would be expected to give a reasonable estimate of the thermal stability and decomposition mechanism, however, it has been found that this is not always the case. Polyvinyl chloride, for example, would be expected to yield hydrogen chloride and an olefinic residue by comparison with simple chloroparaffins. This is in fact what happens, but the reaction is found to occur at temperatures 200° C below that of model compounds. Similarly, polyethyl methacrylate which would be expected to decompose to acid and olefine, does in actual fact break down to monomer, again at temperatures considerably below that of the corresponding model compound. These anomalies can be broadly explained by two factors. Firstly, the existence of labile structural abnormalities in the polymer chain which can act as initiation centres for the decomposition reaction. In spite of their appreciable effect on the stability of the polymer, the concentration of these abnormal linkages is usually so low that they cannot be estimated chemically. Secondly, most polymer molecules tend to decompose by chain processes as opposed to molecular mechanisms in the model compound.

CLASSIFICATION OF THERMAL DEGRADATION REACTIONS.

For the purpose of classification, thermal degradation reactions may be divided into the following two groups.

(a) Depolymerisation or Chain Scission Reactions.

(b) Substituent or Non Chain Scission Reactions.

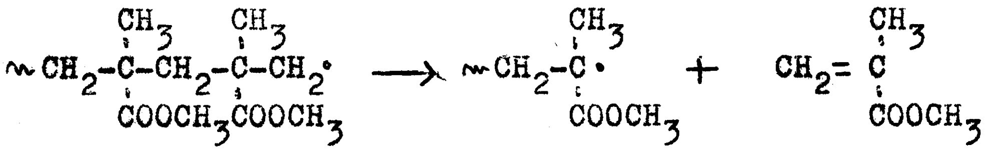
The first group is characterised by the breaking of the main polymer backbone with a corresponding decrease in molecular weight, whereas in the second group, the resulting decomposition reaction involves the substituents attached to the polymer chain. The volatile products in the first group are usually monomer or related compounds while the second group gives essentially non monomeric materials.

(a) Depolymerisation Reactions.

In this group two distinct types of reaction are found which may be broadly distinguished by the nature of the products.

(1) Depolymerisation to monomer.

Polymethyl methacrylate is the best example of this type of reaction where the polymer chain breaks down by a mechanism which is the exact opposite of the propagation step in the polymerisation process,



$$\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2^{\bullet} \longrightarrow \sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\bullet + CH_2=\overset{CH_3}{\underset{COOCH_3}{C}}$$

Grassie and Melville[5] showed that this depolymerisation reaction was initiated at the chain ends. Poly-α-methyl styrene[6] on the other hand decomposes by random chain scission followed by depolymerisation from the active centres formed in the initial scission.

(2) Chain scission giving non monomeric fragments.

The classical example of this type of degradation occurs in polyethylene[7], which breaks down by more or less random scission of the chains to give shorter chain olefinic fragments and small amounts of monomer. The molecular weight falls rapidly to low values. Polypropylene exhibits similar properties.

Between these two extremes are to be found examples such as polystyrene which show characteristic intermediate reactions. In this case, the molecular weight falls rapidly with the evolution of monomer and related fragments such as dimer, trimer, tetramer and pentamer. Monomer accounts for only 42% of the total volatile material.

Poly-m-methyl styrene and polyisobutene break down in a similar manner.

(3) Effect of structure on the nature of depolymerisation.

With the accumulation of experimental data, it is now clear that the above decomposition reactions can be explained on the basis of a single free radical chain mechanism, which can be represented kinetically by the following steps,

Initiation $M_n \longrightarrow P_i^\circ + P_{n-i}^\circ$

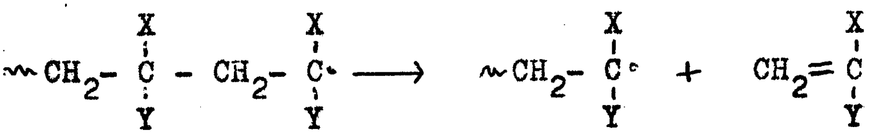
Depropagation $P_i^\circ \longrightarrow P_{i-1}^\circ + M$

Transfer $P_i^\circ + M_n \longrightarrow M_i + P_n^\circ$

Termination $P_i^\circ + P_j^\circ \longrightarrow M_i + M_j$ or M_{i+j}

where n is the chain length of the starting material and M_i, M_j, etc. and P_i°, P_j°, etc. represent respectively dead polymer molecules and long chain radicals, i, j, etc. monomer units in length.

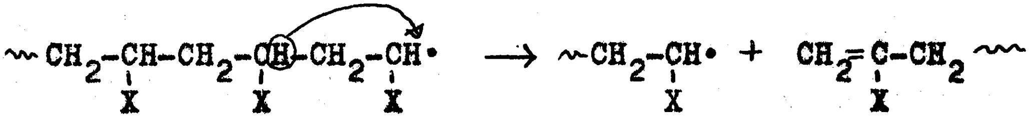
Generally, it has been found that polymers from 1:1 disubstituted monomers tend to break down to monomer in near quantitative yields. Polymers from monosubstituted monomers, on the other hand, rarely give large yields of monomer. These differing behaviours can be explained qualitatively by considering the influence of structure on the depropagation and transfer steps in the degradation mechanism. Transfer is less likely to occur in 1:1 disubstituted polymers which have no tertiary hydrogen atoms on the main chain. Thus, the rapid fall in molecular weight and the formation of low molecular weight fragments which result from transfer are completely suppressed. Also, the intermediate radical formed from 1:1 disubstituted polymers is considerably more stable than that formed from the monosubstituted polymer, hence the monomer producing disproportionation reaction,



$$\sim CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}\cdot \longrightarrow \sim CH_2-\underset{Y}{\overset{X}{C}}\cdot + CH_2=\underset{Y}{\overset{X}{C}}$$

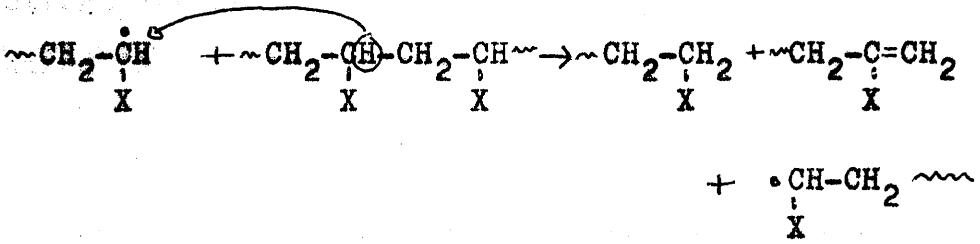
is further favoured at the expense of the hydrogen abstracting transfer process. In the case of monosubstituted polymers where the radical formed is more reactive, transfer reactions tend to predominate.

Generally, the labile tertiary hydrogen atoms can participate in either intramolecular or intermolecular transfer reactions, Intramolecular transfer



$$\sim CH_2-\underset{X}{CH}-CH_2-\underset{X}{C\text{Ⓗ}}-CH_2-\underset{X}{CH}\cdot \longrightarrow \sim CH_2-\underset{X}{CH}\cdot + CH_2=\underset{X}{C}-CH_2\sim$$

Intermolecular transfer



$$\sim CH_2-\underset{X}{\dot{C}H} + \sim CH_2-\underset{X}{C\text{Ⓗ}}-CH_2-\underset{X}{CH}\sim \longrightarrow \sim CH_2-\underset{X}{CH_2} + \sim CH_2-\underset{X}{C}=CH_2 + \cdot\underset{X}{CH}-CH_2\sim$$

The substituent group can also influence the ability of the radical to participate in transfer reactions . In polystyrene, for example, the stabilising effect of the phenyl group on the radical tends to suppress transfer. Transfer reactions are thus just able to compete with the depropagation mechanism, hence polystyrene gives considerable amounts of monomer (42%).

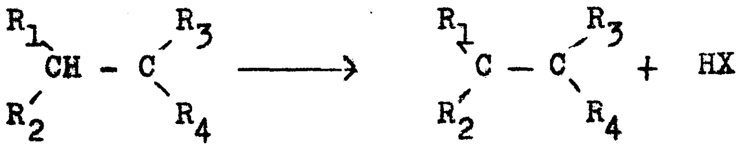
It is thus possible to predict to some extent how a given polymer will break down when subjected to degradation conditions. The above arguments apply only to polymers which decompose by depolymerisation or chain scission mechanisms. The corresponding aspects of substituent or non chain scission reactions are discussed below.

(b) Substituent or Non Chain Scission Reactions.

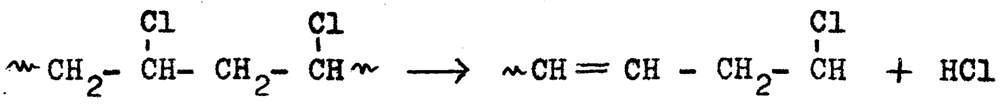
The decomposition reaction mechanism in this group is dependent entirely on the chemical nature of the substituents attached to the backbone of the polymer molecule. Such reactions are usually observed at temperatures lower than that required for depolymerisation to occur (~200°C).

(1) Ester decomposition reactions.

Polymers included in this group are those which break down in a manner similar to the classical ester decomposition reaction,

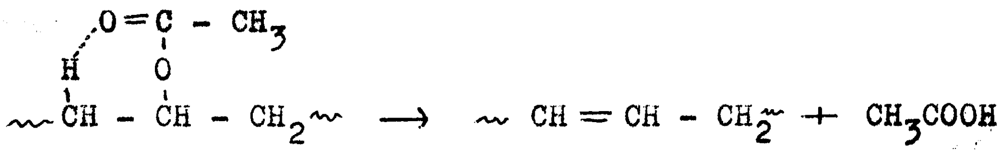


The resulting products are acid and olefine. Typical polymers of commercial interest which decompose by this mechanism are polyvinyl chloride and polyvinyl acetate. Both liberate the corresponding acid leaving a conjugated and thus highly coloured residue,



$$\sim CH_2-\overset{Cl}{\overset{|}{CH}}-CH_2-\overset{Cl}{\overset{|}{CH}}\sim \longrightarrow \sim CH=CH-CH_2-\overset{Cl}{\overset{|}{CH}} + HCl$$

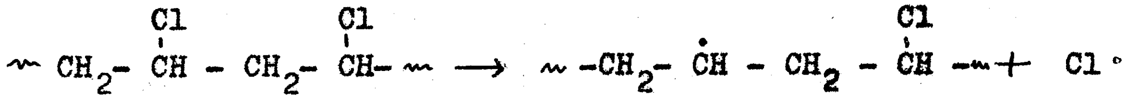
From a consideration of the degradation products it would seem that polyvinyl chloride and polyvinyl acetate might decompose by a similar mechanism. Grassie[8,9] has shown that polyvinyl acetate decomposes by a molecular mechanism,



$$\sim\overset{\substack{H\\ |}}{C}H-\overset{\substack{O=C-CH_3\\ |\\ O\\ |}}{C}H-CH_2\sim\;\longrightarrow\;\sim CH=CH-CH_2\sim + CH_3COOH$$

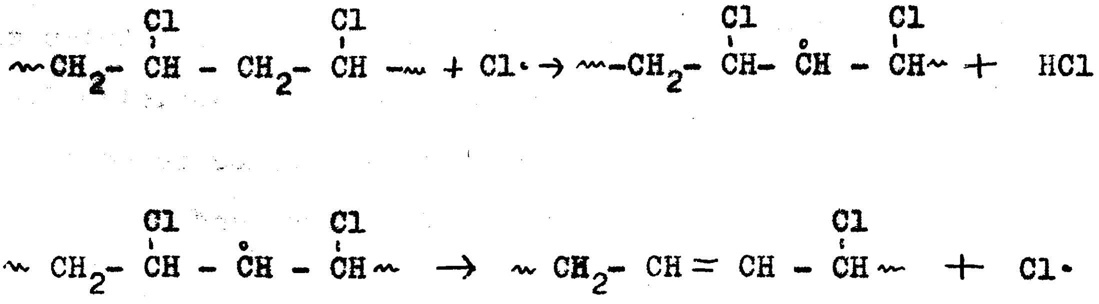
More recently, Arlman[10] has shown that polyvinyl chloride behaves quite differently. It decomposes by a radical mechanism which can be represented by the following sequence of reaction steps,

Initiation



$$\sim CH_2-\overset{\substack{Cl\\ |}}{C}H-CH_2-\overset{\substack{Cl\\ |}}{C}H-\sim\;\longrightarrow\;\sim-CH_2-\dot{C}H-CH_2-\overset{\substack{Cl\\ |}}{C}H-\sim + Cl\cdot$$

Propagation.



$$\sim CH_2-\overset{\substack{Cl\\ |}}{C}H-CH_2-\overset{\substack{Cl\\ |}}{C}H-\sim + Cl\cdot\rightarrow\sim-CH_2-\overset{\substack{Cl\\ |}}{C}H-\dot{C}H-\overset{\substack{Cl\\ |}}{C}H\sim + HCl$$

$$\sim CH_2-\overset{\substack{Cl\\ |}}{C}H-\dot{C}H-\overset{\substack{Cl\\ |}}{C}H\sim\;\rightarrow\;\sim CH_2-CH=CH-\overset{\substack{Cl\\ |}}{C}H\sim + Cl\cdot$$

Termination

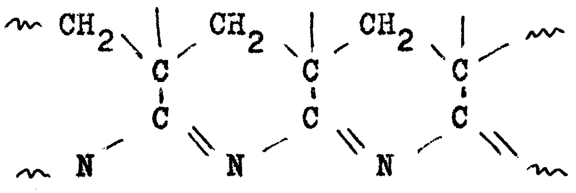
$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

The nitrile polymers, polyacrylonitrile and polymethacrylonitrile are not included in this section, although hydrogen cyanide has been reported[11] as a minor decomposition product of the former. Other reactions which are characteristic of these polymers predominate and are discussed below.

(2) Colouration of nitrile polymers.

One of the most common difficulties which impedes the development of certain synthetic polymers is the tendency to colour either during the processing or in the subsequent use of the material. The prevention of this undesirable deterioration, which is particularly important in the textile industry, has led to considerable investigation into the mechanism of colour formation in polymer molecules. The colouration which occurred on the degradation of polyvinyl chloride and related compounds was explained by the formation of conjugated unsaturated structures in the polymer backbone due to the liberation of hydrogen chloride

Polyacrylonitrile, which is important commercially as a synthetic fibre(Courtelle, Acrilon, etc.) colours without any simultaneous liberation of volatile material. The nature of this colouration process was determined by studies on polymethacrylonitrile[12,13] which were later extended to polyacrylonitrile[11,14,15]. The structure responsible for the colouration was shown to be,



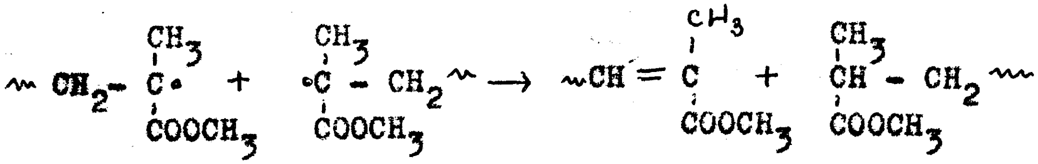
The resulting colour being due to the conjugated ($-C{=}N-$) sequence. The mode of formation of this structure is discussed in a later section.

ABNORMAL LINKAGES AS INITIATION CENTRES FOR DEGRADATION.

In almost every example of polymer degradation which has been extensively studied, it has been found that the decomposition, whether it be by chain scission or non chain scission mechanisms, has been initiated at weak or abnormal linkages present in the polymer chain. Abnormal or labile centres may be introduced into the polymer chain during the polymerisation, either as structural abnormalities or as the result of the incorporation of impurities by copolymerisation. Such linkages may also be formed as a result of the subsequent treatment of the polymer. The examples which follow illustrate how these structures arise.

(i) Polymethyl methacrylate.

Grassie and Melville[5] showed that this polymer decomposed through initiation at the chain ends. It was also shown that not all the molecular chain ends are equally vulnerable, since only 50% of a polymer sample prepared by benzoyl peroxide catalysis was degradable at 220°C. This suggests that one of the chain ends formed in the disproportionation termination step of the polymerisation reaction,

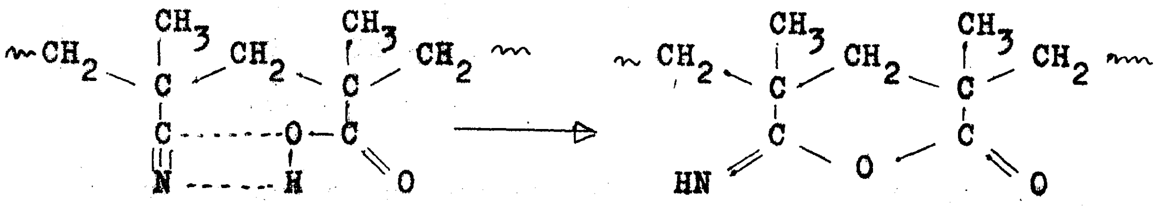


$$\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C\cdot}} + \cdot\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2\sim \longrightarrow \sim CH=\overset{CH_3}{\underset{COOCH_3}{C}} + \overset{CH_3}{\underset{COOCH_3}{CH}}-CH_2\sim$$

is more vulnerable than the other. It was not possible from the experimental data to decide which chain end was the more labile. Later, Grassie and Vance[16] overcame this by preparing polymer samples in benzene which acts as a mild transfer agent. Samples prepared by this method would therefore have saturated and unsaturated chain ends in a different ratio from that obtained by the bulk method. From degradation studies on these polymers it was concluded that the unsaturated chain end was the more labile.

(ii) Polymethacrylonitrile.

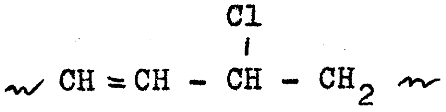
The colouration which occurs in polymethacrylonitrile when heated at temperatures above 100°C is due to the presence of impurities which have been copolymerised into the polymer chain. Grassie and McNeill[12,13] showed that the impurity in question was methacrylic acid, which had been formed by hydrolysis of the methacrylonitrile monomer due to the presence of traces of acetic acid and water. These latter components are by-products of the preparation from acetone cyanhydrin. The colouration mechanism is readily initiated through the methacrylic acid group,



Extensive purification of the monomer by washing with alkali to remove the acid impurity gave a more colour stable polymer.

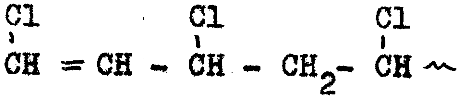
(iii) <u>Polyvinyl chloride</u>.

Stromberg, Strauss and Achhammer[17] suggest that initiation occurs by scission of a C - Cl bond. Such a bond would be activated by an allylic double bond,



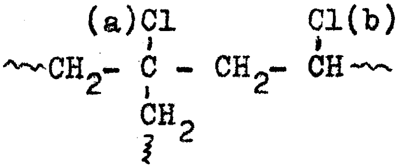
$$\sim CH=CH-\overset{Cl}{CH}-CH_2\sim$$

Since transfer to monomer[18] is the predominant termination process, thermally unstable structures of this type at the chain ends,



$$\overset{Cl}{CH} = CH - \overset{Cl}{CH} - CH_2 - \overset{Cl}{CH}\sim$$

would be expected to initiate the zipper type dehydrochlorination mechanism. Cotman[19] has shown that tertiary chlorides are also present in polyvinyl chloride. These structures (a), which are formed by chain transfer between the growing radical and the dead polymer molecule would be more labile than the secondary chloride groups (b),

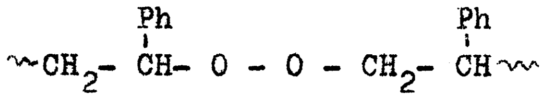


$$\sim CH_2 - \overset{(a)Cl}{\underset{CH_2}{C}} - CH_2 - \overset{Cl(b)}{CH}\sim$$

and would therefore be potential initiation sites. At the present time the exact initiation step of the degradation mechanism has not been resolved.

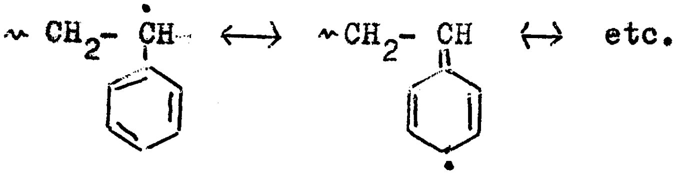
(iv) Polystyrene.

Although it is not generally agreed, it seems, as the result of recent work by Cameron and Grassie[20,21,22], that the rapid initial fall in molecular weight is due to the presence of a number of weak links. Unlike the other examples mentioned above, the exact nature of these labile linkages has not yet been determined. Grassie and Kerr[23, 24] have shown that oxygen copolymerised into the polymer,

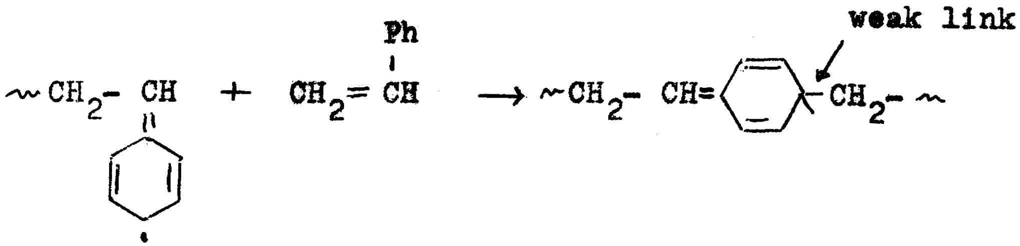


$$\sim CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}-O-O-CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}\sim$$

producing a thermo-labile peroxidic unit, is not the sole cause of weak links in the polymer. Cameron and Grassie concluded that the labile structures present in polystyrene prepared in the absence of oxygen were due to unsaturated structures in the polymer backbone. Quinonoid structures formed by polymerisation through the various canonical forms of the benzene ring,



were suggested as possible labile sites. These structures on polymerisation would give,



However no direct evidence was put forward to show that these structures were in actual fact the weak links responsible for the chain scission.

The above examples demonstrate the principle ways in which labile centres capable of initiating degradation reactions can be introduced into polymer molecules. These may be summarised as follows;

(1) The formation of labile end groups in the termination step of the polymerisation process.

(2) Incorporation of impurities into the polymer chain.

(3) The occurrence of abnormal polymerisation steps e.g. branching head to head additions.

(4) Oxidation.

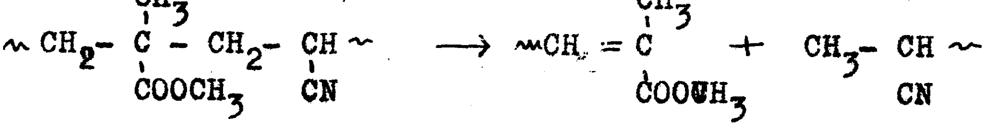
DEGRADATION OF COPOLYMERS.

The stability of homopolymers can be improved by a variety of methods depending on the mechanism by which the polymer decomposes. Photochemical degradation, for example, can be prevented by the incorporation of certain materials capable of absorbing the destructive ultra-violet radiation. The excess energy can then be dissipated as harmless infra-red radiation or as heat. Polyvinyl chloride is a classical example where the use of stabilised polymer has led to considerable commercial development which would otherwise have been impossible. In this case, Winkler[25] suggests that the materials used as stabilisers disrupt the radical chain dehydrochlorination reaction.

In recent years certain copolymers have been used commercially in preference to the homopolymer. The introduction of the second monomer unit may improve the physical properties or it may prevent some undesirable degradation reaction taking place. Copolymers of acrylonitrile and vinylidene chloride represent a recent commercial development which exemplifies this. The non flammable properties of the vinylidene chloride are combined with the fibrous properties of acrylonitrile. The vinylidene chloride units would also prevent the formation of $(-C{=}N-)$ conjugated sequences with a corresponding decrease in the tendency to colouration.

Although the mechanism of thermal degradation of a number of homopolymers has been determined, no similar work has been done on copolymers. This is rather surprising considering that in most cases it has been shown that impurities copolymerised into the polymer chain have a profound effect on the degradation properties of the polymer. Reviews on the theoretical aspects of copolymer degradation have been given by Burnett[26], Jellinek[2] and Wall[27].

The marked change in degradation mechanism due to the presence of small quantities of a comonomer unit was demonstrated by Grassie and Melville[5] using copolymers of methyl methacrylate and acrylonitrile. In this system the introduction of acrylonitrile units temporarily inhibits the depolymerisation reaction. During this induction period, rapid chain scission occurs, the molecular weight tending to a limiting value corresponding to the average distance between acrylonitrile units. The overall characteristics of this system are similar to that observed in the polystyrene homopolymer. Grassie and Melville explain the initial induction period as being due to the accumulation of unsaturated chain end molecules formed in the chain scission reaction,



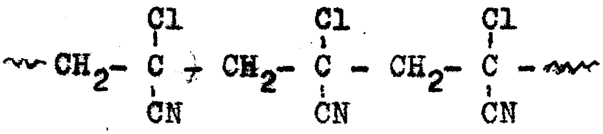
$$\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\underset{CN}{CH}\sim \longrightarrow \sim CH_2=\overset{CH_3}{\underset{COOCH_3}{C}} + CH_3-\underset{CN}{CH}\sim$$

Copolymer degradation studies have also been used to verify the decomposition mechanism of the homopolymer. Such methods have been used by Grassie et al in the colouration studies of polymethacrylonitrile and polyacrylonitrile. Samples of these polymers copolymerised with small amounts of the corresponding acid compound exhibited considerable colouration on heating, thus verifying that these impurities were responsible for the initiation of the colour forming reaction.

A systematic study of the degradation behaviour of copolymer systems would therefore be of considerable interest.

AIM OF THIS WORK.

Since previous workers in this laboratory have been concerned with the colouration reactions of polymethacrylonitrile and polyacrylonitrile, a natural sequel to this work would be a study of poly-α-chloroacrylonitrile,



$$\sim CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{Cl}{\underset{CN}{C}}-\sim$$

This polymer may be capable of several different degradation reactions;

(1) Depolymerisation.

Since this compound is a 1:1 disubstituted polymer, depolymerisation to monomer as in polymethyl methacrylate would be a possible reaction.

(2) Ester decomposition.

i) Poly-α-chloroacrylonitrile can also be considered as a substituted polyvinyl chloride, hence ester decomposition with corresponding liberation of hydrogen chloride could be possible. Such a mechanism would be facilitated due to the resonance stabilisation of the nitrile group on the intermediate radical centre.

ii) A second ester decomposition type of reaction involving loss of hydrogen cyanide could take place. Such a mechanism has been reported for polyacrylonitrile[11], however, this would seem to be highly improbable in the case of poly-α-chloroacrylonitrile where the bond dissociation energy for C - CN would be expected to be greater than that required for C - Cl scission. Also, the stabilising influence of the cyanide group on the radical centres formed in depolymerisation and dehydrochlorination reactions would facilitate these mechanisms.

(3) Colouration.

Poly-α-chloroacrylonitrile should be capable of forming (-C = N-) conjugated sequences leading to colouration as in polymethacrylonitrile.

The initial aim of this work was to study poly-α-chloroacrylonitrile in the light of these possible mechanisms. It will be seen in the chapters which follow that the degradation reaction which actually occurs most readily on heating is loss of hydrogen chloride. Since this occurs at a relatively low temperature, it becomes theoretically possible to introduce unsaturation in the polymer chain in controlled amounts by copolymerising with α-chloroacrylonitrile and heating the resulting copolymer to about 160°C. Thus the effect of such unsaturation on the degradation of the polymers at higher temperatures can be studied. The latter part of this thesis is devoted to this aspect.

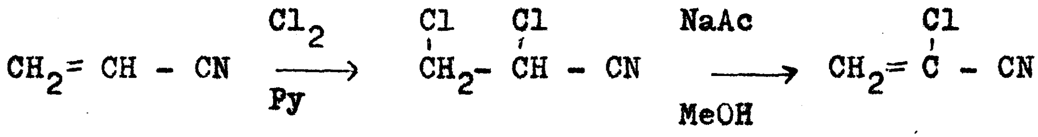
CHAPTER 2

EXPERIMENTAL TECHNIQUES.

1. PREPARATION AND PURIFICATION OF MONOMERS.

(i) α-Chloroacrylonitrile.

α-Chloroacrylonitrile was prepared by the method used by Ivanov and Koton[28],



$$CH_2= CH - CN \xrightarrow[Py]{Cl_2} \overset{Cl}{CH_2}- \overset{Cl}{CH} - CN \xrightarrow[MeOH]{NaAc} CH_2= \overset{Cl}{C} - CN$$

Dry chlorine was bubbled through acrylonitrile (B.D.H.) until the weight increase corresponded to the formation of the dichloro compound. Since this reaction is exothermic, an efficient cooling system(crushed ice) is required. The intermediate dichloride compound was washed with water and distilled under vacuum (0·1mm.) at 36-38°C giving a colourless liquid with lachrimatory properties.

The second stage of the preparation involving dehydrochlorination using sodium acetate in methanol was carried out at 65°C. Overheating was avoided in order to minimise the possibility of polymerisation of the monomer. The α-chloroacrylonitrile was then thoroughly washed with water to remove soluble impurities such as sodium chloride and sodium acetate. The monomer was dried with calcium chloride and distilled in the presence of hydroquinone through a column of copper turnings. The fraction distilling in the range 84-88°C was collected. Further purification (one distillation under atmospheric pressure and two under high vacuum) gave the pure monomer (B.Pt. 86°C.), which is a colourless, lachrimatory liquid with strong vesicant properties. Micro-analysis of the monomer gave:

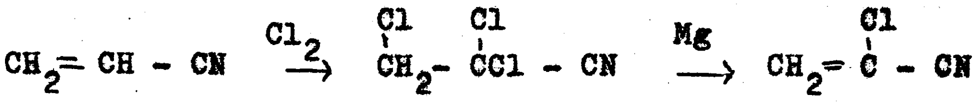
C : 40·5%   H : 2·56%   Cl : 40·73%   N : 16·21%

which is in good agreement with theoretical analysis:

C : 41·13%   H : 2·28%   Cl : 40·5%   N ; 15·99%

The α-chloroacrylonitrile was stored in an amber coloured bottle at 0°C, no stabiliser being required.

α-chloroacrylonitrile can also be prepared by the following method,



$$CH_2{=}CH-CN \xrightarrow{Cl_2} \overset{Cl}{CH_2}-\overset{Cl}{CCl}-CN \xrightarrow{Mg} CH_2{=}\overset{Cl}{C}-CN$$

using magnesium as a dechlorinating agent[29].

(ii) Styrene.

Styrene monomer (Forth Chemicals Ltd.) contained p-tert butyl catechol as inhibitor. This was removed by repeated washing with sodium hydroxide solution until the aqueous layer was colourless. After further washings with water to remove traces of alkali, the inhibitor free monomer was dried over calcium chloride. The styrene was then distilled under reduced pressure, the first portion of the distillate being discarded. The purified monomer was stored at -10°C.

(iii) Methyl methacrylate.

Methyl methacrylate monomer (I.C.I. Ltd.) was freed from inhibitor (0·01% hydroquinone) by washing with sodium hydroxide solution. Purification was carried out as for styrene.

(iv) Vinyl chloride.

Vinyl chloride (ICI.Ltd.) was purified by passing the gas through ammoniacal cuprous chloride solution, water, dilute sulphuric acid, soda lime and silica gel. The pure dry gas was collected on the vacuum line by freezing with liquid nitrogen. The vinyl chloride was stored on the vacuum system at -78°C.

