THESIS FOR THE DEGREE
OF DOCTOR OF
PHILOSOPHY

THERMAL DEGRADATION OF COPOLYMERS

OF

VINYL ACETATE AND VINYL CHLORIDE

by

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SUMMARY.

Thermal degradation of polymeric materials may take place in two general ways. The first way is by splitting off monomer units or several monomer units joined together. The second, and that found in the breakdown of poly (vinyl acetate) and poly (vinyl chloride), is loss of side groups to leave conjugated polyene sequences.

In the first chapter of this thesis, the previous work done on the degradation of poly (vinyl acetate), poly (vinyl chloride) and copolymers of vinyl acetate and vinyl chloride is discussed in terms of the possible mechanisms.

The polymers used in the work described in this thesis were prepared by standard methods and the copolymerisation of vinyl acetate and vinyl chloride was studied before polymers, for degradation, were prepared. The ratios of vinyl acetate to vinyl chloride in the copolymers were determined by nuclear magnetic resonance spectroscopy.

The degradation of the polymers was studied

firstly in the solid phase and later in solution. The degradations in solution were initially performed in ethyl benzoate and later in tri-toluyl phosphate. The reason for this is that the kinetics of the degradations in ethyl benzoate are dependant almost entirely upon the retention of the acetic acid produced in the degradation. This seems to cause a very marked acceleration of the degradation.

The degradations in tritoluyl phosphate solution showed the same relative stabilities of the copolymers as was found in the solid phase. Further investigations in this medium were carried out with the object of investigating the discolouration of the copolymers and the energy of activation of degradation

The rate of discolouration was found to be minimum at 10% VA and 10% VC and at a maximum at 50% to 75% VC.

The energies of activation have a general tendency to increase from PVC to PVA with a slight drop around 50% VC.

The effects of the reaction product and oxygen on the rate of degradation are demonstrated.

The results found are discussed and a mechanism for degradation is postulated. This involves mainly an activation of VA groups by adjacent VC units and then allylic activation by the double bond so formed. The crosslinking reaction is postulated to be a polyene condensation reaction.

The controversy of the radical versus non-radical argument for the degradation of PVC is not resolved but it is concluded that the true mechanism of degradation of PVC is probably a mixture of each, the predominance depending upon the conditions.

Finally, possibilities, for future work are presented and the possible outcome discussed.

PREFACE.

The work described in this thesis was carried out during the period October 1964 to September 1967, in the Department of Chemistry, of the University of Glasgow which is under the general supervision of Professor J.M. Robertson, C.B.E.,F.R.S.

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

I should also like to thank my colleagues in the Macromolecular Chemistry group for useful assistance and discussion and the various members of the Technical staff of the Chemistry Department in particular Mr. G. McCulloch, who carried out most of the molecular weight determinations.

Finally, I wish to thank Drs. N. Grassie and I.C. McNeill for suggesting the problem and for general supervision and encouragement throughout the work.

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CHAPTER 1.

INTRODUCTION.

As this thesis is concerned with polymers and copolymers of vinyl acetate and vinyl chloride, it is convenient throughout to use the abbreviations PVA for poly (vinyl acetate), PVC for poly (vinyl chloride), VA for vinyl acetate monomer and VC for vinyl chloride monomer.

1). Classification of Polymer Degradation Mechanisms.

Degradation reactions may be classified according to the agency or agencies causing them. In this manner, five major classes of degradation may be enumerated --- thermal, oxidative, photo, ultrasonic and mechanical. Some of these major groups may be subdivided by considering the mechanism of degradation. Since this thesis is concerned only with thermal degradation, it alone will be considered here.

Thermal degradation reactions may be classified into two main groups, namely substituent reactions and depolymerisation reactions.

Depolymerisation reactions are characterised by the rupture of the main polymer chain backbone so that at any intermediate stage in the reaction the products are similar to the parent material in the sense that the monomer units are still distinguishable in the chains. New types of terminal groups may or may not appear, depending upon the nature of the chain scission process. The ultimate product will be monomer or closely akin to it. This form of degradation occurs in poly (methylmethacrylate), polystyrene, polyethylene, poly (ethylene terephthalate), etc.

The principal feature of substituent reactions is that the substituents attached to the polymer chain backbone are modified or partially or totally eliminated. Thus the chemical nature of the repeating unit in the macromolecular structure is changed. If volatile products are evolved they will be chemically unlike monomer. This form of degradation occurs in the colouration of nitrile polymers, in poly (methacrylic acid) and in ester decomposition reactions in PVC, PVA and poly (tert-butylmethacrylate).

The degradation of the polymers, with which this thesis is concerned, occurs by a substituent reaction.

2). Degradation of PVC.

PVC now accounts for over 200,000 tons per annum of the thermoplastics production of Great Britain (30% of the total [148]), because of its diversity of applications and low cost. Its original advantage was that it could be processed on equipment developed for the rubber industry but, as the applications diversified, the processing conditions became more demanding and the instability of PVC at elevated temperatures became a problem. Also the poor weathering characteristics of PVC do not allow its full potential in the building industry to be developed.

When PVC is subjected to various agencies such as heat, light, ionising radiation, etc., it liberates hydrogen chloride with accompanying discolouration and a general deterioration of mechanical and electrical properties. Over the years, many types of material have been successfully used to combat degradation but such stabilisers have been evolved empirically and the stabilisation of PVC has been an art rather than a science. It is necessary to understand the degradation processes which occur so that a scientific approach may be made to the problem of stabilisation.

In spite of this necessity and the amount of time and energy put into studying the various degradation processes they are, as is demonstrated below, as yet far from clearly understood.

The degradation of PVC is of very great importance as many of the applications of the polymer require transparent materials and colour develops during the degradation. Whereas in most other materials, the degradation is not important until much higher percentage degradations, when physical properties become affected, in the case of PVC this occurs much later than discolouration and is seen as the material becoming brittle and also as insolubilisation. This latter phenomenon has been accredited to the formation of crosslinked structures (1-5) and studies have been made of the rate of crosslinking (6).

The polymer itself has been shown to have a head to tail structure almost exclusively (7) and studies of the products of degradation below 200°C (8) show that only hydrogen chloride is liberated whereas above 200°C (9-11) small amounts of benzene and other aliphatic and aromatic hydrocarbons have been detected, although chlorinated hydrocarbons are absent. No chlorine or hydrogen is found (9-11) but 4% of the volatile products are unaccounted for (12).

The ultraviolet and visible spectrum of degraded PVC is similar to polyene spectra (1,2,13,14) and the colours produced are reminiscent of carotenoids. These and the head to tail structure suggest that the dehydrochlorinated polymer would have the structure

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

The colour has, however, also been attributed to fulvene structures (15) and, in the case of photodegradation, to a surface layer of carbon (16).

The methods used to study the decomposition are many and varied but common to most of them is measurement of the evolved hydrogen chloride.

When PVC is heated in an inert atmosphere, at temperatures between 150°C and 200°C, it becomes highly coloured during the loss of the first 0.1% of hydrogen chloride (8) and the colour suggests that sequences of seven conjugated carbon-carbon double bonds are present (2,17). Another observation is that, when dehydrochlorination is taken to completion, only very small traces of chlorine remain in the polymer chain (18) whereas, if there was random elimination, one would expect 13% of the chlorine to be left (19). These observations indicate that dehydrochlorination must take place from successive units along the polymer chain rather than at random. This type of behaviour has been termed a "Zipper" (20) reaction.

However three types of mechanism have been proposed for the degradation, namely ionic, unimolecular and radical but before discussing these a brief outline of the work done on the pyrolysis of alkyl chlorides is appropriate.

Alkyl chloride pyrolysis was shown to proceed by one of two mechanisms - radical or unimolecular (21,22). The mechanism of decomposition for certain alkyl chlorides was predicted by Barton (23) by radical intermediate studies and nearly all his predictions have been substantiated. However, this scheme suggests that the decomposition of PVC should be first order, but it loses hydrogen chloride more readily than PVC models. The possible explanation for this lies in the first propagation steps in which, with alkyl chlorides, a tertiary hydrogen is initially abstracted whereas, in PVC, it is a secondary hydrogen which is abstracted first. This is demonstrated in the chlorination of PVC in which the methylene groups disappear first (24).

A). Types of Mechanism.

(i). Unimolecular.

A unimolecular elimination mechanism for PVC dehydrochlorination would be expected to be a random process but allylic activation is believed to be important (3,4,13,25,26,27,28) and is offered as an explanation for the "Zipper" process. There is no direct evidence that allylic activation aids homolytic scission and the idea has been transposed from heterolytic scission mechanism. There is, however, one point in favour of the unimolecular mechanism and that is that most of the PVC stabilisers are not known for their participation in radical reactions.

(ii). Radical.

The radical postulate for thermal dehydrochlorination also has rather vague support. The presence of free radicals has been demonstrated in heat-treated (11) PVC by electron spin resonance spectroscopy. Unfortunately no one has yet studied thermally degrading PVC by electron spin resonance and this could be a possible future development.

Arlman found that free radical initiators increase the rate of loss of hydrogen chloride but Bengough (26) found that they did not. Both of these claims are suspect as benzoyl peroxide for example does not necessarily give an adequate supply of radicals at about 200°C, although the difference could arise from the different phases in which the work was done. Arlman (1) also found that free radical scavengers do not inhibit the reaction and he explains this on the basis of a very stable radical intermediate. He suggests that hydrogen chloride is liberated from the monomer unit adjacent to a radical and the radical is resonance stabilised. Bengough (26) also found that radical scavengers had no effect on the reaction but there is always the possibility that some compounds which are radical scavengers at normal temperatures do not display the same effect at higher temperatures.

Radical-activated elimination mechanisms such as Arlman's (1) have received very little support and the favoured radical mechanisms involve free chlorine atoms. As previously mentioned, no proof of the existence of radicals in thermally degrading PVC has yet been produced but there are several isolated pieces of evidence claimed by Geddes, (29) such as low pre-exponential factors in the rate constant with copolymers of vinylidene chloride (30), increased rate of dehydrochlorination in some cases (1,31,32), when free radical sources are added to the PVC, but not in others, and a claim by Winkler (20) that some PVC stabilisers interfere with radical chain processes.

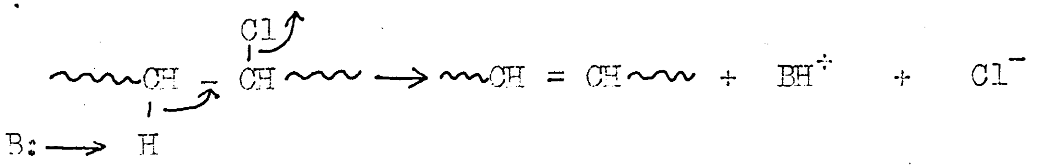
Stromberg (10) and Winkler (20) both postulated radical chain mechanisms for PVC dehydrochlorination, proposing very similar propagation steps but widely differing initiation and termination steps. This difference again suggests that the key to the problem lies in the initiation process.

Stromberg (10) claims that hydrogen chloride could not be eliminated from PVC in a molecular process like the elimination of acetic acid from PVA (33) because of geometrical considerations and thus the elimination must be stepwise as would be the case for an ionic mechanism.

(iii). Ionic.

There is no direct evidence for an ionic mechanism for the thermal elimination of hydrogen chloride from PVC although there is considerable indirect evidence. Alkyl chlorides in the presence of base undergo elimination and substitution reactions to give a mixture of products (34). In PVC there is a similar reaction but substitution is suppressed and the products are similar to the products of thermal dehydrochlorination (7). Highly coloured products are obtained by the treatment of PVC with sodium in liquid ammonia (35), sodium methoxide and lithium chloride in dimethylformamide (36). In the latter case, the chloride anion acts as a strong base and thus the dehydrochlorination is a true ionic chain elimination, substitution having no meaning in this case, and the product is a violet colour which is predicted by Remop (37) who shows that two colours should arise. The first colour is violet when there is elimination only and the second is red when the elimination is occasionally interrupted by substitution. PVC was found to be degraded by sulphuric acid but not by sulphuric acid containing a few percent of nitric acid (38) and it is claimed that the degradation in sulphuric acid is an ionic zipper while, in the latter case, nitric acid adds on to the carbon-carbon double bond, in a faster reaction than that eliminating the next hydrogen chloride, thereby preventing allylic activation.

At 150°C, organic bases, for example benzyl trimethyl ammonium hydroxide, accelerate the dehydrochlorination of PVC (39). The mechanism proposed is a slow initiation step as in (i), then fast



$$\underset{B:\longrightarrow H}{\sim\sim CH} - \overset{Cl}{CH}\sim\sim \longrightarrow \sim CH = CH\sim\sim + BH^{+} + Cl^{-} \qquad (i)$$

attack by the base at the allylic position followed by slow cross-linking termination. If the mechanism of thermal dehydrochlorination of PVC is ionic there would be charge separation at the carbon-chlorine bonds and the catalytic effect of organic bases would be by increasing this polarity (21). The obvious question which arises concerning the ionic mechanism is whether conditions conducive to this type of reaction are found in the thermal degradation of PVC. In answer to this, there is the evidence of the thermal degradation of PVA (33) in which the elimination of acetic acid is concerted but involves a charge separation, and also of Marks et al, (40) who found the dielectric constant of molten PVC at 180°C to be the same as that of nitrobenzene at the same temperature and to be considerably greater than that of the solvents normally used in solution degradation. It is possible that in this case a heterolytic mechanism, involving allylic activation, is occuring.

B). Modes of Initiation.

The crucial step in the reaction is obviously the initiation process, the character of which predetermines the subsequent degradation mechanism i.e. radical initiation imposes a radical mechanism upon the polymer. This applies less to the unimolecular type but it is still essential to know the initiation step. Because of the inherent instability of PVC compared with the expected quite high stability, it is reasonable to assume that irregularities in the chain, or extraneous impurities are causing the initiation.

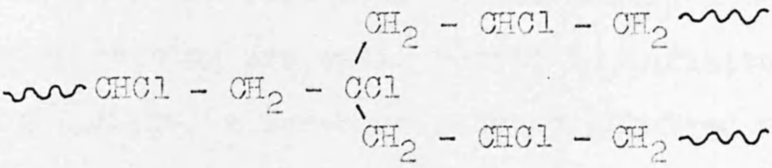
An excellent review of the expected effects of different irregularities has recently been published by Geddes (29) and a brief account will be given here.

Free chlorine atoms could not arise from the spontaneous dissociation of a carbon-carbon bond, which requires 80 k.cal. (41).

Structural irregularities are the obvious point of weakness in the molecule and their type and number depend on polymerisation conditions (42,43,44). One possibility is initiator fragments. If termination is by combination, each chain will have two initiator fragment ends and the linkage at the point of combination will be head to head. If by disproportionation, there will be one initiator fragment per molecule and half of the molecules will have the other end saturated and half will have it unsaturated. The other important terminating process is chain transfer to monomer which gives

$$\sim\!\sim\!\sim CH_2\ CH_2\ Cl\ +\ \sim\!\sim\!\sim CH_2 - CCl = CH_2$$

as the chain ends (45,46). ~~This~~ Transfer to polymer is the predominant terminating reaction in PVC polymerisation (46,47,48) and leads to branch points in the polymer. The tertiary hydrogen is the most reactive for this transfer in PVC and thus the branch point will have a tertiary chlorine atom as in



$$\sim\!\sim\!\sim CHCl - CH_2 - CCl\begin{array}{l} / \ CH_2 - CHCl - CH_2\sim\!\sim\!\sim \\ \backslash \ CH_2 - CHCl - CH_2\sim\!\sim\!\sim \end{array}$$

The detailed structure of the polymer clearly depends upon the relative tendencies for these chain termination reactions to occur. Structural abnormalities may also arise due to changes occuring during storage and handling giving isolated carbon-carbon double bonds and oxygenated structures (49). Extraneous impurities may arise at any stage from the initial manufacture of monomers to the processing of the polymer.

For a full study of all these effects, there must first of all be a quantitative determination of their relative contributions and this means very extensive characterisation of the polymer.

(i). At Chain Ends --- Types of Chain Ends.

Chain end groups could cause initiation of degradation and would obviously give a dependence of the rate of dehydrochlorination on the reciprocal of the molecular weight. This has been studied for fractionated (50,51) and unfractionated (1,26) polymers and shown to occur at temperatures below 200°C and with low molecular weight material but when these results are extrapolated to infinite molecular weight, a non-zero rate is obtained which shows that ends are not the only initiation points. These results do not prove at which of the end-groups initiation is occuring and consideration must therefore be given to the two principal end groups, namely initiator residues and unsaturated chain ends.

(a). Initiator Fragments.

In commercial polymerisation, various initiators are used and a study has been made of dependence of rate of dehydrochlorination upon initiator type.

It has been shown (10,52,53,54) that azoinitiated PVC liberates hydrogen chloride more readily than that initiated by a low-activity peroxide such as lauroyl peroxide. This polymer in turn liberates hydrogen chloride more readily than that initiated by a high-activity peroxide such as benzoyl peroxide.

Ester groups have been found in PVC initiated by acetyl peroxide but hydrolytic removal of them had no effect on the thermal dehydrochlorination (25). The model compound for the end group 2-chloropropyl acetate does not decompose at 170°C, but this means very little as its structure is not very similar to the end group and thus the choice of model is poor. The first evidence suggests that initiator fragments in themselves do instigate thermal dehydrochlorination.

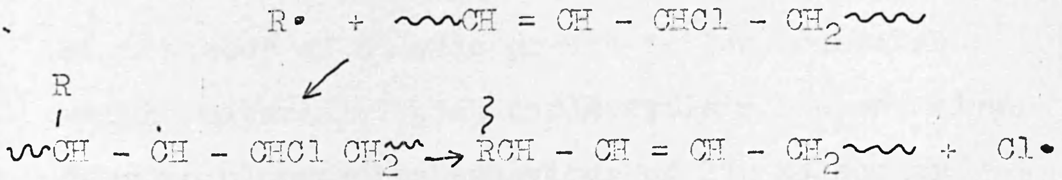
The probable mode of action of initiator fragments would be by breakage of a weak bond in the fragment to give an alkoxy and a macro radical

$$R - CO_2 - CH_2 - CHCl\sim\sim \longrightarrow R - CO\cdot + \dot{O}CH_2 - CHCl\sim\sim$$

If an alkoxy radical is produced which abstracts a secondary hydrogen in PVC, the macro radical of Winkler's (20) propagation step is produced

$$\sim\sim CHCl - \dot{C}H - CHCl - CH_2 - CHCl - CH_2\sim\sim$$

For this to occur it must be assumed (20,50) that the alkoxy radical prefers to abstract the secondary hydrogen. It has been shown, however, that, unlike the chlorine atom which does prefer the secondary hydrogen, the alkoxy radical gives preference to the tertiary hydrogen (55). However, only a small amount of secondary abstraction is necessary to produce a considerable amount of dehydrochlorination, if the kinetic chain of dehydrochlorination is long. The tertiary radicals will act as terminators, or combination sites to give the crosslinks which are found in material degraded in nitrogen or vacuum (1,3,5,6,56). Free chlorine atoms may be formed



$$R\cdot + \sim CH = CH - CHCl - CH_2\sim$$

$$\sim\overset{\overset{R}{|}}{CH} - \overset{\cdot}{C}H - CHCl\ CH_2\sim \rightarrow RCH - CH = CH - CH_2\sim + Cl\cdot$$

and would be formed more readily if the allylic group was terminal.

Before the role of initiator fragments can be established, some method must be developed for measuring their concentration.

Razuvaev (57) has used radiotracers to study the initiation in polymerisation of VC and a similar technique might be useful although no one has yet used it. The concentration of initiator fragments need not be directly related to the oxygen content (8,25,58,59), as the latter does not distinguish initiator fragments from oxidised structures in the chain.

(b). Unsaturated Groups.

Unsaturated end groups are the result of termination by disproportionation or transfer (45,46) and carbon-carbon double bonds in PVC have been detected (2,25) and quantitatively measured by Bengough (60) by ester exchange with allylic chlorine. This work (60) showed an unexpectedly high number of allylic groups in low molecular weight material, which could explain the anomalous dehydrochlorination behaviour of low molecular weight material.

Support for the allylic chlorine initiation site comes mainly from the assumption that the allylic carbon-chlorine bond is more labile (8,10,25). Model compounds (61) decompose more readily than the saturated analogues (62) and have energies of activation comparable to that in PVC (51,26,63,64,146).

These models are, however, prone to peroxidation (65) and this could well be an important factor. The difference between two sets of results (25,61) shows the importance of purification.

The assumption made that allylic groups eliminate hydrogen chloride readily is not necessarily true as the dissociation energy quoted (41) for the allyl carbon-chlorine bond of 58 k.cal/mole is based on very little evidence.

Mild chlorination, causing no substitution, stabilised (25) the polymer. Ozonisation of the virgin polymer gave very little drop in molecular weight but, in spite of this, 0.005% unsaturation could be in the polymer chain and not terminal, which is 20% of the measured unsaturation. The presence of terminal double bonds was shown by the fact that formaldehyde was produced on ozonolysis.

Stromberg's scheme (10) requires free chlorine atoms to be produced with an energy of activation of 40-60 k.cal/mole and the allylic chlorine bond energy has been claimed as 60 k.cal./mole (66). γ irradiation removes hydrogen chloride (66) thus a polymer prepared by initiation by γ irradiation is more unsaturated than that prepared by peroxide initiation. γ initiated polymer is more stable, however, than peroxide initiated polymer, implying that the degradation is not critically dependant upon allylic chlorines.

The stability of allyl chloride itself was used as evidence (20) against unimolecular elimination at chain ends in PVC but they could act as secondary initiation sites reacting with occluded radicals(2) or with radicals derived from dissociation of weak links.

(ii). Possible Sites Within The Chain.

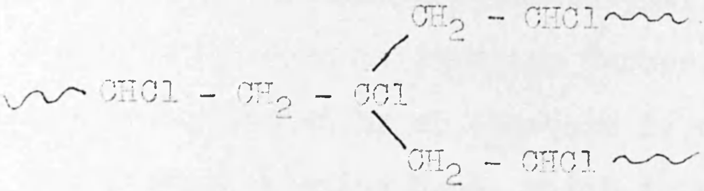
When the rate is plotted against the inverse of the molecular weight a straight line is obtained which does not give zero rate when extrapolated to infinite molecular weight (1,50). This shows that not all the initiation occurs at chain ends. Moreover, Baum and Wartman (25) showed that removal of the carbon-carbon double bonds reduced the rate by 50%, further evidence that some other type of initiation site must be present. These other sites must lie in the polymer chain, and branch points are most strongly suspected although other possibilities must be considered.

(a). Branch Points.

The presence of branch points was predicted from the kinetics of transfer to dead polymer during polymerisation (46,47,48) and has been confirmed only qualitatively.

Reaction with lithium aluminium hydride gives a hydrocarbon polymer with a molecular weight 50% higher than expected (67) indicating some rearrangement. Cotman (68) showed that the number of chain ends per molecule is very much greater than two. Deviation from a linear correlation of weight average molecular weight and intrinsic viscosity in fractionated PVC have been attributed (69) to long branched molecules in the high molecular weight fractions.

Transfer to polymer occurs by abstraction of tertiary hydrogen to give a radical which adds monomer (70) to give a branch at a carbon bearing a tertiary chlorine atom. If the polymerising radical is also capable of abstracting a chlorine atom or a secondary hydrogen atom, three structures are possible



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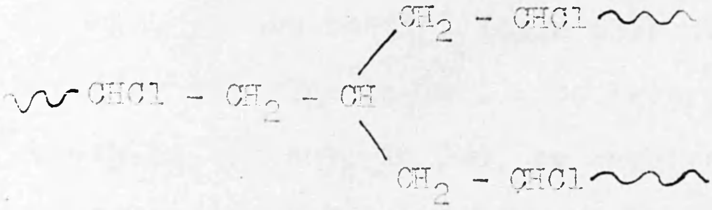

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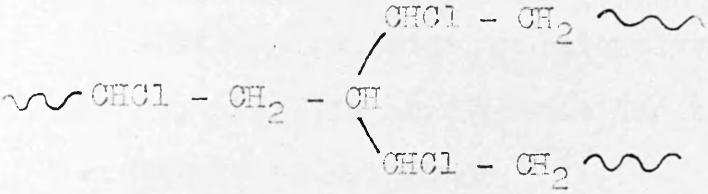
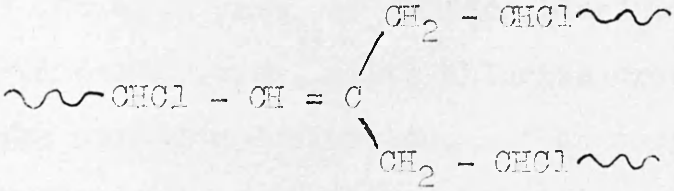


III

Dehydrochlorination of I gives



IV

Tertiary chlorines have been shown to be concentrated in the high molecular weight material(69) as might be expected from the dependence of rate upon the inverse of molecular weight.

The predicted thermal lability of the tertiary carbon-chlorine bond at a branch point is based on analogy with the reactivity to solvolysis (71). Kharasch (55) has argued that this is not valid as there is a decrease in electronegativity from secondary carbon to tertiary carbon but this is more than compensated by an increase in the polarity of the carbon-chlorine bond, which is increased in strength by the partial ionic character. Thus the tertiary chlorine is labile to heterolysis but not homolysis but may, in PVC, be involved as a secondary site of initiation. The high activity of the tertiary chlorine in heterolytic reactions has been put forward as evidence for the ionic nature of the dehydrochlorination (72).

Druesdow (3) claimed that the tertiary chlorine structures gave, by dehydrochlorination or hydrolysis and dehydration, allyl chlorine groups which initiate the dehydrochlorination. When polymerisation is carried to greater than 15% conversion, thus increasing the amount of branching, the rate of dehydrochlorination of the product is also increased, which implies (26) that branches are acting as points of initiation.

A claim that loss of hydrogen chloride was difficult until activated by two conjugated carbon-carbon double bonds was based on copolymers of VC and 2 - chloropropene in which the rate of evolution of hydrogen chloride is proportional to the square of the mole fraction of 2 - chloropropene, which is claimed to be a measure of the number of adjacent co-monomer units.

In poly (α - chloro acroylonitrile), which may be considered as substituted PVC, the carbon-chlorine bond strength is lowered to 60 k.cal./mole (73) which results in increased initiation, giving a higher rate of hydrogen chloride evolution.

The behaviour of tertiary chlorine structures in dehydrochlorination is more in keeping with the unimolecular mechanism rather than the radical one since the formation of a radical at that point is energetically unfavourable, but the structure may lose hydrogen chloride to give allyl groups which are a requirement common to both mechanisms.

(b). Random Unsaturation.

Elimination of molecules of hydrogen chloride by the action of nucleophilic reagents during preparation and storage of polymers would lead to carbon-carbon double bonds in the polymer chain. Small concentrations of carbon-carbon double bonds have been found (2,8) and an indirect determination of their concentration has been accomplished (25) by ozonolysis and molecular weight measurements. This structure has still to be shown to be an initiation site but it has the same claim as terminal double bond groups and, furthermore, is liable to oxidative attack (74) to yield possibly active structures containing carbon-oxygen bonds.

(c). Oxidised Structures.

The evidence for initiation by oxidised structures is inconclusive but they could constitute initiation sites with a low energy of activation. PVC has not been studied in this direction but other polymers have (75,76,77,78). A possible reason for this omission is the complicated pattern of thermo-oxidative breakdown in PVC. The hydroperoxide of polypropylene forms under very mild conditions (79) and can be prepared through the brominated polymer (80) which is similar to PVC.

Probably the best method of estimating hydroperoxides in PVC is by reaction with ferric thiocyanate (81,82,83) and up to 500 p.p.m. (11) has been found. PVC of low particle size may oxidise (49) phenols in the absence of oxygen which is explicable by the existence of peroxide groups. Trace metals give an increase in rate of dehydrochlorination possibly by catalytic decomposition of the hydroperoxide (20). Because of the constancy in rate of dehydrochlorination over periods of hours (1,26,51,64,72,84,85) one must conclude that either the concentration of peroxide remains constant, which means that, unlike most peroxides, it is stable, or a rapid decomposition of peroxide takes place with no termination. It has recently been shown (32) that relatively stable peroxides are capable of initiating the loss of HCl from PVC at elevated temperatures without the necessity of being incorporated in the chain.

It is interesting to note that poly (chloroprene) loses HCl at 140°C (86) only when partially oxidised.

The initiation by oxidised structures is difficult to correlate with a unimolecular mechanism but it is ideal for a radical mechanism.

(d). Head - to - Head Units.

Head - to-head structures have been cited as initiation sites for a molecular chain and these could act by abstraction of a tertiary hydrogen atom by a propagating radical, then rearrangement of the macroradical to give a carbon-carbon double bond and a free chlorine radical as required (23) by Barton's scheme.

However, completely "Head - to - Head" PVC can be made by chlorination of trans -1,4- polybutadiene(87). The stability of this product is only slightly less (86) than that of PVC, suggesting that a single head-to-head unit in 1000 is unlikely to have much effect.

(e). Stereoregularity.

The effect of stereoregularity on the thermal stability has been studied by varying the catalyst (54) or polymerisation temperature (5,51,58) but any effects of stereoregularity achieved are small and overshadowed by the influence of other agencies. It is known in general (87), but not explicitly in PVC, that crystalline regions in polymers are less readily oxidised than amorphous regions. This would suggest that stereoregularity should have some effect.

(f). Extraneous Impurities.

Extraneous impurities may cause much increased dehydrochlorination (4,20,88,89,90) and careful purification (54,56) and characterisation of the polymer is necessary to eliminate these effects.

C). Termination.

The other stage of the dehydrochlorination reaction which has to be carefully studied mechanistically is the termination reaction which controls the final polyene length and the kinetic chain length in a radical mechanism.

The average polyene sequence length has been reported as seven to twelve (1,2,27,91) and this shows that some agent is preventing the dehydrochlorination process going right along the polymer chain. This stoppage could be caused by irregularities in the polymer chain, as inert groups inhibit the extension of the polyene chain (37), but it is most unlikely that the irregularities would occur with sufficient frequency to account fully for the small average length of double bond sequences.

The unimolecular mechanism has strong support here in that after 2 to 3 eliminations the allylic activation is claimed to become weaker and this limits the sequence length (20).

In the radical mechanism two termination steps are possible, namely termination and transfer.

Whichever of these is predominant would depend largely upon the temperature and thus, if this were the case, the colour should vary with reaction temperature but this has never been investigated.

Stromberg (10) postulated three termination steps

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2 \qquad (1)$$

$$Cl\cdot + R\cdot \longrightarrow RCl \qquad (2)$$

$$R\cdot + R\cdot \longrightarrow R-R \qquad (3)$$

and, by neglecting (2) and (3) showed that the rate of dehydrochlorination was proportional to monomer concentration to the power 1.5. This he verified experimentally as did Grassie and Grant (73) for poly (α chloro acrylonitrile) but the measurements in both cases were carried out at about 50% degradation and at a high temperature and thus may not produce the same result as would be found at lower temperatures and lower extents of degradation. This was illustrated by Bengough (26,146) who found the rate to be first order in monomer unit concentration, at lower temperatures and a closer scrutiny of

Stromberg's scheme is therefore called for. The half order is introduced solely by reaction 1 which is combination of two chlorine atoms. This is unlikely because of their high reactivity and low concentration. Also chlorine has never been detected in the reaction products (possibly, however, it could add to unsaturated products).

Winkler [(20)] suggested a set of transfer and termination reactions, their relative importance depending on the temperature, but all of which limit the polyene sequence length.

$$\mathrm{Cl\cdot + \sim\!\sim CH_2 - CHCl\sim\!\sim \rightarrow HCl + \sim\!\sim CH_2 - \dot{C}Cl\sim\!\sim} \qquad (1)$$

$$\mathrm{Cl\cdot + \sim\!\sim CH_2 - CHCl\sim\!\sim \rightarrow HCl + \sim\!\sim \dot{C}H - CHCl\sim\!\sim} \qquad (2)$$

$$\mathrm{Cl\cdot + X\cdot \rightarrow ClX} \qquad (3)$$

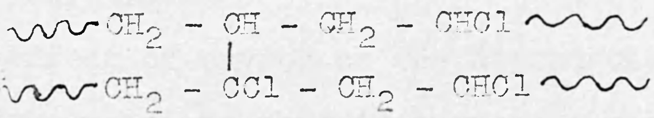
$$\mathrm{\sim\!\sim \dot{C}H - CHCl\sim\!\sim + \cdot X \rightarrow \sim\!\sim CHX - CHCl\sim\!\sim} \qquad (4)$$

$$\mathrm{\sim\!\sim \dot{C}H - CHCl\sim\!\sim + O_2 \rightarrow \sim\!\sim CH(O\dot{O}) - CHCl\sim\!\sim} \qquad (5)$$

Reaction (1) is a transfer reaction in that the tertiary macroradical formed is capable of abstracting a secondary hydrogen from another chain. This reaction would become a termination reaction if the macroradical then combined with another. Reaction (2) is a pure transfer reaction and limits only the polyene sequence length. Reactions (3) and (4) are termination steps, reaction (4) resulting in a crosslink if the radical X is a polymer radical.

The most common explanation for crosslinking is the combination of propagating polymer radicals (2,4,8). Druesdow (3) gave several explanations including copolymerisation of polyene chains and Diels - Alder reactions but the most popular reaction with supporters of the unimolecular mechanism is intermolecular condensation with loss of hydrogen chloride (4,6). Such a reaction would probably require a highly reactive chlorine atom, such as an allylic chlorine, to give crosslinking.

It has been suggested that crosslinking is favoured in stereoregular polymers (5) which have a more favourable spatial arrangement of polymer molecules to give the crosslinked structure,



$$\begin{array}{l} \sim\sim CH_2 - \underset{|}{CH} - CH_2 - CHCl \sim\sim \\ \sim\sim CH_2 - CCl - CH_2 - CHCl \sim\sim \end{array}$$

which is capable of initiating the loss of hydrogen chloride in four directions. This would suggest that crosslinking would be accompanied by an increase in rate of dehydrochlorination and this has been demonstrated (5) experimentally.

Bengough (6) concluded that, as azo-bis-isobutyronitrile had no effect on the rate of crosslinking, the reaction was non-radical. He also concluded that it was mechanistically unrelated to the zipper dehydrochlorination since stabilisers for this reaction in general have no effect on crosslinking.

In unstabilised polymer, crosslinking is of no real importance industrially since, by the time its effects become noticeable, the polymer has become coloured and thus unacceptable. In stabilised polymer, however, where colour is inhibited, the effect of crosslinking may be of considerable importance (96).

D). Effect of Atmosphere.

(i). Oxygen.

The effect of oxygen on the degradation of PVC is very pronounced in that it increases the rate of dehydrochlorination (3,4,25,26,50,63,64,72,88,92); bleaches the degraded polymer (4,8,25,26,36,63,93) and reduces the molecular weight (3,4,26,63,94).

Bleaching may at times be advantageous but may be offset by an increased rate of dehydrochlorination. No change in molecular weight may be obtained in thermal treatment if the rate of scission is made equal to the rate of formation of crosslinks by careful manipulation of oxidative chain scission.

There is experimental evidence (3) for increased rate of dehydrochlorination by the small amounts of oxygen present in technical grade nitrogen compared to highly pure nitrogen. In air or pure oxygen, the rate of dehydrochlorination is accelerating and this has to be borne in mind when postulating a mechanism.

It has been shown (50) that the rate of dehydrochlorination is proportional to the square of oxygen pressure but these measurements were at high temperature and 50% degradation. In solution degradations, no change in rate was reported when the carrier gas was blown over the surface of the solution but the concentration of oxygen at the reaction site would probably be little changed.

Accelerated rates of dehydrochlorination in oxygen have been found even when the reaction is completely isothermal (54) and thus it is not caused by the exothermic nature of the dehydrochlorination reaction in oxygen. Thermogravimetric studies (21) of PVC cannot usefully be made in oxygen because of the incorporation of oxygen into the polymer.

Oxidative degradation is usually a radical process and thus the increased rate of dehydrochlorination in oxygen produces a problem for the supporters of the unimolecular theory. This has, however, been explained away by claiming that it is caused by oxygen attack on the polymer to form labile sites (4,25,95). However, hydroquinone, which has no effect on the rate in nitrogen, reduces the rate in oxygen almost to the same as that in nitrogen (54,72) and this has been interpreted (72) as caused by a non-radical reaction in nitrogen on which is superimposed an oxygen - catalysed radical reaction.

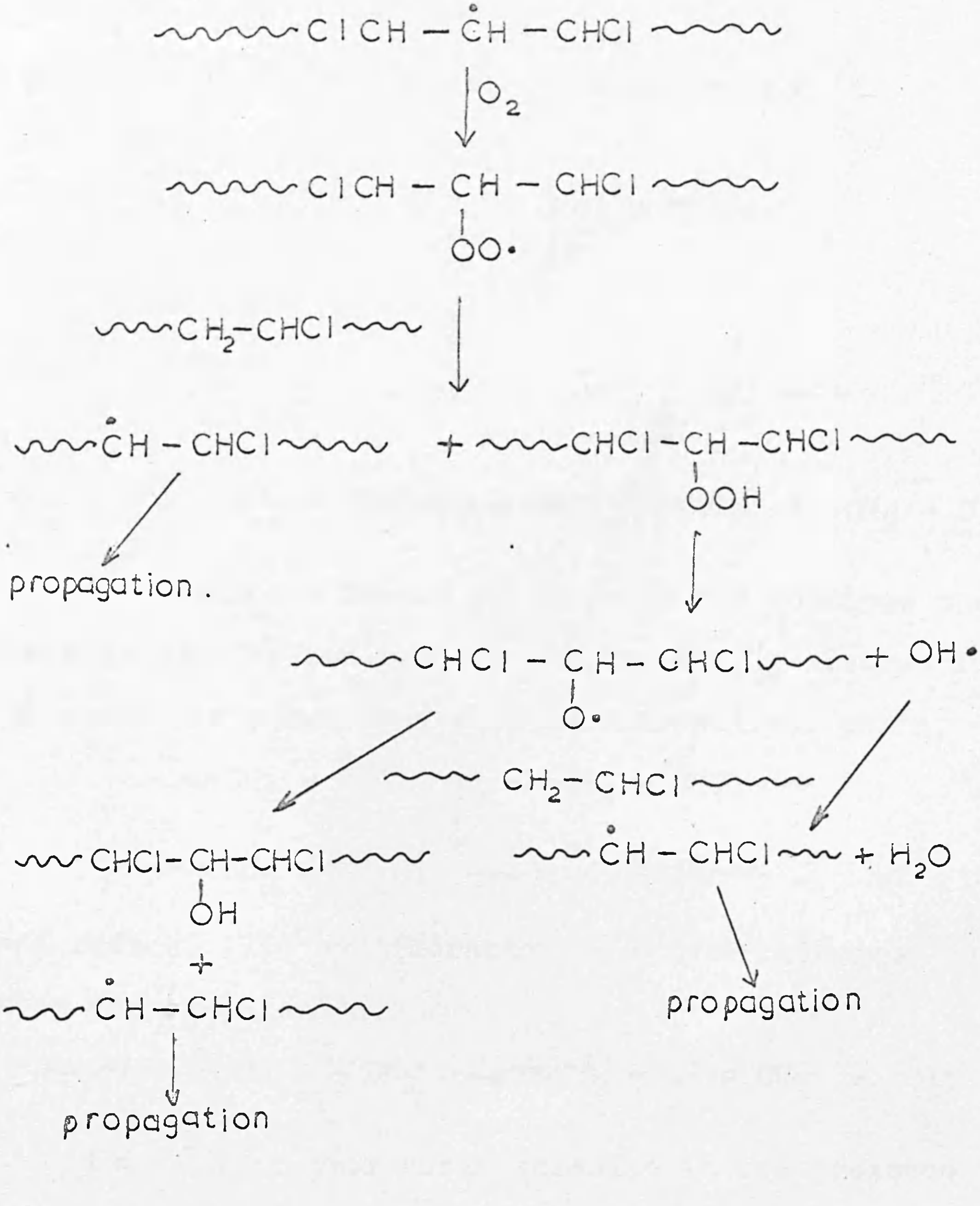
The radical dehydrochlorination theory is easy to reconcile with oxidation. A scheme (20,39,96) has been put forward, Fig.1., in which oxygen adds to a propagating macroradical to give a peroxy radical which abstracts a secondary hydrogen from a PVC chain to give another radical capable of propagation. The hydroperoxide may decompose into two radicals each capable of abstraction of hydrogen giving three kinetic chains from one, causing an acceleration in rate.

Oxygen can also form peroxides with PVC at room temperatures (20,39,72,95,96), thus increasing the number of labile sites.

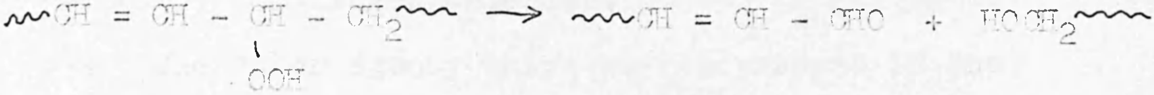
The suggestion (88) that the increased rate of dehydrochlorination in oxygen is caused by the reactivation of termination sites can fit into the termination steps postulated (20) by Winkler. If a chlorine radical abstracts a tertiary hydrogen rather than a secondary hydrogen, a radical is produced which is incapable of propagation but can carry on the kinetic chain by transfer. This radical may also react with oxygen to give a hydroperoxide which is capable of further initiation thereby continuing the kinetic chain.

Chain scission in the presence of oxygen has been explained (6,39) by rearrangement of hydroperoxides,

Figure 1.

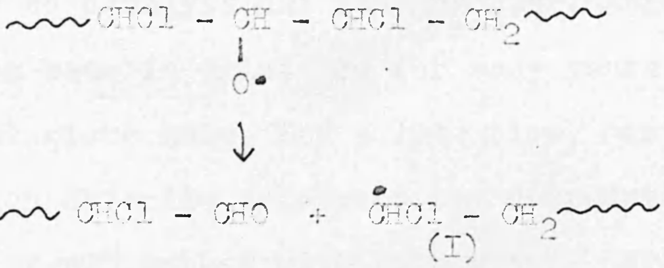


Chain Branching Reaction Mechanism For Dehydrochlorination In Oxygen(29).



$$\sim CH = CH - \underset{OOH}{CH} - CH_2\sim \longrightarrow \sim CH = CH - CHO + HOCH_2\sim$$

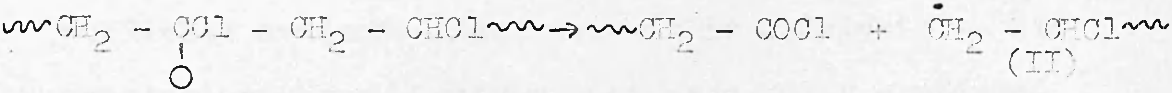
and also by rearrangement of alkoxy radical intermediates (20,96)



$$\sim CHCl - \underset{O\bullet}{CH} - CHCl - CH_2\sim$$

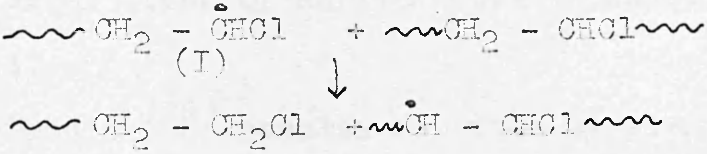
$$\downarrow$$

$$\sim CHCl - CHO + \underset{(I)}{\dot{C}HCl} - CH_2\sim$$



$$\sim CH_2 - \underset{O}{CCl} - CH_2 - CHCl\sim \rightarrow \sim CH_2 - COCl + \dot{C}H_2 - \underset{(II)}{CHCl}\sim$$

The radicals formed by scission can continue the dehydrochlorination reaction, radical I by abstraction of a secondary hydrogen from another polymer chain,



$$\sim CH_2 - \underset{(I)}{\dot{C}HCl} + \sim CH_2 - CHCl\sim$$

$$\downarrow$$

$$\sim CH_2 - CH_2Cl + \sim\dot{C}H - CHCl\sim$$

and radical (II) by liberation of a free chlorine atom for propagation.

$$\sim CH_2 - \underset{(II)}{CHCl - CH_2^{\bullet}} \longrightarrow \sim CH_2 - CH = CH_2 + Cl\bullet$$

Thus the polymer chain scission in the presence of oxygen could be a transfer process.

(ii). Hydrogen Chloride.

The other agency which may be present in the atmosphere immediately surrounding PVC during processing is hydrogen chloride and controversy over its ability to catalyse the dehydrochlorination reaction has been in existence for many years.

Technologists have, for a long time, suspected that hydrogen chloride catalyses the degradation but chemists have not agreed with this view. Arlman (88) published evidence discounting this catalysis. His conclusions have, however, not been fully confirmed and recently evidence in favour of catalysis by hydrogen chloride has become available (40,97). A closer examination of earlier work is therefore required.

Arlman's (88) results obtained by mixing HCl with the carrier gas show that there is a slight accelerating effect on the rate in nitrogen but a slowing down in oxygen, which is to be expected since oxygen is strongly accelerating (3,88,72) and is being replaced by a less strongly accelerating agent.

Druesdow (3) interrupted the flow of carrier gas which allowed the concentration of hydrogen chloride at the reaction site to build up and found the rate to be the same before and after. He claimed this to be evidence against catalysis although he had previously observed that the rate decreased with time when the carrier gas flow was maintained throughout the run.

These results did not justify any firm deductions but the negative conclusions which were drawn were acceptable, because of the difficulty of fitting catalysis by hydrogen chloride into the theories for dehydrochlorination.

Rieche (72) found catalysis in nitrogen, air and oxygen by interrupting the carrier gas flow. Hydrogen chloride normally escapes from the polymer quickly but, in thick films, it is possible for it to remain in contact with the polymer for some time and cause acceleration of dehydrochlorination (97). Talamini (54), using a vacuum system could get up to 25 times the rate of dehydrochlorination in vacuum by adding hydrogen chloride. Two recent papers (40,98) show that when the hydrogen chloride, which has been allowed to build up, is removed, the rate returns to a constant but is higher than the unautocatalysed rate.

This catalysis by hydrogen chloride is very difficult to explain, as homolytic dissociation is unlikely below 200°C and electrophilic addition to conjugated carbon-carbon double bonds would not give any structures capable of initiating further loss of hydrogen chloride. Dissociation of hydrogen chloride is the cause of catalytic pyrolysis of neopentane (99) but this is at a much higher temperature. If it is radical chain mechanism initiated by peroxide, the effect could be explained by the known effect of hydrogen chloride on the decomposition of peroxides (100). It could also react with iron parts of the processing equipment to give ferric chloride which is another catalyst (10,88) for the dehydrochlorination.

Autocalysis has been attributed to another product of degradation namely crosslinked structure (2).

E). Colouration.

The most critical feature of PVC degradation and the first apparent effect of it in unstabilised PVC is discolouration, although in stabilised PVC it may be less important. The colour of the degraded polymer is controlled by dehydrochlorination but all attempts to get a precise relationship have been thwarted. The first obstacle is the quantitative measurement of colour in all forms of degradation and in the presence of additives, in the solid or liquid phase. An approximate sequence of colour is pink --- red --- brown --- black in an inert medium while in oxygen it is yellow --- orange --- brown --- black. The analysis of these colours, with respect to the chemical species present in the degraded PVC, presents two difficulties. The first difficulty is the quantitative measurement of colour and the second is the interpretation of colour with respect to model polyenes. The second is the more difficult problem to overcome.

(i). Measurement of Colour.

Colours are usually compared by eye and this is of course very unsatisfactory. There are various empirical techniques in use for screening stabilisers (101, 102, 103) and some attempts have been made to eliminate human error by colour matching (8, 104) and measurement of transmitted light at a particular wavelength (28,31,105). The last method is not a good one as the absorption spectrum is so spread out.