(v) Acrylonitrile.

Acrylonitrile monomer (B.D.H.) was purified by redistillation under reduced pressure.

2. PREPARATION OF POLYMERS.

In chapter 1 it was shown that small amounts of impurities copolymerised into a polymer chain can have a deleterious effect on its thermal stability. In order to avoid any ambiguities due to such impurities, extensive precautions have to be taken. This involves strict control of monomer purification, polymerisation and after treatment of the polymer.

(i) Purification of Initiator.

Unless stated otherwise, the initiator used in this work was 2:2 azoisobutyronitrile(Eastman Kodak Ltd.)[AIBN], purified by recrystallisation from methanol.

(ii) Purification of Solvents.

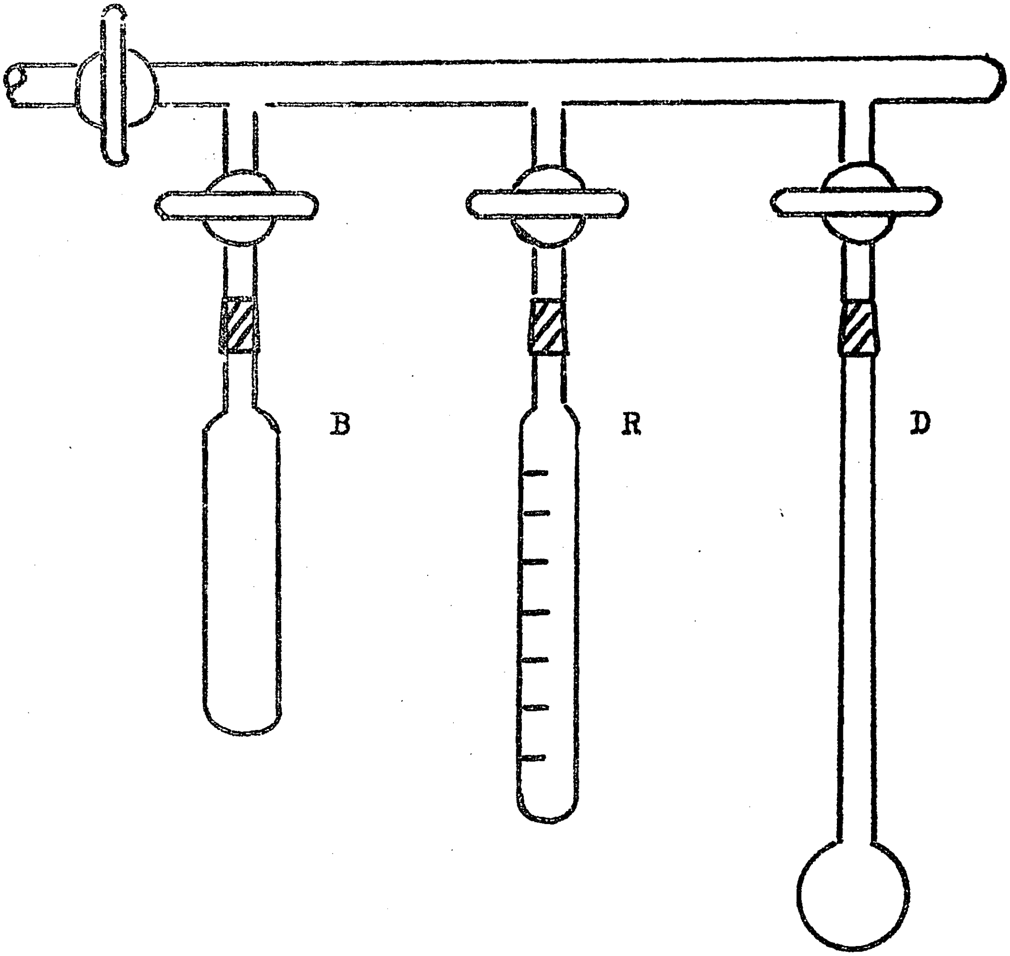
All solvents used in this work were of 'Analar' grade and where necessary further purification was carried out by distillation.

Three main polymerisation techniques were used to prepare the polymers and copolymers used in this work: (a) Bulk polymerisation (b) Solution polymerisation (c) Emulsion polymerisation. In all cases the polymerisations were carried out under high vacuum conditions or, in the case of emulsion polymerisation, in an inert gas atmosphere.

(a) Bulk Polymerisation

Since a large volume contraction occurs during polymerisation a dilatometric method can be used to follow the reaction. Before filling with the reaction components the dilatometers were cleaned and calibrated. To charge a dilatometer, initiator (AIBN) was added in chloroform solution and the chloroform removed by evacuation. The high vacuum apparatus used for filling the dilatometer is shown in figure 1. Evacuation was achieved with a mercury diffusion pump backed by a rotary oil pump, a vacuum of the order of 10^{-5}mm. Hg being obtained. The monomer being used was placed in the reservoir tube and degassed three times under high vacuum using the alternate freezing and thawing method. The first 5% of the distillate was trapped in bulb B and eliminated. After the required amount of monomer had been distilled into the dilatometer, it was sealed off under high vacuum. The dilatometers used in the polymerisation of α-chloroacrylonitrile

FIGURE I



R-Reservoir D-Dilatometer

B-Bulb

APPARATUS FOR FILLING DILATOMETER

were of about 4ml. capacity, those used for styrene, methyl methacrylate and related copolymers were approximately 60ml.. The corresponding capillaries being approximately 3mm. and 5mm. in diameter.

The polymerisations were carried out in the temperature range 45-65°C in a water thermostat controlled to $\pm 0{\cdot}1^\circ$C by a Sunvic H.V.S. type relay regulated by a mercury toluene regulator. The progress of the reaction was followed by observing, with a cathetometer, the fall in level of the liquid in the stem of the dilatometer. The polymerisations were carried to about 10% conversion. The relationship between volume contraction and conversion for α-chloroacrylonitrile was determined from the polymer recovery and final volume contraction. At 55°C the contraction was found to be 34% for 100%polymerisation.

Polymerisations initiated by photo-decomposition of initiator (AIBN) at 25°C were carried out in a thermostat with a silica window, the light source being an Osram 250v, 125w mercury vapour lamp.

(b) Solution Polymerisation.

Solution polymerisation of α-chloroacrylonitrile was carried out by a similar method as in bulk. Methyl ethyl ketone was used as solvent. The solvent and monomer were degassed in the usual manner, distilled into the dilatometer (volume ~ 8·0ml.), containing initiator and sealed off under high vacuum.

(c) Emulsion Polymerisation.

Poly-α-chloroacrylonitrile prepared by bulk and solution methods coloured during the polymerisation reaction and this apparently partially degraded material was regarded as unsuitable for degradation studies. Polymer prepared by emulsion techniques did not exhibit such characteristics and was therefore preferable[30].

The apparatus used for the preparation of poly-α-chloroacrylonitrile by emulsion polymerisation is shown in figure 2.

A mixture of 75 gm. distilled water, 0·5 gm. sodium metabisulphite, 0·25 gm ammonium persulphate, 0·15 gm. gelatin and 0·18 gm. sodium pyrophosphate ($Na_4P_2O_7,10H_2O.$) was placed in the three necked flask. The flask and its contents were then immersed in a water bath at 55°C. The mixture was de-oxygenated by bubbling nitrogen through for one hour. 27 gm. α-chloroacrylonitrile was then added slowly over a period of 30 minutes, the solution being stirred vigorously throughout. The nitrogen was bubbled continuously throughout

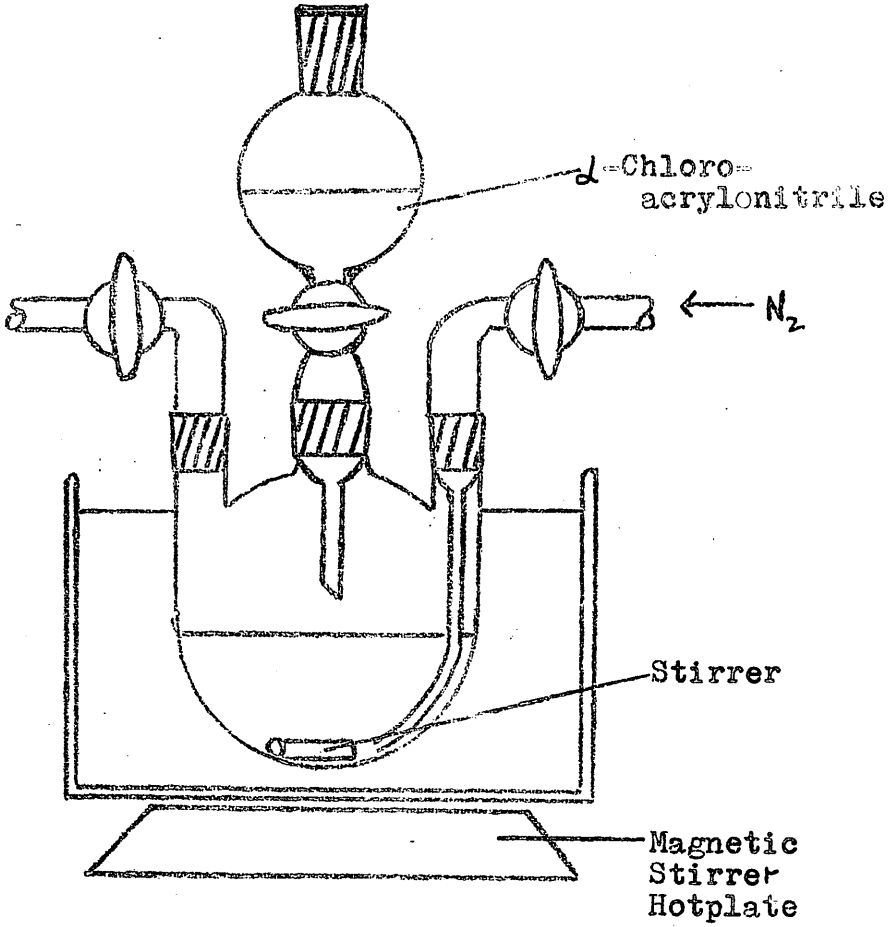


FIG. 2. APPARATUS FOR EMULSION POLYMERISATION.

the experiment(20 hours at 55°C). Polymer prepared by this method was white or very slightly coloured.

3. PREPARATION OF COPOLYMERS.

Apart from systems involving vinyl chloride, the copolymers used in this work were prepared by distillation of the required volumes of the monomers into a dilatometer as described in the above section on bulk polymerisation. Since vinyl chloride is gaseous at room temperature, the above method cannot be applied. This is overcome simply by keeping the vinyl chloride reservoir at -78°C using a solid carbon dioxide/ acetone freezing mixture. The vinyl chloride can then be distilled into the calibrated dilatometer in the usual way.

4. DETERMINATION OF COPOLYMER COMPOSITION.

(a) Copolymer Composition Equation.

Consider a reaction mixture containing two monomers M_1 and M_2. If it is assumed that,(i) the reactivity of the radical is independent of the chain length (2) the reactivity is determined solely by the terminal monomer unit then the propagation reactions occurring in the system may be written as follows,

$$\begin{array}{lllll}
M_1^{\bullet} & + & M_1 & \longrightarrow & M_1^{\bullet} \qquad k_{11} \\
M_1^{\bullet} & + & M_2 & \longrightarrow & M_2^{\bullet} \qquad k_{12} \\
M_2^{\bullet} & + & M_1 & \longrightarrow & M_1^{\bullet} \qquad k_{21} \\
M_2^{\bullet} & + & M_2 & \longrightarrow & M_2^{\bullet} \qquad k_{22}
\end{array}$$

Applying the stationary state approximations for the radicals $M_1^{\bullet}$ and $M_2^{\bullet}$, the ratio of the number of moles of the two monomers $d(M_1)/d(M_2)$ entering the polymer at any instant is given by,

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \cdot \frac{(k_{11}/k_{12})\ (M_1) + (M_2)}{(k_{22}/k_{21})\ (M_2) + (M_1)} \quad \text{——} ①$$

The reactivity ratios r_1 and r_2 are given by,

$$r_1 = k_{11}/k_{12} \qquad\qquad r_2 = k_{22}/k_{21}$$

which on substitution in eqn. ① gives,

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)} \qquad \text{———} \quad ②$$

This equation, generally known as the 'copolymer composition equation' was deduced in 1944 by several workers[31,32,33,34].

If the copolymerisation is restricted to the first few % conversion, during which it is assumed that the monomer concentrations do not change, equation 2 can be written,

$$\frac{(P_1)}{(P_2)} = \frac{(M_1)}{(M_1)} \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)}$$

where $(P_1)/(P_2)$ is the ratio of the molar concentrations of the two monomers in the copolymer and $(M_1)/(M_2)$ is the ratio of the molar concentrations of the two monomers in the feed.

(b) Determination of the Reactivity Ratios.

From the above equations, it can be seen that in order to deduce the composition of a copolymer, it is necessary to know the values of the reactivity ratios of the component monomers. During the last few years, the reactivity ratios of a large number of monomer pairs have been determined[26,35].

However, the reactivity ratios of α-chloroacrylonitrile systems have so far not been reported and thus had to be determined for the purpose of the present work.

(i) α-Chloroacrylonitrile (1) - Styrene (2) System.

Varying monomer mixtures of α-chloroacrylonitrile and styrene were polymerised in vacuo at 60°C using AIBN as initiator. Polymerisation was stopped at 4-5% conversion. The copolymers were precipitated, purified and analysed for chlorine content. The amount of α-chloroacrylonitrile present in the copolymer could then be calculated. The results obtained are shown in table 1 where the subscripts 1 and 2 refer to α-chloroacrylonitrile and styrene respectively.

Table 1.

Copolymer	Monomer	%Cl	Composition monomer feed (moles %)	Composition copolymer (moles %)
2	1	15·7	17·1	43·1
	2		82·9	56·9
3	1	13·5	8·98	37·3
	2		91·0	62·9
4	1	19·6	66·1	52·7
	2		33·9	47·3
5	1	19·1	62·0	52·2
	2		38·0	47·8
6	1	18·1	44·9	49·1
	2		55·1	50·9

The values of $(P_1)/(P_2)$ and $(M_1)/(M_2)$ were substituted in the copolymer equation and r_1 and r_2 determined by the method of Mayo and Lewis[33](Fig. 3.). The reactivity ratios for the α-chloroacrylonitrile- styrene system were found to be,

$$r_1 = 0{\cdot}075 \pm 0{\cdot}01$$

$$r_2 = 0{\cdot}055 \pm 0{\cdot}01$$

These results indicate that the radicals terminated by one monomer unit react more readily with the other monomer molecule. Thus the overall tendency will be to produce a copolymer in which the monomer units alternate.

(ii) α-Chloroacrylonitrile (1) - Methyl methacrylate$^{(2)}$ System.

The results obtained from a similar series of experiments using varying monomer feeds of α-chloroacrylonitrile and methyl methacrylate are tabulated in table 2.

The values of r_1 and r_2 as obtained from the r_1 vs r_2 plot (Fig 4) were,

$$r_1 = 0{\cdot}43 \pm 0{\cdot}03$$

$$r_2 = 0{\cdot}17 \pm 0{\cdot}03$$

FIG. 3.

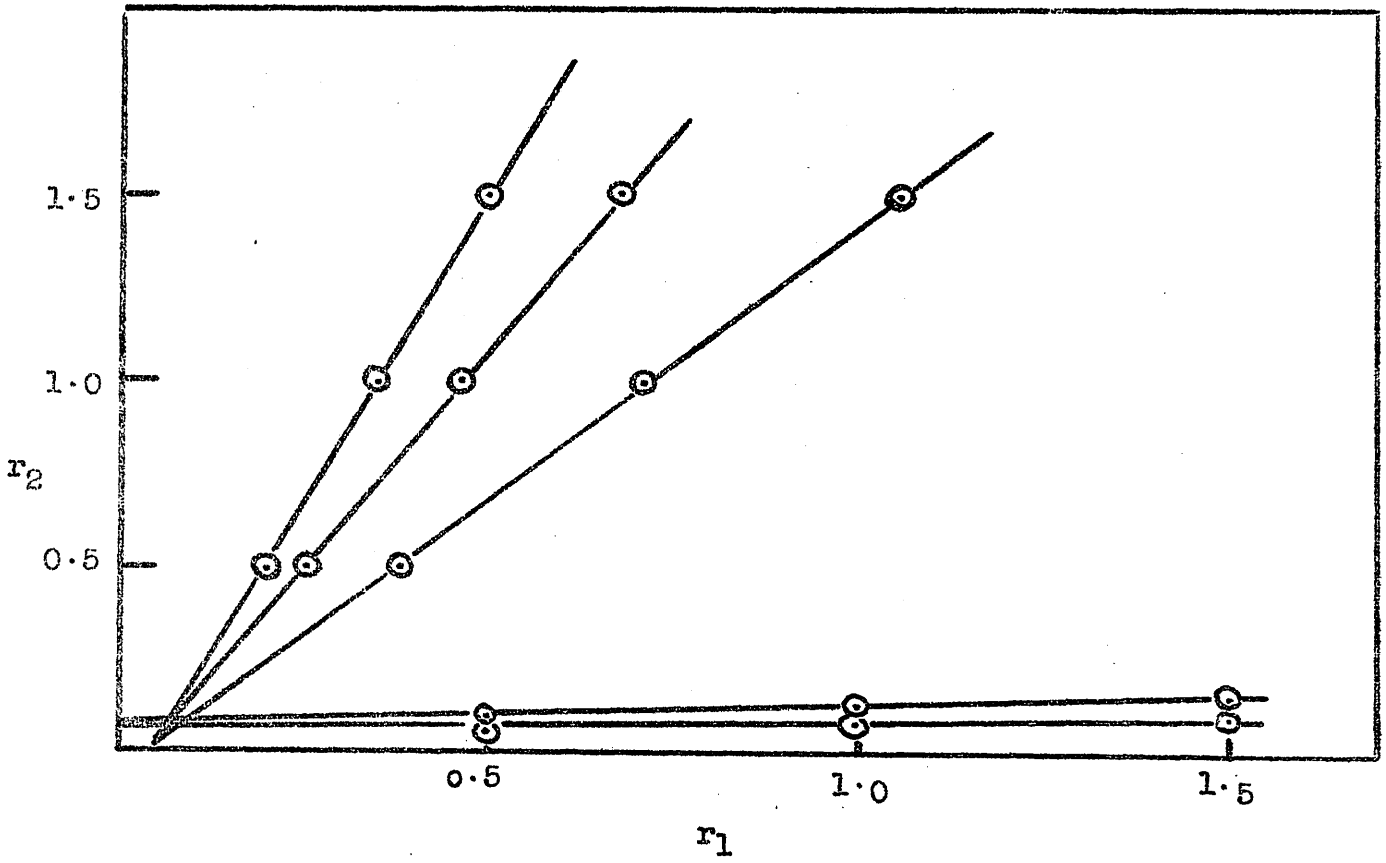


Fig. 4.

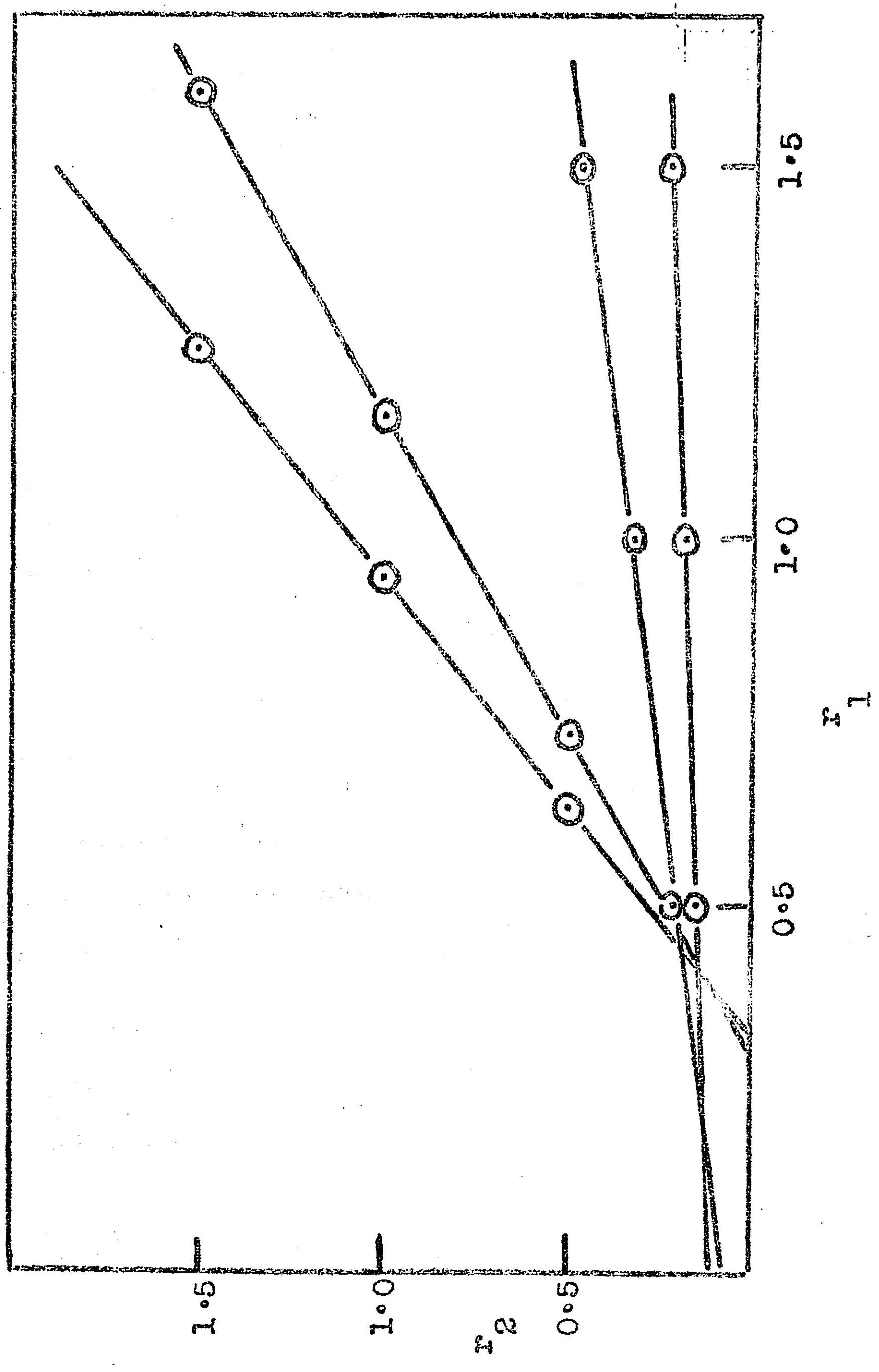


Table 2.

Copolymer	Monomer	%Cl	Composition monomer feed (moles %)	Composition copolymer (moles %)
7	1	14·3	16·73	38·35
	2		83·27	61·65
8	1	22·1	55·7	57·9
	2		44·3	42·1
9	1	22·8	60·4	59·6
	2		39·6	40·4
10	1	17·05	31·2	45·4
	2		68·8	54·6

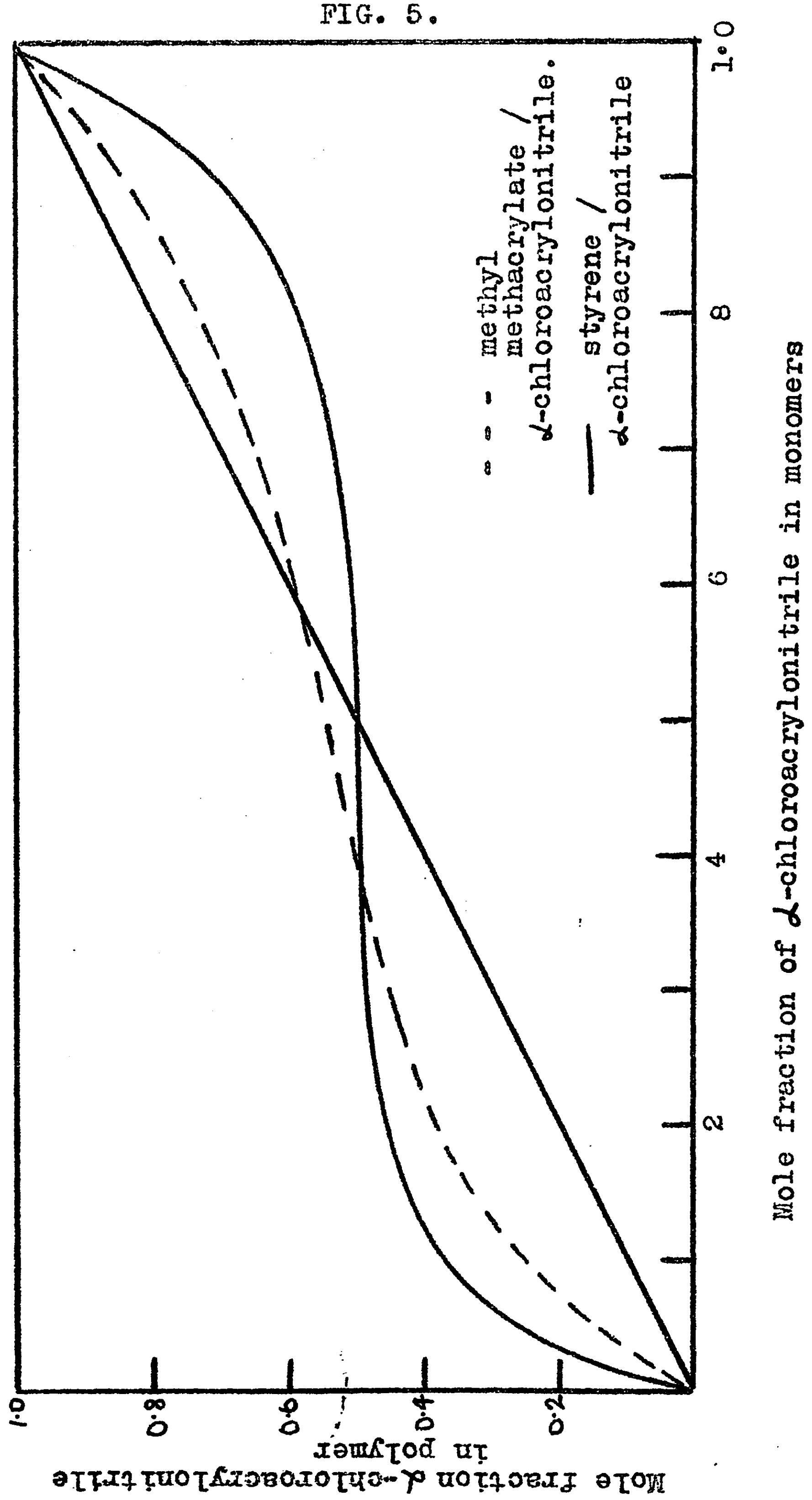
The copolymer composition curves for the above systems calculated from the experimentally determined r values are shown in figure 5.

The reactivity ratios for other systems involving α-chloroacrylonitrile were determined using the Q - e scheme of Alfrey and Price[36]. This scheme expresses each propagation rate coefficient in terms of four parameters representing the reactivities and polarities of the two monomers, as shown below,

$$k_{p_{12}} = P_1 . Q_2 . e^{-e_1 e_2}$$

where P is proportional to the reactivity of the radical,

FIG. 5.


Mole fraction of α-chloroacrylonitrile in monomers
2
4
6
8
1·0
Mole fraction α-chloroacrylonitrile in polymer
0·2
0·4
0·6
0·8
1·0
methyl methacrylate / α-chloroacrylonitrile.
styrene / α-chloroacrylonitrile

Q is proportional to the reactivity of the monomer and e_1 and e_2 represent the charges on monomers 1 and 2 respectively. Styrene is usually chosen as reference monomer and is assigned a value of Q = 1·0 and e = -1·0. The results obtained, using this method, combined with the reactivity ratios of all other systems mentioned in this thesis are shown in table 3.

Table 3.

Monomer$_1$	Monomer$_2$	r_1	r_2	r_1r_2	Ref.
α-chloroacrylonitrile	styrene	0·075	0·055	0·004	Expt.
" "	methyl methacrylate	0·43	0·17	0·073	Expt.
" "	vinyl chloride	5·4	0·001	0·005	Q-e
" "	acrylonitrile	3·33	0·27	0·90	Q-e
styrene	vinyl chloride	17	0·02	0·34	37
styrene	acrylonitrile	0·4	0·05	0·02	38
styrene	vinyl acetate	55	0·01	0·55	39

5. PURIFICATION OF POLYMERS AND COPOLYMERS.

(i) Poly-α-chloroacrylonitrile.

Poly-α-chloroacrylonitrile prepared by the emulsion method was first filtered and then thoroughly washed with distilled water to remove impurities arising from the components of the emulsion system. The polymer was then dried under high vacuum for several days and stored in a desiccator. No attempt was made to reprecipitate the polymer since degradation leading to discolouration is known to occur in solution[40].

(ii) Styrene Copolymers.

Polymerisation was stopped at 5% conversion by immersing the dilatometer in a freezing mixture. The contents of the dilatometer were dissolved in an equal volume of Analar benzene and the copolymer precipitated by adding this solution to ten times its volume of methyl alcohol. The copolymer was filtered off and partially dried in air at 25°C. This process was repeated twice using dioxan instead of benzene. After the final reprecipitation the copolymer was dried in air at 25°C, ground to a fine powder and then extensively dried under high vacuum for several days.

(iii) Polystyrene.

Polystyrene samples were isolated and purified as for the styrene copolymers.

(iv) Methyl Methacrylate Copolymers.

Methyl methacrylate copolymers were treated in a similar manner to the styrene copolymers, 'Analar' acetone, however, was used as solvent.

6. MEASUREMENT OF INFRA-RED SPECTRA.

Infra-red spectra were measured on a Perkin Elmer 237 Grating Spectrophotometer. Samples were prepared for analysis using either the potassium chloride disc or thin film techniques.

(a) Potassium Chloride Disc Technique.

This technique was used for the degradation studies on poly-α-chloroacrylonitrile. 7 mg. of the polymer sample was ground up with 200 mg. of oven dried potassium chloride in an agate mortar under an infra-red light (to prevent adsorption of water from the atmosphere). The resulting mixture was compressed into a disc, by applying a pressure of 5,000 lb./sq.in. for 5 minutes.

(b) Thin Film Technique.

It was found that for polystyrene, methyl methacrylate and copolymers of these compounds, the resolution of the infra-red spectrum could be improved by preparing the samples for analysis as thin transparent films. These films were prepared by dissolving 0·07 gm. of the sample in 3 ml. of Analar chloroform. The solution was then filtered and poured into a 30 ml. beaker containing 15 ml. of clean mercury. After 24 hours the solvent had evaporated, leaving a thin transparent film, 0·07 mm. thick, on the mercury surface. Films were removed from the surface by cutting round the edges with a sharp razor blade. The last traces of solvent were removed by evacuation. Spectra were obtained by mounting the film between two small brass rings which could be placed in a normal disc holder.

7. DEGRADATION APPARATUS.

(a) The Dynamic Molecular Still.

Thermal degradation experiments were carried out in a dynamic molecular still of the type described by Grassie and Melville[5]. With this apparatus it is possible to carry out the experiments in vacuum, thus avoiding the possibility of complicating side reactions and at the same time rapidly remove the volatile products from the reaction zone. Figure 6 shows the arrangement of the glasswork of the degradation apparatus.