The maximum difference in extinction coefficients between 4320 Å and 7260 Å has been taken as an assessment of colour intensity (106) but probably the only meaningful estimation would involve some integration of absorption over a range of wavelengths (102,107).

In the region of the spectrum from 2600 Å to 6000 Å there is a broad background on which are superimposed 10 to 11 peaks (2,14,37,91,103,108-110,147) which are absent in poorly resolved spectra (13,39). The spectra of thermally degraded PVC (2,111) are very similar to that degraded ionically by lithium chloride in dimethylformamide (37). Peaks in the spectra of pressed (14,111) films of thermally degraded PVC are slightly displaced from those in solution spectra but the spectra of PVC, degraded by initiation by irradiation with 1.5 - 2 m.e.v. electrons at - 196°C, are very different (91,109,110).

There is now little doubt that the colour in degraded PVC is caused by conjugated polyenes of the structure

$$\sim\sim CH_2 - (CH = CH)_n - CHCl \sim\sim$$

and a value of n would be of great help in postulating a mechanism for degradation.

Boyer (13) used a statistical approach, assuming a distribution of polyenes with n = 1 upwards. He showed, on the basis of a unimolecular elimination mechanism, that the number average value of n is related to the extent of reaction and the relative reactivity of the allyl activated elimination.

(ii). Analysis of Spectra.

To analyse spectra, spectral details are required of all the individual polyenes concerned, in terms of wavelength and extinction coefficients of the maxima. The absorption spectrum of a simple polyene consists of 4 or 5 peaks (17,112-116) and addition of a further carbon-carbon double bond has the effect of displacing the entire spectrum to higher wavelengths. Thus, for a distribution of polyenes, the presence of fine structure will depend on whether peaks of individual polyenes amplify or cancel each other. Another consideration (40,117,118) is that polyenes will absorb at different wavelengths, depending on their substitution pattern, giving four forms

$$H_2C = CH - (CH = CH)_{n-2} - CH = CH_2 \qquad (I)$$

$$R_1HC = CH - (CH = CH)_{n-2} - CH = CH_2 \qquad (II)$$

$$R_1HC = CH - (CH = CH)_{n-2} - CH = CH_2 \qquad (III)$$

$$R_1R_2C = CH - (CH = CH)_{n-2} - CH = CHR_3 \qquad (IV)$$

There would be a five $m\mu$ shift from I to II, from II to III and from III to IV.

There is a tendency to assume that each "peak" in the spectrum corresponds to the longest wavelength peak of an individual polyene but overlap of several minor peaks may give peaks in the composite spectrum. Several other factors affect the location of absorption maxima such as bathochromic shifts, which are dependant upon the nature of the solvent (114,115,119) and are proportional to the number of carbon-carbon double bonds in conjugation (117). It is also worth noting that trans isomers absorb at higher wavelengths than cis isomers (115).

Polyenes with up to 10 or 12 carbon-carbon double bonds in conjugation have been prepared and their spectra recorded (17,112-116) but polyene sequences much longer than this are required as models for degraded PVC. Since the conjugation theory is not very well defined (117,120-122), however there is no way of calculating the absorption spectra of higher polyenes. Empirical relationships between the value of n and the wavelength of maximum absorption do not hold when n is greater than 10. Many of these are based on the Lewis Calvin equation (123)

$$\lambda = kn$$

but Dewar (124) suggested

$$\lambda = D(1 - a^{-2n-2})$$

in which D and a are constants. These two equations have been combined by Hirayana (125) to give

$$\lambda^2 = A - BC^n$$

None of these predicts the wavelengths of absorption maxima for n greater than 10 very well. Extinction coefficients are only known for low values of n and it is unknown whether they increase or decrease when n is greater than 6.

A minimum number of 5 to 7 carbon-carbon double bonds are needed for colour and most quoted lengths of polyene sequences are between 5 and 20 (1,2). The fine structure ceases at about 5000 Å, which corresponds to the longest wavelength peak of a polyene of about 15 carbon-carbon double bonds (125) in conjugation. The peaks of higher polyenes come very close together and may be so superimposed that they give no fine structure or the spectrometers may be insufficiently sensitive to detect any fine structure which is present.

Dehydrochlorination by some basic catalyst may give polyene sequences running the length of the polymer chain giving a violet coloured polymer. The spectrum of this polymer covers most of the visible range and has a maximum of absorption at 5500 Å with no fine structure (37). When substitution can also occur, the polyene sequences are much shorter, the spectra show fine structure below 5000 Å and are confined to wavelengths below 6000 Å (37)

Polyene sequence lengths reported, of 5 to 12 (1) and 7 to 20, are interpreted (5) as proof of a short chain radical dehydrochlorination process. In a radical chain process, short polyene chains are more likely to be explained in terms of a high transfer rate. The brown colour in degraded PVC has been claimed (27) to be caused by polyenes of length up to 12 with a most probable value of 5 whereas, in the violet material obtained from poly (vinyl bromide), the length is up to 25 with a most probable value of 11.

Oxygen has the effect on thermally degrading PVC, of producing more hydrogen chloride but less colour as previously shown. This lessening of colour has been shown (111) to be caused by a displacement of absorption to the ultra-violet region from the visible region, with loss of fine structure.

The bleaching in oxygen is probably by oxidative attack on long polyene sequences to reduce their length. The classical theory of oxidation of unsaturated polymers is by hydroperoxide formation at allylic positions and then chain scission (74) but it has been suggested that oxidation in PVC is by 1,4 -

addition of oxygen to a diene to give a peroxide which by dissociation and rearrangement gives scission (3,72). It has been suggested that oxidative bleaching of degraded PVC, at ambient temperatures, requires light (63,96,105) but the accompanying photodegradation may cause difficulty in proving this requirement. All the suggestions are for shorter polyene sequences and carbonyl bonds when PVC is degraded in the presence of oxygen and these are borne out by the experimental results.

Any process reducing discolouration is beneficial to stabilisation and it is unfortunate that those materials which prevent a radical chain initiation on propagation may also minimise a beneficial oxidative bleaching. This fact would be well borne in mind when choosing additives for PVC, as many materials can exhibit antioxidant properties at high temperatures and this may be detrimental to stabilisation.

3). Review of the Stabilisation of PVC.

Several reviews (15,43,44,126-133) have been published on the stabilisation of PVC but there is very little known about the precise way in which the materials used interfere with the degradation. Almost the only feature common to all PVC stabilisers is the ability to react with hydrogen chloride, which in practice alleviates the situation caused by the catalytic behaviour of hydrogen chloride but does not prevent the uncatalysed dehydrochlorination. The rate of evolution of hydrogen chloride in the presence of acid acceptors can be very misleading since stabilisation appears to be achieved through a stoichiometric uptake of hydrogen chloride whereas true stabilisation as regards inhibition of colour formation and crosslinking may involve only a very small amount of stabiliser.

When use is made of metal based stabilisers, rapid dehydrochlorination takes place when the stabiliser is saturated and this is attributed to catalysis by the metal chloride (15,96,134,135).

There is little in common among inorganic lead salts, heavy metal soaps, organotin compounds and epoxides except reaction with hydrogen chloride. They may, therefore, act in different ways.

They could act by elimination of labile sites responsible for initiation of dehydrochlorination, or by interference with the propagation mechanism. However even if dehydrochlorination is allowed to occur, the PVC can still be quite acceptable if the stabiliser reacts with the polyene structure to eliminate discolouration. Crosslinking and oxidation are examples of secondary reactions on which certain materials can exert a stabilising influence.

In order to investigate stabilisation, the chemical and physical effects must be separated. An example of this is the dispersion of the stabiliser in the polymer which is dependant upon the physical properties of the stabiliser, its compatibility with the PVC and the work done in the mixing. For example the metal soaps from pure fatty acids are not as good stabilisers as those from industrial fatty acids and it has been suggested (136) that this is caused by the less pure industrial sample having a lower melting point.

Some compounds, incapable of having any influence on the degradation by themselves, can enhance the action of others and this has been ascribed (136) to an improved lubrication of the mixing, by plasticising the PVC or emulsifying the stabiliser.

Commercial PVC, from which extraneous impurities have been removed, is more stable (54) than commercial but basic lead phosphite lowers the rate of degradation of unpurified PVC to that of purified PVC alone (98). This action is presumably by stopping extraneous impurities from causing initiation of the dehydrochlorination.

Labile groups on the polymer backbone may be deactivated in several ways but the most obvious is direct substitution. It has been shown that some metal soaps and dialkyl tin dicarboxylate stabilisers are retained by the polymer after heat treatment (135,137-139). Usually, this retention is less than 1% but it could be sufficient to block all the reactive sites. The carboxylate part of the stabiliser is the part mostly retained (139). By repeated solution and precipitation these stabilisers could be removed slowly and could be rapidly removed by treatment with hydrogen chloride.

This suggests that the stabiliser is weakly bound by some coordinated bond to the polymer at the reactive sites. By rearrangement of this coordinated structure, it is suggested that chlorine atoms could exchange with carboxylate groups and this might explain why the carboxylate group is retained to a greater extent than the alkyl groups and this new ester group in PVC is more resistant to thermal decomposition than was the tertiary or allylic chlorine replaced by it and thus degradation is postponed. Support for this has recently come from Bengough's work (60) on ester exchange between cadmium acetate and tertiary and allylic chlorines in PVC.

Peroxide structures are possible initiation sites and thus on examination of the behaviour of stabilisers to peroxides is of value. Some antioxidants are used as auxiliary stabilisers.

The primary purpose behind the addition of alkyl and aryl phosphites is for action as chelating agents to eliminate the catalytic effect of metal chlorides in the system but they may also act by deactivating hydroperoxide initiation sites (140) in the following way.

Alkyl Phosphite + ROOH Alkyl phosphate + ROH.

Redox systems (49) are capable of decomposing peroxides in a harmless manner and some sulphur compounds (141,-143) can deactivate hydroperoxides in a non-homolytic fashion. This deactivation by sulphur compounds is more efficient than normal antioxidant chain inhibition mechanisms and could account for the enhanced stabilising activity of organo tin compounds containing sulphur (137).

Organo tin compounds similar to those used for stabilising PVC react with hydroperoxides to give products which do not affect PVC (144). It has been shown (20) that conventional stabilisers retard the decomposition of hydroperoxides and PVC stabilisation is possibly accomplished in a similar manner.

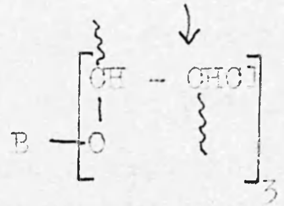
Catalytic conversion of hydroperoxides to alcohols is the basis of a novel system (104) which involves metal borates with hydrochloric acid giving boric acid which catalyses the conversion of peroxides in PVC to alcohols. At elevated temperatures, the boric acid gives metaboric acid which forms esters with the alcohol groups.

$$\mathrm{MeB_4O_7} + 2\mathrm{HCl} + 5\mathrm{H_2O} \longrightarrow 4\mathrm{B(OH)_3} + \mathrm{MeCl_2}$$

$$\sim\sim\mathrm{CH(OOH)} - \mathrm{CHCl}\sim\sim \xrightarrow{\mathrm{B(OH)_3}} \sim\sim\mathrm{CH(OH)} - \mathrm{CHCl}\sim\sim$$

$$\mathrm{B(OH)_3} \xrightarrow{150^\circ\mathrm{C}} \mathrm{BO(OH)} + \mathrm{H_2O}$$

$$\mathrm{BO(OH)} + 3\left[\sim\sim\mathrm{CH(OH)} - \mathrm{CHCl}\sim\sim\right]$$



$$\downarrow$$

$$\mathrm{B} - \left[\mathrm{O} - \overset{\sim}{\mathrm{CH}} - \underset{\sim}{\mathrm{CHCl}}\right]_3$$

It has been suggested (94) that stabilisation may occur by disruption of the radical chain propagation step because radioactivity appeared in the polymer when ^{14}C butyl labelled dibutyl tin diacetate stabiliser was used. Transfer to butyl was proposed as the termination of the molecular chain but this was later repudiated (137).

Polyvinylenes and other long conjugated polyene systems such as dehydrochlorinated PVC exert a stabilising influence possibly by formation of resonance stabilised conjugated biradicals which have insufficient energy to continue the propagating chain (18,145).

The principal aim of stabilisation is normally to prevent colour and, in this light, increased transfer would work. If loss of hydrogen chloride is increased, discolouration can still be prevented if the conjugated system is modified, possibly by dienophiles which could disrupt the system so that the absorption is only in the ultra violet region. It is possible that a number of systems function in this way (14,20,72,96,137,139). Another similar effect is observed in oxidation and some metal-based stabilisers have been identified as oxidation catalysts (3,4,20,130). Antioxidants are obviously to be avoided if oxidative bleaching is desired.

It would appear that, although stabilisers function in a number of ways, the same overall result is obtained.

4). Review of the Thermal Degradation of PVA.

PVA does not have the same variation in uses that has made PVC one of the plastics produced in very large quantities at the present day. PVA does have the advantage over PVC that, in an unstabilised form, it is far more thermally stable.

Because of the rather limited uses of PVA, its degradation has not been studied by so many workers as has PVC degradation. Another reason for this may be that the degradation behaviour of PVA was elucidated very clearly by Grassie (33,149). Thus, a review of the work carried out on the degradation of PVA virtually amounts to a review of Grassie's work.

PVA was found to be stable in vacuum up to 190°C and, at higher temperatures, lost acetic acid leaving a polyacetylene chain as in PVC. The reaction was shown to be a chain reaction proceeding without the agency of free radicals. Initiation was found to occur at the ends of the polymer chains and could occur at any of the possible end structures. The initiation and propagation reactions were interpreted in terms of well known chemical reactions.

A highly coloured conjugated residue was obtained and this was interpreted as suggesting that acetic acid is evolved, not molecule by molecule at random but one after another along the chain. Another piece of evidence put forward in favour of a chain reaction was the fact that small amounts of oxygen inhibited the reaction completely and it was suggested that this was by reaction with the double bond at the reactive point in the chain.

This chain reaction was explained by the fact that removal of a molecule of acetic acid leaves a carbon-carbon double bond which has a methylene group in the α position adjacent to an acetyl group. This methylene group will be highly reactive and thus loss of a further molecule of acetic acid is facilitated.

It was supposed that initiation was by some mechanism similar to the pyrolysis of simple acetate esters (150,151).

The propagation is presumed to go through the chain to the far end and this is quite reasonable since the polymer has a head-to-tail structure (152,153). It is possible that structural irregularities in the chain may arrest the progress of the reaction.

The overall energy of activation was 53.6 k.cal/mole and branches caused deviations in the kinetic measurements.

Thus, PVA has been shown to degrade by a non-radical chain mechanism which is very different to the most widely accepted mode of PVC degradation.

The products of degradation (162) have been examined by mass spectrometry and found to be nitrogen, carbon monoxide, ethylene, carbon dioxide, acetic acid, benzene and toluene.

5). Review of Degradation and uses of Copolymers of VA and VC.

These copolymers have a wide variety of uses, very often as a substitute for PVC. Their main uses are for gramophone records, vinyl flooring and adhesives. The purpose of adding VA to PVC is to lower the glass transition temperature thus making the polymer processable at lower temperatures and therefore more economically.

The interest in the degradation of the copolymers stems from their tendency to begin to degrade at the processing temperature as they are more unstable than PVC. Also new uses of the polymer have been found in the manufacture of transparent articles, such as transparent egg boxes, where it would be advantageous to avoid discolouration while using injection moulding.

Very little published literature is available on the degradation of these copolymers. One paper (103) purports to discuss the mechanism of their breakdown and compare it with the mechanism for PVC. This claim is not substantiated and no information is to be obtained from this paper.

The only other paper which reports the degradation of these copolymers describes the use of G.L.C. (164) to separate the two acid products - acetic acid and hydrogen chloride. The ratio of acetic acid to hydrogen chloride found was almost identical to the ratio of VA to VC obtained by infra-red spectroscopy. Also, by the nature of the calculations, it was shown that the predominant products by far are acetic acid and hydrogen chloride.

In the stabilisation of these copolymers at present the tendency is simply to add in something which will stabilise PVC, hoping that it will work reasonably well.

6). The purpose of this Work.

The purpose of this work was to examine the different facets of the degradation of copolymers of VA and VC in an attempt to find out how they degrade, why they degrade and also how to arrest the degradation. It was also hoped that the study of the copolymers would help to clarify the present very confused position regarding the mechanism of PVC degradation.

CHAPTER II.

EXPERIMENTAL.

1). Preparation of Polymers.

A). Purification of Monomers.

VA (Hopkin and Williams Ltd.) was distilled under an inert atmosphere, the fraction distilling at 70°C - 72°C was used. This procedure removed both inhibitor and impurities.

VC (I.C.I. Ltd.) was used from the cylinder and treated as described in the next section.

B). Filling Dilatometers.

The initiator for polymerisation was azo-bis-iso-butyronitrile (Eastman Kodak Ltd.), previously recrystallised from ethanol. It was introduced in the form of a solution in benzene, the benzene then being removed on a suction pump.

VA was poured into a reservoir, degassed four times, distilled into a graduated reservoir and, finally, distilled into the dilatometer containing initiator.

VC was distilled from the cylinder, through a needle valve, into a reservoir, degassed five times, distilled into a graduated reservoir then distilled into the dilatometer. The distillations were carried out from a reservoir at - 65°C at which temperature the vinyl chloride is a liquid.

C). Polymerisation.

Polymerisations were carried out in bulk at 60°C by normal dilatometric methods to 10% conversion. Care had to be exercised as certain monomer mixtures for preparation of a copolymer with VC content around 95% exploded during polymerisation.

D). Precipitation and Drying of the Polymers.

The polymers were precipitated in two ways depending on composition.

(a). Copolymers of high VC content were dissolved in cyclohexanone and precipitated in methanol. This process was repeated three times and the copolymer was dried in a vacuum oven for several days at about 45°C.

(b). Copolymers with over about 40% vinyl acetate were precipitated from acetone solution in a suitable water/methanol mixture, the composition of which had to be varied with copolymer composition. The copolymer was then "freeze-dried" using benzene as solvent.

2). Liquid Phase Degradation.

The apparatus in which these degradations were performed is shown in figure 2. The liquid in the flask A was continuously boiled, the degradation tube being heated by the distilling vapour. This system has the advantage of maintaining a stable, reproducible temperature. Fluctuations caused by changes in atmospheric pressure were small enough to be neglected as was evidenced by a thermocouple placed in the apparatus.

A). In Ethyl Benzoate.

The degradation tube for the reactions in ethyl benzoate, (Mersey Chemicals Ltd.), which was distilled before use, is shown in detail in figure 3. Nitrogen was passed over the surface of the solution, the concentration of which was about 100 mg. of copolymer in 10 ml. of ethyl benzoate. Degradation yielded a mixture of hydrogen chloride and acetic acid. The hydrogen chloride was carried over by the nitrogen and collected in the water trap. The acetic acid was retained by the ethyl benzoate from which it was removed by extraction with water. The

Figure 2

Apparatus for Solution Degradations.

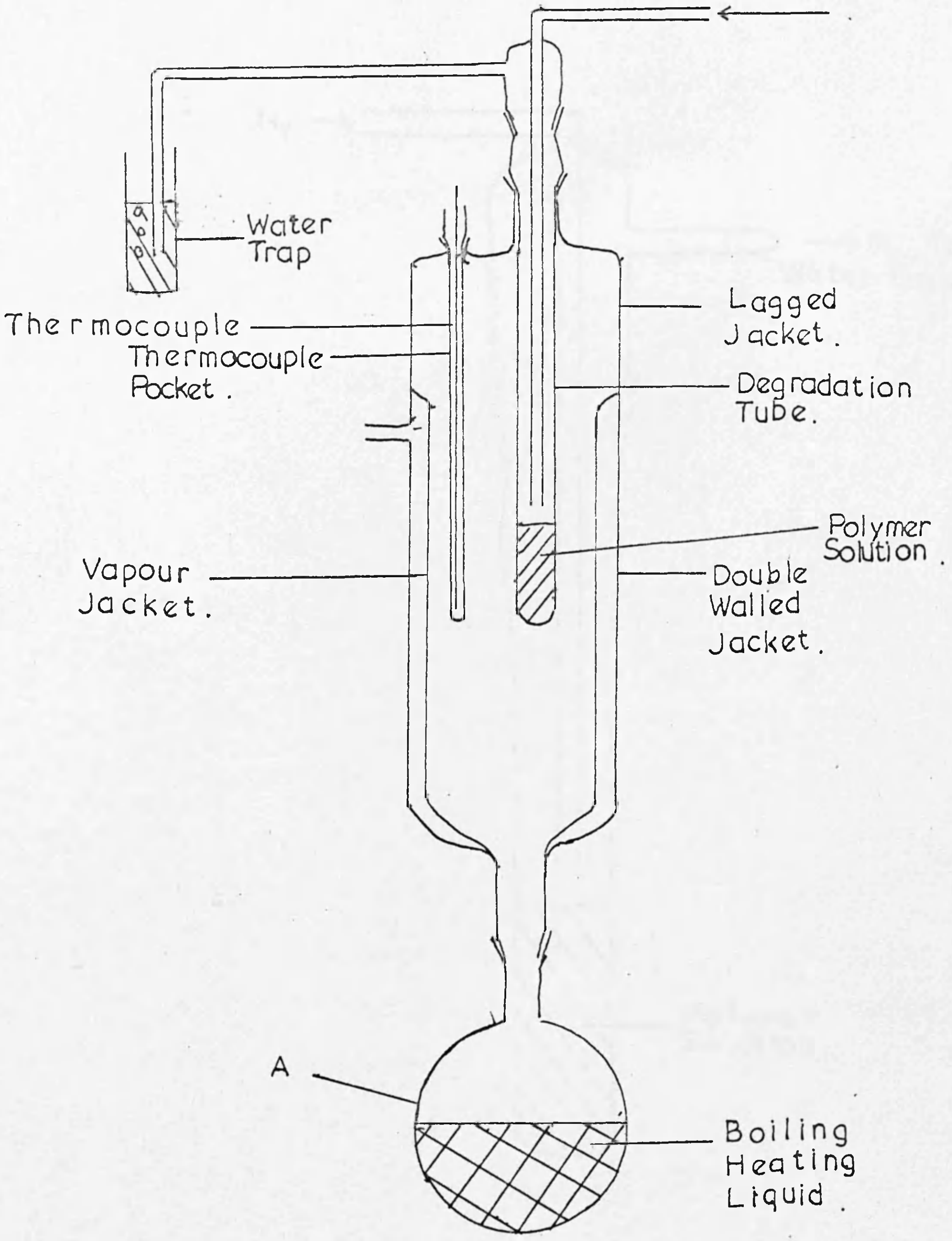
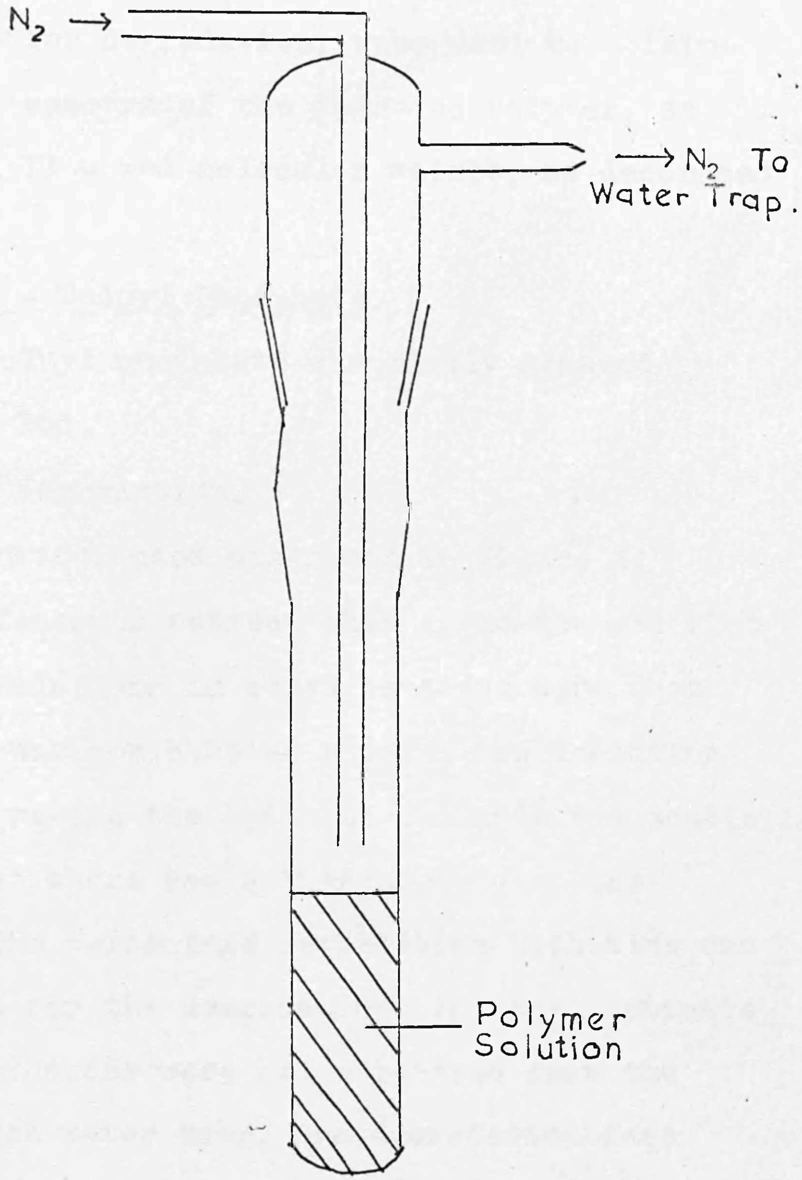


Figure 3
Apparatus for Degradations in Ethyl Benzoate



amounts of each acid liberated over successive time intervals were determined by titration as described in II 2 B (ii).

In another series of degradations the polymer solutions, after degradation, were used to obtain ultra-violet spectra of the degraded polymer, as described in II 4 and molecular weight, as described in II 5.

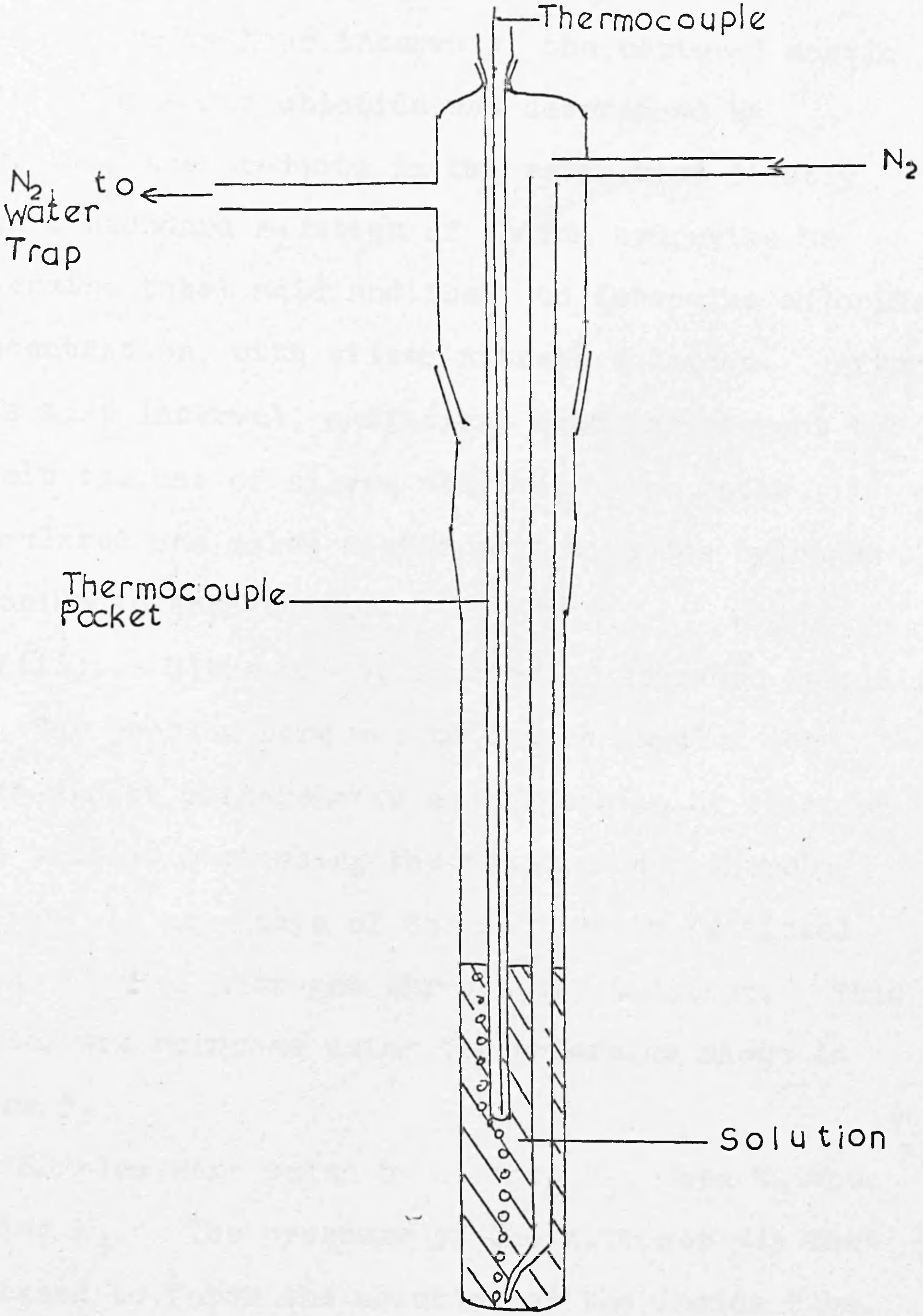
B). <u>In Tri - Toluyl Phosphate.</u>

Tri - toluyl phosphate was kindly donated by British Geon Ltd.

(i). Degradation.

The apparatus used was shown in figure 4. The only differences between this apparatus and that used for degradations in ethyl benzoate were that the nitrogen was now bubbled through the degrading solution, to remove the hydrogen chloride and acetic acid, and that there was a thermocouple in the solution. The percentage degradation with time was calculated as for the degradations in ethyl benzoate but, as the products were being removed from the system into the water trap, one degradation gave as much information as many separate degradations

Figure 4
Apparatus for Degradations in Tritoluyl Phosphate.



in ethyl benzoate.

(ii). Ratios of Products.

At twelve hour intervals, the ratio of acetic acid to hydrogen chloride was determined by titrating the products in the water trap firstly with a standard solution of sodium hydroxide to determine total acid and then, to determine chloride concentration, with silver nitrate solution. After this time interval, sufficient acid was present to permit the use of silver nitrate. The ratio calculated was moles acetic acid to moles hydrogen chloride in each case.

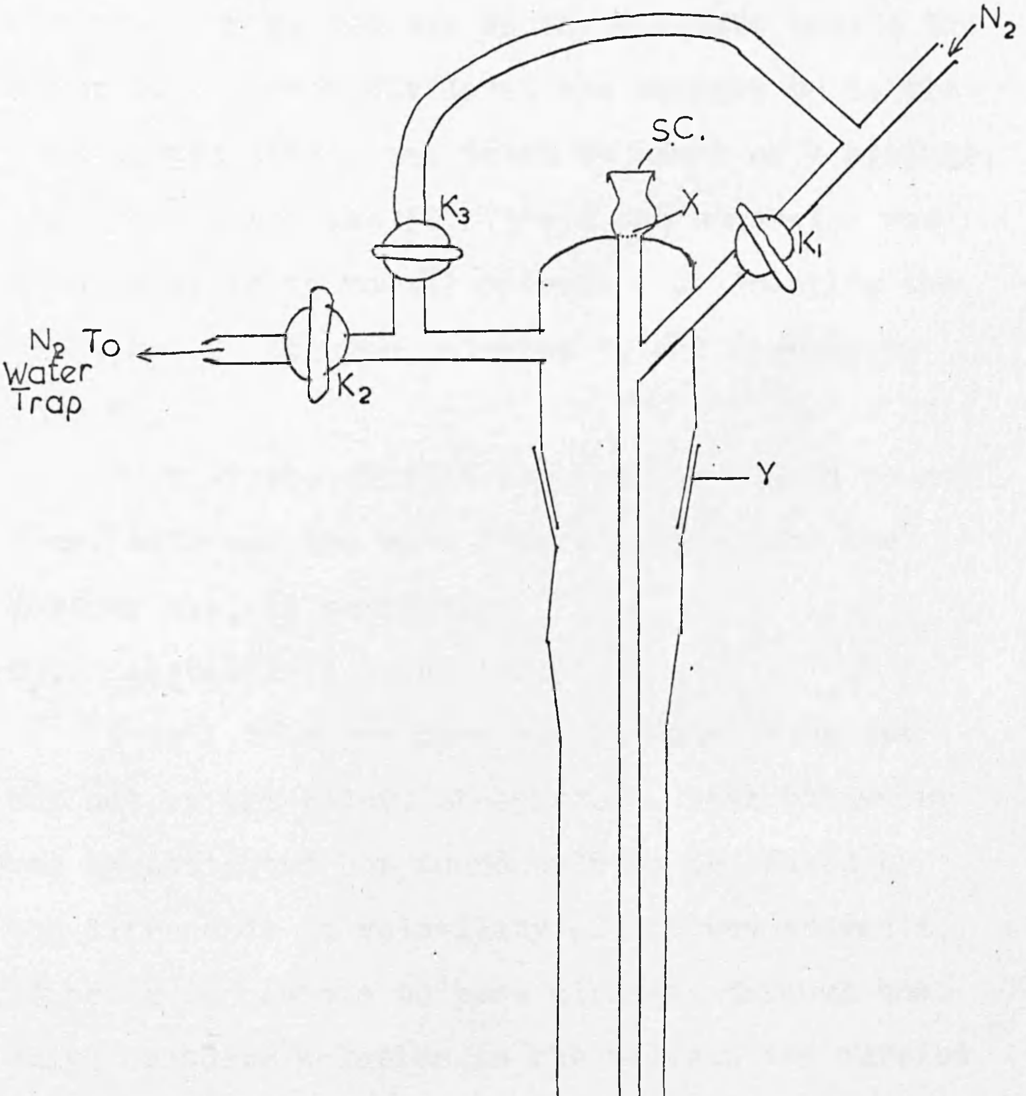
(iii). Ultra-violet Spectra of Degraded Solutions.

The problem here was to obtain samples for ultra-violet measurements as a function of reaction time without disturbing the reaction and thereby taking full advantage of the continuity permitted by the flow of nitrogen through the solution. This problem was overcome using the apparatus shown in figure 5.

Samples were taken by closing K_1, then K_2 then opening K_3. The pressure of the nitrogen was then increased to force the solution up the inside tube.

Figure 5.

Apparatus for Solution Samples.



The joint Y had to be held by hand to prevent its springing apart because of the pressure inside the apparatus. Then the level was brought up to the mark X, the sample was taken by means of a syringe, through a serum cap (S.C.) and the apparatus was then returned to normal operation by lowering the pressure of nitrogen, closing K_3 and opening K_2 then K_1.

Part of the aliquot removed was placed in a 2 mm. cell and the rest into a sample tube for further use, if necessary.

C). Acetic Acid Retention.

Acetic Acid was retained by ethyl benzoate but not by tri-toluyl phosphate. This behaviour was investigated but found only to be caused by the difference in volatility of the two solvents, it being impossible to pass nitrogen through the ethyl benzoate solution as the solvent was carried over.

D). Effect of Solvent.

The effect of solvent on the characteristics of the degradation reaction was studied for PVA and PVC by using different solvents to make up the solution for degradation. The solubilities of the polymers restricted the number of possible solvents to ethyl benzoate, di-chloro-napthalene and benzophenone, the last being very poor for PVA. The apparatus used was as in figure 3.

E). Effect of Temperature.

These studies were carried out on tri-toluyl phosphate solutions by changing the continuously distilling liquid in the flask A at the base of the vapour jacket. The apparatus used was as in figure 4.

3). Solid Phase Degradations.

A). In Dynamic Molecular Still.

Initial degradations in the solid phase were carried out using a dynamic molecular still apparatus which is shown in figure 6. This apparatus was basically similar to that used by Grassie and Melville (154). The polymer sample was placed in a stainless steel tray and a sintered stainless steel lid was screwed in place. This tray was then screwed into the heating block, which was also of stainless steel, the system was evacuated and the degradation carried out. The products were trapped in the three-armed tube, dissolved in water and titrated.

During the degradation, the system is continuously pumped out.

B). Thermal Volatilisation Analysis.

The samples were degraded in the apparatus shown in figure 7 which is that of McNeill (155). This apparatus is also continuously pumped.

(i). Initial.

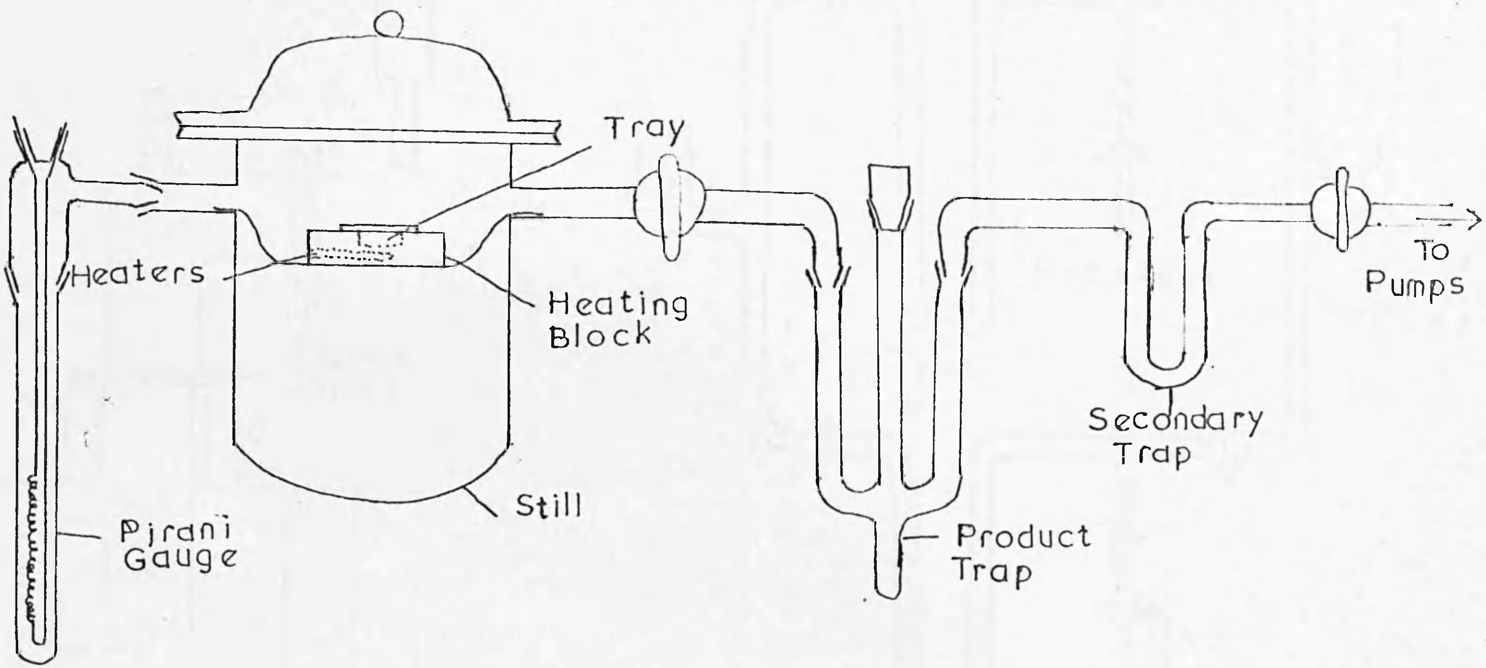
These were done in the solid phase on samples of about 25 mg., the exact weight being noted in each case. The output of the pirani gauge was continuously traced on a recorder chart, marks being put on this trace at one hundred degree intervals in the temperature of the inside base of the degradation tube, which has been previously determined with respect to the oven temperature.

In this series of experiments, the volatiles were merely pumped away, no attempt being made to collect them from the trap after the run had been completed.

(ii). Further.

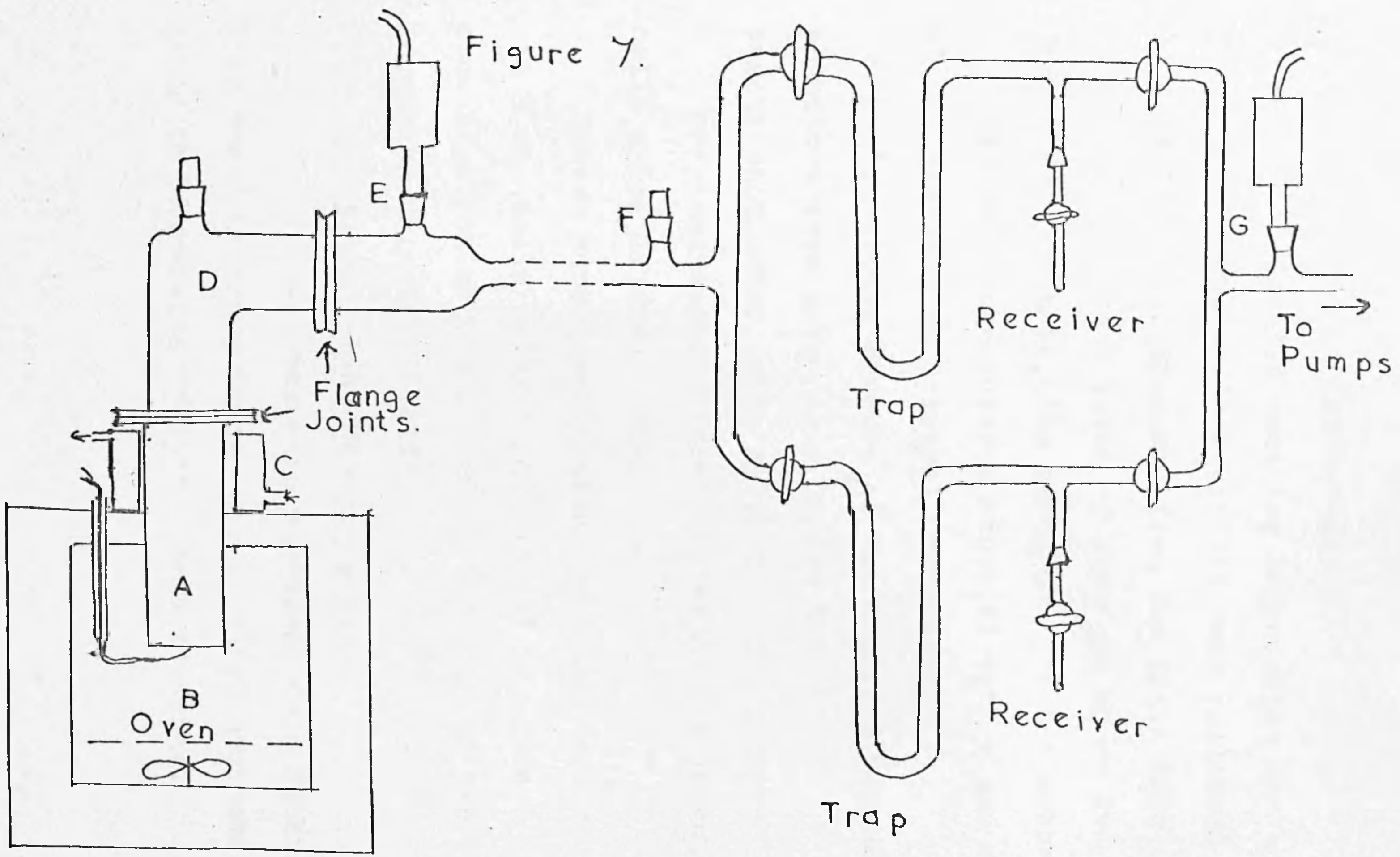
It was intended to trap the products from the two main peaks, separate them by gas liquid chromatography, and run mass spectra on the effluent

Figure 6.



Dynamic Molecular Still.

Figure 7.



Thermal Volatilisation Analysis Apparatus.

from the gas liquid chromatograph.

The sample size used for degradation was about 100 mg., and the product samples were collected by distilling the products from the traps into conveniently shaped tubes of the form shown in figure 8. In this, the serum cap was for extraction of a sample of the gaseous material with a gas syringe.

4). Ultra-violet Spectral Measurements.

Ultra-violet spectra of the degraded polymer solutions were taken on a Unicam S.P.800 spectrophotometer, with solvent in the reference beam.

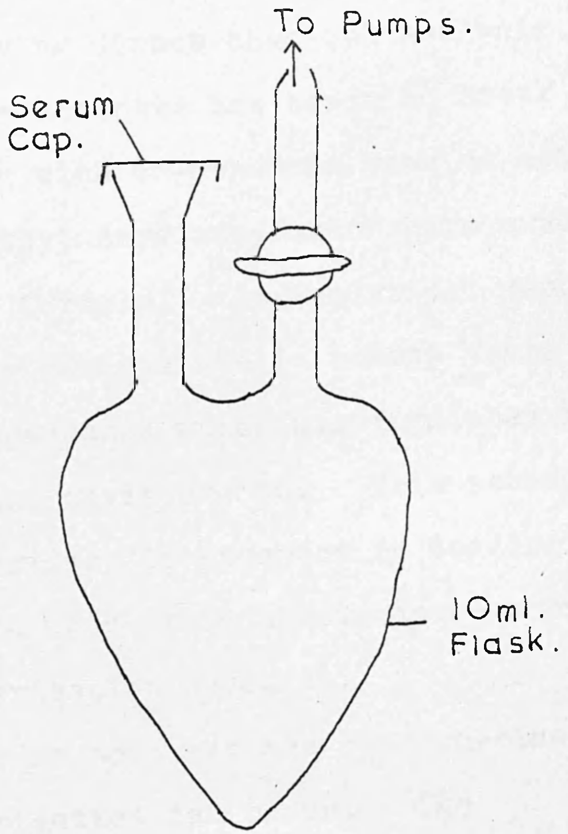
Original spectra were carried out in 10 mm. cells using diluted solutions.

Later, more quantitative, spectra were measured in 2 mm. cells using a solution of the same concentration as the degrading solution or the degrading solution itself.

5). Molecular Weight Measurement.

Molecular weights were measured, on a Mechrolab High Speed Membrane Osmometer, in ethyl benzoate, using an Ultracella "feinst" grade membrane.

Figure 8.



Product Collection Vessel for T.V.A.

CHAPTER III.

Determination of the Reactivity Ratios for the Copolymerisation of Vinyl Acetate and Vinyl Chloride.

One of the first essentials in dealing with copolymers is to be able to determine their compositions. Several methods have been used in the past, usually involving direct chemical analysis. This method can be quite accurate but tends to break down when one is dealing with co-monomers such as methyl methacrylate and ethyl acrylate, which have exactly the same molecular formula. An analytical method which has come into general use in recent years is nuclear magnetic resonance which distinguishes between protons in different environments. This method was deemed to have considerable prospect in dealing with the copolymers with which this thesis is concerned.

1). The Copolymerisation Equation.

When two or more monomers are copolymerised together copolymerisation can occur. The composition of the copolymer obtained may be varied by varying the concentrations of the monomers.