The still (Quickfit Ltd.) consists of a heavy glass envelope with a removable desiccator lid. The furnace block was supported on a glass cradle slung across the still. Electrical leads to and fron the furnace block and tray were led through a manifold in one of the B 24 sockets and sealed with Picien wax.

(b) Furnace Construction and Control.

The copper furnace block and degradation tray are shown in figure 7. Heat was supplied by three 50w/24v cartridge heaters (Hedin Ltd. type 22092). Two of the heaters were connected in series while the third was regulated by an Ether Transistrol Temperature Controller (type 991A) controlled by the copper/ constantan thermocouple housed in the furnace block. The voltage across the heaters was controlled by two Variac Voltage Regulators. The electrical circuits for the heating system are shown in figure 7. The single intermittant heater was sufficient for reaction temperatures below 200°C. For higher temperatures the constant heaters

FIG. 6.

DEGRADATION APPARATUS

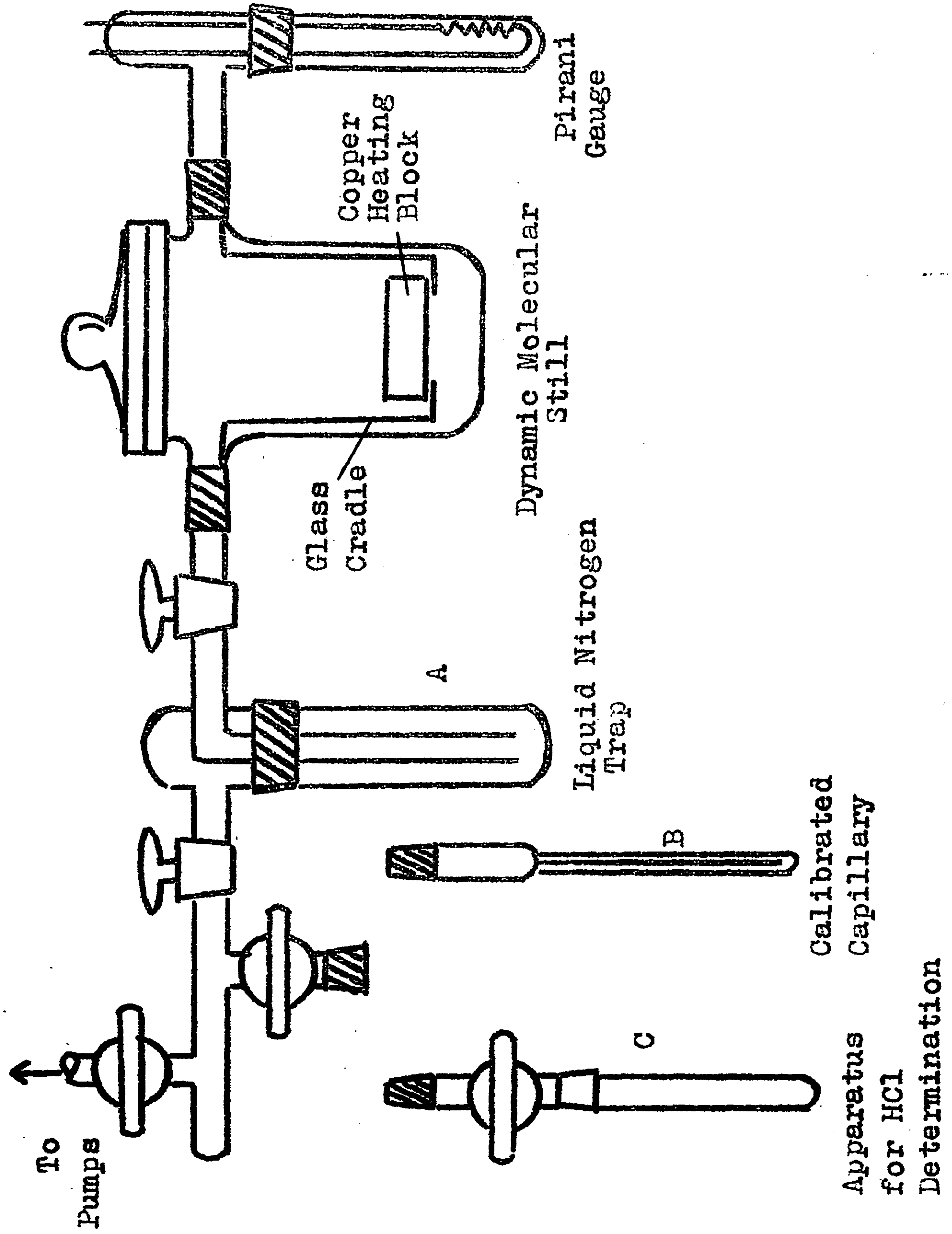
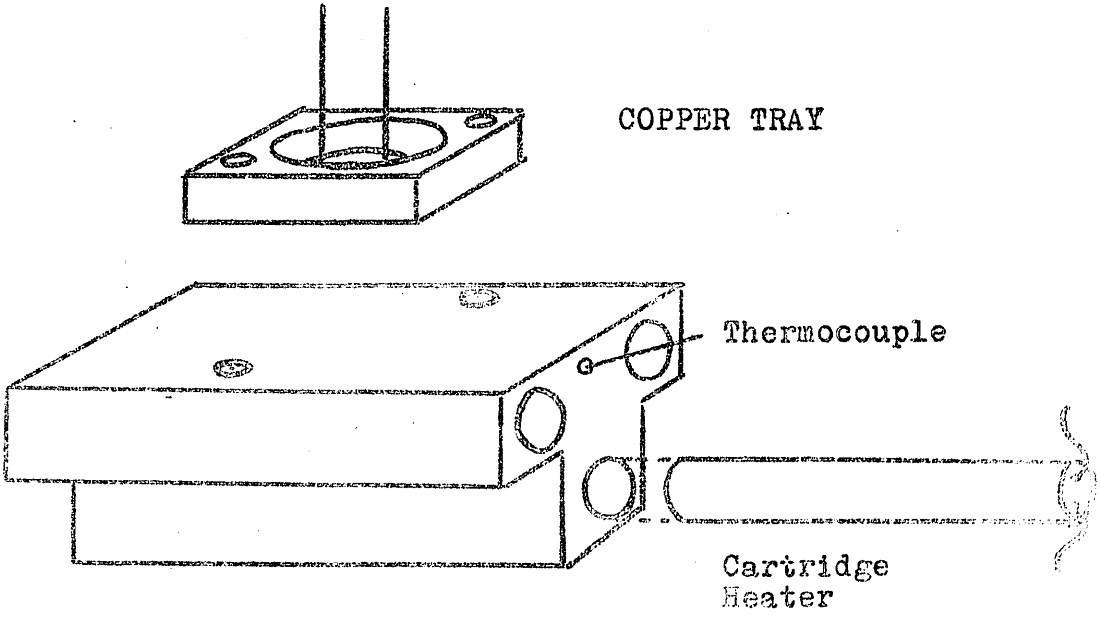
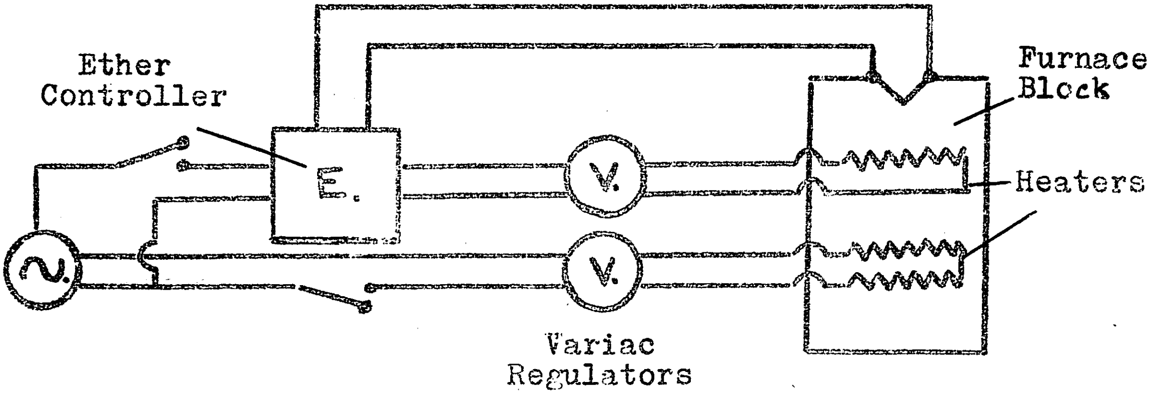


FIG. 7.



COPPER FURNACE BLOCK



FURNACE CIRCUITS

were required in addition. With this system the temperature of the furnace could be controlled to ± 0·5°C.

(c) The Degradation Tray.

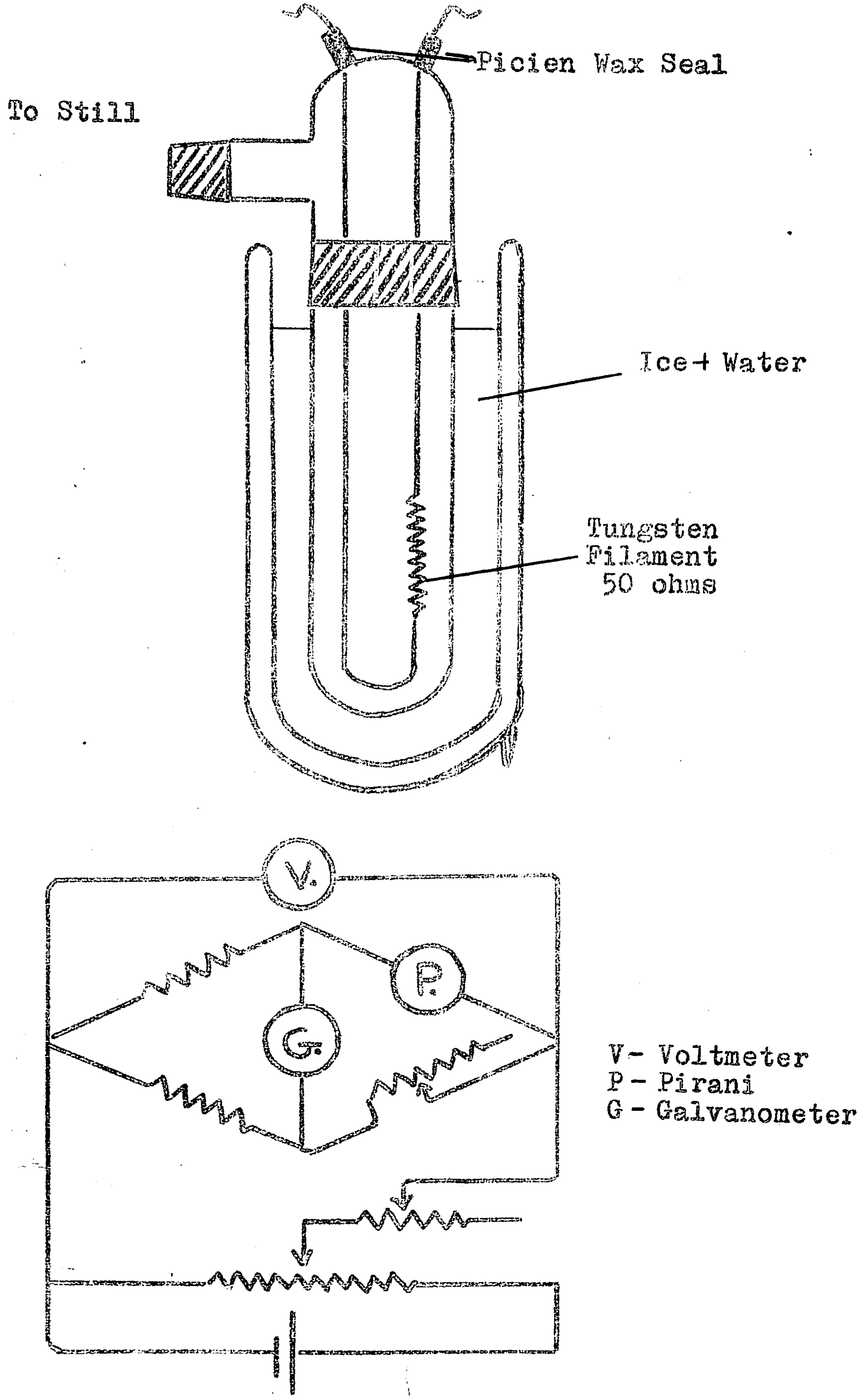
This consists of a copper tray with a circular cavity as shown in figure 7. During a degradation experiment the temperature of the tray was recorded by a copper/ constantan thermocouple silver soldered to the tray surface. The thermocouple, wired to a similar circuit as used in the degradation apparatus, was calibrated by heating in an oil bath.

To ensure good thermal contact, the tray and the furnace block were screwed firmly together before each experiment. To minimise temperature gradients and to eliminate 'sputtering' in the sample, previous workers using this degradation technique have covered the polymer sample with a thin layer of copper powder. Grassie and Mathewson[41], however, have shown that for polyvinyl chloride the copper powder reacted with hydrogen chloride, the main decomposition product, forming a complex compound. Wolkober[42] has shown that sand can be used as a satisfactory substitute. A fine grain acid washed sand was therefore used in all degradation experiments where hydrogen chloride was expected as a decomposition product.

(d) The Pirani Gauge.

The Pirani gauge and Wheatstone Bridge circuit are shown in figure 8. The gauge consists basically of a stretched tungsten filament ($\sim 50\Omega$) supported between two copper wires. With increasing pressure in the still, the greater number of gas molecules colliding with the hot filament causes it to cool, thus decreasing its resistance. In order to balance the bridge a greater voltage must therefore be applied across it. If V is the voltage required to give zero deflection on the galvanometer at a given pressure and V_o is the corresponding initial voltage when the system is evacuated, then $V^2 - V_o^2 / V_o^2$ is a measure of the pressure. For quantitative work the gauge must be calibrated with the material responsible for the pressure change. Since in the present work the Pirani gauge is used in a purely qualitative way, such a calibration is not required. The voltage V is thus used to give a relative measure of the pressure in the still. During operation the gauge was thermostatted at 0°C to eliminate effects due to changes in ambient temperature.

FIG 8.


Picien Wax Seal
To Still
Ice + Water
Tungsten
Filament
50 ohms
V.
P.
G.
V- Voltmeter
P - Pirani
G - Galvanometer

(e) Estimation of the Decomposition Products.

The three main decomposition products to be estimated in this work are styrene, methyl methacrylate and hydrogen chloride. Since styrene and methyl methacrylate are liquids at room temperature, they can be estimated by distillation from the trap A (fig.6) into a calibrated capillary tube B. Hydrogen chloride on the other hand is gaseous at room temperature and cannot be estimated in this way. Due to its high solubility in water it can, however, be readily dissolved in water and the resulting solution analysed using volumetric, p_H determination or conductivity methods. The hydrogen chloride was thus distilled from the trap A (fig.6) into a pre-evacuated tube C (fig.6) containing 10 ml. of distilled water at -196°C. Tap D was then closed and the apparatus removed from the vacuum line. The water was then thawed out, the tube shaken to dissolve the hydrogen chloride and the resulting solution analysed using the above mentioned techniques.

8. MOLECULAR WEIGHT DETERMINATIONS.

Molecular weights of the various polymer and copolymer samples were determined using a P.C.L. Suspended Level

Viscometer. The measurements were carried out in a water bath maintained at 25±0·05°C by a mercury toluene regulator and Sunvic H.V.S. Relay. Analar acetone was used as solvent for poly-α-chloroacrylonitrile studies, while Analar chloroform was used for the styrene/α-chloroacrylonitrile, methyl methacrylate/α-chloroacrylonitrile and styrene/ vinyl chloride copolymer systems. With degraded samples the residue was extracted from the copper tray with the required solvent, the solution filtered and made up to 10ml. in a graduated flask. Determinations were carried out in the usual manner, the time of flow for several dilutions being noted for each sample. Solution concentrations were determined by evaporating 3ml. of the initial solution in a weighing bottle at 100°C.

The intrinsic viscosity $[\eta]$ was obtained by extrapolation of the η_{sp}/C versus C curves to zero concentration. Molecular weights could then be calculated from the equation,

$$[\eta] = KM_v^a$$

For polystyrene[43], $K = 1·12 \times 10^{-4}$ and $a = 0·73$.
The corresponding values for methyl methacrylate[44] are,

$$K = 4·8 \times 10^{-5}, \quad a = 0·80.$$

Since the copolymers used contain only a small concentration of co-monomer, it was assumed that the above values hold also for the copolymer. Corresponding values for poly-α-chloroacrylonitrile are not available.

It must be emphasised, however, that due to the limitations of this method[45], the results obtained can only be regarded as qualitatively accurate. Number average molecular weight determinations would obviously be preferable and necessary for quantitative interpretation of the experimental results. Due to the difficulties involved in such determinations and the limited time available, it was found most convenient to use the viscometry method.

Details of all the polymers and copolymers used in this work are given in table 4.

Table 4

No.	Ppn.	Polymer	Temp. Polym.	Initiator %w/v	% Polym.	% Comp. moles C.A.N.	$[\eta]$	$M_v 10^{-3}$
P.E.1	E	P.C.A.N.	55°C	Redox				
P.E.3	E	P.C.A.N.	55°C	Redox				
C.P.13	B	styrene/C.A.N.	60°C	AIBN (0·05%)	5	9·2	1·20	337
C.P.14	B	styrene/C.A.N.	60°C	AIBN (0·05%)	5	2·4	1·20	332
C.P.27	B	styrene/C.A.N.	60°C	AIBN (0·05%)	5	5·0	1·22	344
PS05/60	B	Polystyrene	60°C	AIBN (0·05%)	5		1·27	359
C.P.16	B	M.M.A./C.A.N.	55°C	AIBN (0·04%)	6	6·1	2·60	830
C.P.19	B	M.M.A./C.A.N.	55°C	AIBN (0·04%)	5	16·0	2·02	604
C.P.22	B	styrene/V.C.	60°C	AIBN (0·05%)	5	2·6	0·86	210
C.P.23	B	styrene/V.C.	60°C	AIBN (0·05%)	5	7·6	0·53	108
C.P.25	B	styrene/V.C.	60°C	AIBN (0·05%)	5	0·5	1·24	347
C.P.15	B	styrene/ acrylonitrile	60°C	AIBN (0·05%)	5	3·9	1·29	366

C.A.N. - α-chloroacrylonitrile M.M.A. - methyl methacrylate

V.C. - vinyl chloride B - Bulk E - Emulsion

CHAPTER 3

THE BULK POLYMERISATION OF α-CHLOROACRYLONITRILE.

1. INTRODUCTION.

Many kinetic studies have been made on bulk polymerisation reactions in which homogeneous conditions prevail, that is, in which the polymer formed is soluble in the monomer. Under these conditions the kinetics of polymerisation are relatively simple. In the case of acrylonitrile, vinyl chloride and other halogenated vinyl monomers, however, heterogeneous conditions arise, the polymer formed being precipitated from its monomer. Kinetic studies on these compounds have shown that the normal relationships, as derived for homogeneous polymerisation, may break down. However, in the presence of sufficient quantities of solvent for the polymer, relationships such as the rate dependence on the square root of the initiator concentration are strictly obeyed.

α-Chloroacrylonitrile, as expected, exhibits such properties, the polymer precipitating early in the reaction. Figure 9 shows the progress of a typical bulk polymerisation

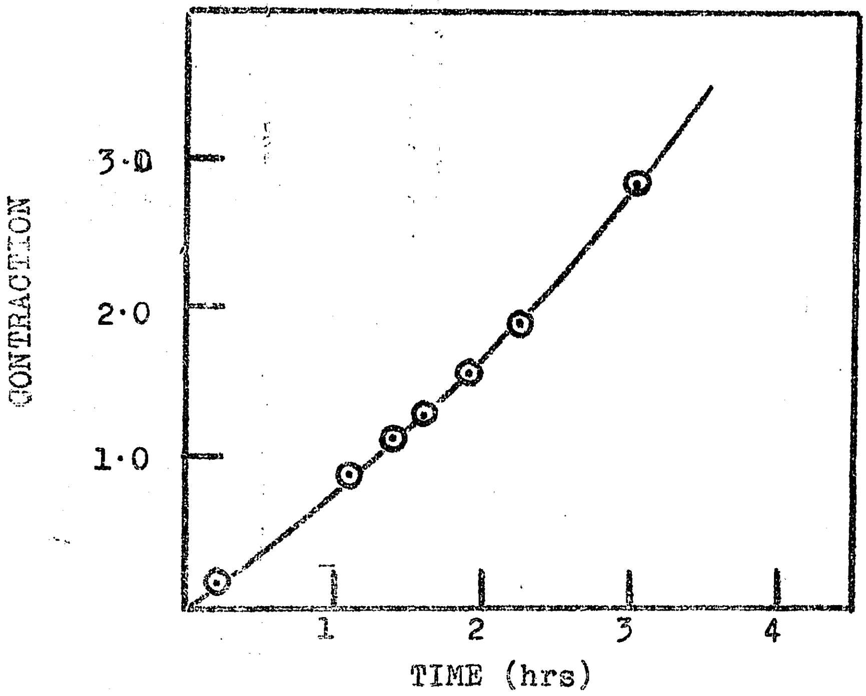


FIG. 9. Thermal catalysed bulk polymerisation at 65°C; catalyst 1·0% AIBN.

of α-chloroacrylonitrile initiated by catalyst (AIBN). The reaction is autocatalytic to at least 20% conversion. Gradual elimination of a retarder, present in the system, could be responsible for this acceleration. However, a similar catalysed polymerisation carried out in sufficient quantities of solvent(M.E.K.) to prevent precipitation, exhibits no similar rate acceleration (Fig. 10). Comparison of these two systems indicates that the autocatalytic effect in the bulk polymerisation is not due to impurities or retarders.

This apparent autocatalysis contrasts with the behaviour of homogeneous systems, where the rate diminishes with time due to the consumption of monomer (Fig.10) and since the viscosity of the medium does not increase with polymerisation, it is also different from the typical 'gel effect' obtained at high conversions. It follows therefore, that this autocatalytic effect results from the precipitation of the polymer. Similar conclusions have been derived for other systems which polymerise in heterogeneous conditions.

2. POLYMERISATION STUDIES.

(i) Variation of Rate with Catalyst Concentration.

The effect of different concentrations of initiator on

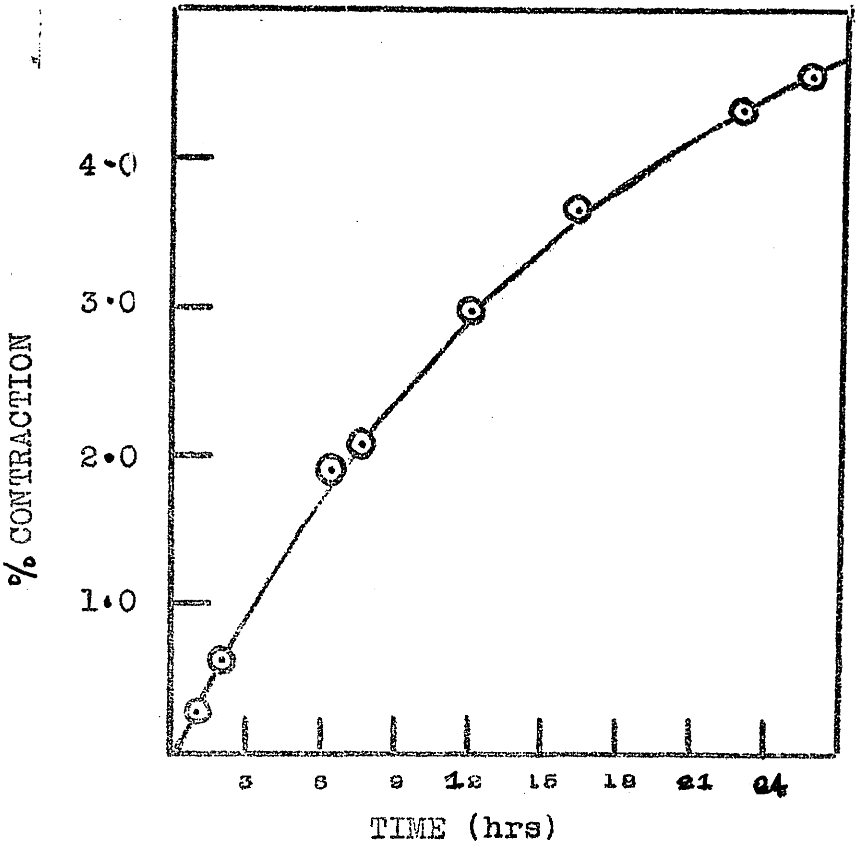


FIG. 10. Thermal catalysed polymerisation in methyl ethyl ketone solution at 65°C: catalyst 1·0% AIBN.

the rate of bulk polymerisation of α-chloroacrylonitrile at 55°C is shown in figure 11. It can be seen that the rate of polymerisation increases with increasing concentration of initiator, the general autocatalytic effect being apparent with as much as 2% initiator. The increase in rate is most prominent in the first 5% conversion.

Since the rate is not constant at any time during the reaction, a study of the effect of initiator concentration on the rate of polymerisation must be carried out at constant temperature and at constant %conversion. The plot of the rate of polymerisation at 5 and 10% conversion against the square root of the initiator concentration is shown in figure 12. The resulting linear plots indicate that the rate of polymerisation varies as the square root of the initiator concentration.

(ii) Variation of Rate with Temperature.

The effect of temperature on the polymerisation of α-chloroacrylonitrile initiated by 1% AIBN is shown in figure 13. The autocatalytic effect is still apparent at 65°C. The overall activation energy for the reaction was obtained from the gradient of the Arrhenius Plot (Fig.14), constructed by plotting the logarithm of the rate at 0·5%

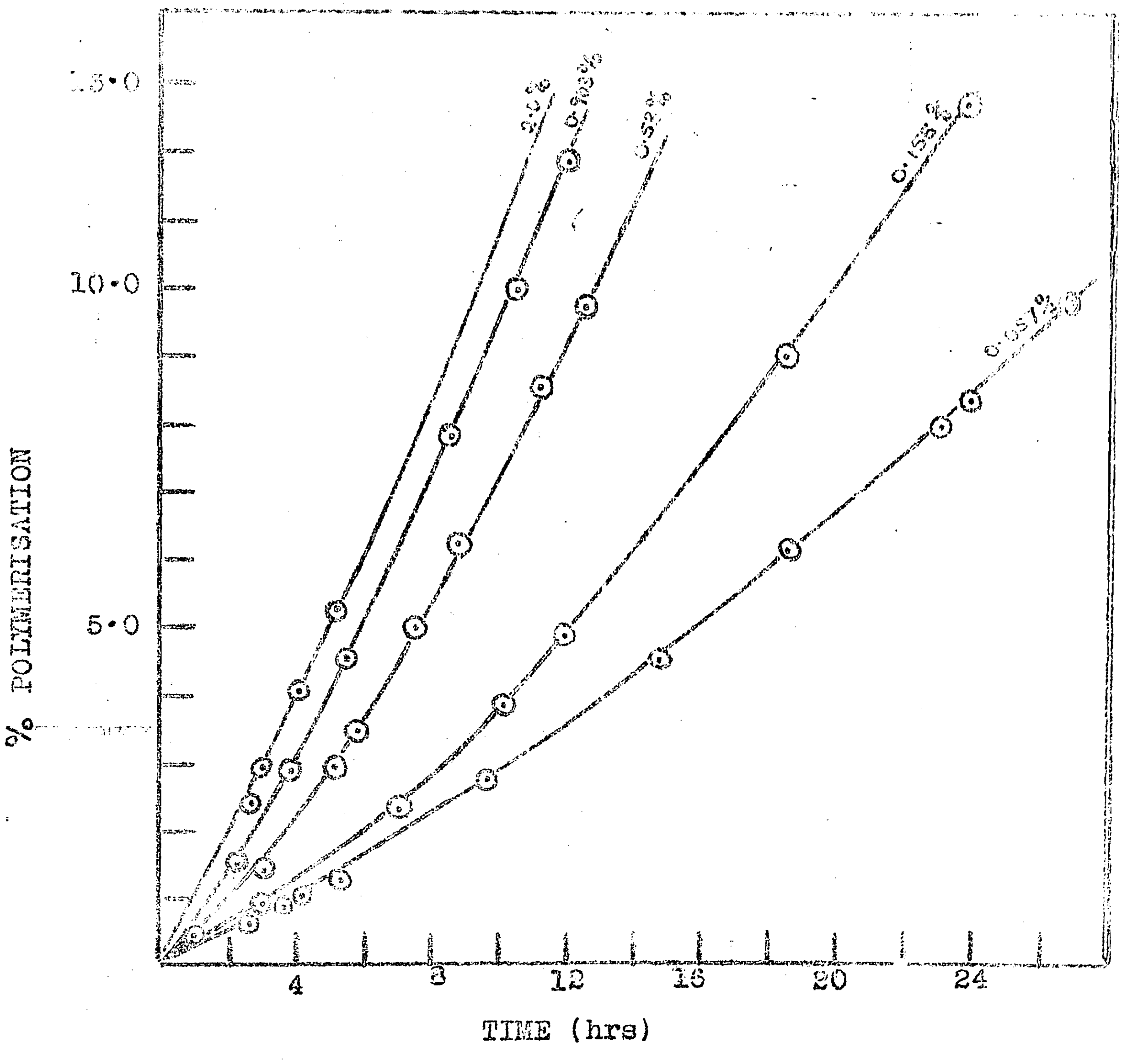


FIG. 11 Thermal catalysed bulk polymerisation at 55°C.

FIG: 12.

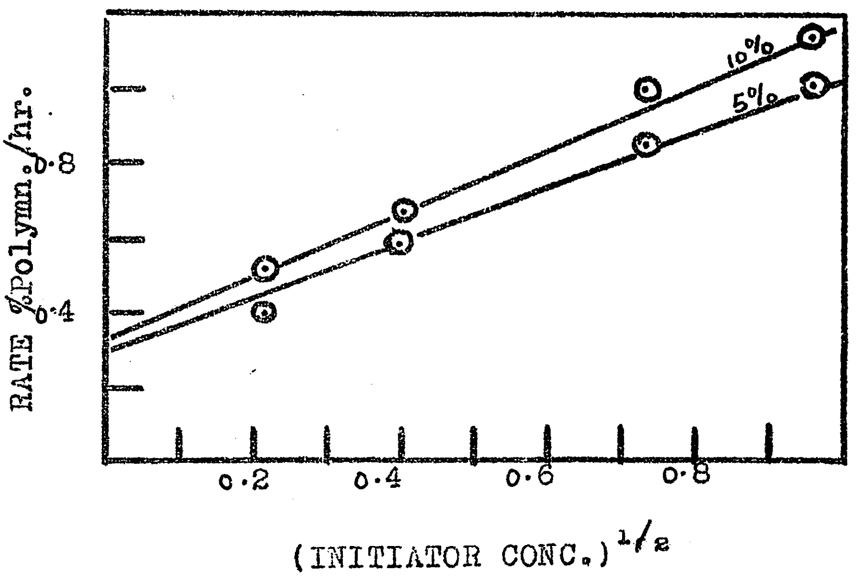


FIG. 13.