The composition of the copolymer will depend on the reactions which use up monomer namely the propagation reactions. In the copolymerisation of two monomers M_1 and M_2, four propagation steps are involved as follows:-

Propagation $\quad M_1^* + M_1 \dashrightarrow M_1^* \qquad k_{11}$

$M_1^* + M_2 \dashrightarrow M_2^* \qquad k_{12}$

$M_2^* + M_1 \dashrightarrow M_1^* \qquad k_{21}$

$M_2^* + M_2 \dashrightarrow M_2^* \qquad k_{22}$

in which M_1^* and M_2^* are the radicals derived from M_1 and M_2 respectively. The rate at which monomer 1 is used up is

$$-\frac{d\left[M_1\right]}{dt} = k_{11}\left[M_1^*\right]\left[M_1\right] + k_{21}\left[M_2^*\right]\left[M_1\right] \qquad (X)$$

and the rate at which monomer 2 is used up is

$$-\frac{d\left[M_2\right]}{dt} = K_{12}\left[M_1^*\right]\left[M_2\right] + k_{22}\left[M_2^*\right]\left[M_2\right] \qquad (Y)$$

In the stationary state, the concentrations of M_1^* and M_2^* must be constant and also the rate of conversion of M_1^* into M_2^* must be equal to the rate of conversion of M_2^* into M_1^*, therefore

$$k_{21} \left[M_2^*\right]\left[M_1\right] = k_{12}\left[M_1^*\right]\left[M_2\right]$$

$$\left[M_2^*\right] = \frac{k_{12}\left[M_2\right]}{k_{21}\left[M_1\right]}\left[M_1^*\right]$$

If this value of $\left[M_2^*\right]$ is substituted in equations (X) and (Y) and the equation resulting from equation (X) is divided by the equation resulting from equation (Y),

$$\frac{d\left[M_1\right]}{d\left[M_2\right]} = \frac{k_{11}\left[M_1^*\right]\left[M_1\right] + \dfrac{k_{21}\;k_{12}\left[M_2\right]}{k_{21}\left[M_1\right]}\left[M_1^*\right]\left[M_1\right]}{k_{12}\left[M_1^*\right]\left[M_2\right] + \dfrac{k_{22}\;k_{12}\left[M_2\right]}{k_{21}\left[M_1\right]}\left[M_1^*\right]\left[M_2\right]}$$

which reduces to

$$\frac{d\left[M_1\right]}{d\left[M_2\right]} = \frac{\left[M_1\right]}{\left[M_2\right]} \cdot \frac{r_1\left[M_1\right] + \left[M_2\right]}{r_2\left[M_2\right] + \left[M_1\right]}$$

which, when solved for r_2, gives

$$r_2 = \frac{\left[M_1\right]}{\left[M_2\right]}\left\{\frac{d\left[M_2\right]}{d\left[M_1\right]} \cdot \left(1 + \frac{\left[M_1\right]}{\left[M_2\right]}\;r_1\right) - 1\right\} \qquad (Z)$$

in which $\left[M_1\right]$ and $\left[M_2\right]$ are the molar concentrations in the monomer mixture, and $d\left[M_1\right]$ and $d\left[M_2\right]$ are the concentrations of the monomer units in the polymer chain. If, now, the molar ratio of monomers in the monomer mixture and the ratio of the monomer units in the polymer chain are known, a graph of r_1 versus r_2 may be drawn using equation (Z). If this procedure is carried out for several copolymers, a series of straight lines is obtained. The coordinates of the point at which they meet represents the solution of the simultaneous equations and thus give the true values of r_1 and r_2. However, in practice, it is rarely found that all the lines are concurrent and the limits of error are usually estimated from the magnitude of the area in which the intersections occur. A typical plot of r_1 versus r_2 is shown in figure 13.

2). Experimental.

By virtue of there being different numbers of protons in each of two energy states, transitions between the states can be induced which will give a nett absorption of energy which is called resonance. This energy is in the radio frequency range and this method is called nuclear magnetic resonance spectroscopy.

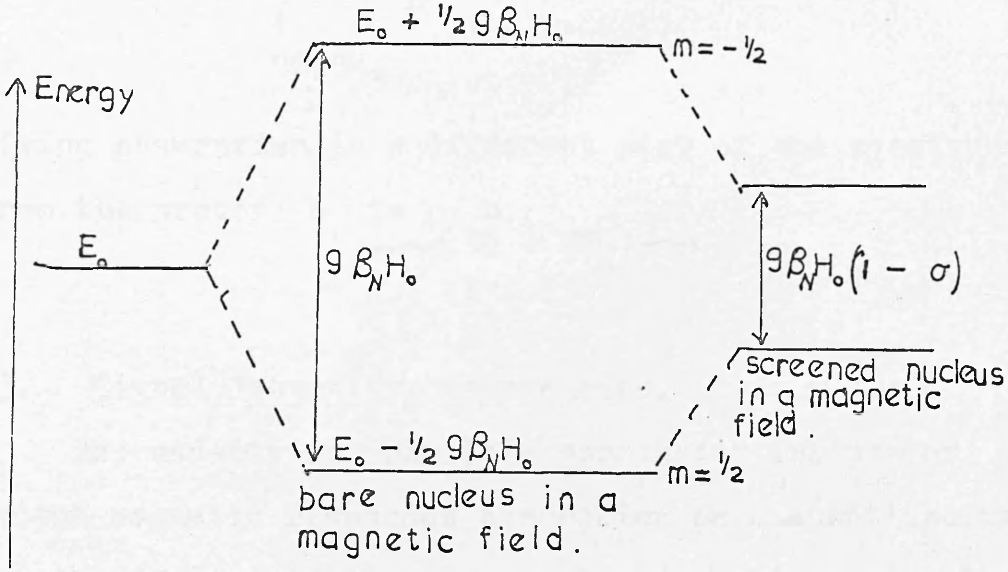
A). Magnetic Shielding.

If an atom of a molecule is placed in a magnetic field, it acquires a magnetic moment by virtue of the induced orbital motion of its electrons. The magnitude of this secondary magnetic field is proportional to the applied field H_o. The local magnetic field at the position of the nucleus is not H_o, but differs slightly from H_o

$$H \text{ (local)} = H_o \quad (1 - \sigma)$$

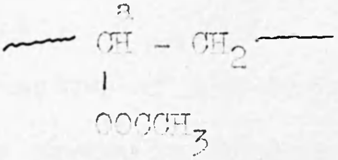
in which σ is a non-dimensional constant called the screening constant. The screening reduces the separation of the nuclear energy levels in a magnetic field as shown in figure A.

Figure A.



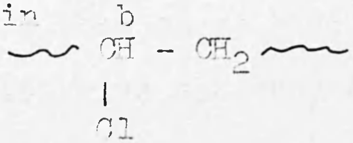
As a result, the energy quantum required for a transition between states is smaller, and therefore resonance will occur at a lower frequency, or at a higher applied field.

For a series of protons in different chemical environments, there is a corresponding series of screening constants. As a result, resonance will occur in a different part of the spectrum for each chemically distinct proton. This displacement is known as chemical shift. This results in the proton a in



$$\sim \underset{\mathrm{OOCCH_3}}{\underset{|}{\overset{a}{\mathrm{CH}}}} - \mathrm{CH_2} \sim$$

giving absorption in a different part of the spectrum from the proton b in



$$\sim \underset{\mathrm{Cl}}{\underset{|}{\overset{b}{\mathrm{CH}}}} - \mathrm{CH_2} \sim$$

B). Signal Intensity Measurements.

The underlying principle permitting the use of proton magnetic resonance absorption as a quantitative measure of a particular substance is that the signal strength is proportional to the number of protons giving rise to that signal. The intensity of a signal is measured by taking the area under the appropriate peak in the spectrum and this is made possible by an integration technique which may be built into the spectometer.

C). Preparation of the Copolymers.

The copolymers for analysis were prepared in the same way as those for degradation (see chapter II). 10 ml. quantities were polymerised in bulk at 60°C.

using 2,2' - azobis - (2 - methylpropionitrile) as initiator. They were precipitated in various ways depending on the composition (see also chapter II).

3). Results.

The spectra of the copolymers -- a typical spectrum is shown in figure 9 -- were compared with those of PVA and PVC as shown in figures 10 and 11 respectively. It was thus shown that the tertiary protons in the VA units give the peak A at 4.8τ the tertiary protons in the VC units give the peak at 5.8τ . The absorption at 8 is associated with the methyl and methylene protons in both units.

The nuclear magnetic resonance spectra (N.M.R.) were obtained in $CDCl_3$ solution using a Perkin - Elmer R10 60 Mc/s spectrometer. The compositions of the copolymers were calculated from the ratio of the areas under the two tertiary proton peaks as measured by the attached integrator. An integrated spectrum is shown in figure 12. The results obtained for the ratios of monomer units in the copolymer chains, along with the molar ratios of monomers in the original monomer mixtures Shown in Table I.

Table I.

Copolymer Composition Data*

	Monomer Mixture $[M_1] / [M_2]$	Copolymer $d[M_1] / d[M_2]$
1.	2.00	0.703
2.	0.30	0.115
3.	34.00	7.67
4.	8.15	3.195
5.	0.364	0.147

* M_1 = Vinyl Acetate, M_2 = Vinyl Chloride.

The reactivity ratios were obtained using the equation

$$r_2 = \frac{[M_1]}{[M_2]} \left\{ \frac{d[M_2]}{d[M_1]} \cdot \left(1 + \frac{[M_1]}{[M_2]} r_1 \right) - 1 \right\}$$

and the resulting plot r_1 versus r_2 is shown in figure 13.

Figure 9.

Typical N.M.R. Spectrum of a Vinyl Acetate/Vinyl Chloride Copolymer.

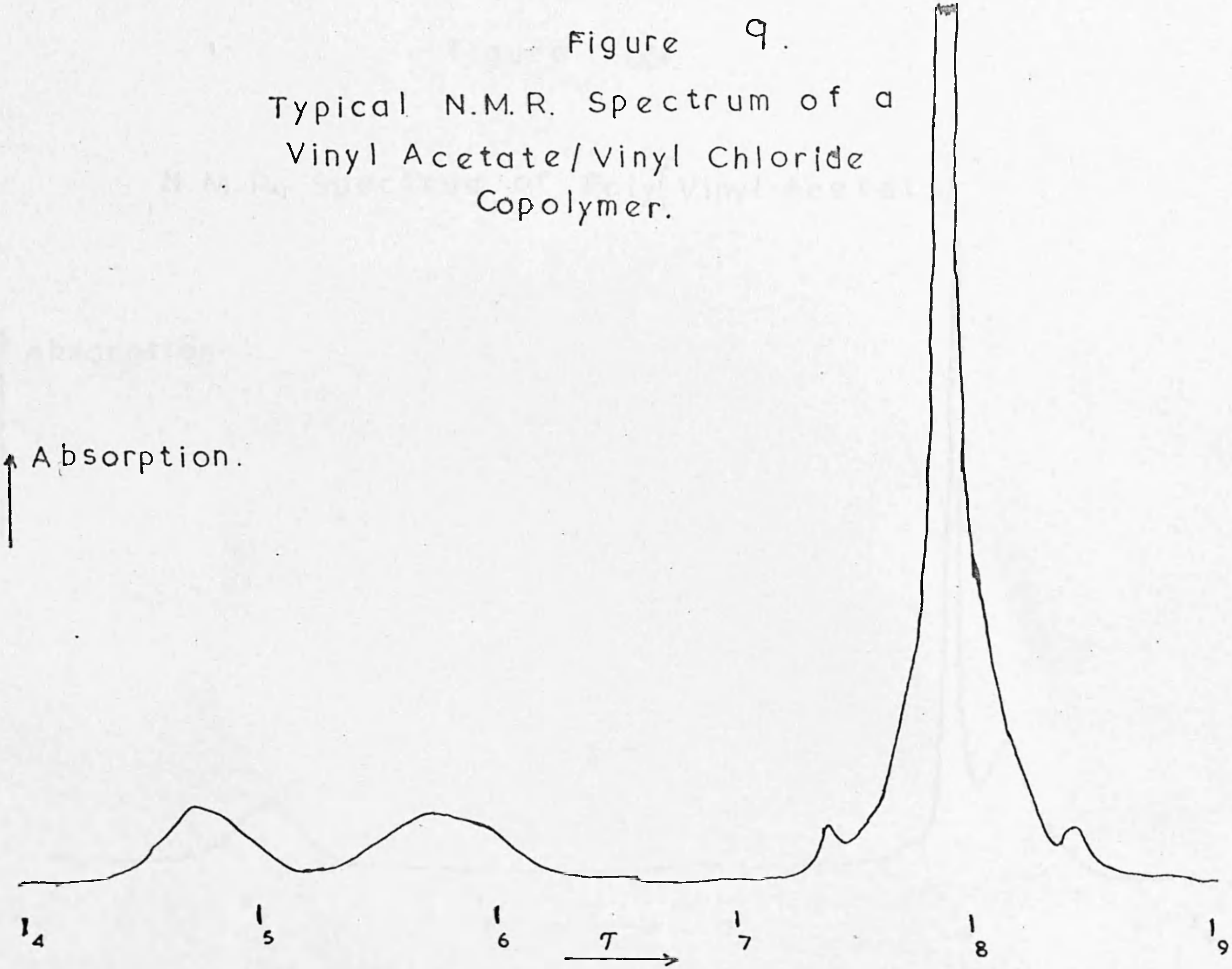


Figure 10.

N.M.R. Spectrum of Poly(Vinyl Acetate).

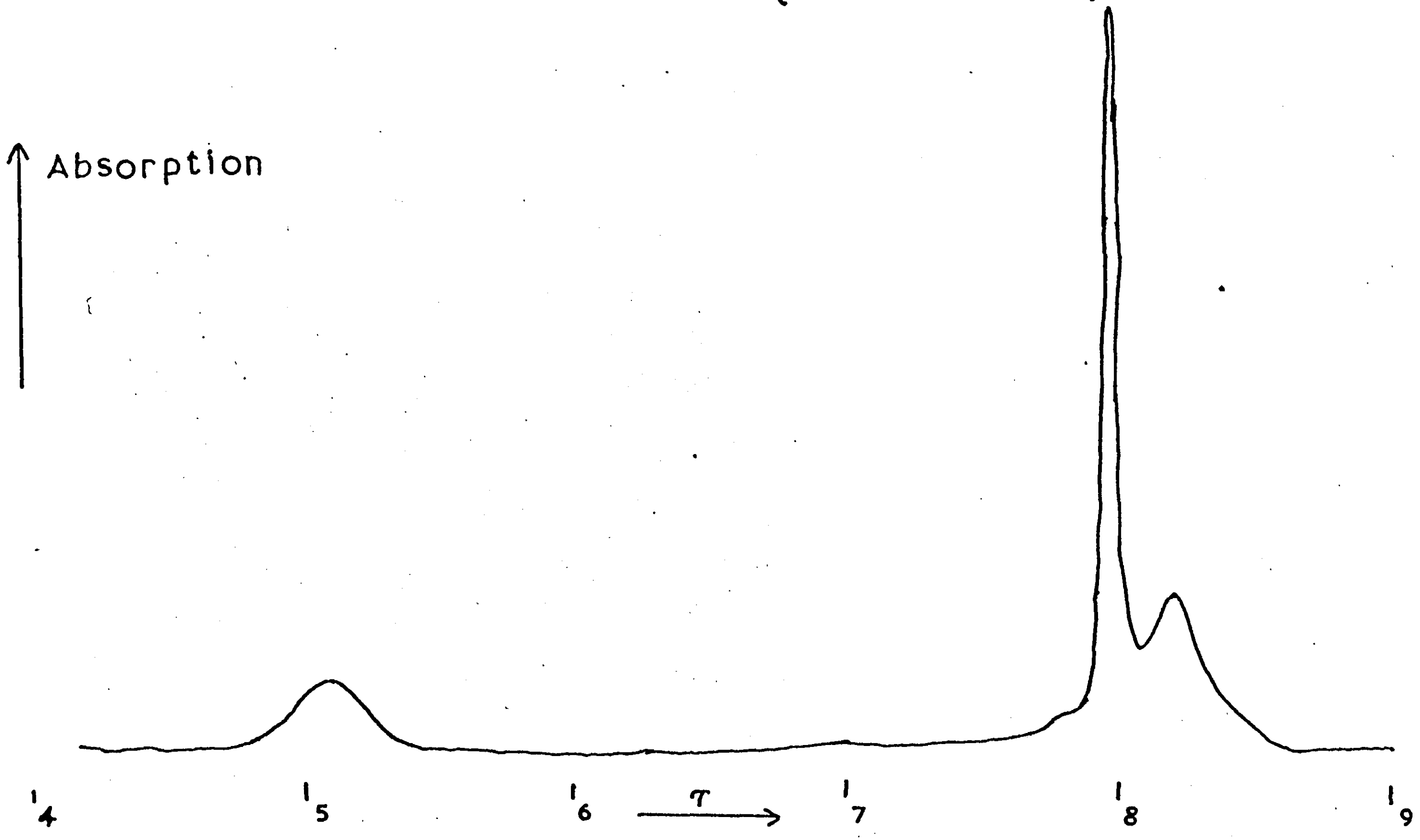
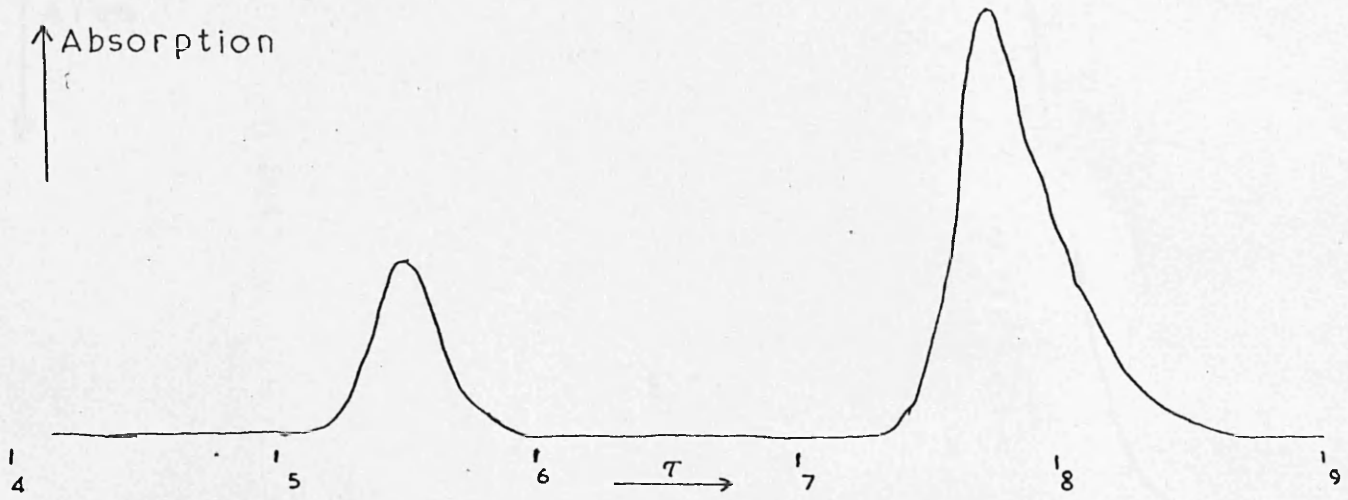


Figure 11.

N.M.R. Spectrum of Poly(Vinyl Chloride).



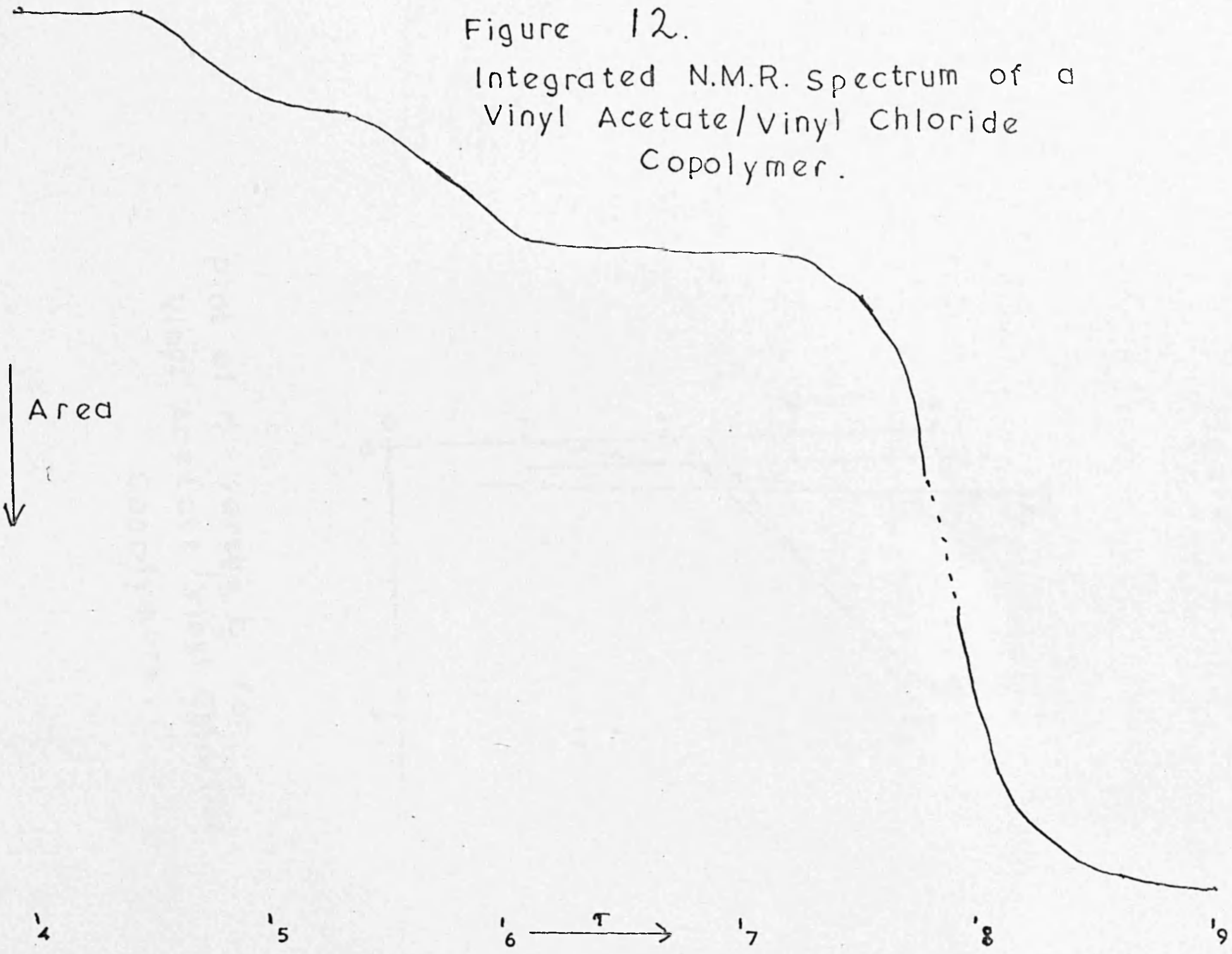
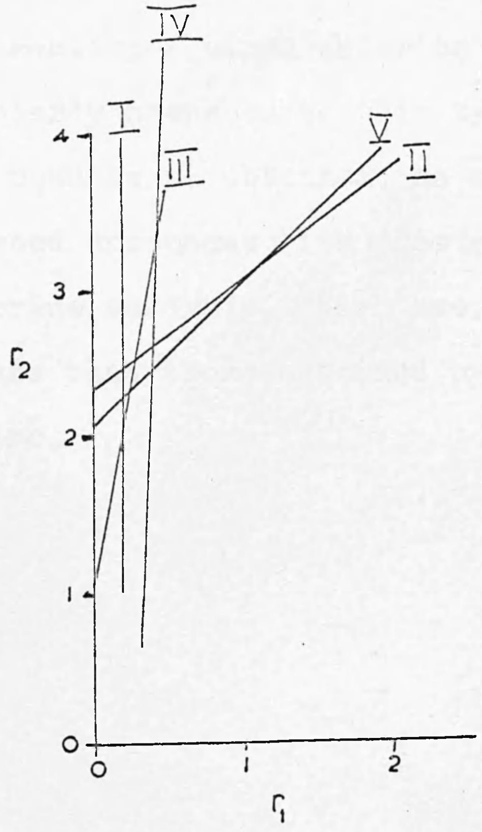


Figure 12.

Integrated N.M.R. Spectrum of a Vinyl Acetate/Vinyl Chloride Copolymer.

Figure 13.



Plot of r_1 versus r_2 for Vinyl Acetate/Vinyl Chloride Copolymers.

The results derived from figure 13 are shown in table 2 along with other results obtained previously, noting the methods by which they were obtained.

4). Discussion.

Thus the vinyl acetate / vinyl chloride system proves to be particularly amenable to this type of analysis and the results so obtained, as shown in table 2, are in good agreement with previous values based on chlorine analysis, which are probably more accurate than those obtained by dehalogenation by zinc.

Table 2.

Reactivity Ratios for the Copolymerisation of Vinyl Acetate (M_1) and Vinyl Chloride (M_2).

r_1	r_2	Temp., °C.	Analytical Method.	Ref.
0.6	1.8	40	Dehalogenation by zinc	(156)
0.23 ± 0.02	1.68 ± 0.08	60	Chlorine Estimation	(157)
0.3	2.1	68	Chlorine Estimation	(158)
0.30 ± 0.08	2.45 ± 0.15	60	Present Work	(161)

CHAPTER IV.

Initial Investigations.

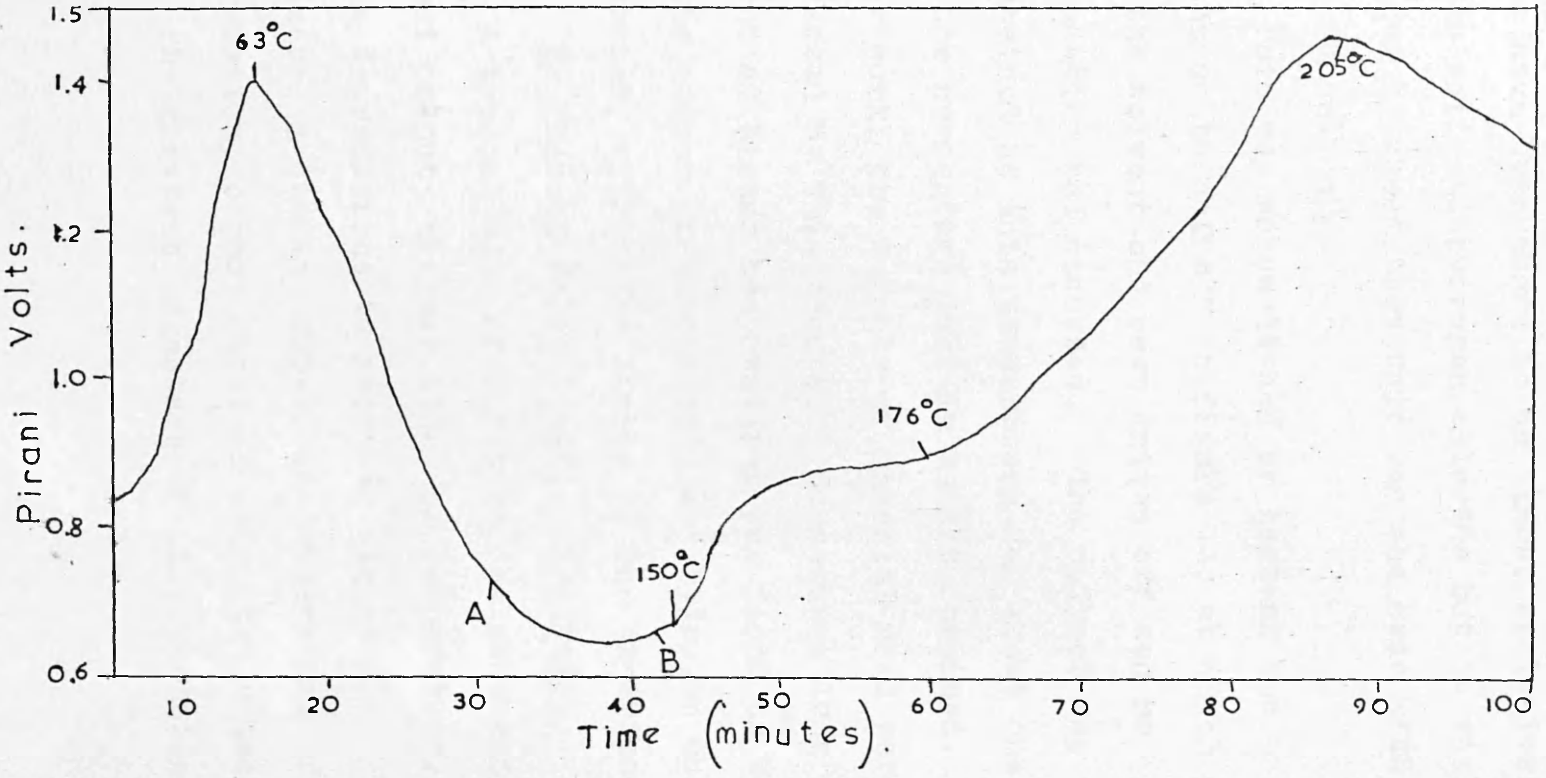
1). In the Dynamic Molecular Still.

The approximate temperature at which degradation proceeds at a conveniently measurable rate was determined by inspection of a Pirani gauge plot, as in figure 14, which illustrates the relative rate (volts) of production of volatile material as a function of time and temperature. The first peak in figure 14 is attributable to trapped solvent being released from the polymer on melting, and the second to volatile products of degradation.

At the point A on this plot, the degradation is proceeding at a measurable rate and this would be a reasonable minimum temperature at which to perform isothermal degradations. It is clear from figure 14 that temperatures around 180°C would be most convenient for detailed studies.

Another requirement before detailed degradation work may be commenced is a knowledge of the products of the reaction. As stated in the introduction,

Figure 14.



Typical Plot of Pirani Volts Against Time for a 50/50 VA/VC Copolymer these have been shown to be almost exclusively acetic acid and hydrogen chloride but it was decided to check that this was the case with the present polymers.

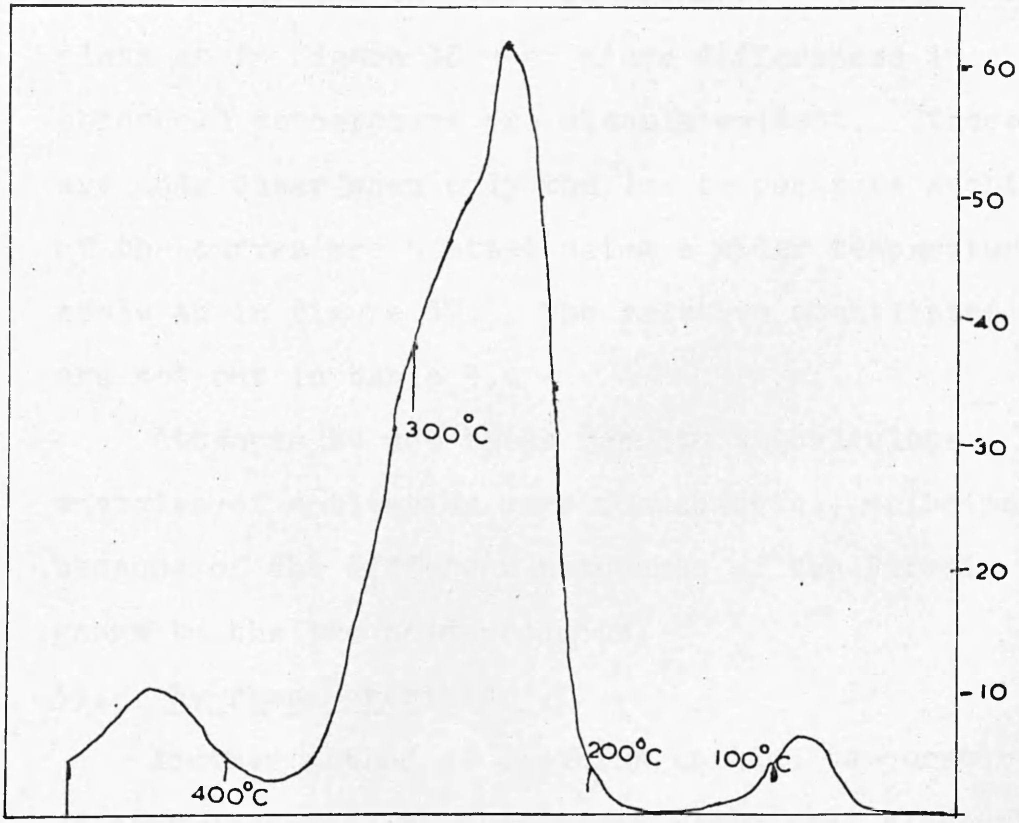
This was accomplished by heating the polymer sample up to point B in figure 14, at which point all the solvent had been driven off and no degradation had occurred. The polymer was maintained at this temperature for about one hour and the percentage loss in weight obtained. In later work, the weights of material used were corrected by this amount. Subsequent loss in weight at higher temperatures was found to be equal to the amount of acetic acid and hydrogen chloride collected, within the limits of the experiment.

2). By Thermal Volatilisation Analysis.

A typical plot of pressure, as measured by Pirani output, against time, or temperature, for these degradations is shown in figure 15. This indicates a similar threshold temperature of degradation to that obtained using the molecular still.

The greatest advantage of this technique is its

Figure 15.



Typical Plot of Pirani Reading Against Temperature by Thermal Volatilisation Analysis for a 50/50 VA VC Copolymer.

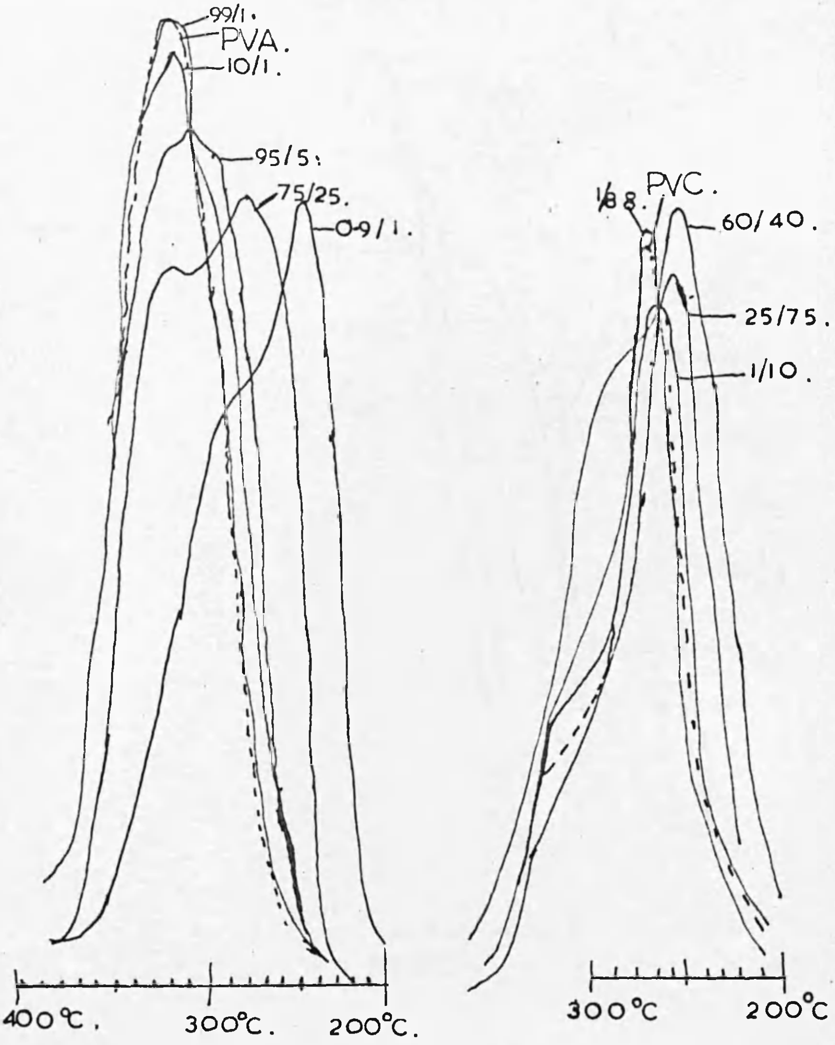
ability to demonstrate the relative stabilities of the different copolymers. This is done simply by superimposing the various pressure / temperature plots as in figure 16 when minor differences in threshold temperature are clearly evident. These are made clear when only the low temperature sections of the curves are plotted using a wider temperature scale as in figure 17. The relative stabilities are set out in table 3.

Attempts to use these results to calculate energies of activation were unsuccessful, principally because of the different responses of the Pirani gauge to the two acid products.

3). By Thermogravimetry.

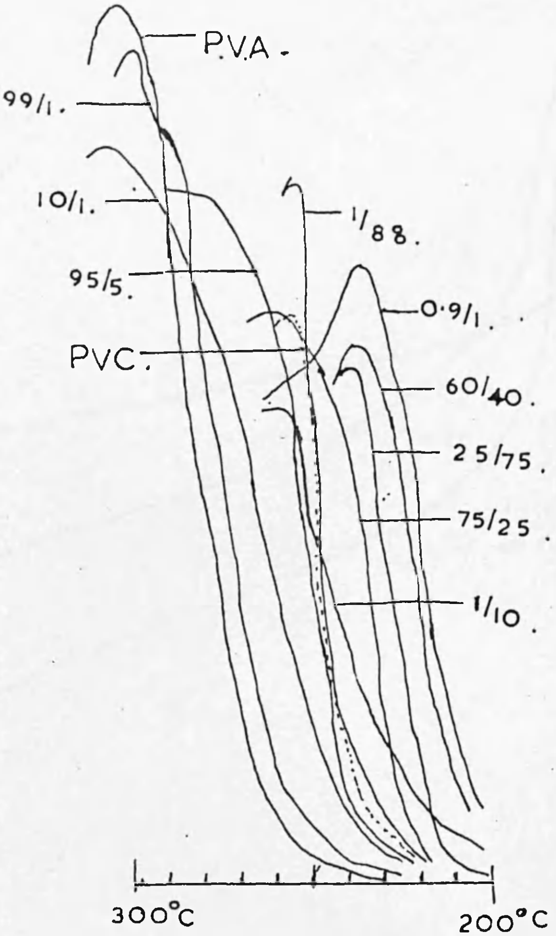
Another method of checking initial temperatures of degradation is by thermogravimetry and, although this technique was not used extensively in the present work, figure 18 shows thermograms for PVA, PVC and a 50/50 copolymer, obtained using a Du Pont 950 thermal analyser. The fact that these are single step curves suggests that there is only one mechanism whereby volatiles are being produced at temperatures below 425°C.

Figure 16



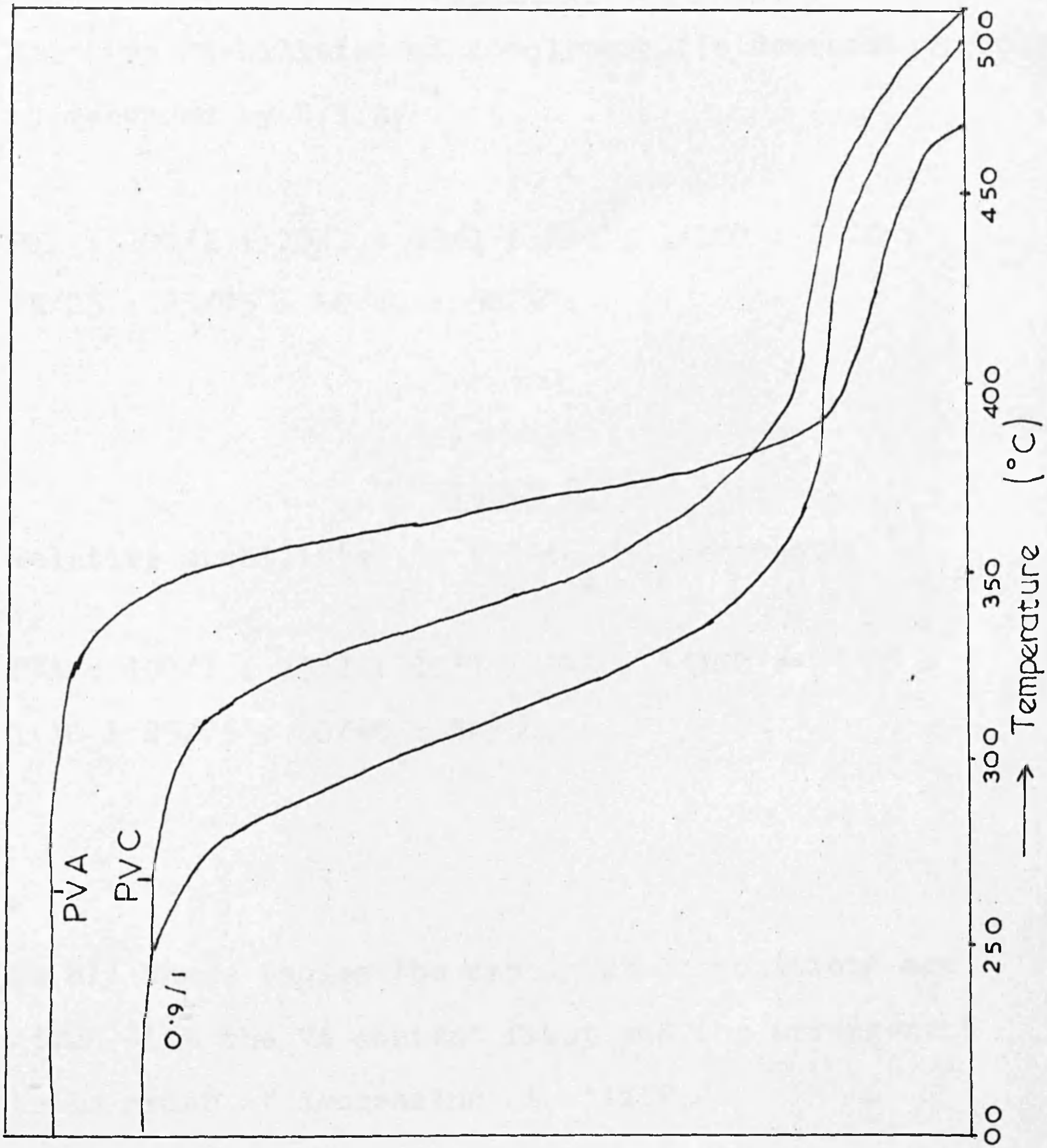
Traces from T.V.A for Various Copolymers (Ratios are VA/VC).

Figure 17.



Trace of Pressure Against Temperature for all Polymers (VA Content First).

Figure 18.



Thermograms of PVA, PVC and a 0·9/1 Copolymer.

TABLE 3.

Relative stabilities of copolymers (in decreasing order) as measured by T.V.A. *

PVA : 100/1 : 10/1 : 19/1 : PVC : 1/100 : 1/10 : 75/25 : 25/75 : 60/40 : 50/50.

TABLE 5.

Relative stabilities in tri-toluyl phosphate. *
at 180°C

PVA : 100/1 : 19/1 : 10/1 : PVC : 1/100 : 75/25 : 1/10 : 25/75 : 60/40 : 50/50.

*

In all these tables the copolymer compositions are given with the VA content first and the arrangement is in order of decreasing stability.

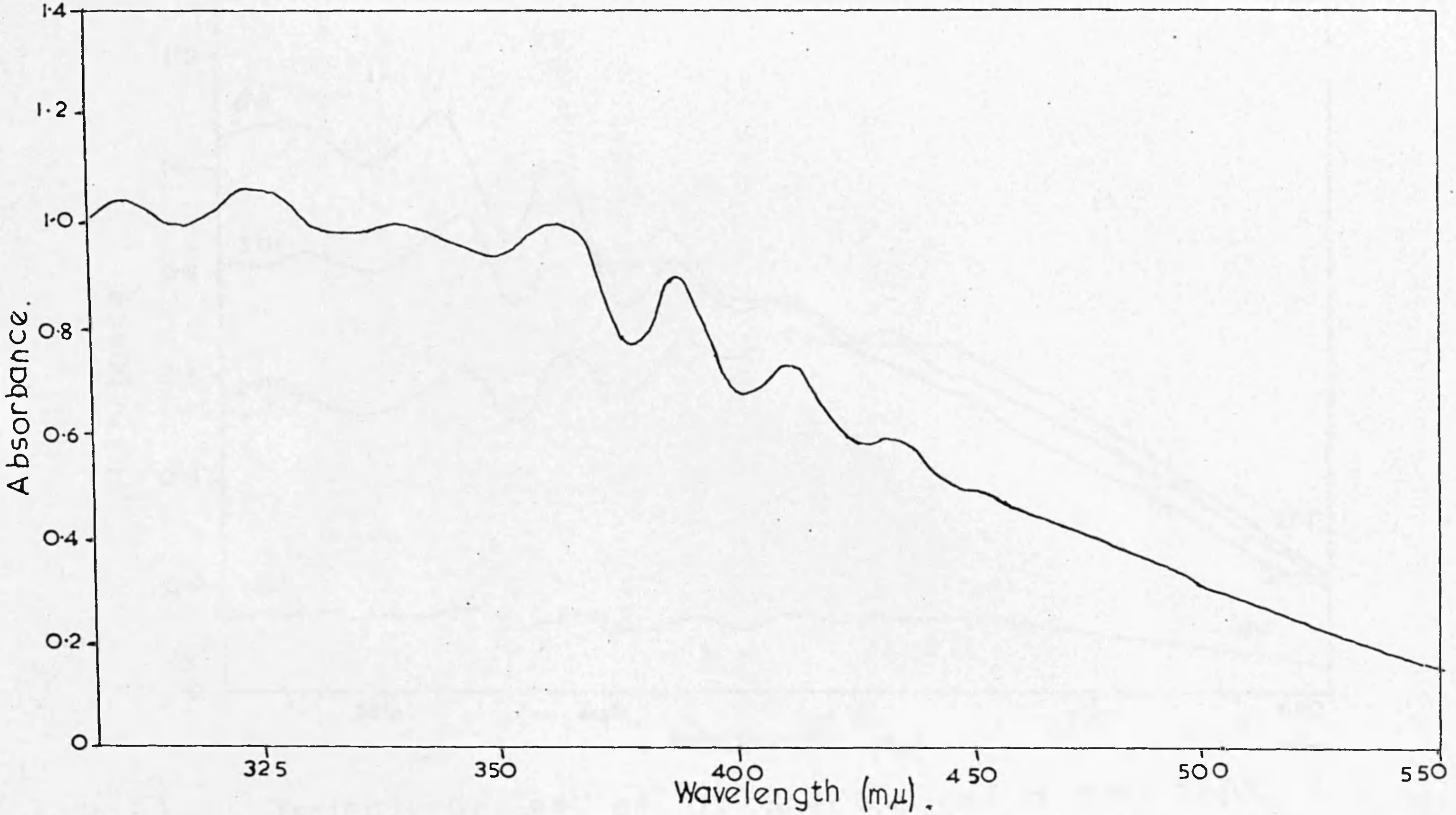
4). In Ethyl Benzoate Solutions.

An attempt to measure rates of degradation, by making continuous observations of the pH in the water trap, proved fruitless, possibly because a mixture of a strong and a weak acid was concerned and the weak acid is relatively undissociated at low pH.

Thus, another method had to be devised for following the degradation reaction in ethyl benzoate solutions. It was noticed that the solutions, after degradation, were quite intensely coloured and, therefore, that ultra-violet spectra of the degraded solutions might give a useful measure of the extent of degradation. A typical ultra-violet spectrum of a degraded polymer is shown in figure 19 and a typical series, illustrating the effect of time of degradation, is shown in figure 20.