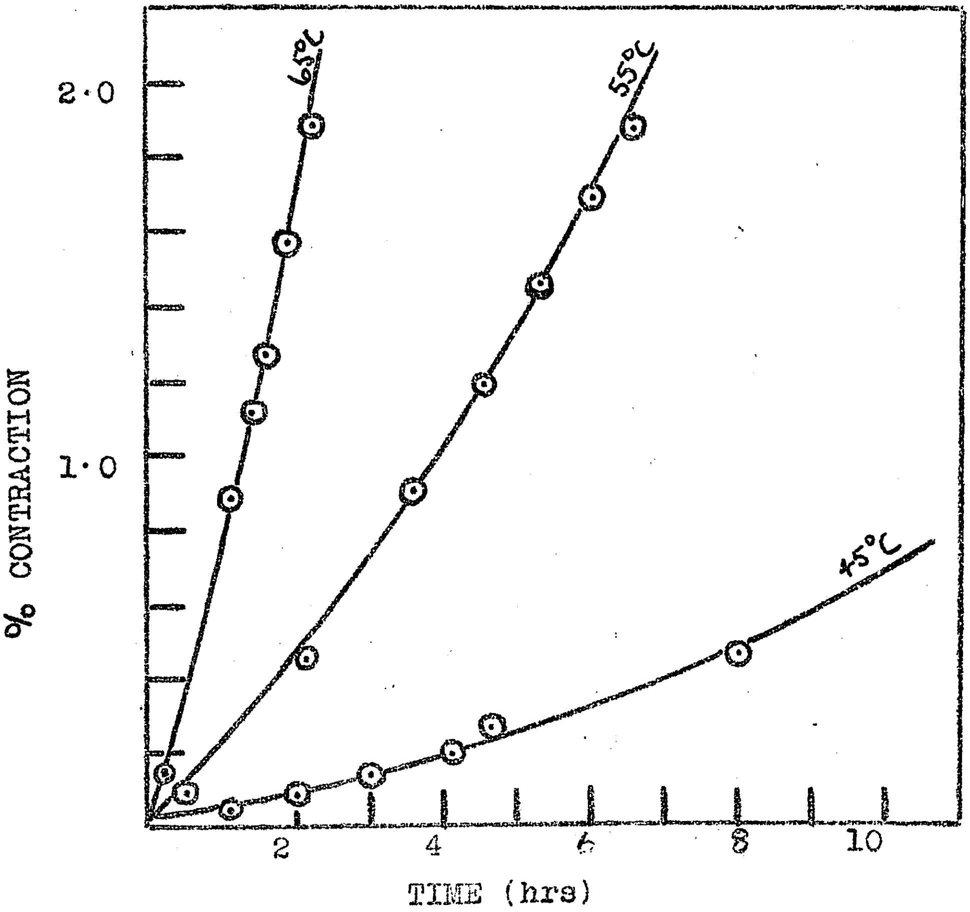
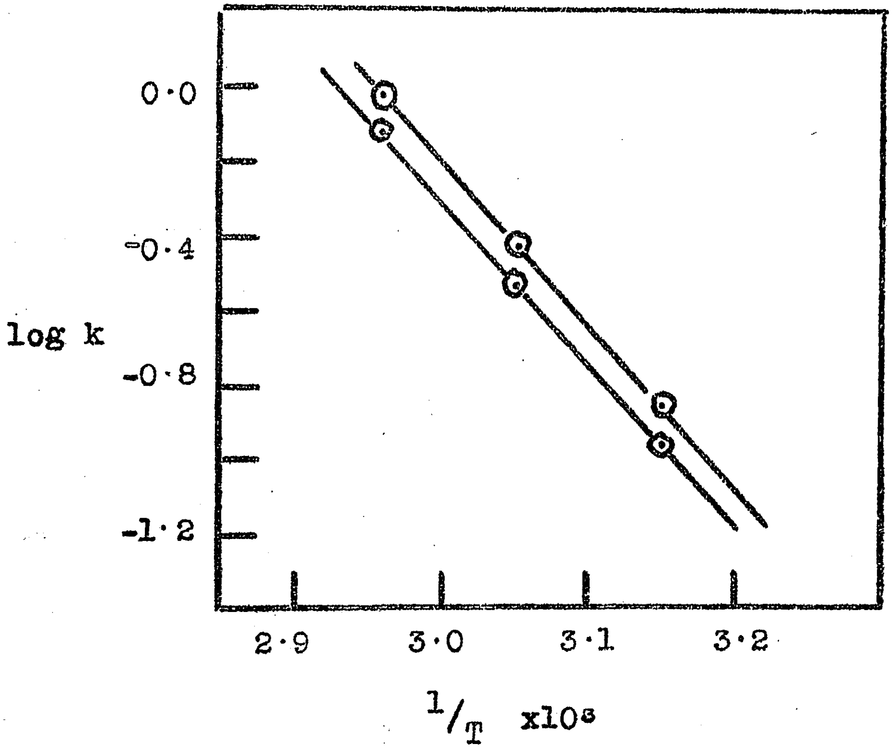


FIG. 14.



contraction against the reciprocal of the absolute temperature. A straight line of similar gradient was obtained using the corresponding rates at 1·5% contraction. The results obtained are tabulated in table5.

Table 5.

Temp.°C	$1/T \times 10^3$	%contr-action	k %contr/hr.	log k
45	3·145	0·5	0·107	-0·9706
55	3·049	0·5	0·291	-0·5364
65	2·959	0·5	0·752	-0·1238
45	3·145	1·5	0·137	-0·8617
55	3·049	1·5	0·369	-0·4330
65	2·959	1·5	0·934	-0·0297

The overall activation energy was found to be 23·0 kcal/mole.

(iii) Molecular Weight Measurements.

The molecular weight, measured by the intrinsic viscosity $[\eta]$, of the polymers prepared at 55°C using various initiator concentrations is shown in table 6.

Table 6.

Cat. conc.	%Conversion	$[\eta]$
0·90	5·48	1·085
0·90	11·82	1·055
0·155	12·68	1·10
0·10	8·30	1·01
0·057	4·57	0·962

From table 6 it can be seen that the molecular weight is independent of the initiator concentration. This indicates that transfer to monomer,

$$P_n^{\bullet} + M \longrightarrow M_n + P_1^{\bullet}$$

is important in the system. Prat[46], Bengough and Norrish[18] have obtained similar results for polyvinyl chloride.

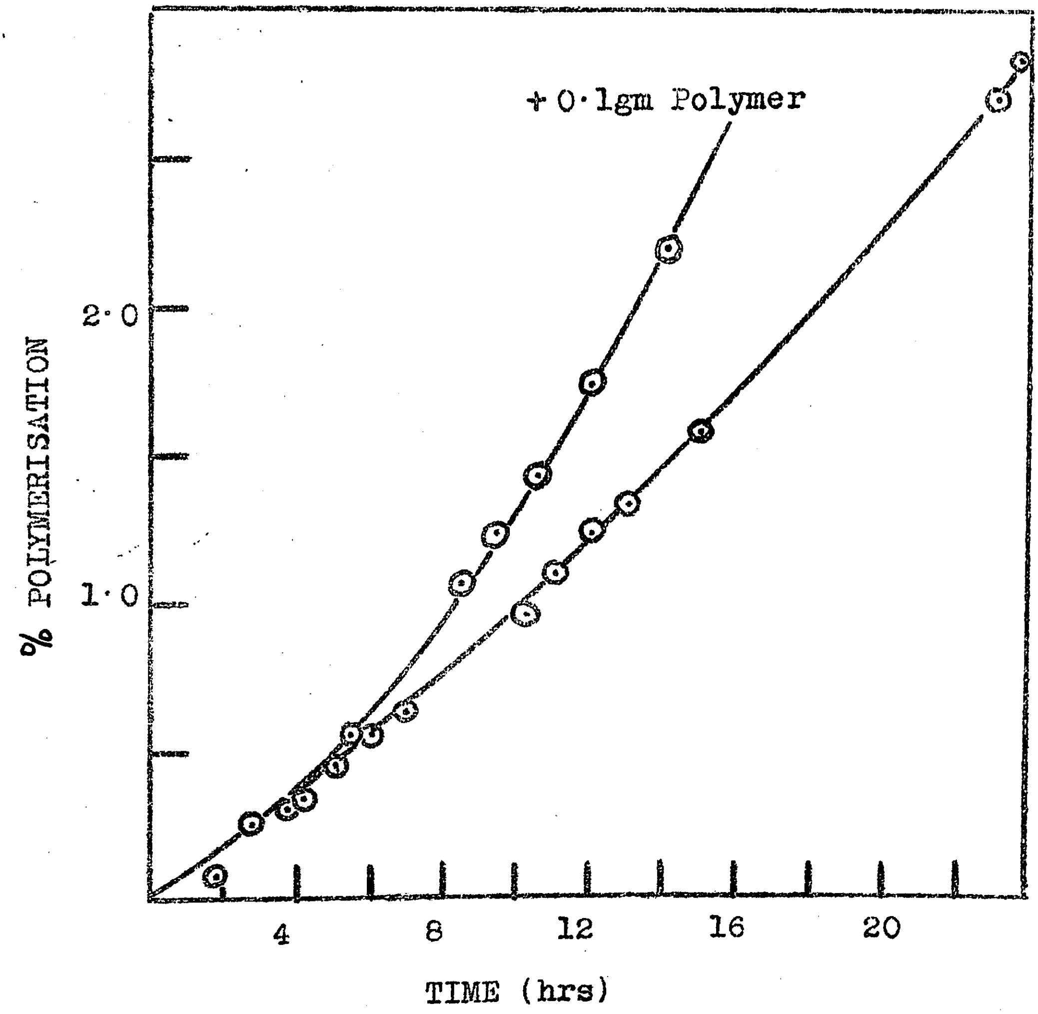
(iv) Addition of Dead Polymer.

From the nature of the results obtained so far, it is apparent that the abnormal effects produced are not due to impurities initially present, but must be associated with the precipitation of the polymer. This was confirmed by carrying out a polymerisation (0·1% AIBN at 55°C) in the presence of 0·1 gm. of poly-α-chloroacrylonitrile. The polymerisation curve obtained is compared in figure 15 with a similarly initiated reaction. From this it can be seen that the addition of polymer increases the rate of polymerisation.

(v) <u>Colouration</u>.

In nearly every case, the polymers prepared by bulk polymerisation of α-chloroacrylonitrile were found to be slightly coloured, the intensity of the colour increasing with extent of conversion and initiator concentration. Polymer prepared by thermal initiation was also found to be coloured. This colouration is presumably due to the development of conjugation in the polymer but it is not clear exactly how this occurs. It was possible to show, however, that a sample of poly-α-chloroacrylonitrile in solution did not colour at the temperature of polymerisation even in the presence of initiator. This suggests that polymerising monomer is necessary and that the colouration reaction runs parallel with polymerisation and is probably a radical process. In the polymerisation experiments, the formation of colour was restricted as far as possible by using small concentrations of initiator and limiting conversion

FIG. 15.



to 10%.

Colouration of acetone solutions of poly-α-chloroacrylonitrile occurred readily on addition of a few drops of sodium hydroxide solution. No decrease in colour resulted on leaving this solution to stand for a few days, indicating that the reaction responsible for the colouration was not reversible. Precipitation of the polymer from the alkali coloured solution gave a red brown coloured material which had a strong absorption band in the infra-red spectrum at 1650-1500 cm^{-1}. This absorption could be assigned to the formation of an unsaturated conjugated structure[47].

3. DISCUSSION.

(i) General.

It is obvious from the above results that the bulk polymerisation of α-chloroacrylonitrile represents a typical example of a heterogeneous phase polymerisation. Unlike simple homogeneous polymerisations, the rate of reaction increases with increasing conversion. In recent years systems behaving similarly, including vinyl chloride, acrylonitrile, vinylidene chloride and trifluorochloroethylene have been investigated. It is now clear that these systems have many features in common. Disagreement has, however, arisen over the reaction mechanism responsible for the accelerative effects. Bamford, Barb, Jenkins and Onyon[48] observed similar autocatalytic phenomena for the bulk polymerisation of acrylonitrile, the initiator order, however, was 0•9 and the overall activation energy 35•0 kcal/mole. These workers proposed a radical occlusion theory whereby the active polymer radicals are trapped in the precipitating polymer. These occluded radicals can still participate in propagation and transfer reactions although bimolecular termination reactions in the polymer are restricted. This reduction in the rate of termination would lead to an overall increase in the rate of polymerisation.

An alternative explanation was proposed by Bengough and Norrish[18] for the bulk polymerisation of vinyl chloride which displayed similar properties, the autocatalytic effect being observed up to 40% conversion. The initiator order was 0•5 and the overall activation energy 22•0 kcal/mole. Bengough and Norrish explained their observations on the basis of a transfer reaction involving dead polymer. This results in immobile free radicals being formed on the surface of the polymer particles. The radical activity can be removed by transfer to monomer. According to this theory, the rate acceleration is proportional to the particle surface area.

Bamford and his colleagues have suggested that the occlusion theory could be applied to vinyl chloride, whereas the surface transfer mechanism cannot be applicable to polyacrylonitrile which does not undergo transfer reactions readily. Recently Mickley, Michaels and Moore[49] have confirmed the results of Bengough and Norrish and have proposed a simplified moving boundary treatment of diffusion of radical activity into the polymer to explain the observed rate dependence on the polymer concentration.

The results obtained for α-chloroacrylonitrile indicate a close resemblance to those obtained for vinyl chloride. Similarity in initiator order and overall energy of activation suggests that both monomers polymerise by the same mechanism.

The possibility of occlusion occurring as proposed by Bamford et al for acrylonitrile was investigated for α-chloroacrylonitrile. Similar irradiation experiments as conducted by the above authors on acrylonitrile were repeated on α-chloroacrylonitrile. These consisted of subjecting a mixture of α-chloroacrylonitrile and initiator suitable for thermal polymerisation at 60°C, to irradiation at 25°C at which temperature the thermal rate is low. In the case of acrylonitrile it was found that after photochemical pre-polymerisation, the mixture when heated to 60°C polymerised very rapidly over the first few minutes. After this period the rate rapidly declined to its normal value. A similar 'fast' reaction was not observed for α-chloroacrylonitrile, indicating that occluded radicals were not present in the precipitated polymer. Also, the value of 0·5 for the initiator order would not be acceptable in terms of the occlusion theory.

From these experiments and the fact the addition of polymer to the polymerising monomer produces an accelerative effect, it may be concluded that the occlusion theory of Bamford, Barb, Jenkins and Onyon does not hold for α-chloroacrylonitrile. The close similarity observed between the α-chloroacrylonitrile and the vinyl chloride systems suggests that the autocatalytic effect of the former is due to transfer reactions as proposed by Bengough and Norrish. Certainly poly-α-chloroacrylonitrile should be capable of undergoing transfer reactions even more readily than polyvinyl chloride since the chlorine atom in the former will be additionally labilized by the resonance stabilising effect of the nitrile group attached to the same carbon atom. The fact that chain transfer reactions play an important part in the polymerisation of α-chloroacrylonitrile is further evident from the constant values of molecular weight obtained over a wide range of initiator concentrations. Such a result which is indicative of a transfer reaction, in this case most probably with monomer, has also been observed with vinyl chloride. Once more, the cyanide group should be expected to influence this reaction.

So far no mention has been made of the relationship between molecular weight and conversion. From table 6 it can be seen that the molecular weight is independent of the conversion, a result which is consistent with the proposed mechanism. This is in contrast with the increase in molecular weight which results when a 'gel' effect takes place.

(ii) The Mechanism and Kinetics of Polymerisation.

The various steps discussed above may be summarised in the following kinetic scheme;

Reactions in the liquid phase

Initiation	$Cat + M \longrightarrow P_1^{\bullet}$	$k_1 [Cat]$
Propagation	$P_r^{\bullet} + M \longrightarrow P_{r+1}^{\bullet}$	k_p
Transfer	$P_r^{\bullet} + M \longrightarrow M_r + P_1^{\bullet}$	k_{tr}
Termination	$P_r^{\bullet} + P_s^{\bullet} \longrightarrow M_{r+s}$ or $M_r + M_s$	k_t

Reactions at the polymer surface

Transfer to polymer	$P_s^{\bullet} + M_r \longrightarrow M_s + \overset{*}{M_r^{\bullet}}$	k_a
Propagation	$\overset{*}{M_r^{\bullet}} + M \longrightarrow \overset{*}{M_{r+1}^{\bullet}}$	k_p
Termination	$\overset{*}{M_r^{\bullet}} + M \longrightarrow M_r + P_1^{\bullet}$	k_{tr}

where M_r, M, P represent dead polymer, monomer and all mobile radicals respectively. $\overset{*}{M_r^{\bullet}}$ represents the radicals formed on the surface of the polymer. In the above kinetic scheme it is assumed that $\overset{*}{M_r^{\bullet}}$ can propagate and transfer at rates similar to that in the liquid phase.

The rate of formation of radicals in the system is given by the following equations,

$$d(P^{\bullet})/dt = k_i - k_t(P^{\bullet})^2 - k_a(P^{\bullet})(M_r) + k_{tr}(\overset{*}{M_r^{\bullet}})(M) \quad \text{———} \quad ①$$

$$d(\overset{*}{M_r^{\bullet}})/dt = k_a(P^{\bullet})(M_r) - k_{tr}(\overset{*}{M_r^{\bullet}})(M) \quad \text{———} \quad ②$$

Applying stationary state conditions;

$$d(P^{\bullet})/dt = 0 \qquad \text{and} \qquad d(\overset{*}{M_r^{\bullet}})/dt = 0$$

Adding ① and ② gives $(P^{\bullet}) = (k_i/k_t)^{1/2}.(Cat)^{1/2}$

Substituting in ② gives,

$$(M_r^{\overset{*}{\bullet}}) = (k_i/k_t)^{1/2}.(Cat)^{1/2}.k_a(M_r)/k_{tr}(M)$$

The rate of polymerisation is given by;

$$-d(M)/dt = k_p(P^{\bullet})(M) + k_p(M_r^{\overset{*}{\bullet}})(M)$$

$$= k_p(M)\left[(P^{\bullet}) + (M_r^{\overset{*}{\bullet}})\right] \text{ ———— } ③$$

Substituting values for $(P^{\bullet})$ and $(M_r^{\overset{*}{\bullet}})$ in ③ gives,

$$-d(M)/dt = (Cat)^{1/2}.(M).k_p k_i^{1/2}/k_t^{1/2}.\left[1 + k_a(M_r)/k_{tr}(M)\right]$$

$$= K_p.(Cat)^{1/2}\left[(M) + K'(M_r)\right] \text{ ———— } ④$$

where $K_p = k_p k_i^{1/2}/k_t^{1/2}$ and $K' = k_a/k_{tr}$

Equation 4 confirms the rate dependence on the square root of the initiator concentration obtained experimentally. The above equation also demonstrates the influence of precipitated polymer on the rate of polymerisation. Since the transfer reactions with the polymer would be expected to occur at the surface, the weight of polymer present raised to the power of two-thirds (surface area) could be substituted for (M_r), in equation 4,

$$-d(M)/dt = K_p(Cat)^{1/2}\left[(M) + K'w^{2/3}\right] \text{ ———— } ⑤$$

The dependence of the rate on the weight of polymer raised to the two-thirds power can be verified if the value of K_p can be determined. An accurate evaluation of this could be obtained from polymerisation experiments carried out in solution. A fairly good approximate value, however, can be obtained if it is assumed that the rate over the initial stages of the polymerisation is equal to the rate when no polymer is present. Using this assumption it was found that the average value of K_p for the experiments at 55°C was 0·057.

Equation ⑤ can now be written,

$$R_p/(\mathrm{Cat})^{1/2} = -d(M)/dt/(\mathrm{Cat})^{1/2} = 0{\cdot}057\left[(M) + K'w^{2/3}\right]$$

$$\therefore \Delta R_p = R_p/(\mathrm{Cat})^{1/2} - 0{\cdot}057(M) = K''w^{2/3}$$

The values of ΔR_p for the polymerisation initiated by 0·9% AIBN at 55°C are recorded in table 7. The plot of $\log \Delta R_p$ against $\log w$ is shown in figure 16, a linear relationship being obtained. The gradient of the straight line was 0·70 which is in good agreement with the theoretically expected value of 0·67. Similar results were obtained for the other polymerisations carried out at 55°C.

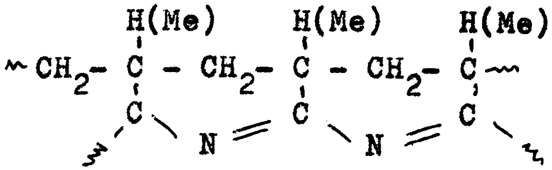
Table 7.

R_p (%poly/hr)	ΔR_p	$\log \Delta R_p$	w (gm/l)	log w
0·743	0·148	−0·8297	10	1·0000
0·830	0·238	−0·6234	20	1·3010
0·910	0·325	−0·4881	30	1·4771
0·984	0·400	−0·3979	40	1·6021
1·025	0·445	−0·3516	50	1·6990
1·085	0·506	−0·2958	60	1·7782
1·121	0·546	−0·2628	70	1·8451
1·224	0·589	−0·2299	80	1·9031

(iii) Colour Formation.

Recent studies, as indicated in chapter 1 have shown that the development of colour in polymer molecules is usually associated with the formation of unsaturated conjugated structures. Outstanding examples of this are to be found in polyvinyl chloride (I) and poly(meth)acrylonitrile (II), the structures responsible being,

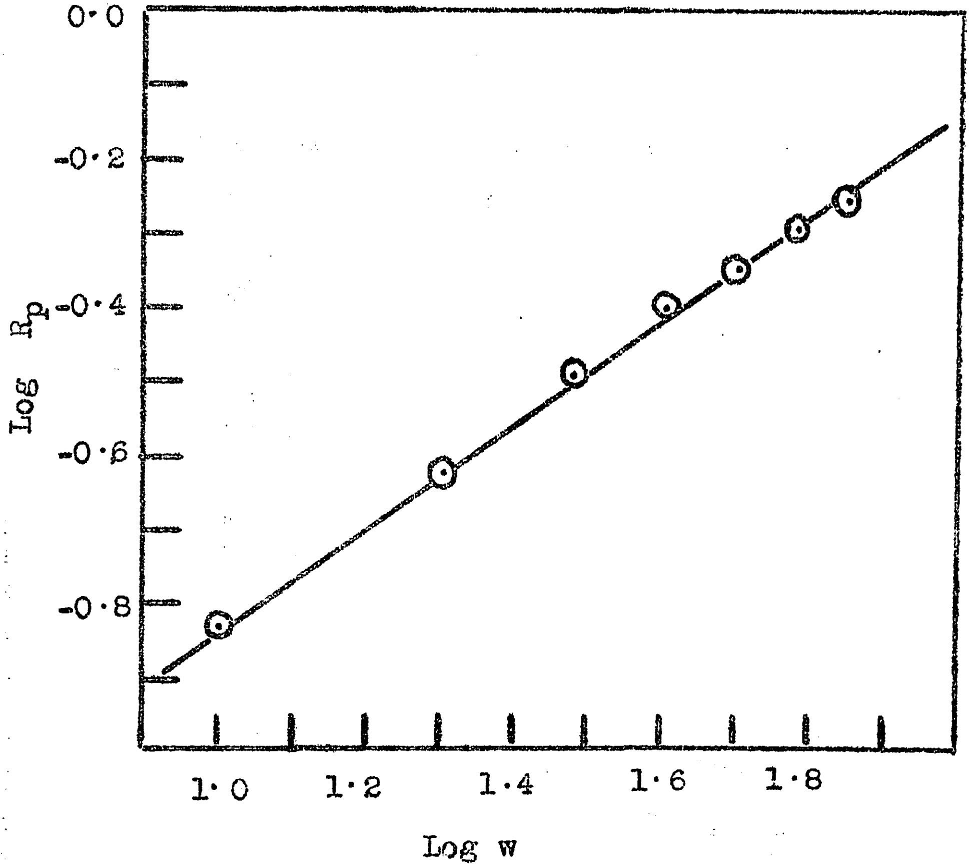
$$-CH=CH-CH=CH-$$



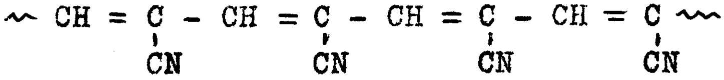
$$\sim CH_2-\underset{\displaystyle C}{\overset{H(Me)}{C}}-CH_2-\underset{\displaystyle C}{\overset{H(Me)}{C}}-CH_2-\underset{\displaystyle C}{\overset{H(Me)}{C}}\sim$$

(I) (II)

FIG. 16.



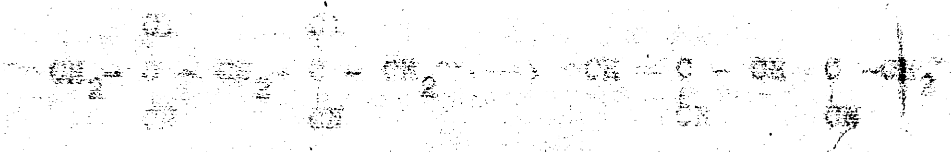
Structure I is formed by the loss of hydrogen chloride and structure II results from the linking up of adjacent nitrile groups. Comparison with poly-α-chloroacrylonitrile shows that both structures may be formed. Grassie and McNeill[50] have shown that the alkali induced colouration of polymethacrylonitrile solutions is reversible, a red solution, for example, reverts to yellow on standing for a few days at room temperature. The chemical structure responsible for the colour is clearly unstable in solution. In the case of poly-α-chloroacrylonitrile no such reversibility was detected, a red coloured solution being stable over a period of two months. It would seem, therefore, that the structure responsible for colouration in poly-α-chloroacrylonitrile is,



$$\sim CH=\underset{CN}{\underset{|}{C}}-CH=\underset{CN}{\underset{|}{C}}-CH=\underset{CN}{\underset{|}{C}}-CH=\underset{CN}{\underset{|}{C}}\sim$$

Additional evidence in support of this will be presented in the following chapter where it will be shown that poly-α-chloroacrylonitrile decomposes readily with the liberation of hydrogen chloride and subsequent formation of a backbone unsaturated conjugated structure. It is not, however, possible to predict whether the dehydrochlorination reaction occurs simultaneously with the propagation step or as a secondary degradation reaction. In both cases the nitrile group would be expected to exert a strong stabilising influence on any intermediate radical. Once the initial unsaturated structure is formed, the dehydrochlorination would be readily propagated by allylic activation to give sequences sufficiently long enough (~7 units) for colour development.

(b) Dehydrochlorination



$$\sim CH_2-\underset{CN}{\overset{Cl}{C}}-CH_2-\underset{CN}{\overset{Cl}{C}}-CH_2\sim \longrightarrow \sim CH=\underset{CN}{C}-CH=\underset{CN}{C}-CH_2$$

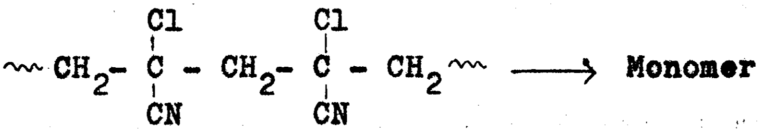
(c) Nitrile Cyclisation

CHAPTER 4.

THE THERMAL DEGRADATION OF POLY-α-CHLOROACRYLONITRILE.

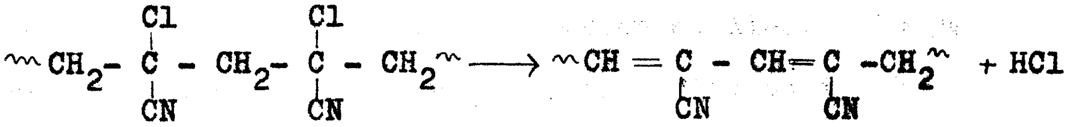
Poly-α-chloroacrylonitrile is capable, theoretically, of three different degradation reactions;

(a) Depolymerisation



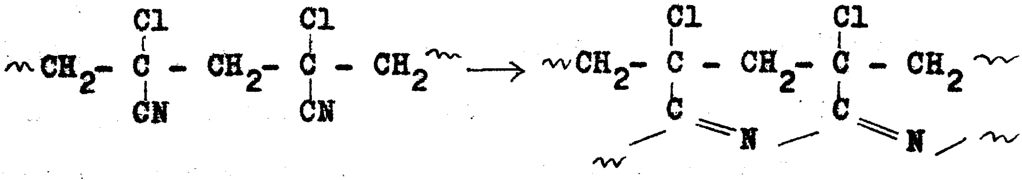
$$\sim CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2\sim \longrightarrow \text{Monomer}$$

(b) Dehydrochlorination



$$\sim CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2\sim \longrightarrow \sim CH=\underset{CN}{C}-CH=\underset{CN}{C}-CH_2\sim + HCl$$

(c) Nitrile Colouration



In section 1 of this chapter, investigations of the thermal degradation reaction occurring in poly-α-chloroacrylonitrile are described. Section 2 deals with kinetic aspects of the decomposition reaction.

1. MODE OF DEGRADATION.

(i) Sample Purity.

In the previous chapter it was shown that poly-α-chloroacrylonitrile prepared by bulk techniques was invariably coloured due to the formation of unsaturated structures in the polymer backbone. Experience with other polymeric systems has shown that the presence of such structures would be expected to influence the degradation properties of the polymer. Hence, samples of poly-α-chloroacrylonitrile prepared by this method are not suitable for degradation studies. Polymer prepared by emulsion techniques is not coloured to the same extent and is thus preferable. Other factors which favour the use of the emulsion technique are faster rates, lower temperatures of polymerisation, better yields and higher molecular weights. The main disadvantage of this method is the possibility of impurities from the emulsion components being incorporated chemically or adsorbed into the polymer. The samples used were always thoroughly washed to remove adsorbed impurities.

(ii) Thermal Decomposition of Poly-α-chloroacrylonitrile.

Poly-α-chloroacrylonitrile (P.E.1) was heated under high vacuum in the dynamic molecular still, the liberation of volatile material being followed on the Pirani Gauge. A typical Pirani plot is shown in figure 17 where it can be seen that considerable liberation of volatile material occurs at temperatures greater than 150°C. During degradation it was noticed that the evolution of the decomposition products coincided with a rapid colouration of the residue. The solubility of the polymer in acetone, methyl ethyl ketone and other ketonic solvents also decreased substantially.

(iii) Examination of the Decomposition Products.

Fractionation of the decomposition products indicated the presence of two compounds. The first, was gaseous at -80°C, soluble in water giving a strong acid solution while the second was liquid at room temperature, strongly acid and turned anhydrous copper sulphate blue. Analysis of the residue showed that the chlorine content had decreased considerably. From this it may be concluded that the volatile decomposition products of the thermal degradation of polychloroacrylonitrile are hydrogen chloride and water.

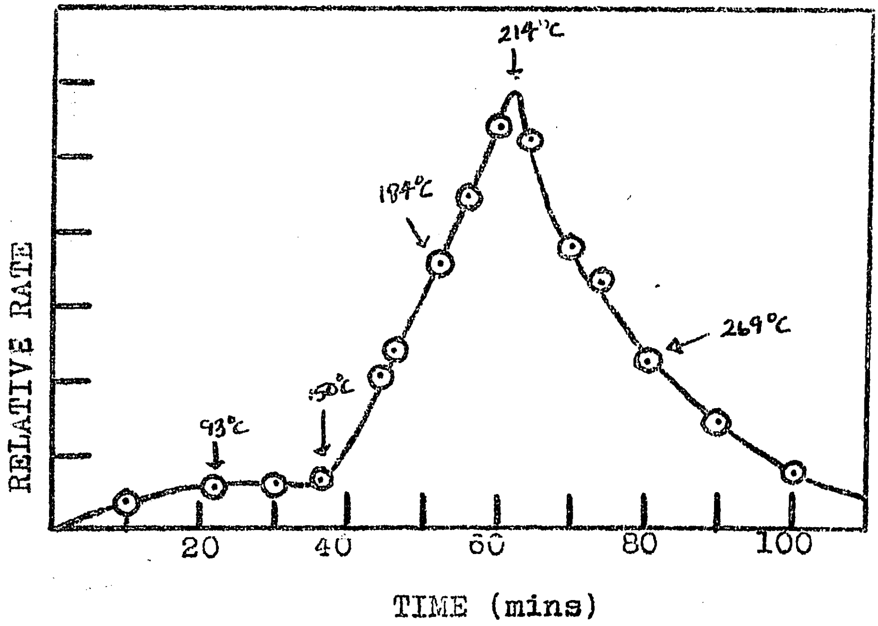


FIG.17. Pirani plot for the degradation of poly-α-chloroacrylonitrile.

Since the polymer was prepared by emulsion techniques, the presence of water is readily explained, the acidity being due to the large solubility of hydrogen chloride in water. Extensive drying by pre- heating at 100°C in vacuum reduced the amount of water liberated but traces were always detectable.

(iv) Changes in Infra-red Spectrum.

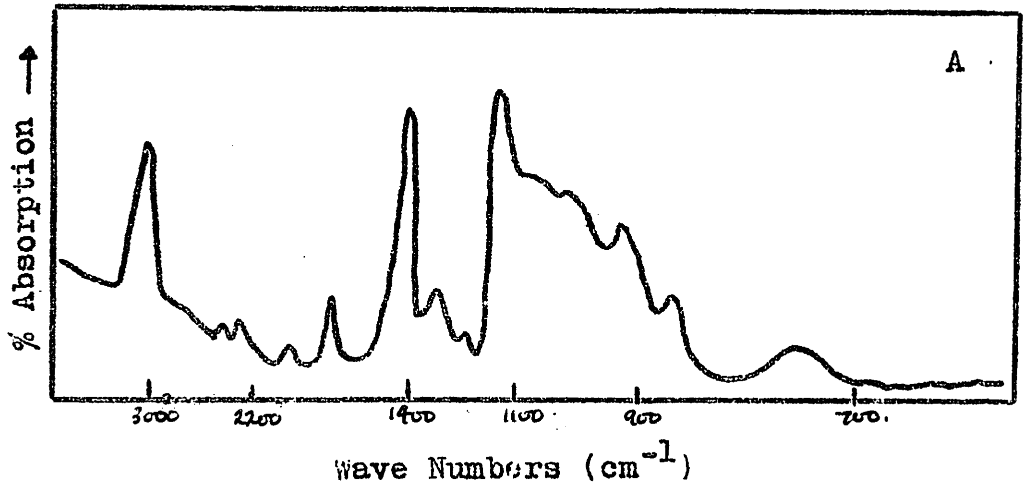
When poly-α-chloroacrylonitrile is heated at temperatures above 140°C considerable changes occur in the infra-red spectrum. These are shown in figure 18 where the infra-red spectrum of poly-α-chloroacrylonitrile, degraded for two hours at 195°C, is compared with that of the undegraded material. The increased scatter resulting from the change in refractive index of the degraded sample tends to restrict a detailed study of the absorption changes in the region 4000 - 2500 cm^{-1}. Outwith this region new absorption peaks are found at 2260 - 2210, 1650 - 1500, 1426 - 1200 and 805 cm^{-1}. Figure 19 shows the effect of time of heating at 142°C on the spectrum of poly-α-chloroacrylonitrile in the region 2500 - 1400 cm^{-1}.

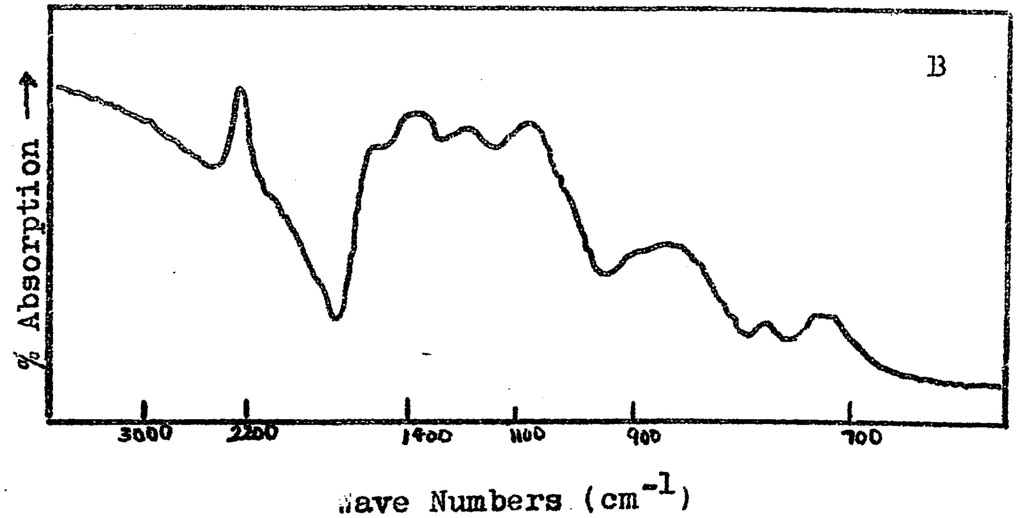
(v) Discussion.

Interpretation of Infra-red Data. 2260 - 2210 cm^{-1}

Absorption in this region corresponds to changes in the

FIG. 18.

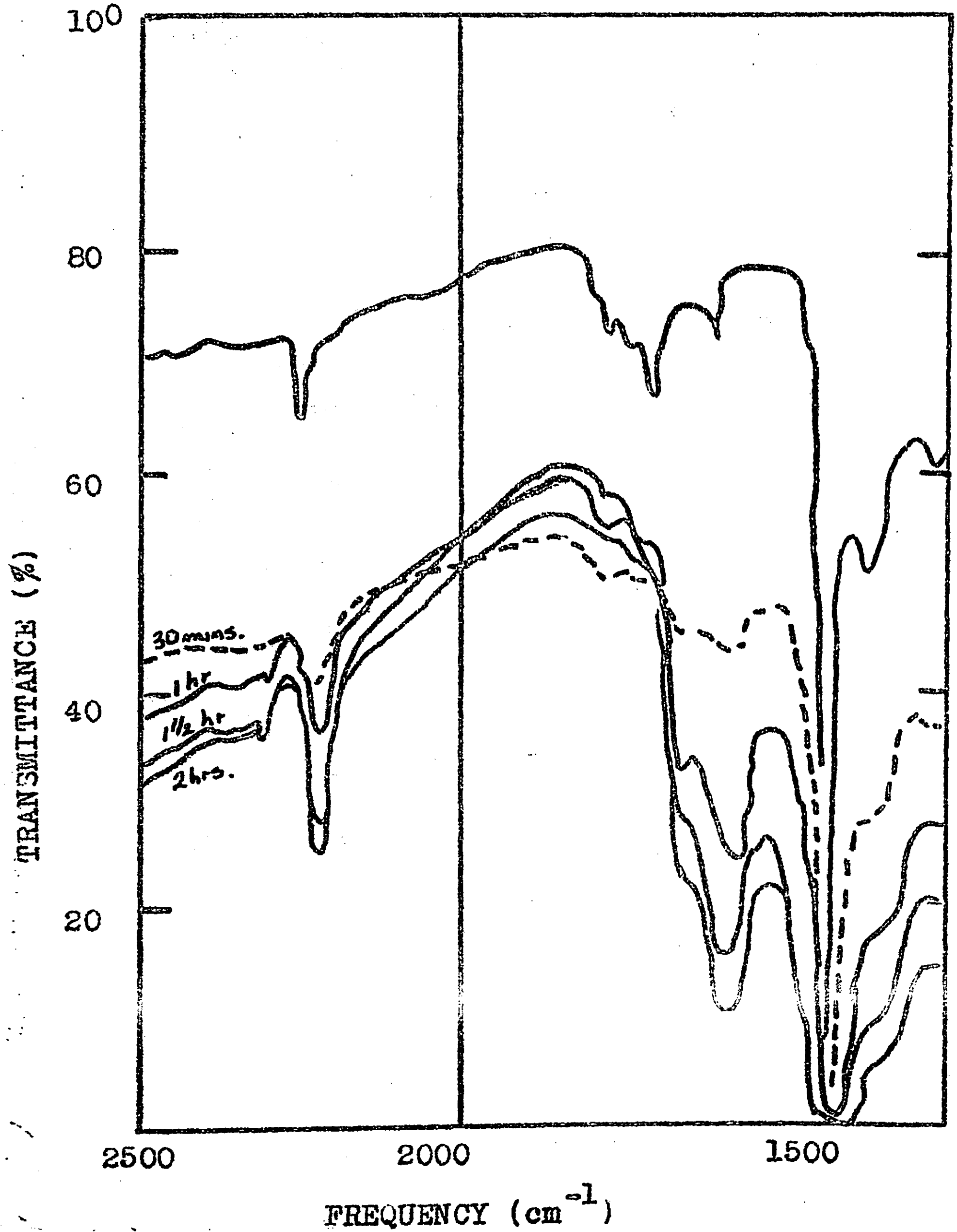




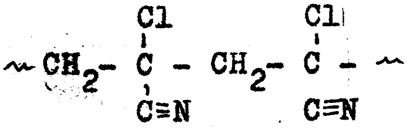
A Undegraded

B Degraded 2hrs/ 195°C

FIG. 19.

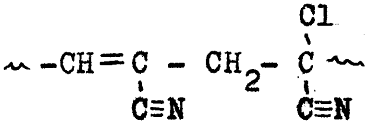

100
80
60
40
20
TRANSMITTANCE (%)
2500
2000
1500
FREQUENCY (cm^{-1})
30 mins.
1 hr
1½ hr
2 hrs.

stretching vibration of the $C\equiv N$ group. The undegraded sample as shown in figure 19 exhibits an absorption band of low intensity in this region. This is rather remarkable considering the large concentration of nitrile groups present. The most probable explanation of this phenomena is that the chlorine atom exerts a 'quenching' effect on the intensity of this band. Bellamy[51] reports a similar occurrence in acetone cyanohydrin where the hydroxyl group 'quenches' the $C\equiv N$ absorption intensity to a remarkable extent, the intensity being about a third of the normal. With the removal of the chlorine atom on dehydrchlorination and the consequent formation of conjugated unsaturated bonds there is an increase in intensity and a subsequent frequency shift to 2210 cm^{-1}.



$\sim CH_2-\underset{C\equiv N}{\overset{Cl}{C}}-CH_2-\underset{C\equiv N}{\overset{Cl}{C}}-\sim$

2260 cm^{-1}



$\sim -CH=\underset{C\equiv N}{C}-CH_2-\underset{C\equiv N}{\overset{Cl}{C}}\sim$

2210 cm^{-1}

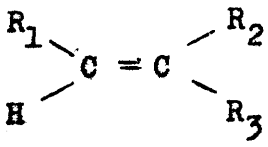
The $C\equiv N$ stretching vibration of the monomer, which possesses a similar unsaturated structure to the above, is found at 2205 cm^{-1}.

1650 - 1500 cm^{-1}.

The gradual build up of absorption in this region can be assigned to the formation of conjugated unsaturated sequences involving C=C or C=N bonds. Degraded polyvinyl chloride[52] and polymethacrylonitrile[50] exhibit similar absorption bands. Since the frequencies of these conjugated systems are virtually identical, it would be extremely difficult to attempt to assign the absorption bands in this region to the correct group without recourse to some other independent evidence. In this case it is obvious from the nature of the decomposition products that the structure responsible for absorption in this region is the $(-C=C-)_n$ conjugated system. The reappearance of the C≡N stretching vibration on degradation also supports this.

$1500 - 650$ cm^{-1}.

Assignment of the various absorption bands in the first part of this region is rather complicated due to the complex nature of the various C - C deformation modes. The absorption at 805 cm^{-1} can be assigned to the formation of a tri-substituted unsaturated structure[53],



(vi) Conclusion.

In the light of the chemical and spectroscopic evidence presented above, it is apparent that the principle degradation reaction occurring in poly-α-chloroacrylonitrile when pyrolysed in vacuum at temperatures above 140°C is dehydrochlorination with the consequent formation of conjugated unsaturated sequences in the polymer backbone. The formation of these structures being responsible for the insolubility and colouration of the residue. The rapidity with which these characteristics - dehydrochlorination, insolubility and colouration occur, suggests that the reaction takes place preferentially at groups of adjacent units, possibly by a radical mechanism.

The overall conclusion to be deduced from this and the previous chapter is that both in its polymerisation behaviour and in the degradation behaviour of its polymer, α-chloroacrylonitrile is behaving as a substituted vinyl chloride.

2. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF POLY-α-CHLOROACRYLONITRILE.

(i) Introduction.

In this section kinetic studies of the dehydrochlorinatiom reaction which occurs on heating poly-α-chloroacrylonitrile at temperatures above 140°C are described. Investigation of the corresponding reaction in polyvinyl chloride has attracted considerable attention. In the earlier studies of the dehydrochlorination mechanism of polyvinyl chloride, it was suggested by a number of workers[54] that the reaction is autocatalysed by the hydrogen chloride. More recent evidence reported by Arlman[10] disproves this and he explains the decomposition mechanism in terms of a free radical reaction similar to that proposed by Barton and Howlett[55] for the corresponding reaction in 1:2 dichloroethane. Stromberg, Straus and Achhammer[17] have presented a kinetic treatment based on such a mechanism, which explains, to some extent, the accumulated experimental evidence. A study of poly-α-chloroacrylonitrile along these lines should therefore be of considerable interest.

(ii) Reaction Rates.

Since the sole degradation product apart from residual solvent impurities is hydrogen chloride, the simplest and most accurate method of following the reaction rate is by measurement of the weight loss. This was confirmed by degrading P.E.1. at various temperatures in the range 155 - 195°C where it was found that the measured weight loss corresponded within experimental error, to the amount of hydrogen chloride determined by titration. It was therefore decided to use this method to follow the reaction. However, as a check, titration and pressure readings were also recorded.

The weight loss versus time data for the pyrolysis of P.E.1. are plotted in figure 20. This gives a series of curves similar to that obtained for polyvinyl chloride, the temperature range, however, being some 80°C lower. Stromberg, Straus and Achhammer in their kinetic treatment of polyvinyl chloride propose a relationship of the form,

$$-dC/dt = kC^n \qquad \text{——} \qquad ①$$

where C is the fraction of undegraded monomeric units, that is, the mass of potential hydrogen chloride in the sample at time t divided by the mass in the undegraded sample. k is a rate constant. The order of the reaction n for poly-α-chloroacrylonitrile assuming that a similar rate expression holds, was determined for the pyrolysis of P.E.1. at 195°C by plotting log dC/dt against log C. The results obtained are tabulated in table 8.

The value of n obtained from the gradient of the resulting straight line graph (Fig. 21) is 1·58. Further experiments

FIG. 20.

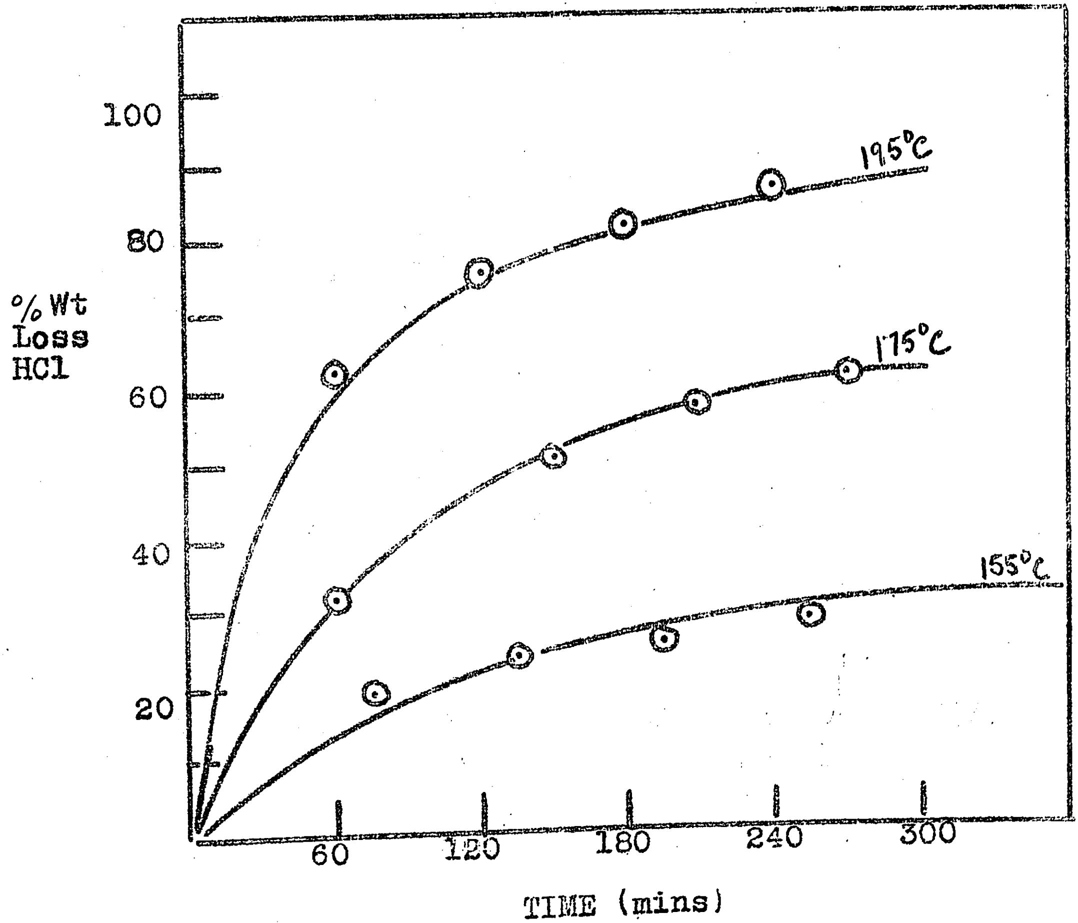
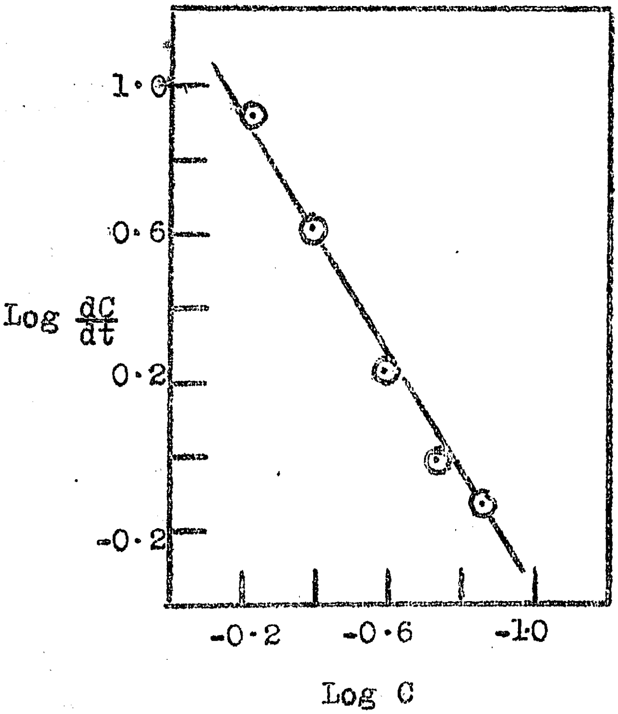

100
80
60
40
20
% Wt
Loss
HCl
195°C
175°C
155°C
60
120
180
240
300
TIME (mins)

FIG. 21.



on P.E.1. and P.E.3. at various temperatures gave values of <u>n</u> in the range 1·5 ± 0·1.

Table 8

Time (mins)	dC/dt x10^2 /min	log dC/dt	C	log C
30	8·33	0·9206	0·60	-0·2218
60	4·07	0·6096	0·41	-0·3872
120	1·71	0·2330	0·26	-0·5850
180	0·968	-0·0141	0·185	-0·7328
240	0·736	-0·1331	0·140	-0·8539

The close correlation between the experimental data and the postulated rate equation suggests that the pyrolysis of poly-α-chloroacrylonitrile can be represented by a three halves order equation of the form,

$$-dC/dt \quad = \quad kC^{3/2}$$

as was also shown by Stromberg et al for polyvinyl chloride. On integration this gives,

$$C^{-1/2} \quad = \quad C_o^{-1/2} \quad + \quad 1/2\ kt$$

where C_o is the original fraction of undegraded monomeric units. Curves obtained by plotting $C^{-1/2}$ versus time for P.E.1. degraded in the temperature range 155 - 195°C are shown in figure 22. The rate constants obtained from the slopes of the straight lines are shown in table 9.

Table 9

Temp. °C	k x10^3 /min
155	0·81
175	3·77
195	12·92

When an Arrhenius type plot of the above data is constructed, a straight line is obtained as shown in figure 23. The overall energy of activation obtained from the slope of this line is 29·4 kcal/mole.

(iii) Discussion.

It is generally agreed that polyvinyl chloride decomposes by a radical chain mechanism and not by a molecular mechanism as proposed by Grassie[56] for polyvinyl acetate. The close similarity between the behaviours of poly-α-chloroacrylonitrile

FIG. 22.

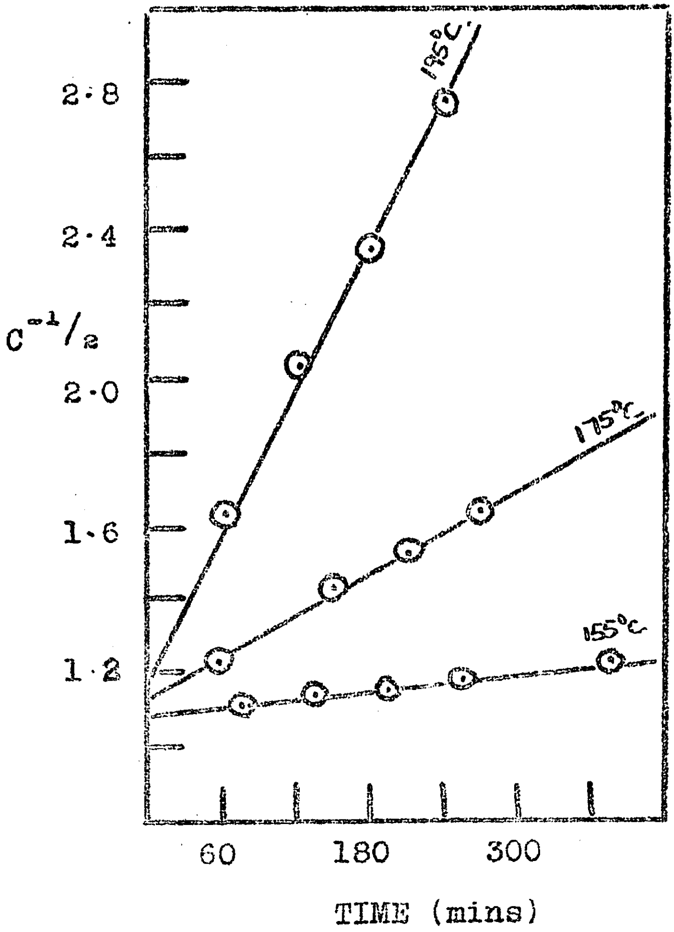
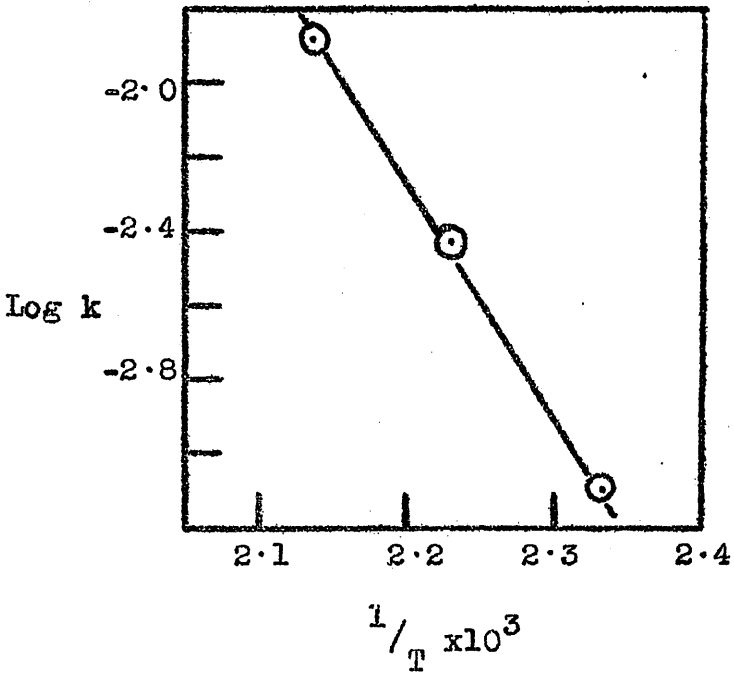
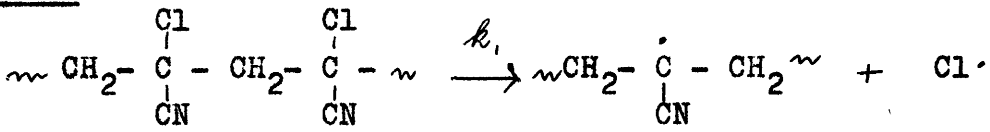


FIG. 23.



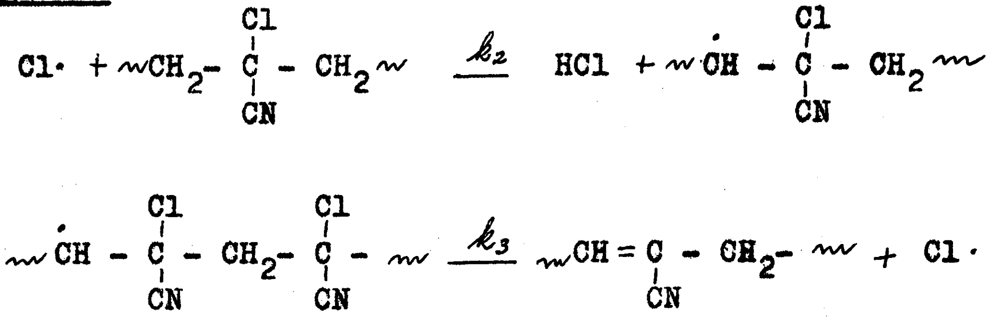
and polyvinyl chloride suggests that the former decomposes by a similar mechanism. A free radical chain mechanism which explains the above experimental data can be formulated as follows.

Initiation



$$\sim CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{Cl}{\underset{CN}{C}}-\sim \xrightarrow{k_1} \sim CH_2-\underset{CN}{\dot{C}}-CH_2\sim \quad + \quad Cl\cdot$$

Propagation



$$Cl\cdot + \sim CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2\sim \xrightarrow{k_2} HCl + \sim\dot{C}H-\overset{Cl}{\underset{CN}{C}}-CH_2\sim$$

$$\sim\dot{C}H-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{Cl}{\underset{CN}{C}}-\sim \xrightarrow{k_3} \sim CH=\underset{CN}{C}-CH_2-\sim + Cl\cdot$$

Termination

$$Cl\cdot + Cl\cdot \xrightarrow{k_4} Cl_2$$

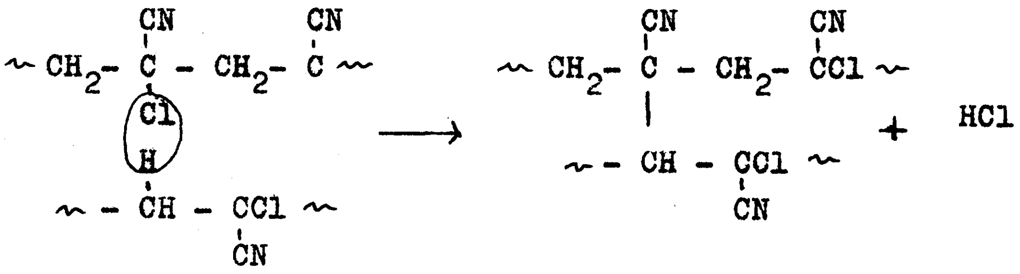
$$P_m\cdot + P_n\cdot \xrightarrow{k_5} P_m - P_n$$

$$P_m\cdot + Cl\cdot \xrightarrow{k_6} P_m - Cl$$

The C - Cl bond should be the weakest in the chain due to the resonance stabilisation of the radical formed. Electron impact studies[57] have shown that the bond dissociation energy for the C - Cl bond in allyl chloride is 58 kcal, which is approximately 20 kcal less than the corresponding bond dissociation energy for ethyl chloride (80 kcal)[58]. This difference of ~ 20 kcal. is attributed to the resonance stabilisation of the allyl radical. Although no corresponding values for a system incorporating a nitrile group are available, the theoretical expected value should be of a similar magnitude to that for allyl chloride.

This increased lability of the C - Cl bond in poly-α-chloroacrylonitrile should therefore favour initiation at this point. The conjugative influence of the nitrile group should also facilitate the abstraction of the chlorine atom in the second step of the propagation reaction. The reduced stability of poly-α-chloroacrylonitrile compared with polyvinyl chloride can therefore be interpreted as being due to the influence of the nitrile group on the initiation and propagation steps.

From the nature of the radicals involved, it can be seen that three possible termination reactions can result. The combination of free radicals resulting in cross linking is probably responsible for some termination in the early stages of the reaction. Such combination could account for the resulting insolubility of the residue, but it seems more likely that the bulk of the cross linking is the result of dehydrochlorination from adjacent chains,



As the reaction proceeds , the mobility of the chain radicals would be diminished and termination by their combination in pairs would be inhibited. Termination by combination of the mobile chlorine radicals would then become relatively more probable. Free chlorine has not been detected in the present work and was not reported in previous polyvinyl chloride work. However, its detection in such small amounts would be exceedingly difficult in the presence of the large amounts of hydrogen chloride evolved.

If a steady state condition is assumed for the chain carriers, the following equations can describe the system.

$$d(Cl\cdot)/dt = k_1 C - k_2(Cl\cdot).C + k_3(P\cdot) - k_4(Cl\cdot)^2 = 0 \qquad \text{———————} ①$$

$$d(P\cdot)/dt = k_2(Cl\cdot).C - k_3(P\cdot) = 0 \qquad \text{———————} ②$$

Adding ① and ②

$$k_1C = k_4(Cl\cdot)^2$$

$$\therefore (Cl\cdot) = (k_1/k_4)^{1/2}.C^{1/2}$$

Now

$$-dC/dt = k_2(Cl\cdot).C$$

$$\therefore -dC/dt = k_2(k_1/k_4)^{1/2}.C^{3/2} \qquad ③$$

Equation 3 explains the experimentally obtained rate dependence on the concentration of monomeric units raised to the three halves power.

With this mechanism the overall activation energy would be given by,

$$E_a = E_1/2 + E_2 - E_4/2$$

The value of E_2 for the extraction of the hydrogen atom in the propagation step would be quite small. Steacie[59] predicts a value of ~8 kcal. for this type of reaction. The activation energy of the termination step, the combination of two radicals should also be of comparable magnitude to E_2. The initiation step would therefore make the largest contribution to the overall activation energy. On this basis E_1 is of the order of 59 kcal. which is in good agreement with the theoretically expected value.