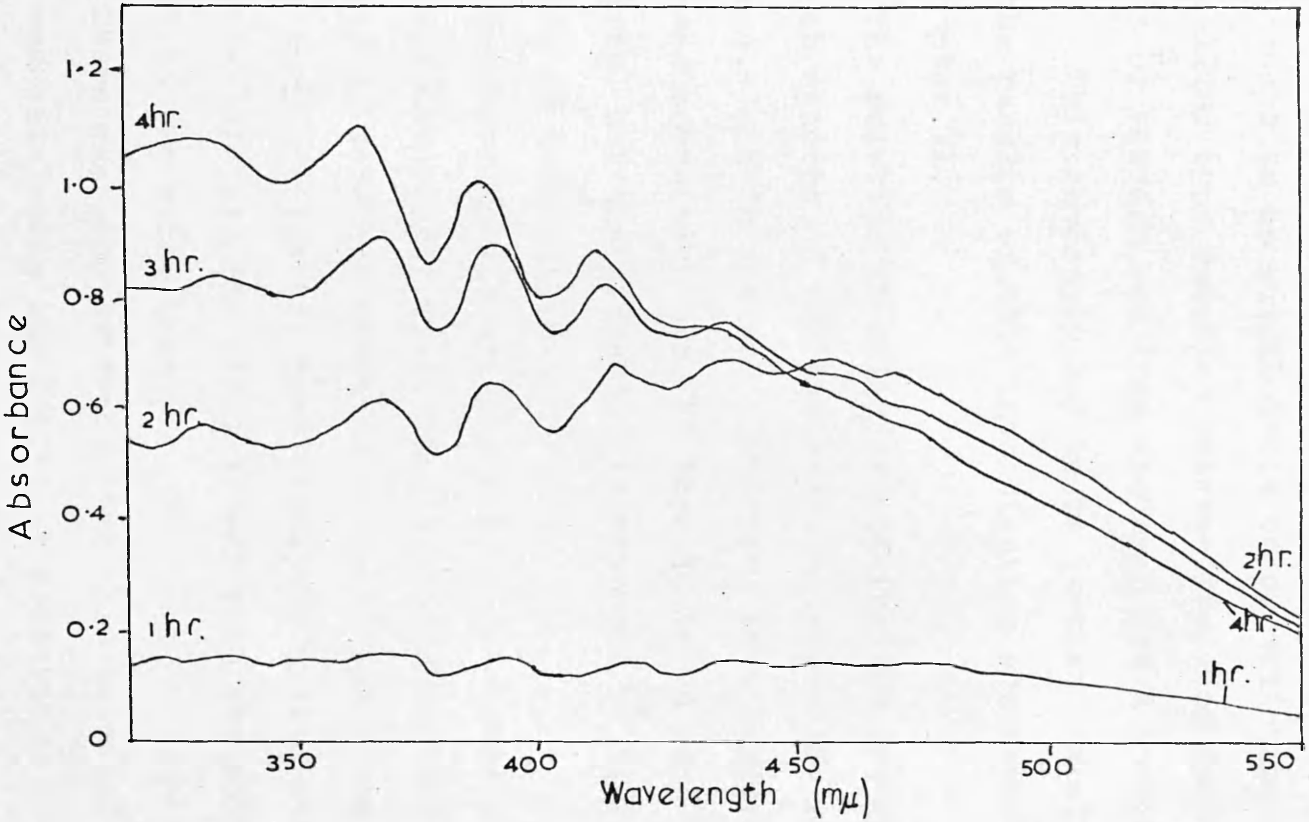
As already discussed in chapter 1, the peaks in these spectra are due to carbon-carbon double bond conjugation of various lengths. The series in figure 20 shows that there is, after a certain time of degradation, a decrease in the actual number of

Figure 19.



Typical Ultra-Violet Spectrum of a 75/25 VA/VC Copolymer
Degraded for 4 hours at 180°C

Figure 20.



Typical Series of U.V. Spectra of a 0·9/1 VA/VC Copolymer Degraded for Different Times. at 180°C long polyene sequences while there is a very sharp increase in shorter sequencies. This phenomenon was thought to be attributable to crosslinking by a Diels-Alder type reaction between two long conjugated chains or between one long sequence and a double bond. This obviously had to be further investigated and the results of this investigation are reported in Chapter VI.

The relative stabilities obtained by inspection of such spectra of the various copolymers are shown in table 4. It is obvious that there is a tendency for polymers containing more VA than VC to be more stable at first, but the situation is reversed at higher extents of degradation.

Attempts to measure the ratios of acetic acid to hydrogen chloride titrimetrically, as described in Chapter 2, were unsuccessful since it was found that, under the experimental conditions, the acetic acid was not being efficiently carried over from the reaction vessel to the water trap.

There was also evidence that this retained acetic acid was catalysing the degrading reaction.

This led to a modification of the technique which involved extraction of the acetic acid with water from the ethyl benzoate solution. It was thus possible to measure rates of degradation in ethyl benzoate solution and obtain the ratios of acetic acid to hydrogen chloride in the degradation products.

This improved technique also made possible a more quantitative estimate of the relative stabilities of the polymers in ethyl benzoate solution. This was done by plotting the percentage degradation, achieved in a fixed time, against the percentage VC in the polymer as shown in figure 21.

5). In Tri-toluyl Phosphate.

These degradations, performed in the apparatus shown in figure 4, also gave a coloured solution which was diluted and the ultra-violet spectrum measured. Because of the fact that all acid products were blown out of the tri-toluyl phosphate solution, it was possible to measure continuously the amounts of acid coming over into the water trap.

In the light of previous experience with pH

TABLE 4.

Relative stabilities of copolymers in ethyl benzoate.*
at 180°C

Time	Relative Stabilities.
1 hr.	PVA : PVC : 100/1 : 1/100 : 19/1 : 1/10 = 10/1 : 25/75 : 50/50 : 60/40 : 75/25.
2 hr.	PVC : 1/100 : PVA : 100/1 : 1/10 : 19/1 = 25/75 : 10/1 : 75/25 : 60/40 : 50/50.
3 hr.	PVC : 1/100 : PVA : 100/1 : 1/10 : 19/1 : 25/75 : 10/1 : 75/25 : 60/40 : 50/50.
4 hr.	PVC : 1/100 : PVA : 100/1 : 1/10 : 19/1 : 25/75 : 10/1 : 75/25 : 60/40 : 50/50 .

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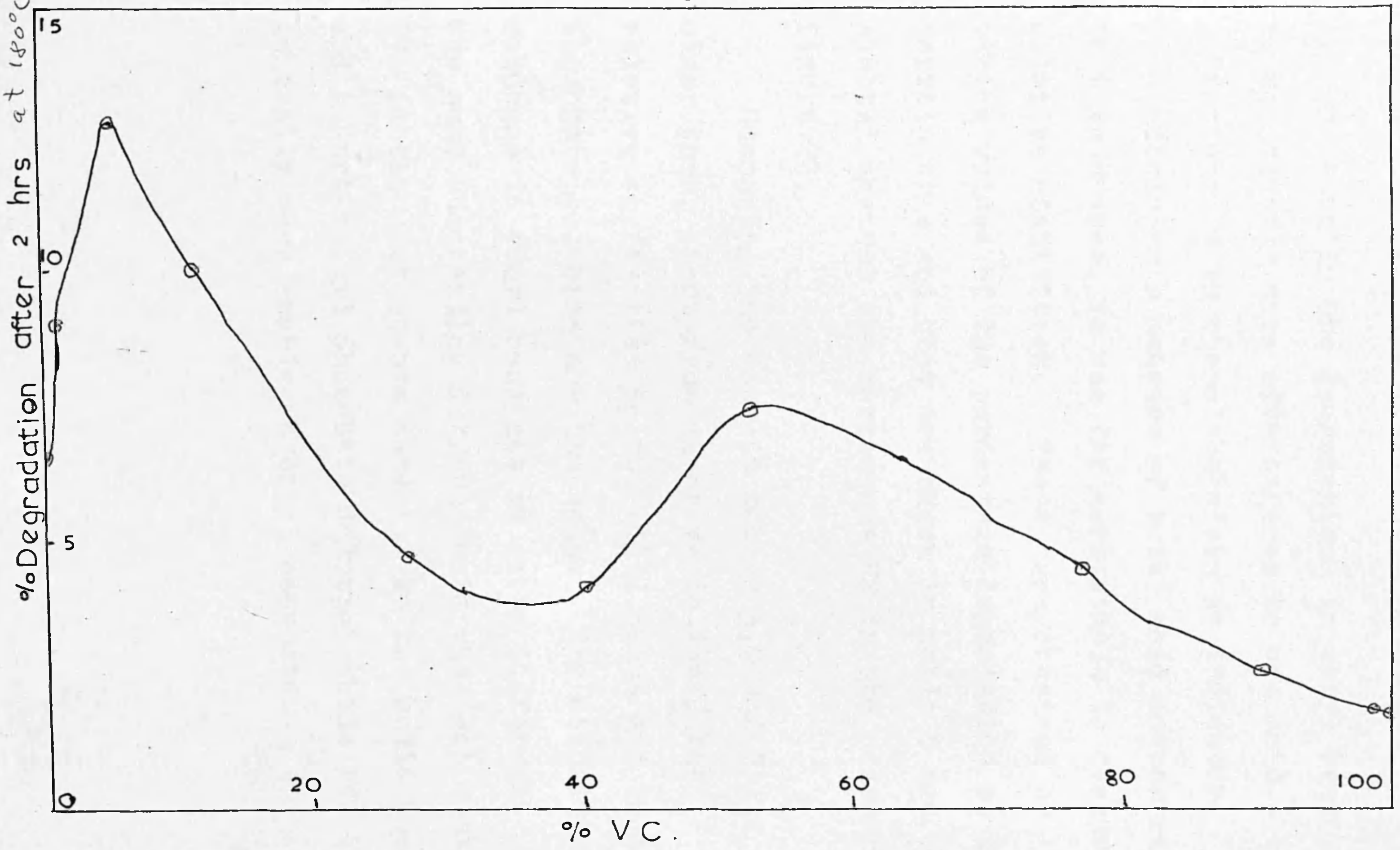
*

In all these tables the copolymer compositions are given with the VA content first and the arrangement in order of decreasing stability.

Figure 21.

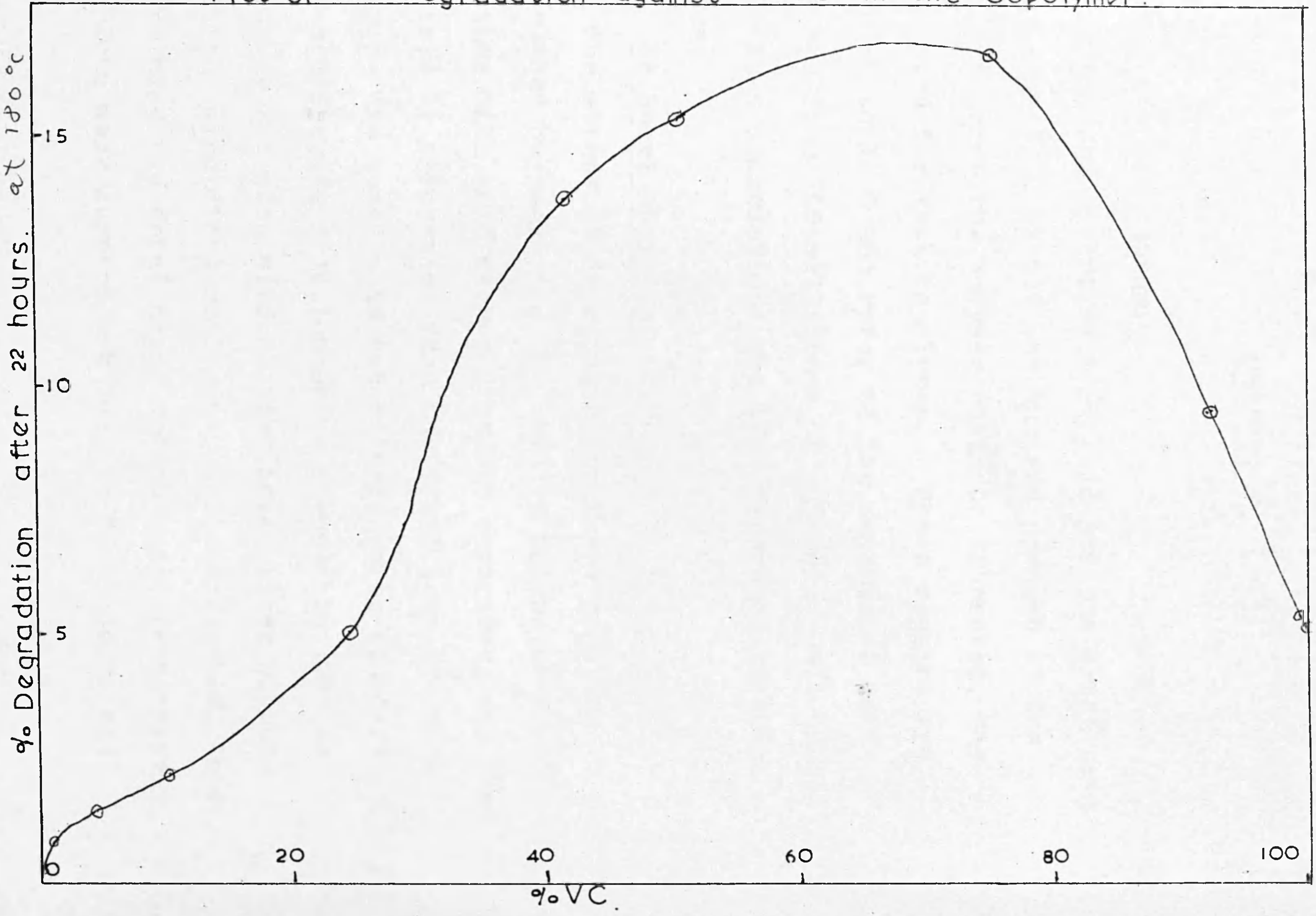


Plot of % Degradation against % VC in the Copolymer.

measurements in the degradations in ethyl benzoate, it was clearly more advantageous to use acid - base titrations, with phenolphthalein as indicator, thus obtaining a measure of total acid concentration. In this system, it was far more simple to measure the relative stabilities. These were obtained by taking values of the percentage degradation at a certain time and they are shown in table 5 and also, plotted against the percentage VC in the polymer, in figure 22.

Comparing the data in tables 3,4 and 5, it is clear that, apart from minor variations, the relative stabilities in the solid phase and in tri-toluyl phosphate solution are the same. The stability sequence in ethyl benzoate is quite different. Perhaps the most outstanding difference is the fact that PVA is the most stable material in the solid phase and in tri-toluyl phosphate solution while PVC is generally more stable in ethyl benzoate.

Figure 22.
Plot of % Degradation against % VC in the Copolymer.



CHAPTER V.

Volatile Products.

1). Rate of Reaction.

The total amount of each acid and the total acid to be expected, should one hundred percent of the acid groups on the polymer chain be liberated, was calculated for each copolymer. These results are shown in table 6 and refer to the amounts of acid expected from 100 milligrams of polymer. All quoted percentage degradations are with reference to these values.

A). In Ethyl Benzoate.

The extent of degradation in these runs was calculated by measuring the acid in the water trap together with acid washed from the apparatus, and that obtained by extraction from the ethyl benzoate with water. The total acid was titrated with standard sodium hydroxide solution using phenolphthalein as indicator and then with standardised silver nitrate solution using dichlorofluorescein as indicator, thus determining the total acids and chloride respectively.

Runs were carried out lasting from one to six

TABLE 6.

Quantities of Acids Representing 100% Degradation of Different Copolymers.

Copolymer Composition VA/VC.	Millimoles of Acid Expected from 100 mg.		
	Total Acid	Acetic Acid	Hydrogen Chloride
PVA	1.163	1.163	-
88/1	1.168	1.155	0.01328
19/1	1.180	1.121	0.0590
10/1	1.191	1.083	0.1083
75/25	1.235	0.97	0.2645
60/40	1.306	0.783	0.522
0.9/1	1.360	0.644	0.715
25/75	1.462	0.366	1.097
1/10	1.547	0.146	1.401
1/82	1.596	0.01923	1.577
PVC	1.6	-	1.6

hours. The percentage degradations for each time interval were then calculated and plotted against the percentage VC in the polymer as shown in figures 21 (page 108) and 23. These demonstrate two stability maxima at 5-10% VC and 50-60% VC. The highest stability of all is seen to be at 100% VC, i.e. PVC. Since bulk PVA is known to be quite considerably more stable than bulk PVC, however, degradation in ethyl benzoate is clearly abnormal.

Another indication of abnormality is the plot of percentage degradation against time of degradation which is shown in figure 24. This illustrates the fact that small concentrations of VA units catalyse the reaction while at high VA concentrations the reaction curve takes on autocatalytic characteristics.

These two pieces of evidence suggested that either the solvent was catalysing the degradation, and it is difficult to imagine in what manner it could, or the retained acetic acid was acting as a catalyst. That acetic acid is retained almost quantitatively in the reaction tube under the experimental conditions is confirmed by the fact that, when acetic acid is added to ethyl benzoate containing

Figure 23.

Plot of % Degradation against % VC for Various Times.
at 180°C

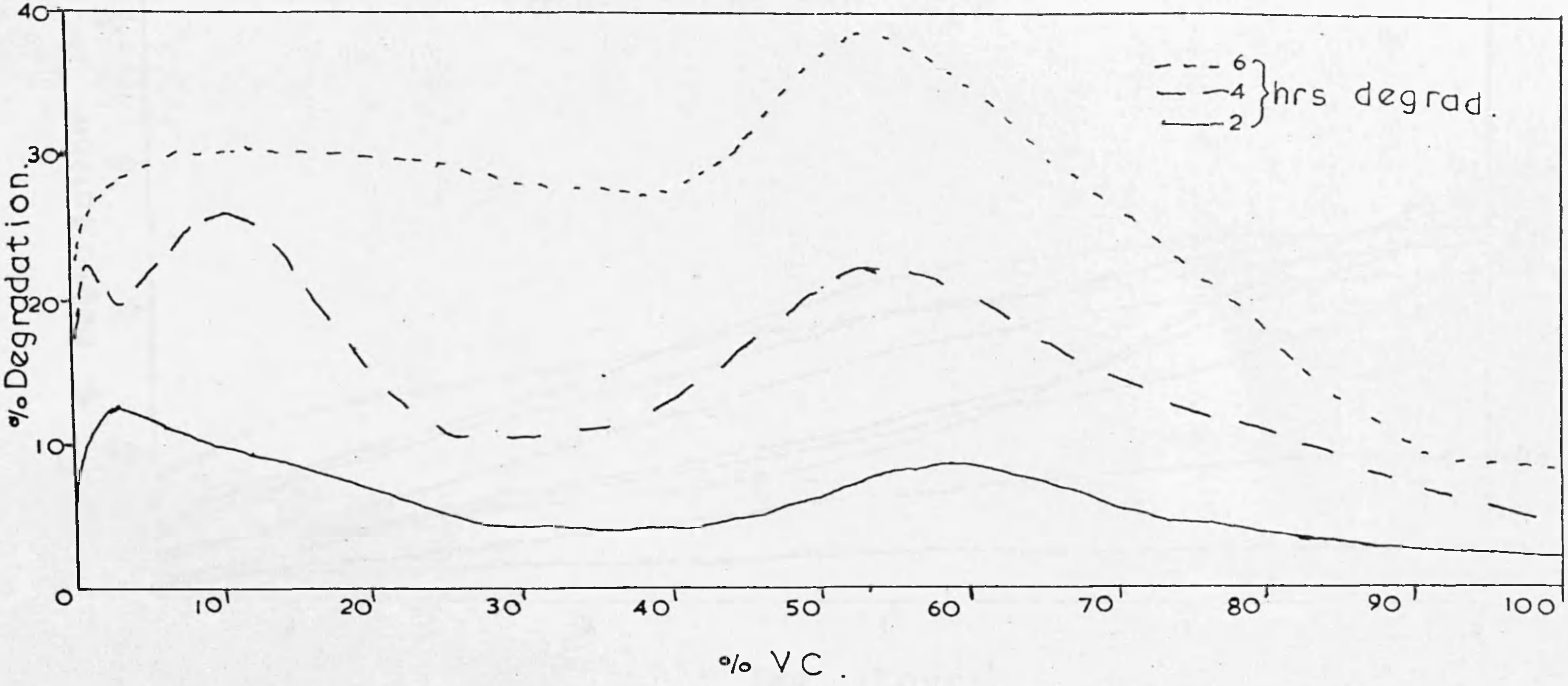
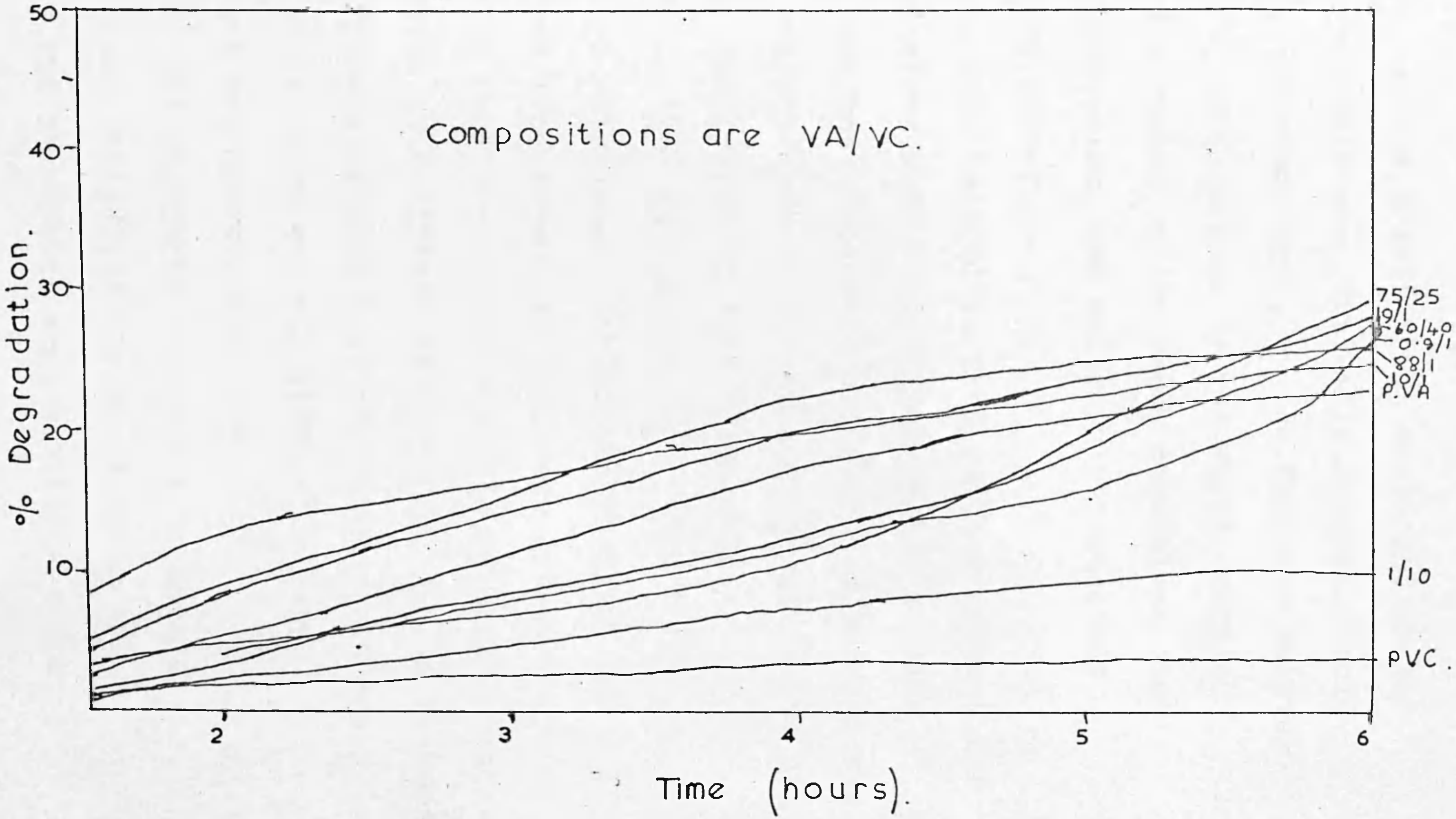


Figure 24.