Stromberg, Straus and Achhammer in their treatment of polyvinyl chloride obtained an activation energy of 60 kcal. for the initiation step. This suggests that the initiation step occurs at the C - Cl bond in the allylic position to an unsaturated structure. Such a structure would be expected to exist at the chain ends as a result of transfer to monomer during polymerisation. Stromberg and his colleagues, however, denote the initiation step in their reaction scheme by k_1C which implies that every monomer unit is a possible initiation centre. Such a step obviously invalidates the resulting kinetic scheme.

Arlman[10], Baum and Wartman[60] and Talamini and Pezzin[61] have produced evidence to suggest that the initiation in polyvinyl chloride does occur at the chain ends. Baum and Wartman go further to suggest that the initiation occurs at the chain ends at low temperatures while initiation at tertiary chloride structures becomes predominant at higher pyrolysis temperatures.

The kinetic scheme proposed by Stromberg, Straus and Achhammer cannot therefore represent a true picture of the decomposition mechanism of polyvinyl chloride. It may be argued that similar labile groups should be present at the chain ends in poly-α-chloroacrylonitrile, however, the close agreement of the experimental results with the proposed reaction scheme suggests that this is not so and that the predominant initiation step occurs at random.

[illegible] [illegible]styrene as being due to the existence of a number of bonds distributed at random in the polymer. Grassie an Kerr[23,24,64] have produced considerable evidence support this theory. Opposing it, Simha and Wall[65] have interp these molecular weight changes on the basis of a random scission reaction resulting from inter and intramolecula transfer. Gordon[66] has also claimed, from a theoretica standpoint, that they can be explained by a transfer mechanism. Recently, Cameron[67] has reviewed both theor and has produced additional evidence[20,21,22] in support weak links. A brief summary of possible weak link stru was given in chapter 1, a more detailed account is now g

Jellinek suggested that the incorporation of oxyge into the polymer chain may lead to the formation of labi

CHAPTER 5.

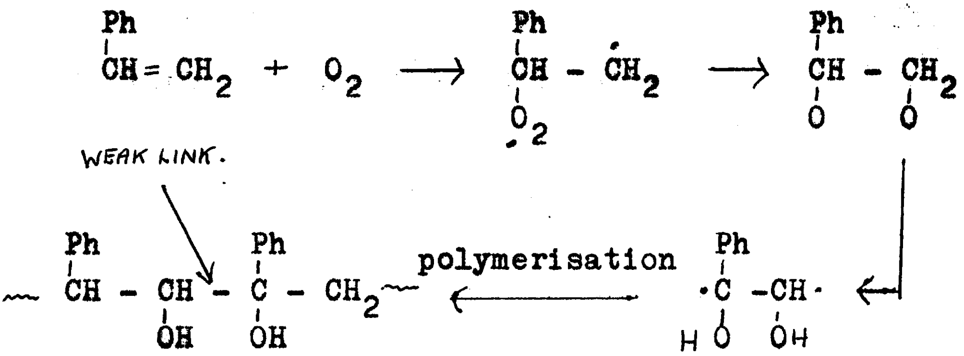
DEGRADATION OF STYRENE/α-CHLOROACRYLONITRILE COPOLYMERS.

1. INTRODUCTION.

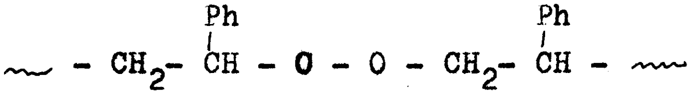
(i) Weak Link Theory of Polystyrene.

This theory, first proposed by Jellinek[62,63] explained the initial fall in molecular weight which occurs on heating polystyrene as being due to the existence of a number of weak bonds distributed at random in the polymer. Grassie and Kerr[23,24,64] have produced considerable evidence supporting this theory. Opposing it, Simha and Wall[65] have interpreted these molecular weight changes on the basis of a random scission reaction resulting from inter and intramolecular transfer. Gordon[66] has also claimed, from a theoretical standpoint, that they can be explained by a transfer mechanism. Recently, Cameron[67] has reviewed both theories and has produced additional evidence[20,21,22] in support of weak links. A brief summary of possible weak link structures was given in chapter 1, a more detailed account is now given.

Jellinek suggested that the incorporation of oxygen into the polymer chain may lead to the formation of labile structures;



This seemed a possible explanation since it was known that polystyrene prepared in the absence of oxygen is more stable than polymer prepared in the presence of oxygen. However, such a mechanism is extremely doubtful since it is known that styrene copolymerises with oxygen forming a polyperoxide,

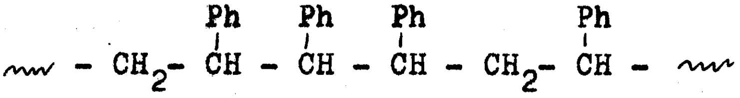


$$\sim - CH_2 - \overset{Ph}{CH} - O - O - CH_2 - \overset{Ph}{CH} - \sim$$

which would certainly be thermo labile.

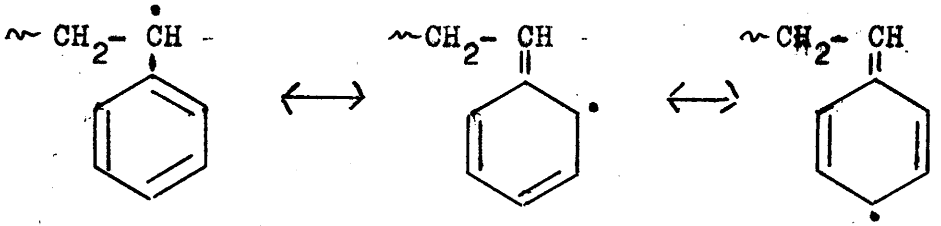
Grassie and Kerr showed, however, that labile structures result even when polymerisation is carried out with complete exclusion of oxygen. Investigation of the polymerisation variables showed that the number of weak links depended on the temperature of polymerisation, the concentration of such links increasing with temperature. Thus the formation of weak links occurs during the polymerisation process.

Recently, Cameron and Grassie, using radio-active stilbene copolymerised with styrene,

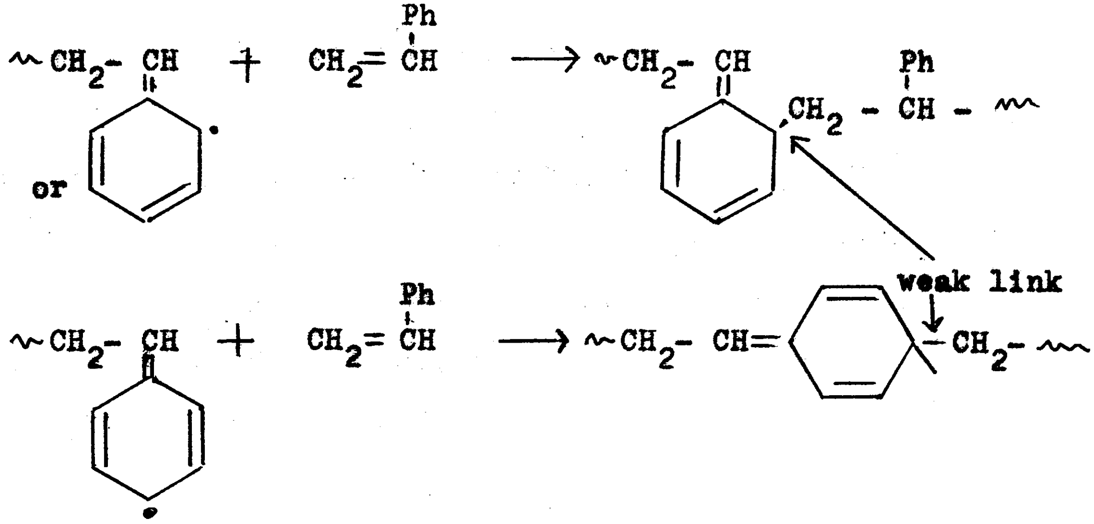


$$\sim -CH_2-\overset{Ph}{\overset{|}{CH}}-\overset{Ph}{\overset{|}{CH}}-\overset{Ph}{\overset{|}{CH}}-CH_2-\overset{Ph}{\overset{|}{CH}}-\sim$$

have shown that head to head linkages cannot be responsible for the chain scission. They suggest that structures formed by polymerisation through the canonical forms of the benzene ring,



may be responsible. On polymerisation the following structures would arise,



Cameron and Grassie attempted to estimate these quinonoid type structures using ozonolysis. Results showed that polystyrène contained backbone unsaturated structures in the same concentration as its weak links. However, no evidence was put forward to indicate that these unsaturated bonds were in actual fact due to quinonoid type structures. A reaction scheme based on these structures explaining relevant experimental data was also proposed.

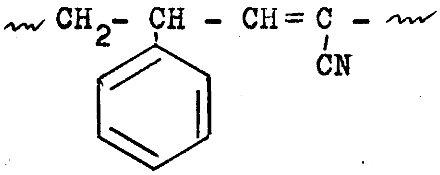
(ii) Use of α-Chloroacrylonitrile in Weak Link Investigations.

In the previous chapter it was shown that poly-α-chloroacrylonitrile degrades by ester decomposition with liberation of hydrogen chloride. This decomposition reaction occurred at measurable rates at temperatures as low as 155°C. Since this temperature lies well below that required to degrade polystyrene (~300°C), it should, theoretically, be possible to introduce unsaturated bonds into a polystyrene chain simply by copolymerising with α-chloroacrylonitrile followed by subsequent dehydrochlorination at 155°C. A slightly higher initiation temperature may be required to eliminate the hydrogen chloride but this should still be well below 300°C. Hence, by using this technique it may be possible to study the effect of unsaturated bonds, present in the polymer backbone, on the degradation mechanism.

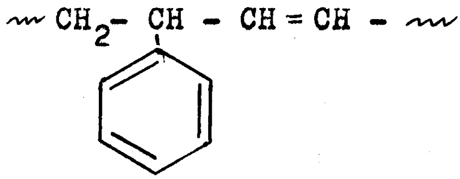
Vinyl chloride/ styrene copolymers could similarly be used but α-chloroacrylonitrile is preferred since;

(a) dehydrochlorination occurs more easily, hence eliminating the possibility of secondary thermal effects on the polystyrene.

(b) the presence of the nitrile group (I) creates an environment nearer to that of the phenyl group than that obtained from the hydrogen atom of the vinyl chloride (II),



(I)



(II)

(c) the reactivity ratios of the styrene/α-chloroacrylonitrile system are more favourable.

The main drawback in the use of α-chloroacrylonitrile is the possibility of the formation of alternating sequences in the chain due to the relatively high reactivity of the radicals for the opposite monomer. In order to minimise this, very small amounts of α-chloroacrylonitrile have to be used.

2. THERMAL DEGRADATION.

(i) Decomposition Products.

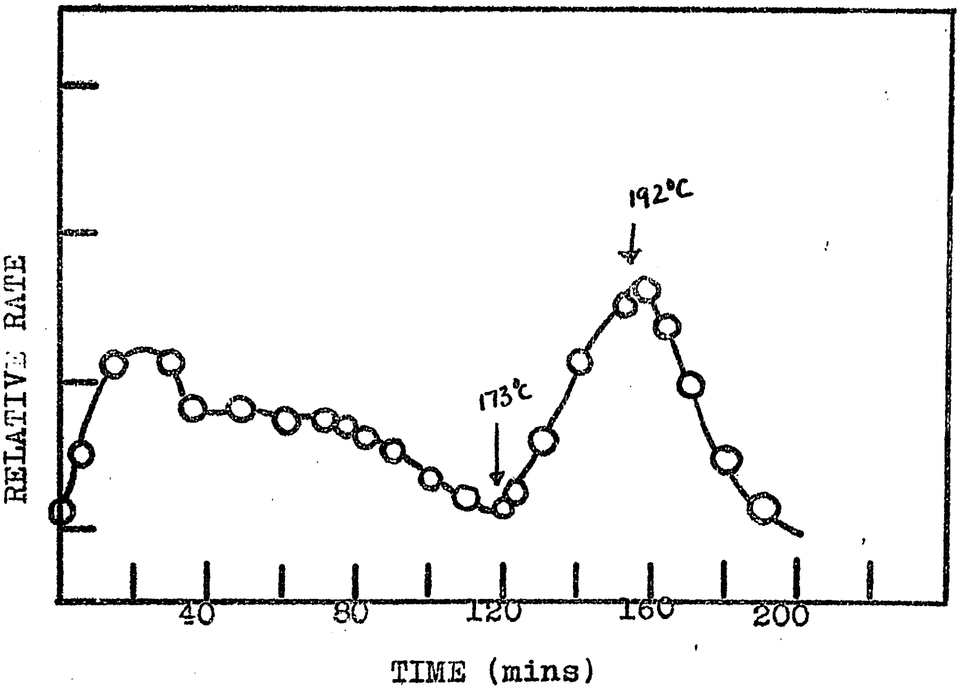
The liberation of volatile material from the copolymers on heating in vacuum was determined using the Pirani gauge. A typical plot for C.P.13. in the temperature range 25 - 200°C is shown in figure 24. The initial peak is due to the liberation of occluded solvent material. The second peak corresponded to the evolution of a gaseous material which was identified as hydrogen chloride. Analysis of the residue, which showed a decrease in chlorine content, confirmed this. No styrene monomer was detectable at this point. Continued heating at much higher temperatures was found to be necessary for the liberation of styrene and related compounds. The styrene monomer was identified by infra-red and V.P.C. techniques.

The main decomposition products of styrene/α-chloroacrylonitrile copolymers are thus hydrogen chloride, styrene and related compounds. α-Chloroacrylonitrile monomer was not detected.

(ii) Molecular Weight Changes.

Molecular weight changes occurring during degradation were measured using copolymers containing small proportions

FIG. 24.

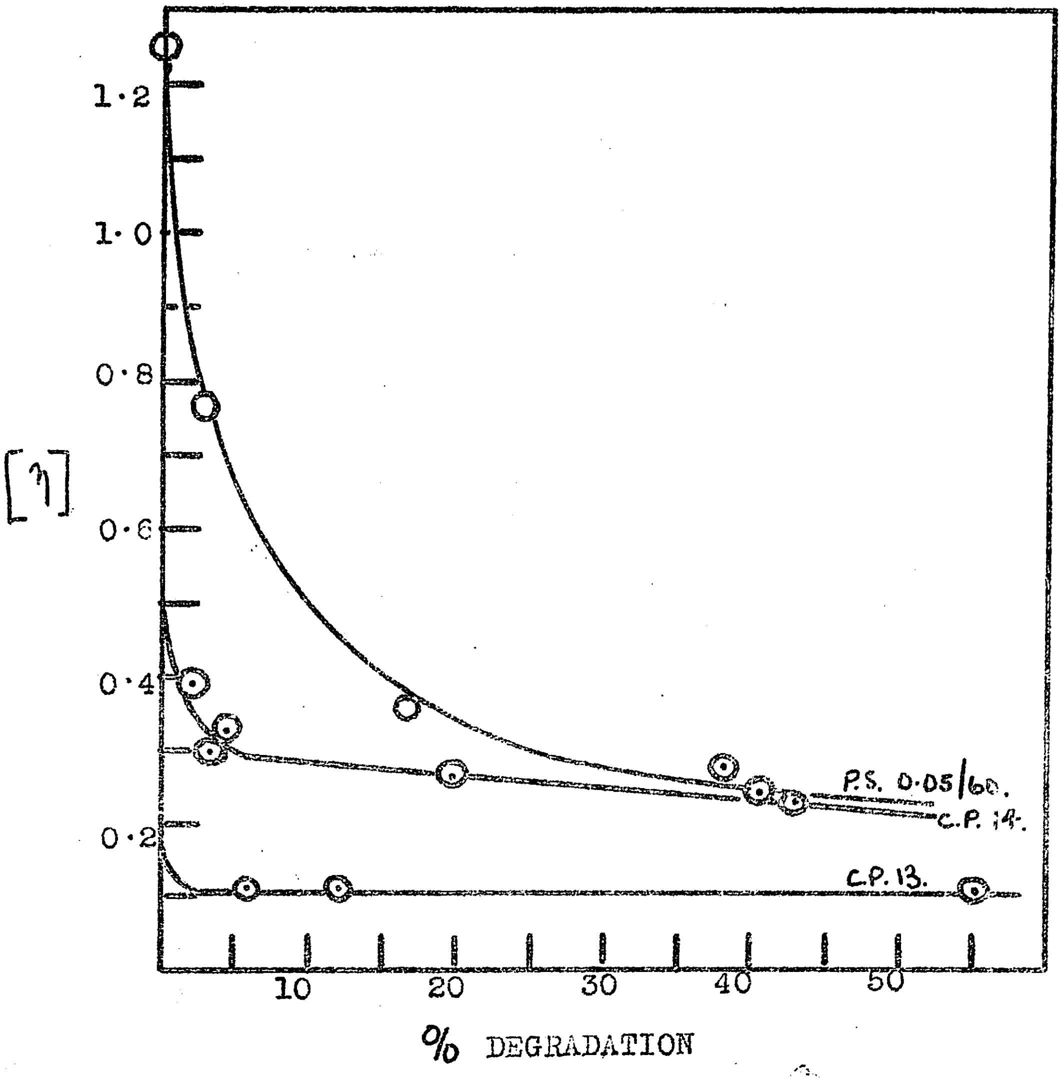


of α-chloroacrylonitrile, namely, C.P.13. and C.P.14. The results obtained are shown in figure 25 where the intrinsic viscosity $[\eta]$ is plotted against %degradation measured by weight loss. The degradation experiments were carried out at various temperatures in the range 220 - 344°C.

Comparison with the corresponding results obtained from a polystyrene sample (P.S. 0·05/60) of similar molecular weight indicate a difference in the reaction mechanisms. The copolymers undergo a very rapid initial fall in molecular weight to values below that of the homopolymer. A gradual decrease with volatilization follows. In the case of C.P.13 the molecular weight remains constant with increasing degradation. The accuracy of the molecular weight determination in this case is questionable since the values being measured $M_v < 10,000$ are below the accurate working range for viscosity determination of molecular weight.

The rapid initial fall in molecular weight over the first few percent degradation suggests that the copolymers undergo a rapid random chain scission reaction which is independent of the ensuing depolymerisation. This is similar to the overall picture of polystyrene degradation except that in the copolymer, chain scission occurs relatively much more readily. Putting this in another way, it may be

FIG. 25.



said that in polystyrene the chain scission and depolymerisation reactions occur simultaneously while in the copolymer, chain scission is complete before significant amounts of depolymerisation have occurred.

Since the only essential difference between the copolymers and the homopolymer is the presence of α-chloroacrylonitrile units in the polystyrene chain, it follows that these units are directly responsible for the rapid initial fall in molecular weight. The α-chloroacrylonitrile units may thus be considered as potential weak links. The molecular weight would therefore be expected to fall to a definite chain length corresponding to the complete rupture of all the weak links. This was shown in figure 25 where it can be seen that the initial fall in molecular weight is dependent on the concentration of α-chloroacrylonitrile units.

Generally, therefore, the introduction of α-chloroacrylonitrile units into a polystyrene chain does not lead to essentially different degradation characteristics. Apparent differences are due to different relative rates of weak link scission and depolymerisation. The degradation studies carried out so far, have been at temperatures above 220°C. If the above reactions occur independently, it should be theoretically possible to separate them simply by lowering the temperature. If, however, the depolymerisation reaction occurs simultaneously with the chain scission, such separation should not be possible. This is investigated in the following section where the above copolymers are degraded at temperatures in the range 155 - 185°C.

(iii) Low Temperature Degradation.

The changes in molecular weight occurring when C.P.13 is heated at 155°C are shown in figure 26. From this and the fact that no significant weight loss was detectable, it may be concluded that at this temperature, chain scission is the sole degradation reaction.

Assuming that the chain scission reaction is due entirely to the α-chloroacrylonitrile units and not to any other inherent weak links. Then

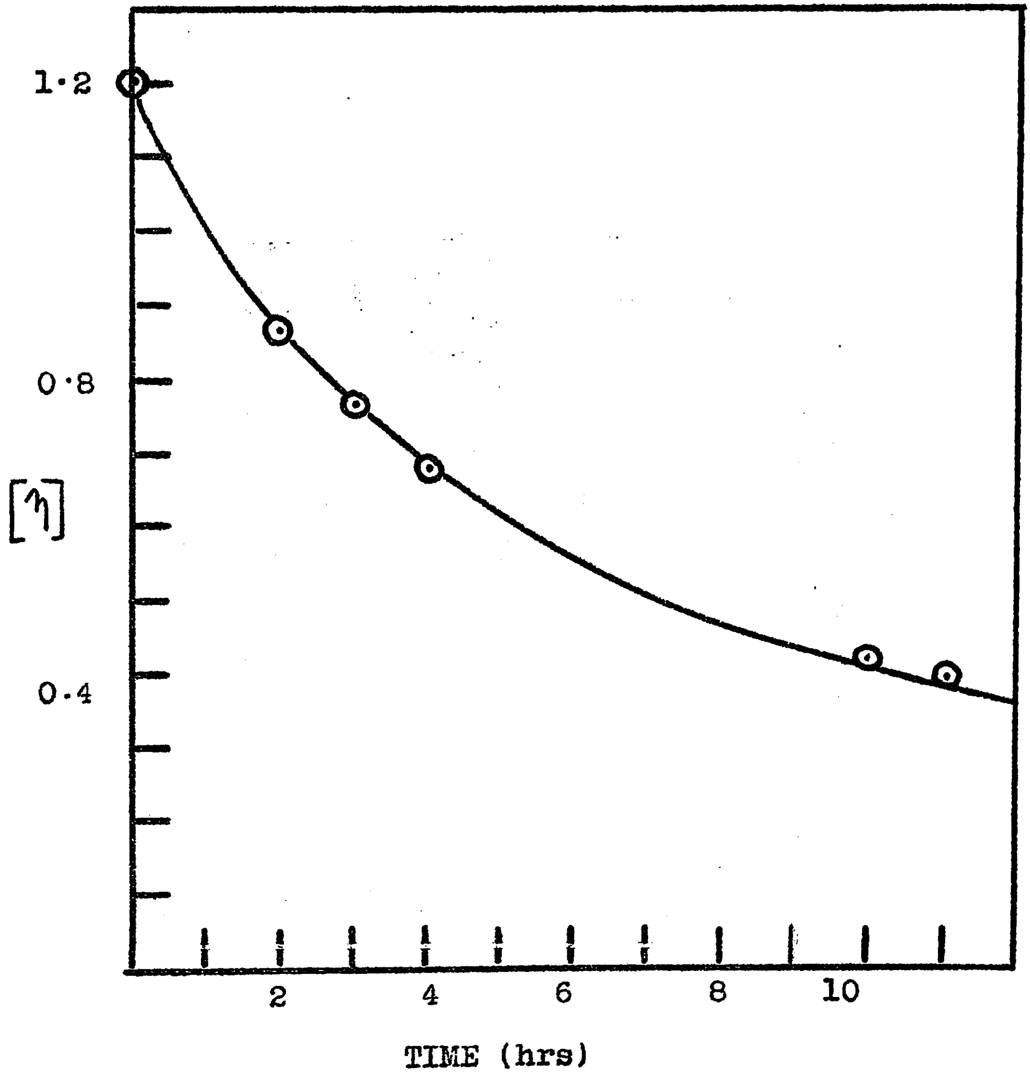
$$-dw/dt = kw \quad \text{———————} \quad ①$$

where w is the number of weak links in the system at time t. Now α the degree of degradation is defined

$$\alpha = s/P_0 - 1$$

which reduces to s/P_0 when P_0 is large, P_0 being the initial chain length and s the average number of links broken per

FIG. 26.



original chain of length P_o.

If w_o is the number of weak links initially present, then

$$w = w_o(1 - \alpha)$$

Substituting and integrating in ①, gives

$$-\ln(1 - \alpha) = kt$$

For small values of α,

$$-\ln(1 - \alpha) \triangleq \alpha$$

Hence

$$\alpha = kt$$

$$\therefore \; s/P_o = kt$$

Since

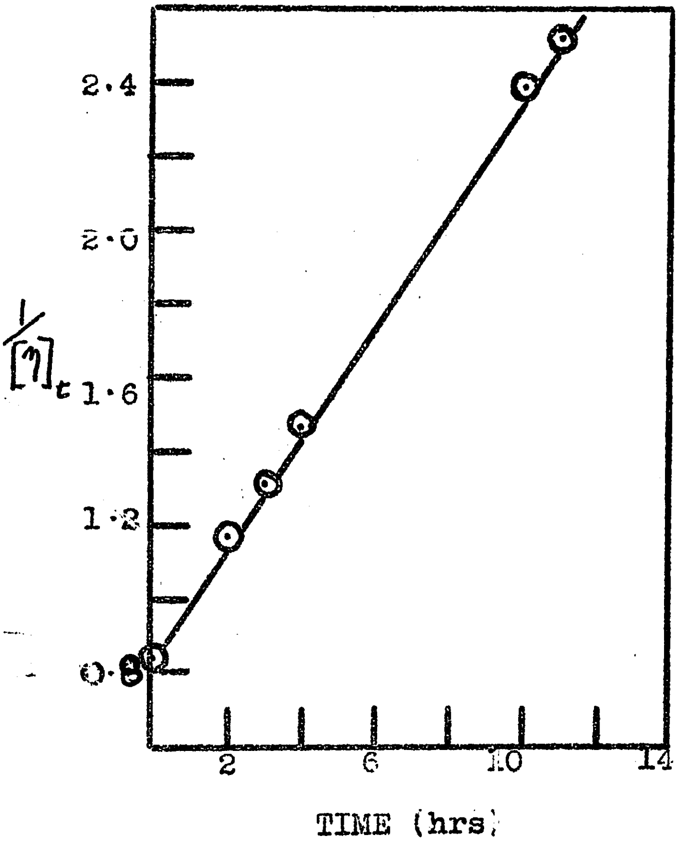
$$s = P_o/P_t - 1$$

$$\therefore \; 1/P_t - 1/P_o = kt \quad \text{———} ②$$

This random chain scission expression holds irrespective of the cause of degradation[68].

Representing the experimental data for C.P.13 at 155 °C by plotting $1/[\eta]_t$ against degradation time, a straight line is obtained (Fig. 27), the intercept corresponding to the

FIG. 27.



experimental value of $1/[\eta]_0$. Linear plots were also obtained for C.P.14 and C.P.27 degraded at 155°C.

The effect of temperature on the chain scission is shown in figure 28, where samples of C.P.14 degraded in the temperature range 155 - 185°C are compared. The rate constants obtained from the slopes of the lines are tabulated in table 10.

Table 10.

Temp. °C	k $\times 10^5$ /sec	log k	$1/T \times 10^3$
155	1·92	-4·7167	2·336
164	3·59	-4·4449	2·289
175	10·95	-3·9605	2·232
185	39·43	-3·5467	2·184

The activation energy of the chain scission reaction obtained from the slope of the Arrhenius plot(Fig. 29) is 40·5 kcal /mole. Similar experiments on C.P.27 gave an activation energy of 41·0 kcal./mole.

Since the amount of hydrogen chloride evolved during the degradation of these low α-chloroacrylonitrile content copolymers is obviously very small and undetectable by weight loss or Pirani gauge measurements, a more sensitive method

FIG. 28.

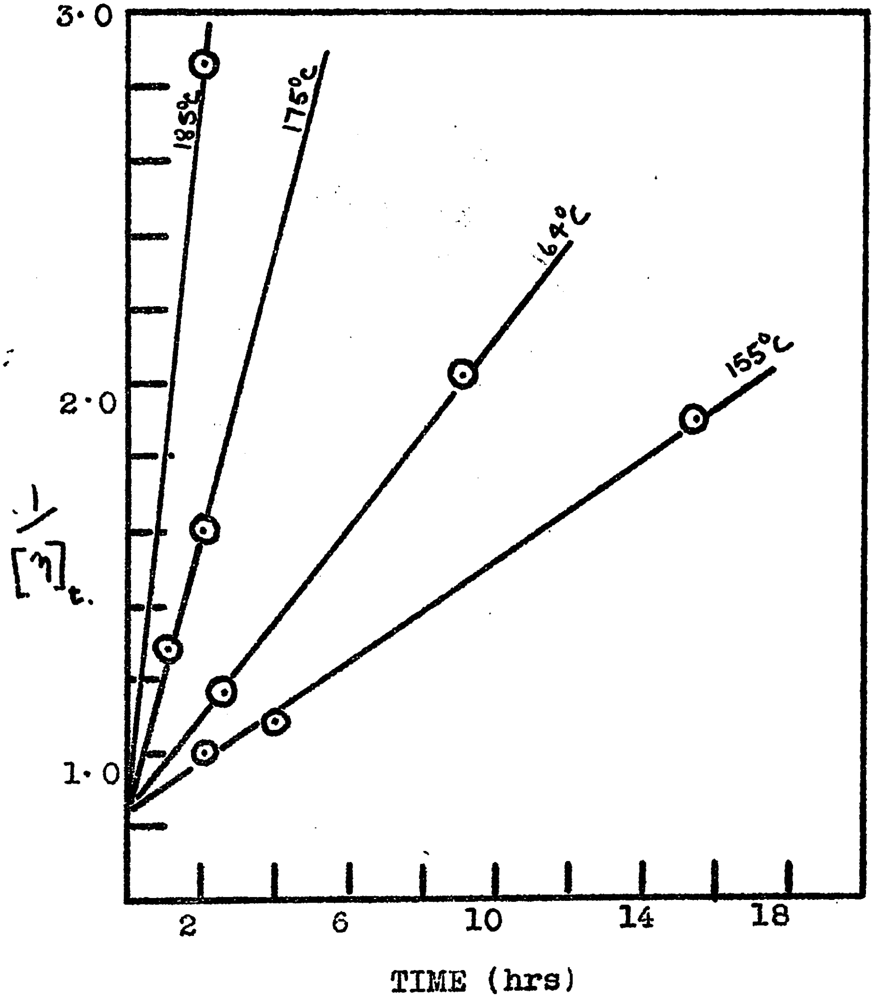
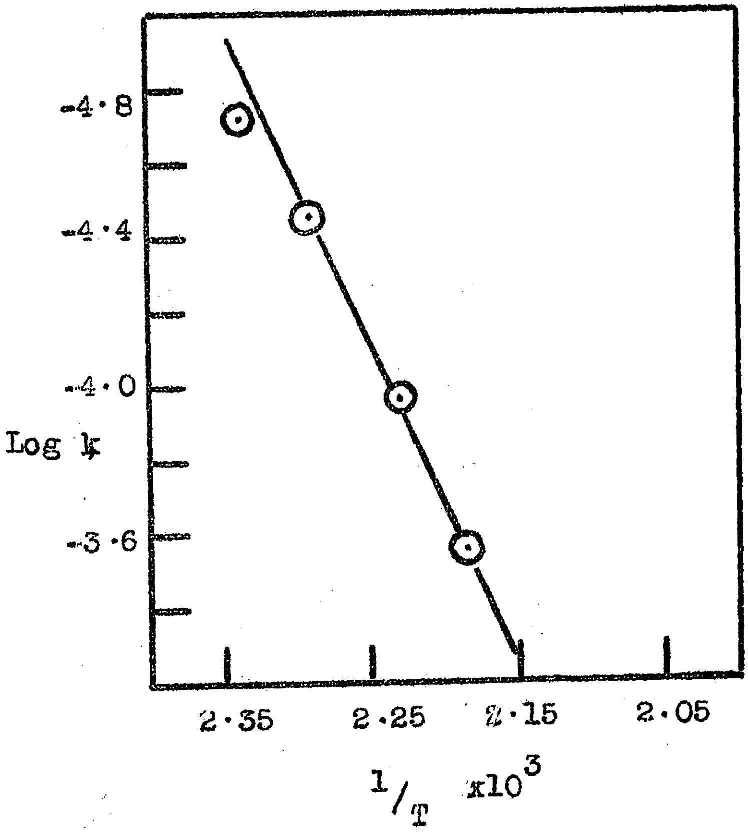


FIG. 29.



is required. Solution in water followed by pH measurement is obviously ideal, amounts as small as 10^{-8} moles of hydrogen chloride being readily detectable.

C.P.27 was heated for varying times at 180°C, the volatile material being dissolved in water and the resulting pH measured. The results obtained are tabulated in table 11 with the corresponding intrinsic viscosities.

Table 11.

Time min.	pH	$[\eta]$
30	5·30	0·980
120	3·90	0·713
180	3·22	0.499

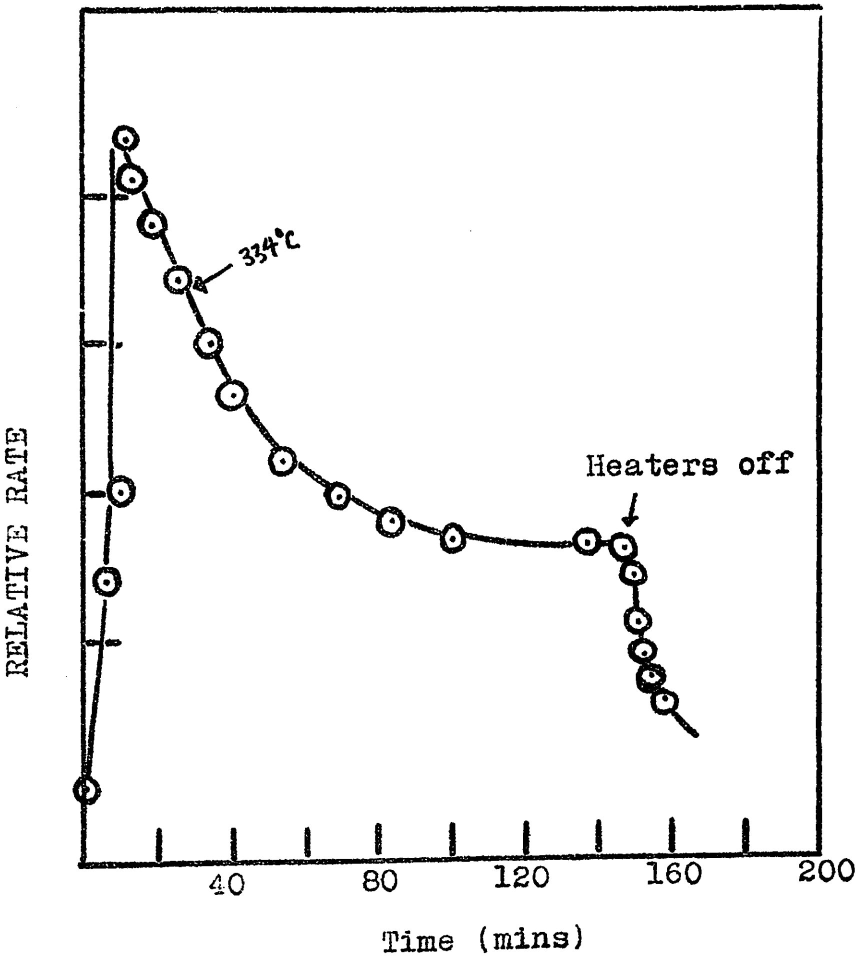
Due to the limitations imposed by the molecular weight determination, it is not possible to relate quantitatively the hydrogen chloride evolved with the number of bonds broken. Nevertheless, this series of experiments has shown that hydrogen chloride is evolved while chain scission is occurring. A natural assumption from this is that the two reactions must be related, since no other degradation reaction is known to occur with polystyrene at such a low temperature.

(iv) High Temperature Degradation.

This section deals with the degradation of the copolymers at temperatures (> 250°C) above that required for weak link scission. At these temperatures the predominant reaction is depolymerisation. Figure 25 showed that after the initial chain scission, the molecular weight decreased gradually with increasing degradation as was the case for polystyrene after weak link scission is complete. A typical Pirani plot for C.P.27 degraded at 334°C is shown in figure 30. From this it can be seen that the rate of depolymerisation does not pass through a maximum value as in the case of polystyrene. This discrepancy is due to the difference in the rate of chain scission between the copolymer and the homopolymer. Thus, since the rate of depolymerisation depends on the number of chain ends present, it goes through a maximum at about 25% degradation in polystyrene while in the copolymer in which weak link scission is complete early in the depolymerisation the rate decreases continuously from a maximum value. It follows therefore, that the reaction occurring on heating the copolymers at high temperatures is similar to that occurring in polystyrene after weak link scission is complete.

A summary of a series of degradation experiments on the copolymers in this temperature range is shown in table 13.

FIG. 30



These results indicate that under similar temperature conditions the copolymer depolymerises more readily than the homopolymer. Such a result is expected since the more rapid rate of chain scission in the copolymer results in the more rapid build up in the concentration of degradable chain ends.

5. DISCUSSION.

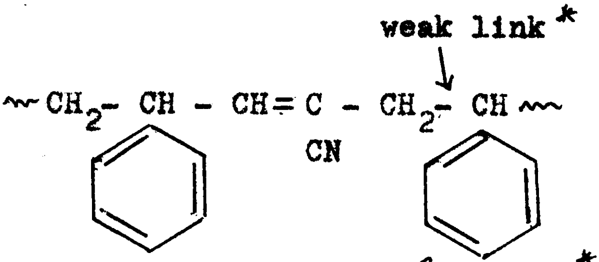
Before discussing the reactions occurring during the thermal degradation of styrene / α-chloroacrylonitrile copolymers and their subsequent contribution to the 'Weak Link Theory', it would be opportune at this point to compare the degradation characteristics of the copolymer with those of the homopolymer.

It has been established that the copolymer undergoes two separate reactions, namely, random chain scission and depolymerisation. The chain scission reaction can be followed in the temperature range 155 - 185°C. For depolymerisation to occur, higher temperatures are required. In the case of polystyrene similar reactions occur but from the shape of the degradation curve it can be seen that both reactions take place simultaneously, chain scission being complete at approximately 25% degradation. Obviously, the structures responsible for the chain scission reaction in the copolymer are far more labile than the corresponding structures in the homopolymer. The effect of the differing rates of weak link scission on the depolymerisation process can be readily seen from a study of the corresponding Pirani rate curves. In the case of the homopolymer the rate goes through a maximum value at 25% degradation whereas in the copolymer the rate decreases continuously from a maximum value.

(i) Mechanism of Chain Scission.

Since no chain scission is known to occur in polystyrene at temperatures as low as 155°C, it is therefore assumed that the α-chloroacrylonitrile units are responsible for this reaction. The effect of inherent or natural weak links is therefore neglected.

In chapter 4 it was shown that the decomposition of poly-α-chloroacrylonitrile was initiated by scission of the C - Cl bond, the energy of initiation being 59 kcal. Since weak link scission of the copolymer and the evolution of hydrogen chloride occur in the same temperature range as that required to decompose poly-α-chloroacrylonitrile, it follows that the initiation step in the copolymer degradation is also most probably scission of the C - Cl bond. On dehydrohalogenation, an unsaturated bond would be formed in the polymer backbone,



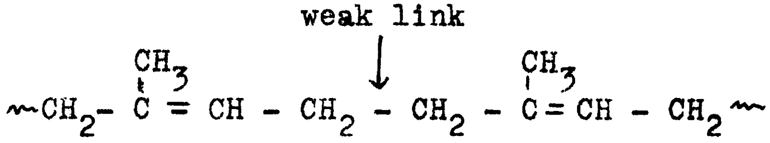
The carbon - carbon bond in the βposition* to the unsaturated bond should therefore be considerably weaker than the normal carbon - carbon bonds. Table 12 shows the bond dissociation energies for similar model compounds.

Table 12.

System	Dissoc. Energy kcal.	Stabilisation Energy	Ref.
C - C	81·0	-	69
$CH_2 = CH - CH_2 — CH_3$	62·0	19·0	70
$C_6H_5 - CH_2 — CH_3$	63·0	18·0	71

From table 12 it can be seen that the bond dissociation energy for a carbon - carbon bond in the βposition to an unsaturated group is reduced by 19 kcal. In the copolymer this value may be modified somewhat by the presence of the conjugated nitrile group.

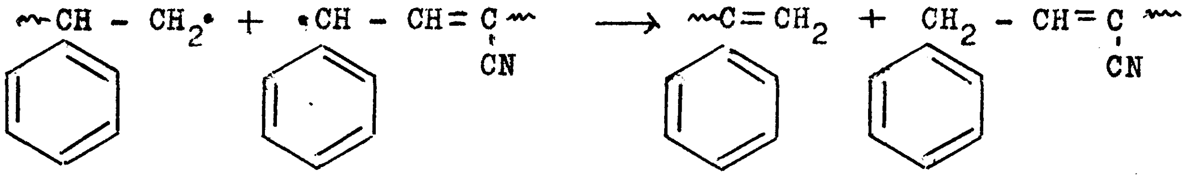
Applying these values to the labile carbon-carbon bond which is activated by both the unsaturated structure and the benzene ring, the expected dissociation energy would be 81-19-18 = 44 kcal., which is comparable with that obtained experimentally (41 kcal.). A similar situation arises in polyisoprene,



$$\sim CH_2-\overset{CH_3}{C}=CH-CH_2\overset{\text{weak link}}{\overset{\downarrow}{-}}CH_2-\overset{CH_3}{C}=CH-CH_2\sim$$

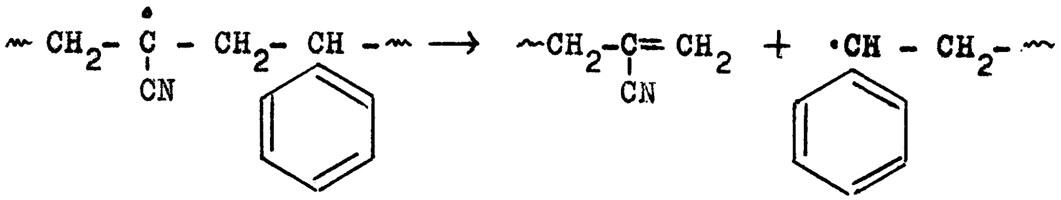
which decomposes by a chain scission mechanism at ~200°C. Jellinek[72] predicts E_A for this chain scission to be 43 kcal.

The radicals formed in the chain scission reaction could form stable molecules by a hydrogen transfer mechanism,

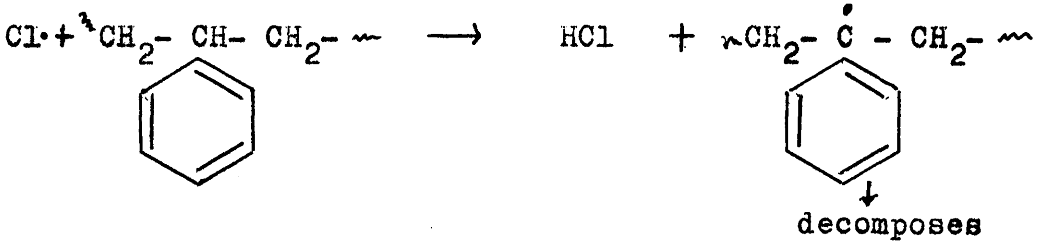


The presence of these unsaturated groups at the chain ends would readily initiate the depolymerisation reaction.

The radical formed by the initial rupture of the C - Cl might conceivably undergo an alternative radical decomposition reaction which would lead to chain scission and the liberation of hydrogen chloride. This may be represented,



This chain scission reaction may occur directly as in the above case or as result of attack of the initially formed chlorine radical on a labile tertiary hydrogen atom,



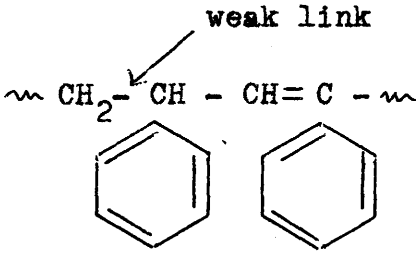
Steacie[73] suggests an activation energy of ~24 kcal for the decomposition of a non conjugated radical. In the above examples both decomposing radicals are resonance stabilised, hence, if it is assumed that this resonance stabilisation energy is approximately 19 kcal as evaluated in table 12, the expected value for the decomposition of the above radicals would be $24 + 19 = 43$ kcal.

Due to the energetic similarities between the two mechanisms, it is not possible at this stage to decide which one is responsible for the chain scission. It seems possible that both mechanisms may contribute to the overall chain scission reaction.

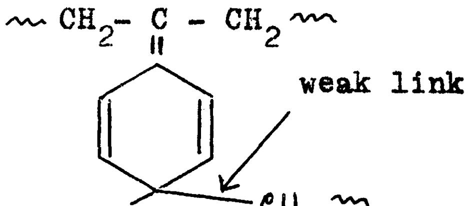
(ii) The Degradation of Styrene/α-Chloroacrylonitrile Copolymers and the Weak Link Theory.

In this respect, the use of styrene/α-chloroacrylonitrile copolymers has not been as successful as first hoped. The rapid chain scission at low temperatures combined with the inability to distinguish the mechanism responsible for this, makes it extremely difficult to form any definite conclusions. However, if it is assumed that the chain scission follows upon the formation of unsaturated bonds in the polymer backbone, some conclusions concerning the effect of unsaturated centres on the stability of polystyrene may be derived.

Cameron and Grassie suggest that the following two labile structures,



I



II

may be inherently present in the polymer. Structure I could be formed by transfer between the polystyrl radical and the tertiary hydrogen atom. The mode of formation of structure II has already been mentioned. In both cases a carbon - carbon bond in the β position to two unsaturated structures results. Comparing structures I and II, on the basis of the activating influence of the unsaturated groups, with that responsible for chain scission in the copolymer would seem to indicate that these structures should produce chain scission at lower temperatures than that observed. Since this is not the case the structures proposed by Cameron and Grassie could not be inherently present in the polymer.

It must be emphasised once again that the above conclusions are entirely speculative and are based on the assumption that the chain scission in the copolymer is due to the presence of unsaturated centres in the polymer backbone and not to the equally probable radical decomposition mechanism.

Table 13.

Summary of Degradation Experiments.

Polymer	Temp. °C	Time of Heating (Hrs.)	%volatilisation	$[\eta]$
P.S. 0·05 /60	322	1	2·7	0·762
"	328	3	16·4	0·358
"	334	2	16·0	0·295
"	334	4	38·0	0·275
"	347	1¼	40·2	0·242
C.P.13	226	2	5·7	0·11
"	240	2	12·0	0·11
"	322	1	55·0	0·11
"	155	2	-	0·86
"	155	3	-	0·76
"	155	4	-	0·68
"	155	10	-	0·41
"	155	11	-	0·39
C.P.14	226	2	3·1	0·297
"	226	8	4·3	0·33
"	290	1½	19·8	0·26

Table 13 cont.

Polymer	Temp. °C	Time of Heating	%volatilisation	$[\eta]$
C.P.14	322	1	42·8	0·22
"	155	2	-	1·00
"	155	4	-	0·93
"	155	15¼	-	0·527
"	164	2½	-	0·86
"	164	9	-	0·497
"	175	1	-	0·78
"	175	2	-	0·625
"	185	2	-	0·35
C.P.27	155	3	-	1·05
"	155	8	-	0·98
"	170	2	-	0·86
"	170	4	-	0·78
"	180	½	-	0·98
"	180	2	-	0·713
"	180	3	-	0·50

CHAPTER 6.

THE THERMAL DEGRADATION OF METHYL METHACRYLATE/α-CHLOROACRYLONITRILE COPOLYMERS.

1. INTRODUCTION.

In the previous chapter, it was shown that the incorporation of a small number of α-chloroacrylonitrile units into a polystyrene chain fundamentally altered the degradation characteristics from that of the homopolymer. The exact nature of the resulting rapid chain scission reaction which occurred on heating at temperatures above 155°C was not determined. The experimental data, however, indicated that dehydrochlorination of the α-chloroacrylonitrile units was in some way associated with this chain scission. A similar investigation using another copolymer system would therefore be of considerable interest. Not only would it be comparable with that of the styrene/α-chloroacrylonitrile system but might possibly provide further information about the mechanism responsible for the chain scission.

It was decided, therefore, to carry out a similar investigation using copolymers of methyl methacrylate and α-chloroacrylonitrile. Factors which favour the choice of methyl methacrylate are :

(a) the decomposition mechanism of the homopolymer is well understood.

(b) complicating side effects, arising from transfer reactions through labile tertiary hydrogen atoms as in polystyrene, are avoided.

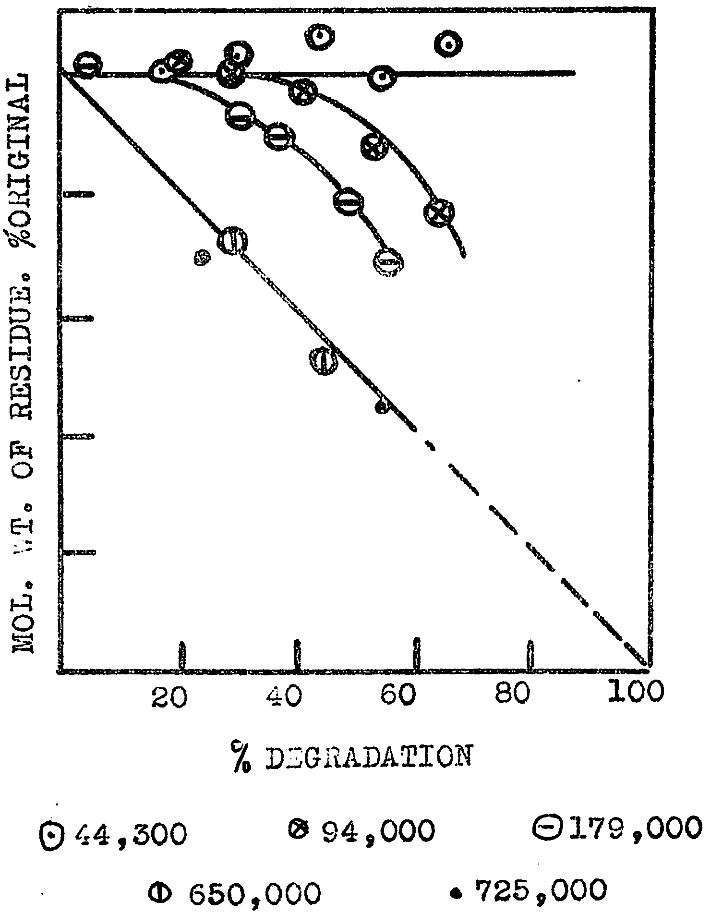
(c) the polymer is comparatively stable at the temperatures at which decomposition of the α-chloroacrylonitrile units occur.

(d) the reactivity ratios of the system are more favourable than those of the styrene/α-chloroacrylonitrile system.

(i) The Thermal Degradation of Polymethyl Methacrylate

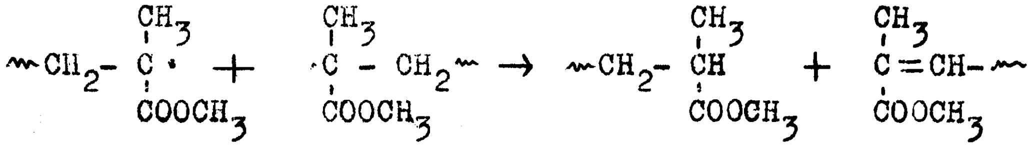
Polymethyl methacrylate is one of the few examples of a polymeric system which decomposes to give near quantitative yields of monomer. Grassie and Melville[5] showed that the decomposition could be regarded as a simple reverse polymerisation reaction. The molecular weight changes taking place during degradation are shown in figure 31. For low molecular weight material, it was found that complete unzipping of the chains occurred, the molecular weight of the residue being maintained at its initial value. For high molecular weights (>300,000), where the molecular chain length

FIG. 31.



MOL. WT. OF RESIDUE. %ORIGINAL
20
40
60
80
100
% DEGRADATION
⊙ 44,300
⊗ 94,000
⊖ 179,000
⦶ 650,000
• 725,000

is greater than the kinetic zip length, the molecular weight curve lies along the diagonal. From the shape of the curves it was evident that the depolymerisation was initiated at the chain ends. In this polymer the disproportionation termination reaction during polymerisation results in 50% each of the molecules being terminated by saturated and unsaturated chain ends,



$$\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot + \cdot\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2\sim \rightarrow \sim CH_2-\overset{CH_3}{\underset{COOCH_3}{CH}} + \overset{CH_3}{\underset{COOCH_3}{C}}=CH-\sim$$

Grassie and Melville were also able to show that not all chain ends were equally vulnerable, since only 50% of the polymer sample was degradable at 220°C, a higher temperature being required to volatilise the residue. This suggested that one of the above chain ends was more labile than the other. Grassie and Vance[16] have presented evidence to show that the unsaturated end group was the more labile.

2. THERMAL DEGRADATION.

(i) The Decomposition Products.

The relative rate of the evolution of volatile material when C.P.16 is heated to 200°C in the still is shown in figure 32. From this it can be seen that evolution of volatile material occurs at temperatures above 150°C. Examination of this material indicated that two components were present. The first, which was gaseous at room temperature, soluble in water and giving a strong acid solution was hydrogen chloride. Infra-red and V.P.C. analysis of the second component, which was a clear liquid at room temperature, showed the presence of methyl methacrylate monomer.

(ii) Molecular Weight Changes .

The changes in intrinsic viscosity occurring when C.P.16 is heated in the temperature range 145 - 170°C are shown in figure 33. Comparison with the results obtained by Grassie and Melville (Fig. 31) for polymethyl methacrylate demonstrate that the copolymer undergoes a different decomposition mechanism. The rapid initial fall in molecular weight suggests the presence of a random chain scission reaction similar to that occurring in polystyrene and styrene/α-chloroacrylonitrile copolymers.

In figure 34 the relative decrease in molecular weight for C.P.16 and C.P.19 is plotted against the %degradation. From this graph it can be seen that the extent of molecular weight decrease is independent of the degradation temperature and is dependent on the concentration of α-chloroacrylonitrile

FIG. 32.

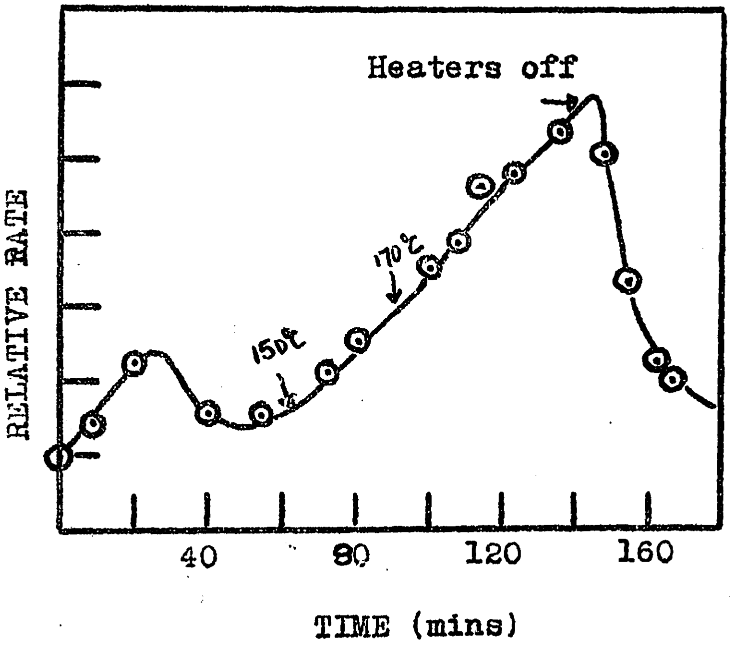


FIG. 33.

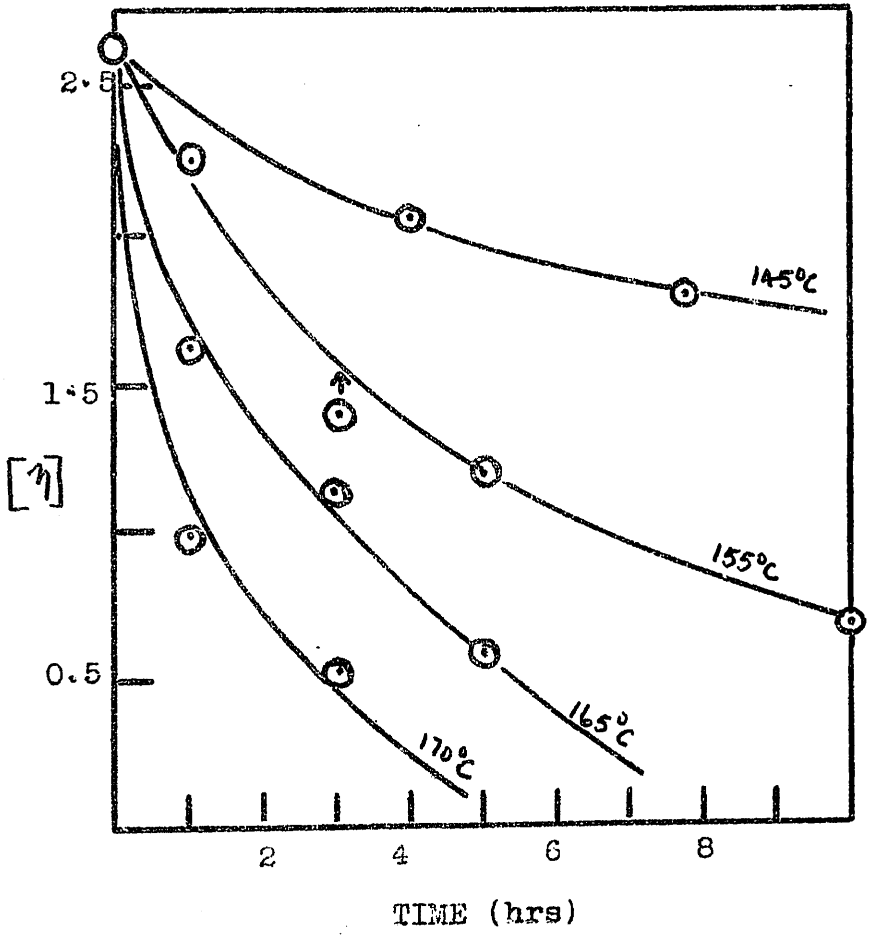
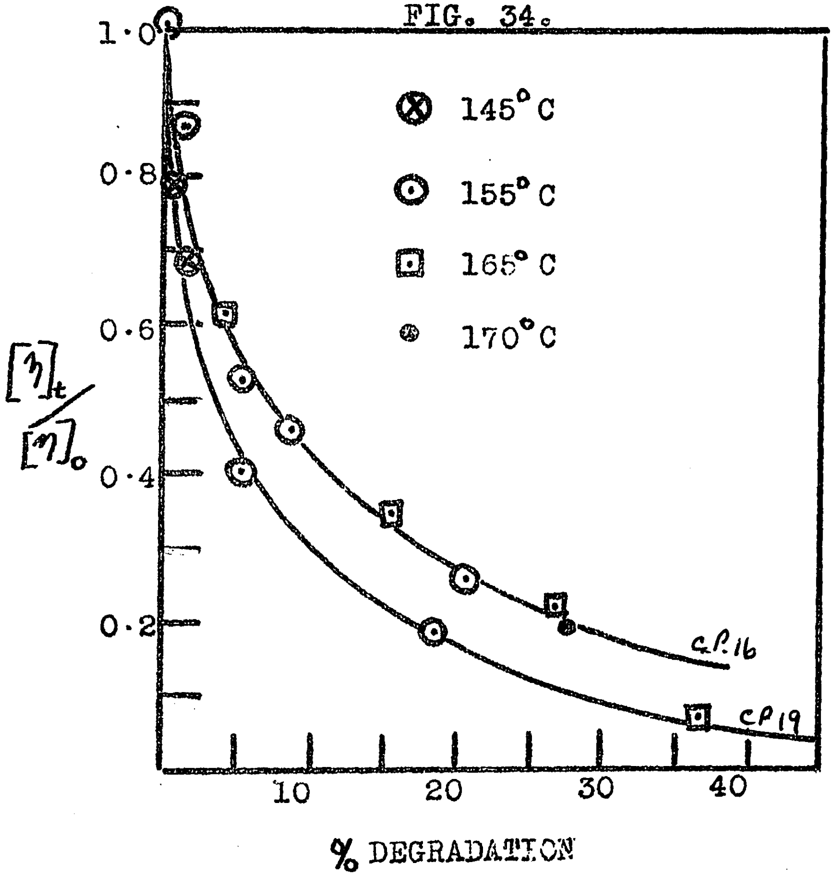


FIG. 34.


1·0
0·8
0·6
0·4
0·2
⊗ 145° C
⊙ 155° C
⊡ 165° C
● 170° C
$[\eta]_t / [\eta]_o$
10
20
30
40
% DEGRADATION
C.P.16
CP19

units. Since depolymerisation is also taking place, as indicated by the presence of monomer in the decomposition products, the curves obtained are similar in appearance to those obtained for polystyrene.

As the α-chloroacrylonitrile units are distributed at random in the copolymer, chain scission dependent on these units must also be of a random nature. It was shown for the styrene/α-chloroacrylonitrile copolymers that the initial stages of the resulting random chain scission could be represented by,

$$1/P_t - 1/P_o = kt$$

where P_o and P_t are the chain lengths initially and at time t respectively. k is a rate constant. Provided the zip length of the depolymerisation is not large compared with the molecular chain length, a similar relationship should hold for the methyl methacrylate/α-chloroacrylonitrile system. This was verified, using C.P.16 degraded in the range 145 - 170°C, by plotting $1/[\eta]_t$ against time of heating (Fig.35.) The intercept of the resultant linear plots corresponded to the experimentally determined value of $1/[\eta]_o$. The rate constants calculated from the slopes of the straight lines are shown in table 14.

FIG. 35.

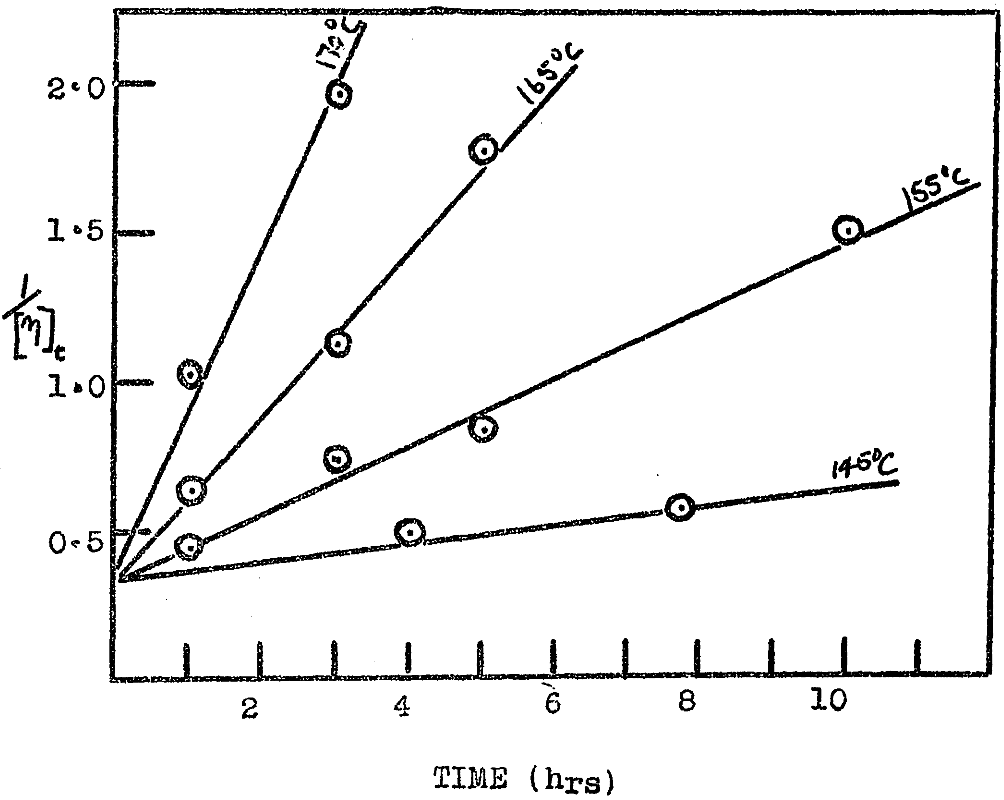


Table 14.

Temp. °C	k x10^3 /sec	log k	1/T x10^3
145	0·531	-3·2749	2·392
155	1·925	-2·7156	2·336
165	4·67	-2·3307	2·283
170	9·58	-2·0186	2·257

The activation energy of the chain scission reaction, calculated from the slope of the linear Arrhenius Plot (Fig.36), was found to be 43 kcal/mole which is similar in magnitude to that obtained for the corresponding chain scission in the styrene/α-chloroacrylonitrile copolymer.

(iii) Production of Monomer.

From figure 37 it can be seen that in the initial stages of the chain scission, the monomer produced follows a linear relationship with the time of heating. A comparison of these plots with the corresponding chain scission data (Fig.35) indicates that the evolution of monomer runs parallel to the number of chain ends. It follows, therefore, that as random chain scission takes place, unzipping of monomer units occurs at the newly formed chain ends.

FIG. 36.

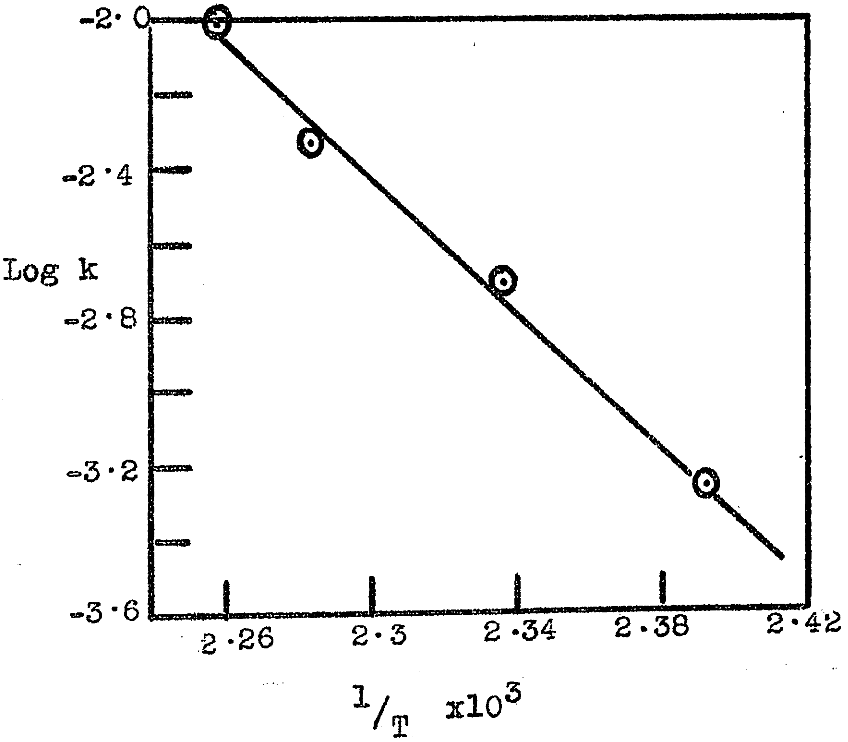
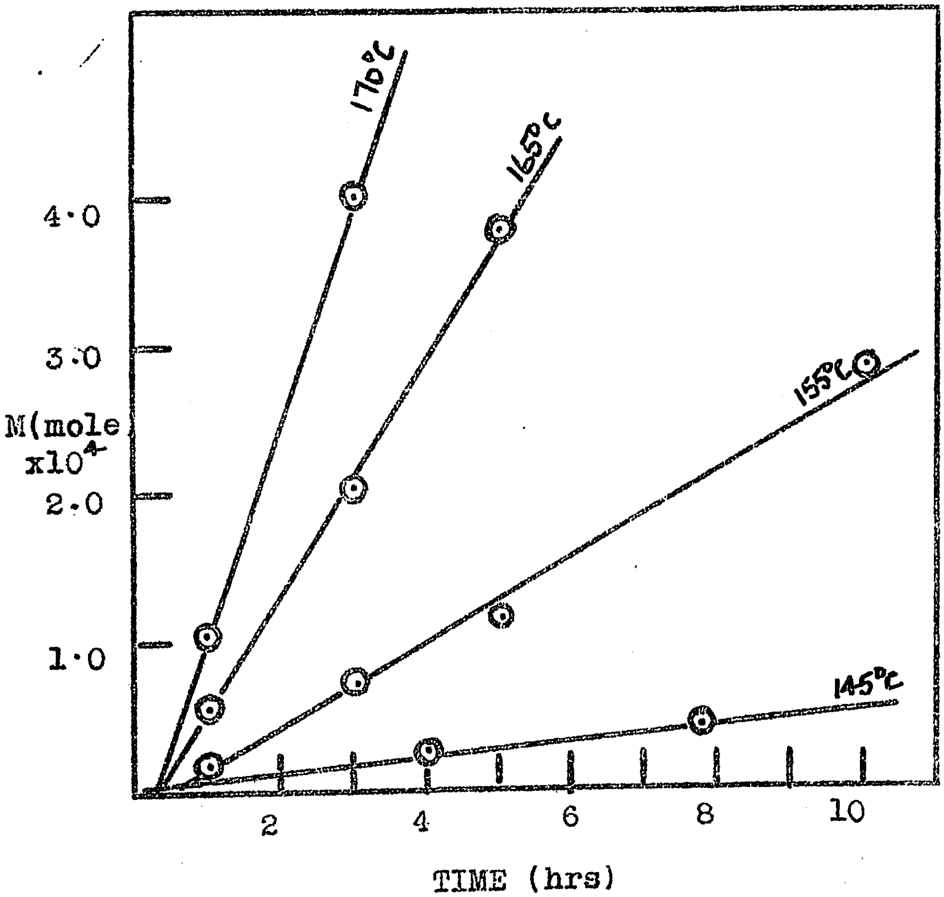


FIG. 37.



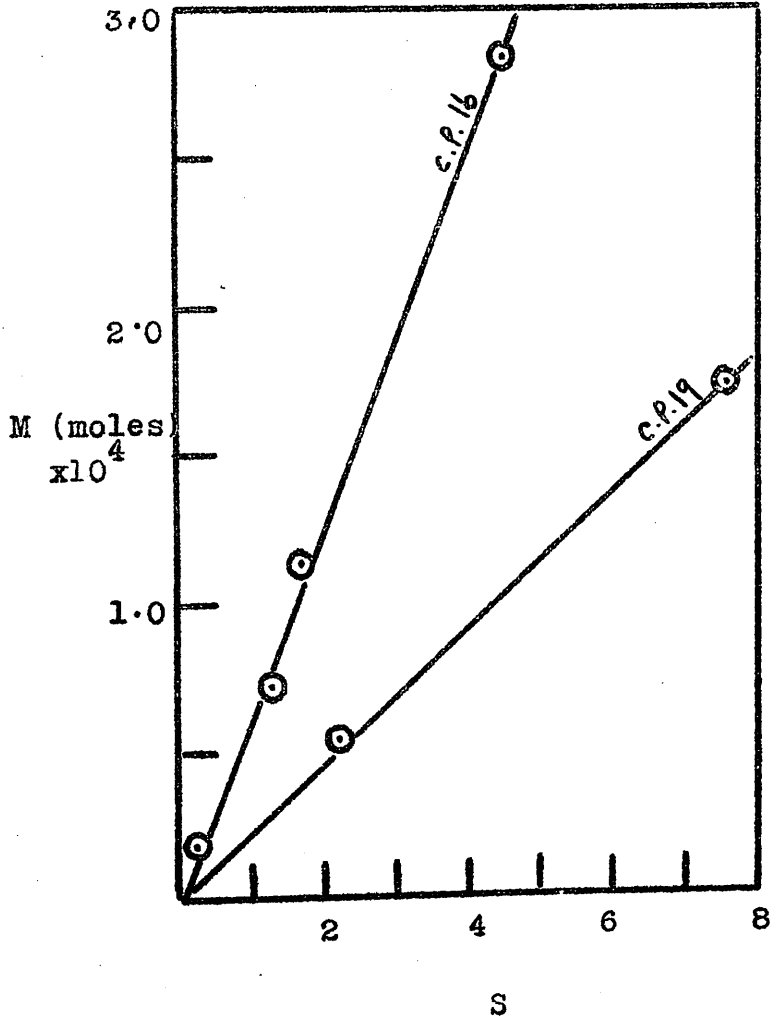
(iv) Variation of Copolymer Concentration.

The resulting increase in the number of weak links corresponding to an increase in the concentration of α-chloroacrylonitrile units in the copolymer has already been shown in figure 34 for C.P.19 and C.P.16. The number of α-chloroacrylonitrile units present also influences the production of monomer as shown in figure 38, where the amount of monomer produced for C.P.16 and C.P.19 degraded at 155°C is plotted against the average number of chain scissions **s** per original chain. Assuming that the chain length of the depolymerisation reaction is small, an approximate value of **s** can be obtained from the viscosity data using,

$$s = P_o / P_t - 1$$

It will be shown later that the chain length of the depolymerisation reaction is in actual fact quite small. The slopes of the obtained linear plots (Fig.38) were inversely proportional to the concentrations of the α-chloroacrylonitrile units in the copolymers. From this it may be concluded that the kinetic chain length of the depolymerisation reaction is dependent on the number of methyl methacrylate units between successive α-chloroacrylonitrile groups.

FIG. 38.

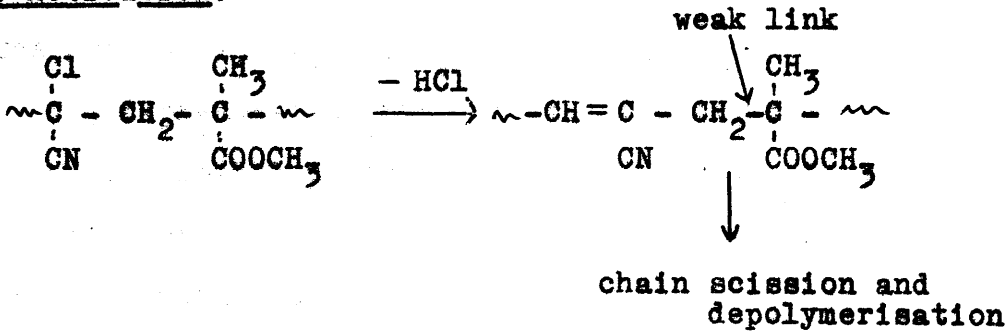


3. DISCUSSION.

(i) General.

From the molecular weight data, it can be, seen that styrene / α-chloroacrylonitrile and methyl methacrylate/ α-chloroacrylonitrile copolymers exhibit similar chain scission properties when heated in vacuum in the temperature range 145 - 185°C. This combined with the close correlation in activation energies suggests that the basic reaction taking place is the same in both copolymers. Since dehydrochlorination of the α-chloroacrylonitrile units occurs in parallel with chain scission, they are most probably related in some way. In the previous chapter, two possible mechanisms of dehydrochlorination which could also account for the chain scission were proposed. Similar arguments may be applied to the methyl methacrylate/α-chloroacrylonitrile copolymer as shown below;

Allylic Activation.

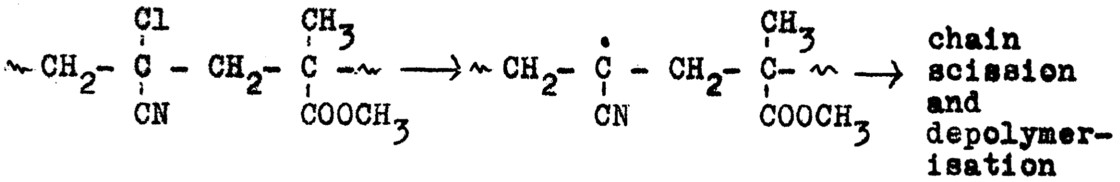


$$\sim\underset{CN}{\overset{Cl}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\sim \xrightarrow{-HCl} \sim-CH=\underset{CN}{C}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\sim$$

weak link

chain scission and depolymerisation

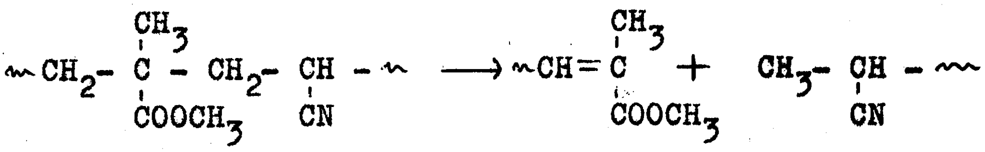
Radical Decomposition.



$$\sim CH_2-\overset{Cl}{\underset{CN}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-\sim \longrightarrow \sim CH_2-\overset{\bullet}{\underset{CN}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-\sim \longrightarrow \text{chain scission and depolymerisation}$$

In both mechanisms, using a similar thermochemical treatment as applied to the styrene/α-chloroacrylonitrile system, the theoretically expected activation energy of the chain scission reaction would be approximately 43 kcal/mole which is in agreement with the experimentally determined value. Like the styrene/α-chloroacrylonitrile copolymer system it is not possible from the experimental data to decide which mechanism is responsible for the chain scission. The results from the methyl methacrylate system, however, indicate that it may not be necessary to invoke transfer reactions involving labile tertiary hydrogen atoms to explain the behaviour of the styrene/α-chloroacrylonitrile system.

The outstanding difference between the two copolymer systems is the presence of monomer in the decomposition products of the methyl methacrylate copolymers. Such a result is not unexpected from a consideration of the stabilities of the corresponding homopolymers. The close correspondence between the amount of monomer produced and the number of chain ends indicates that depolymerisation takes place from the newly formed radical centres. Grassie and Melville obtained a similar molecular weight curve for methyl methacrylate/acrylonitrile copolymers degraded at 220° C. However, in their case an induction period, during which the molecular weight decreased rapidly, occurred before depolymerisation was detectable. The above authors explained this on the basis of a disproportionation chain scission reaction forming stable chain ends,



$$\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\underset{CN}{CH}-\sim \longrightarrow \sim CH=\overset{CH_3}{\underset{COOCH_3}{C}} + CH_3-\underset{CN}{CH}-\sim$$

The absence of a similar induction period and the high initial rate indicates that this does not hold for the methyl methacrylate/α-chloroacrylonitrile copolymers.

(ii) Reaction Mechanism.

The above experimental results can be explained in terms of a random chain scission process with production of monomer from the newly formed chain ends. This can be represented.

Initiation $M_n \longrightarrow P_i^{\bullet} + P_{n-i}^{\bullet}$

Depropagation $\qquad P_i^{\cdot} \longrightarrow P_{i-1}^{\cdot} + M$

Termination $\qquad P_s^{\cdot} \longrightarrow M_s$

Where M_n, P_i, M and M_s represent the undegraded polymer molecules, the depolymerising polymer radicals, monomer and dead polymer molecules respectively. From this scheme it can be seen that,

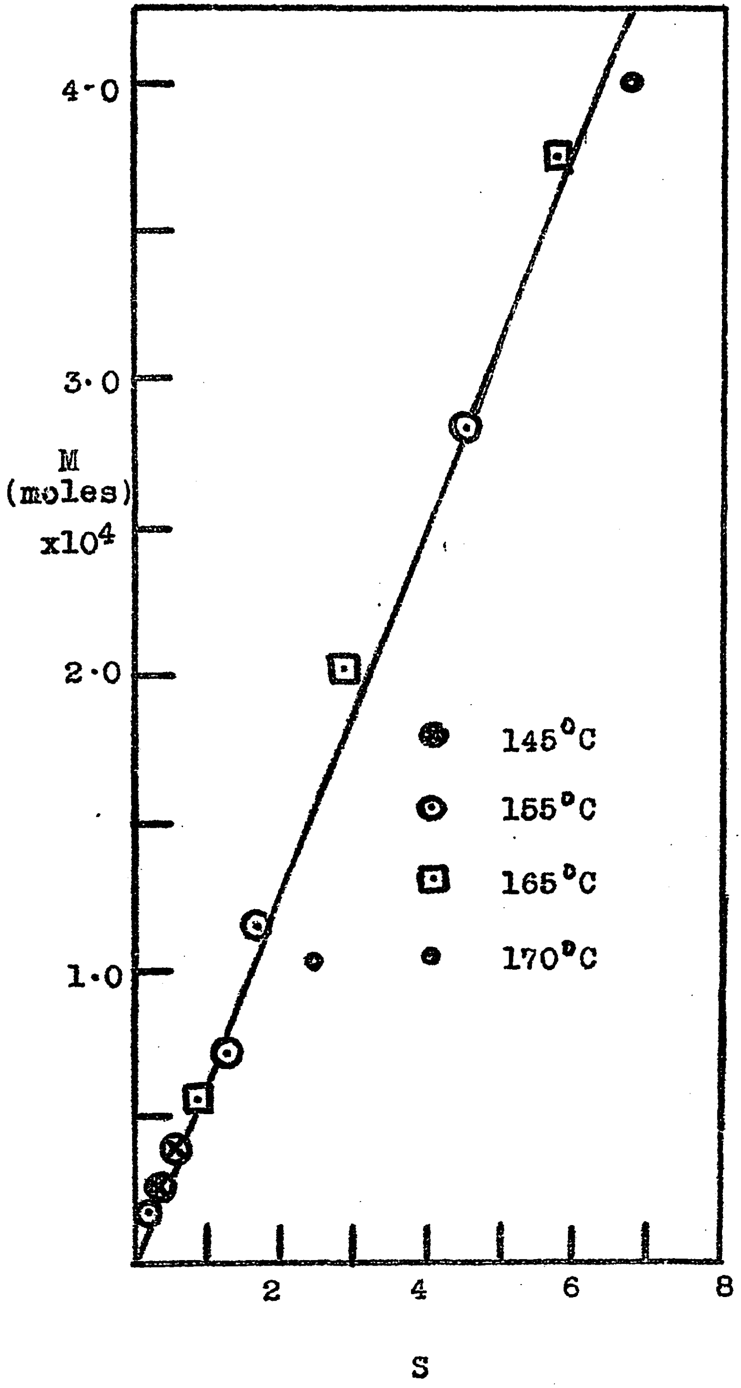
$$dM/_{dt} = \epsilon\, ds/_{dt}$$

where ϵ and s represent the kinetic chain length of the depolymerising radicals and the average number of chain scissions per original chain. For the early stages of the degradation this can be simplified to,

$$M = \epsilon N = \epsilon sw/_{M_n}$$

where N and w represent the total number of scissions and the weight of sample degraded(0·15gm) respectively. This was verified for the degradations carried out at 155°C as shown in figure 38. However, on plotting the corresponding values of M and s for the degradations in the range 145 - 170°C, it was found that the value of ϵ remained constant (Fig.39). The most obvious explanation for this is that the unzipping

FIG. 39.



chain radical is being terminated when it reaches the next α-chloroacrylonitrile unit. Such a termination step would be first order, which is in agreement with the proposed kinetic scheme. If, however, the termination step was bimolecular, the relationship between the monomer evolved and the number of chain scissions would be,

$$M = \xi N^{1/2}$$

A linear relationship.was not obtained on substitution of the experimental data into this equation.. Also, the probability of termination by radical combination in the initial stages would be low due to the relative immobility of the polymer radicals.

From figure 39 it is calculated that for C.P.16 four monomer units are liberated per chain break. Considering the limited accuracy of the molecular weight determinations, this is of a similar magnitude to the theoretically expected value (14 units) calculated from the copolymer composition.

It is therefore concluded that the simple kinetic scheme proposed, satisfactorily represents the decomposition mechanism of methyl methacrylate/α-chloroacrylonitrile copolymers when heated in the temperature range 145 - 170°C.

Table 15.

Summary of Degradation Experiments.

C.P.16.

Temp. °C	Time of heating (hrs)	[η]	M_v x10	s	M (moles) x10^4	%Degdn
145	4	2·05	615	0·346	0·249	0·33
"	7½	1·78	530	0·565	0·387	1·56
155	1	2·25	689	0·210	0·177	1·20
"	3	1·36	367	1·26	0·718	5·38
"	5	1·19	311	1·66	1·148	8·60
"	10	0·67	151	4·49	2·835	20·60
165	1	1·60	450	0·842	0·551	3·94
"	3	0·90	219	2·79	2·018	15·3
"	5	0·57	124	5·69	3·75	26·6
170	1	0·98	244	2·4	1·038	6·45
"	3	0·51	107	6·7	4·00	27·30

C.P.19.

Temp. °C	Time of heating (hrs)	[η]	M_v x10	s	M (moles) x10^4	%Degdn
155	1	0·80	189	2·19	0·532	5·44
"	2	0·37	71	7·53	1·720	18·54

CHAPTER 7.

GENERAL DISCUSSION.

1. SUMMARY.

It is clear from the studies of both the bulk polymerisation of α-chloroacrylonitrile and the thermal degradation of the resulting polymer that, α-chloroacrylonitrile, which can be considered either as a cyano substituted vinyl chloride or as a chloro substituted acrylonitrile, exhibits generally properties characteristic of the former.

Studies on the bulk polymerisation of α-chloroacrylonitrile described in chapter 3, show that heterogeneous conditions prevail, the polymer formed being insoluble in the monomer. Like other heterogeneous systems, it was found that the rate of polymerisation increases with conversion. This accelerative effect has been attributed to surface transfer reactions between a radical centre and the precipitated polymer. The chlorine atom in this case would be very easily abstracted due to resonance stabilisation of the resulting radical. Molecular weight studies of the polymers formed support this concept that chain transfer reactions are important in the polymerisation of this monomer. A kinetic scheme is proposed to account for the experimental results.

A study of the thermal degradation of poly-α-chloroacrylonitrile (Chpt. 4) has shown that this polymer, which might conceivably decompose by one of three common mechanisms; namely

(1) Depolymerisation, as found in most 1:1 disubstituted vinyl polymers.

(2) Ester Decomposition, as in polyvinyl chloride.

(3) Nitrile Colouration, as in polymethacrylonitrile .

does in fact decompose by the dehydrochlorination mechanism (2). The temperature required (155°C) to bring about this reaction is considerably lower than that for the similar reaction in polyvinyl chloride. During dehydrochlorination, the residue colours and becomes insoluble. A free radical mechanism, initiated by random scission of the labile C - Cl bonds, consistent with the reaction data for a three halves order, is postulated.

Thermal degradation studies (Chpts.5&6) of styrene and methyl methacrylate copolymers with low α-chloroacrylonitrile contents have shown that these copolymers are considerably more prone to degradation than styrene and methyl methacrylate homopolymers. Experiments carried out at temperatures at which poly-α-chloroacrylonitrile undergoes dehydrochlorination have shown that in both copolymer systems the α-chloroacrylonitrile units act as weak link sites leading to random chain scission. In the methyl methacrylate system, depolymerisation occurred from the newly formed chain ends whereas in the styrene system, degraded in the same temperature range (155 - 185°C), no monomer was detected. Possible mechanisms, resulting from dehydrochlorination of the α-chloroacrylonitrile units, are proposed to explain the observed chain scissions. Some speculative references on the stability of inherently present 'weak links' in polystyrene are discussed.

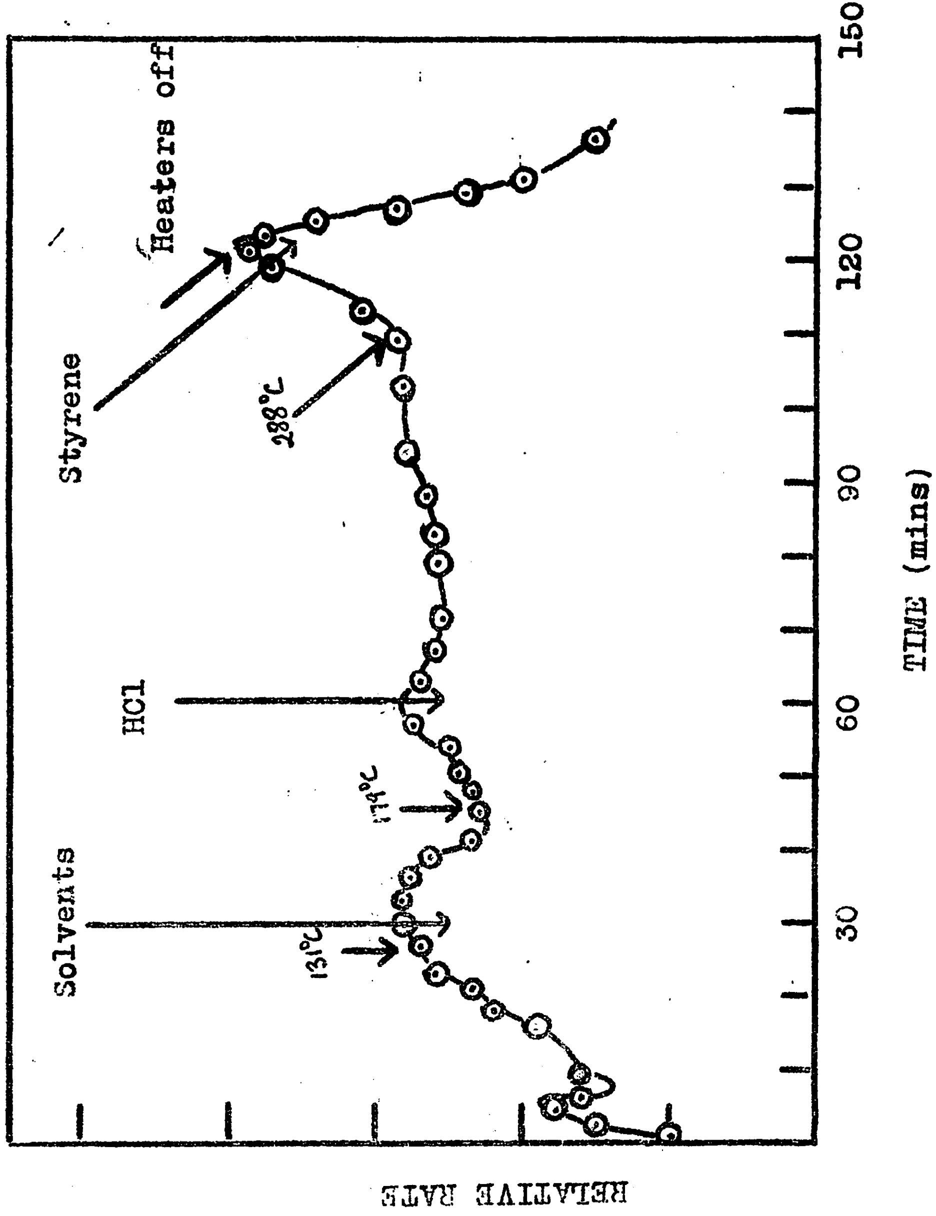
2. THE PROBLEM REVIEWED.

Before discussing points arising from this work and possible further courses of investigation, the results obtained from a few preliminary experiments on the thermal degradation properties of other copolymer systems indirectly related to the systems described above will be mentioned.

(a) Styrene/ Vinyl Chloride.

Studies on this system indicate that certain anomalies, inconsistent with the styrene/α-chloroacrylonitrile copolymers, occur. Figure 40 shows how the rate of evolution of volatile material varies as C.P.23 is heated slowly to 290°C in the dynamic molecular still. Examination of the decomposition

FIG. 40


Heaters off
Styrene
288°C
HCl
174°C
Solvents
131°C
30
60
90
120
150
TIME (mins)
RELATIVE RATE

products indicated that hydrogen chloride and styrene were liberated. From further degradation experiments on C.P.22, C.P.23, and C.P.25 it was apparent that no chain scission occurs at temperatures below 226°C, even though hydfogen chloride is evolved.

(b) Styrene/ Acrylonitrile.

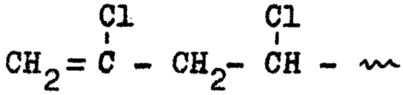
No chain scission reaction was detectable on heating a copolymer of styrene and acrylonitrile (C.P.15) at 226°C.

(i) Discussion.

The completely unexpected chain scission reaction resulting from the decomposition of α-chloroacrylonitrile units copolymerised with styrene and methyl methacrylate, emphasises once more the need for a systematic study of copolymer degradation. Such an investigation is desirable on two counts, firstly, the increasing use of copolymers as commercial materials and secondly to understand the effect of impurities on the properties of polymers in general.

Various methods of classifying copolymer degradations come to mind, the simplest and probably the most reasonable would be on the basis of the decomposition reactions of the individual components. The α-chloroacrylonitrile systems described here could then be classified as being composed of depolymerisation and ester decomposition components. As a further study on the behaviour of copolymers classified under this heading, it would be interesting to investigate systems incorporating vinyl chloride and vinyl acetate, both of which decompose by well established ester decomposition reactions. Preliminary experiments on styrene/ vinyl chloride copolymers indicate that large scale chain scission does not occur in this case. Further studies to explain this would therefore be of considerable interest.

The thermal degradation work on poly-α-chloroacrylonitrile presents further evidence in support of the generally accepted radical decomposition reaction which occurs in polyvinyl chloride. However, the random initiation mechanism proposed for poly-α-chloroacrylonitrile has not generally been accepted for polyvinyl chloride, although Stromberg, Straus and Achhammer have in recent years postulated a similar mechanism for this polymer. As indicated in chapter 4, their experimental results were not in agreement with a mechanism of this kind. Other authors have proposed a chain end initiated reaction in which unsaturated structures at the chain ends are the initiation centres for the 'zipper' like dehydrochlorination. Baum and Wartman have indicated that the most probable chain end structure would contain a β-chloro-unsaturated group,



$$CH_2=\overset{Cl}{C}-CH_2-\overset{Cl}{CH}-\sim$$

Such a structure would not, however, possess a labile allylic C - Cl bond. An α-chloro unsaturated chain end formed by a disproportionation termination step would be expected to be more labile, however, Baum and Wartman consider the formation of this structure most unlikely. Further studies on polyvinyl chloride must therefore clarify the exact nature of the chain ends if support is to be given to a chain end initiated mechanism of degradation.

On poly-α-chloroacrylonitrile itself, degradation studies in solution would be of considerable interest although solvent participation might complicate such an investigation.

On the immediate problem of inherent weak links in polystyrene, the study using styrene/ α-chloroacrylonitrile copolymers has not been as fruitful as first hoped. Any further investigation using this system would first have to verify that the chain scission reaction was due to the formation of unsaturated structures in the polymer backbone. This might be possible if number average molecular weight measurements were combined with accurate determinations of the hydrogen chloride evolved. An alternative approach to this problem may be possible by using copolymers of styrene with various substituted 1:3 butadiene monomers. In this case an unsaturated bond would be initially present in the polymer backbone.

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