Plot of % Degradation against Time for all Polymers at 180°C



no polymer and the solution is subjected to the degradation conditions, virtually no acetic acid appears in the water trap, unless the tube leading from the degradation tube to the water trap is continuously heated, under which conditions some acetic acid appears, but not in a reproducibly quantitative manner.

It was thus decided to find another solvent for the degradations which had a much higher boiling point so that the nitrogen could be blown through the solution and not over it, in an attempt to remove all the acetic acid, without loss of solvent.

B) In Tri-toluyl Phosphate.

Dioctyl phthalate, dichloronaphthalene, and benzophenone were tried but they were either too difficult to handle quantitatively (e.g. dichloronaphthalene which is a mixture of solid and liquid isomers having different melting points), or they did not dissolve PVA (which was the difficulty with benzophenone and dioctylphthalate).

Tri-toluyl phosphate was easier to handle quantitatively, dissolved the whole range of copolymers and had a high enough boiling point.

It was thus decided to use it for degradations.

It was later found, however, that tri-toluyl phosphate could not be used in a Mechrolab High Speed Osmometer because of its high viscosity, and the polymers could not be precipitated from it.

Thus, molecular weight measurements were confined to samples degraded in ethyl benzoate.

To ascertain whether acetic acid could be removed quantitatively from tri-toluyl phosphate, concentrations of acetic acid, of the order of those expected during degradation runs, were added to tri-toluyl phosphate containing no polymer. This was subjected to the conditions of degradation and it was found that, although some acid probably condensed inside the apparatus before eventually entering the water trap, all the added acetic acid had arrived at the trap within 90 minutes.

Before proceeding to an extensive quantitative investigation of the reaction in tri-toluyl phosphate, it was considered advisable to check that the temperature in the reaction vessel was constant over a period of 7 days, which was the approximate duration of the projected longest runs. A thermocouple, protected by a glass sheath, was placed in the solution and its output fed into a recorder. This showed that any variations in temperature were within the limits ± 0.5°C.

The reproducibility of the experiments was also checked and figure 25 shows the results of two degradations on the same copolymer. This shows complete reproducibility and gave confidence that the experimental techniques were satisfactory for kinetic work.

In tri-toluyl phosphate, the degradations were continuous in that measurements could be made on the extent of degradation at various times throughout the experiment, since the products were removed completely from the system. Thus, only one experiment was required to obtain a series of values of percentage degradation against time, which has many obvious advantages over the situation in ethyl benzoate, when a series of degradation runs had to be carried out for each system.

As in the case of degradations in ethyl benzoate, the percentage degradation for a fixed time was plotted against percentage vinyl chloride, as shown in

Figure 25.

Plot of % Degradation against Time for a 25/75 VA/VC Copolymer to show Reproducibility in Tri-toluyl Phosphate, at 180°C

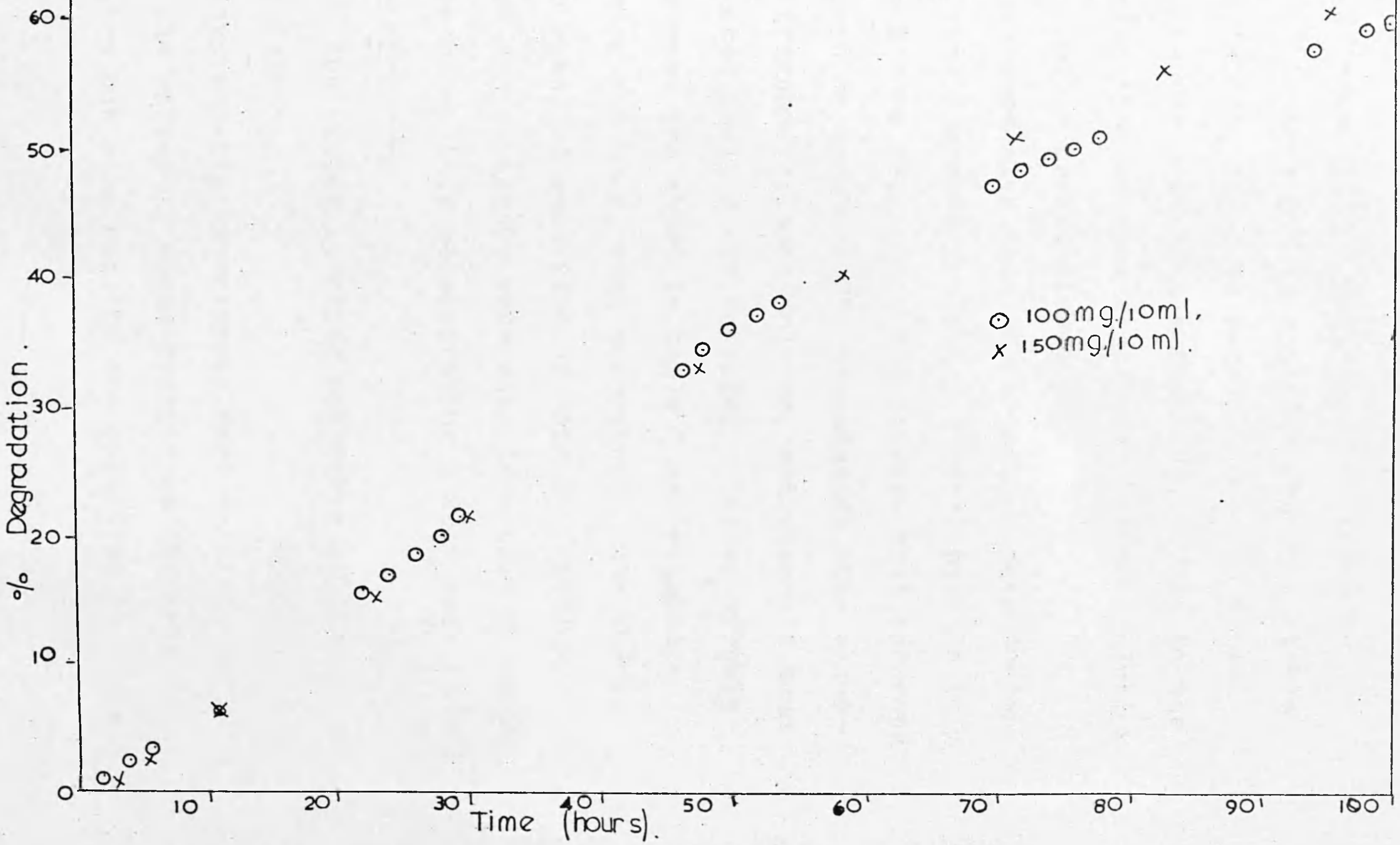


figure 22 (page 110). This shows a minmum in stability at about 65% VC and also the most stable material is PVA, which is reasonable since it is known to be far more stable than PVC. This is the first indication of some similarity between solution and solid phase degradations.

Plots were also made of percentage degradation against time for each run and a typical example is shown in figure 26. This illustrates that the rate is constant up to about 25% degradation, the value being different for each polymer, and there is then the expected falling off in rate. Values of this constant rate are shown in table 7 as percentage degradation per hour, with composition also shown. Absolute rates of evolution of acid in tritoluyl phosphate are obviously very much less than those in ethyl benzoate, thus necessitating a very much longer time for each run.

An ultra violet spectrum was taken at the end of the degradation.

No systemmatic experiments were carried out to examine the effect of concentration on the rate of degradation but some results are collected in table 8.

Figure 2 6.

Typical Plot of %Degradation against Time for a 50/50 VA/VC Copolymer in Tri-toluyl Phosphate at 180°C

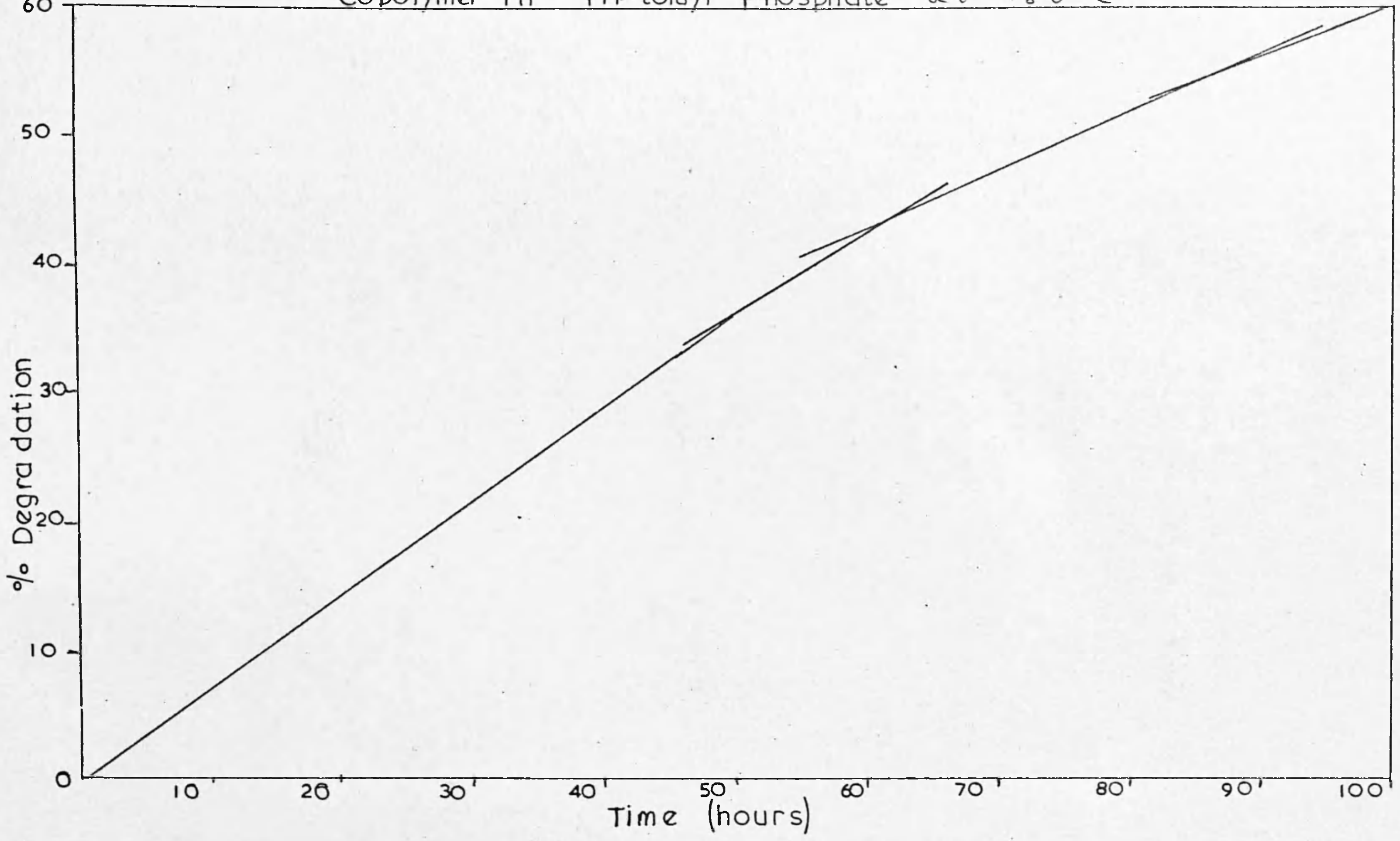


TABLE 7.

Copolymer Composition VA/VC	Rate at 180°C % degradation / hour.
PVA	0.001
100/1	0.012
19/1	0.0458
10/1	0.128
75/25	0.291
60/40	0.810
0.9/1	0.812
25/75	0.820
1/10	0.430
1/82	0.18
PVC	0.164

TABLE 8.

Copolymer Composition VA/VC	Polymer Composition	
	100 mg/ 10 ml	150 mg/ 10 ml
	Rate (% degrad. / hour) at 180°C	
19/1	0.0458	0.0707
75/25	0.291	0.401
60/40	0.810	0.923
0.9/1	0.812	1.135
25/75	0.820	0.867
1/10	0.430	0.543
1/82	0.18	0.233

These indicate that, throughout the copolymer composition range, there is some dependence of rate upon concentration of polymer. Unfortunately, there is insufficient data to permit any conclusions to be drawn from these results.

The effect of change of temperature on the rate of degradation will be discussed later. No attempt was made to study the effect of molecular weight of the copolymers on the rate of degradation, as this would have been a very difficult and time-consuming exercise and the results would have been extremely difficult to interpret.

C) Effect of Oxygen.

This could not be investigated in ethyl benzoate, since it would have been necessary to pass the oxygen over the surface of the solution, which would not necessarily have changed the concentration of oxygen in the bulk of the solution.

In tri-toluyl phosphate, however, a blank experiment demonstrated noticeable discolouration of the tri-toluyl phosphate and, although little evolution of phosphoric acids was noticed, it was decided not to undertake a quantitative investigation.

Qualitatively, a very decided catalytic effect was observed as shown in figures 27 (a-d). It is not clear from these results whether the oxygen catalyses the breakdown of the polymer, or catalyses the breakdown of the tri-toluyl phosphate to give products which catalyse the polymer degradation.

D) Effect of Products.

This was investigated by shutting off the nitrogen flow then switching it on again after some time. The effect of this was that after the acids, which had accumulated in the solution while the nitrogen was switched off, had been removed, the rate settled down to a constant value once more and this constant value was the same as the uncatalysed rate. A typical run is illustrated in figure 28a.

These results showed that hydrogen chloride catalysed the dehydrochlorination of PVC, acetic acid catalysed the degradation of PVA and either one or both of the products catalysed the degradation of the copolymers. It would be reasonable to expect both products to catalyse the degradations of the copolymers, since they catalyse their corresponding homopolymer.

Figure 27a.

Plot of % Degradation against Time for PVA under O_2. at 180°C

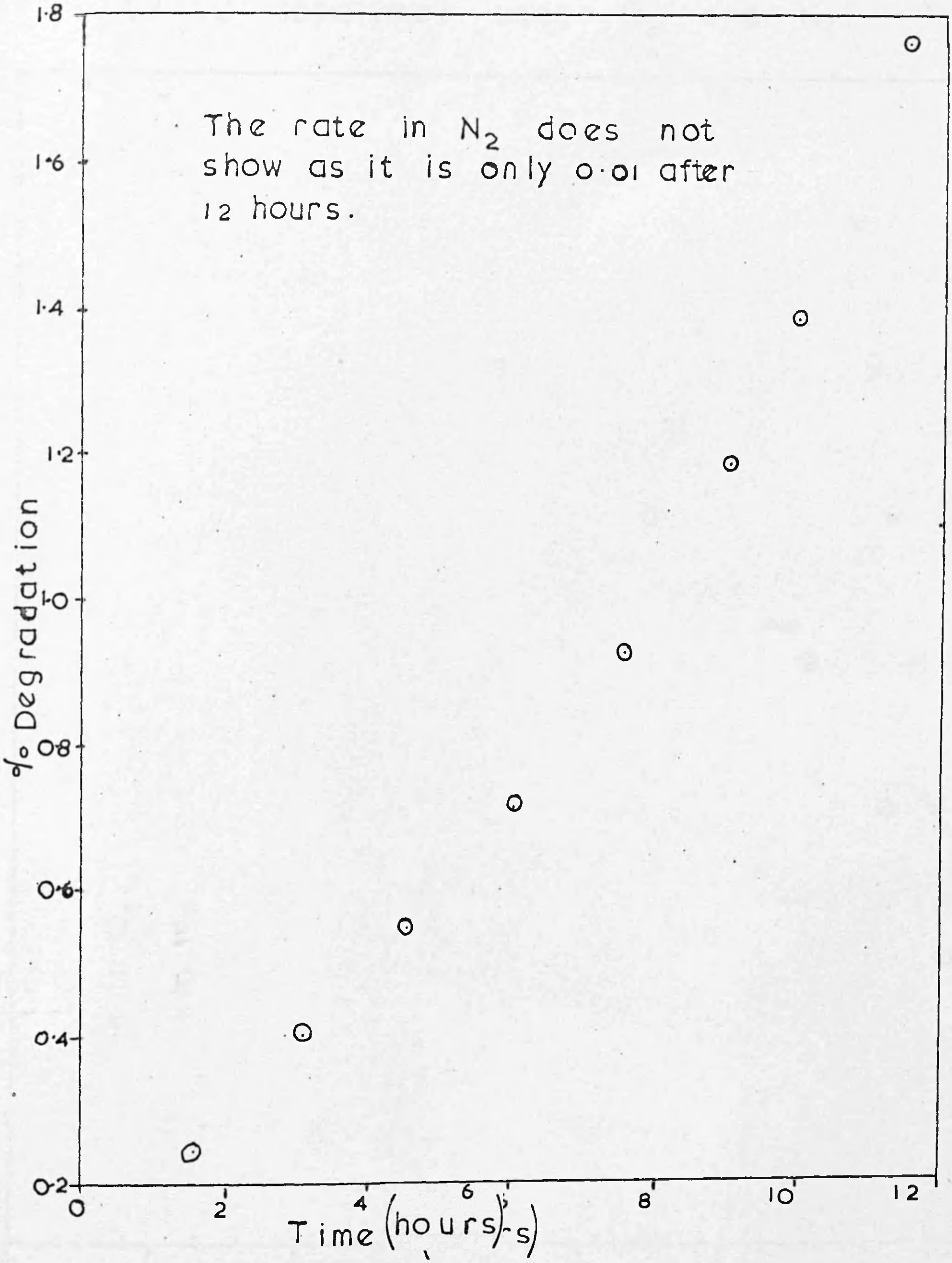


Figure 27. b.

Plot of Degradation against Time for a 0.9/1 VA/VC Copolymer under O_2 and N_2. at 180°C

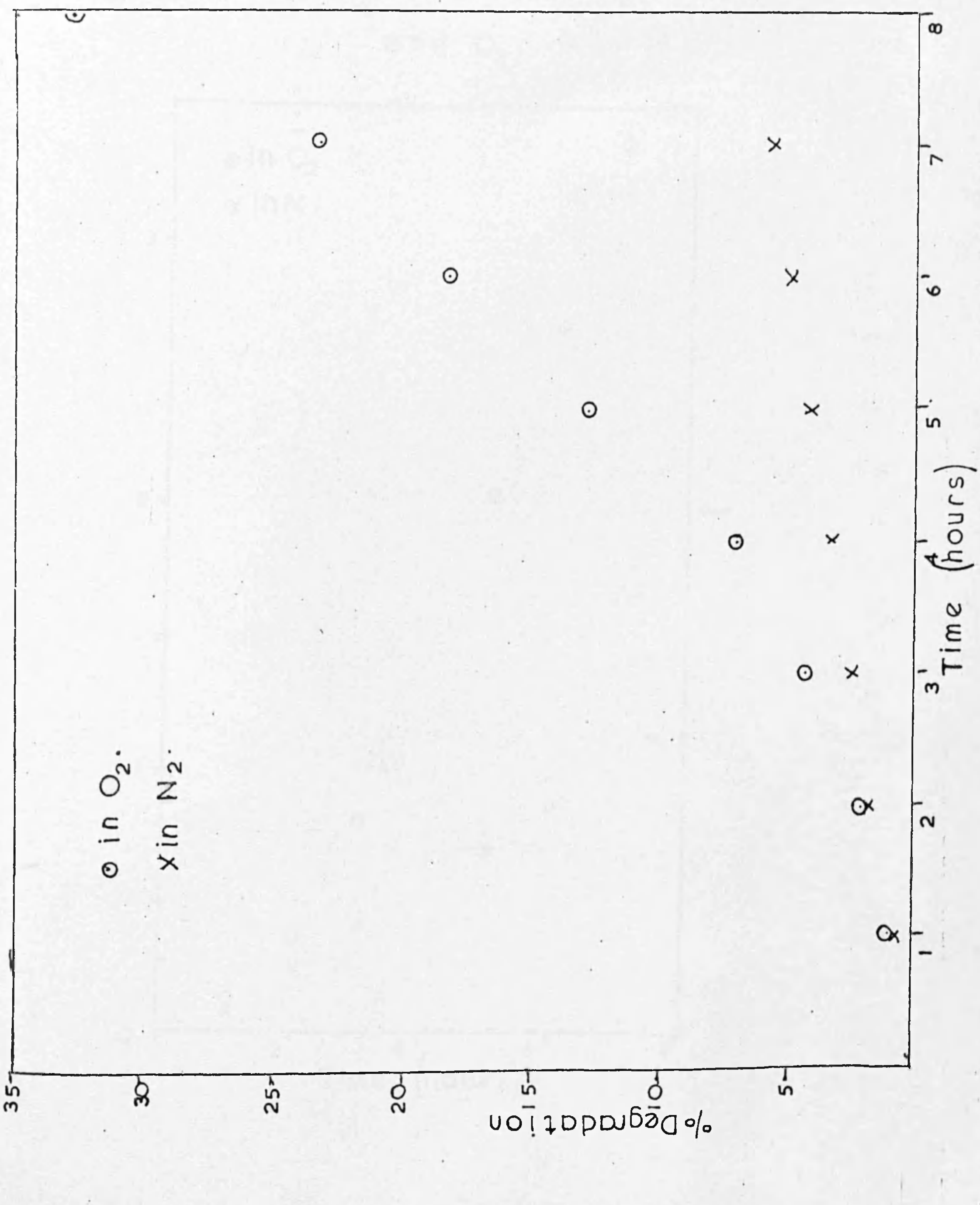


Figure 27c.

Plot of % Degradation against Time for PVC under N_2 and O_2. at 180°C

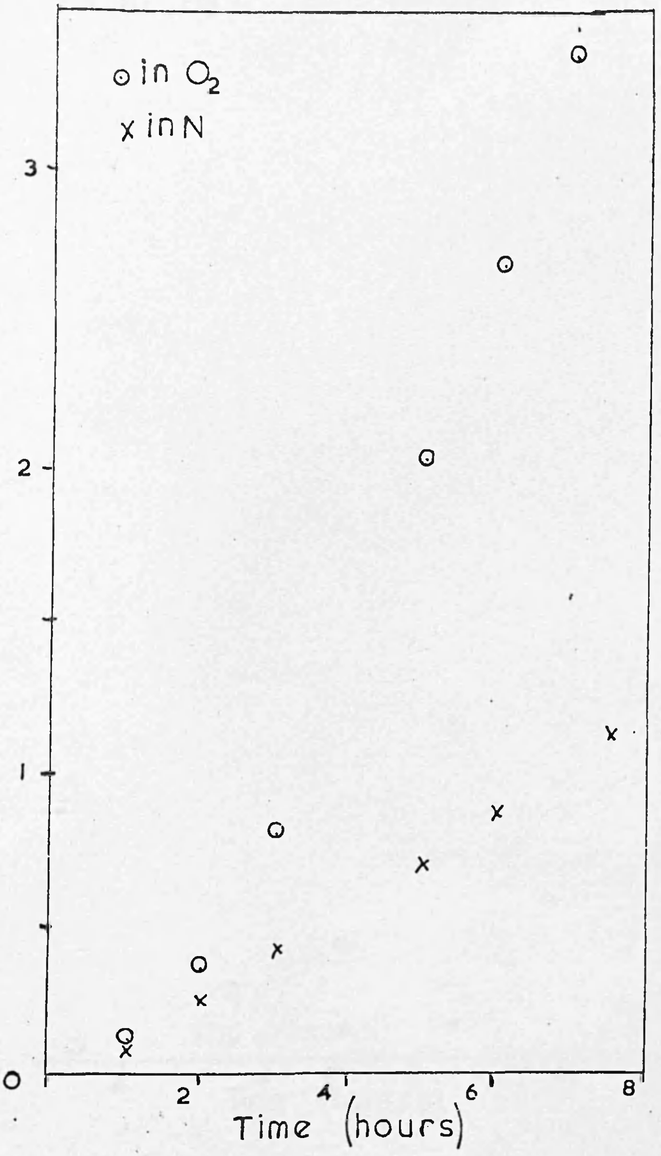


Figure 27d.

Plot of % Degradation against Time for a 10/1 VA/VC Copolymer under O_2 and N_2. at 180°C

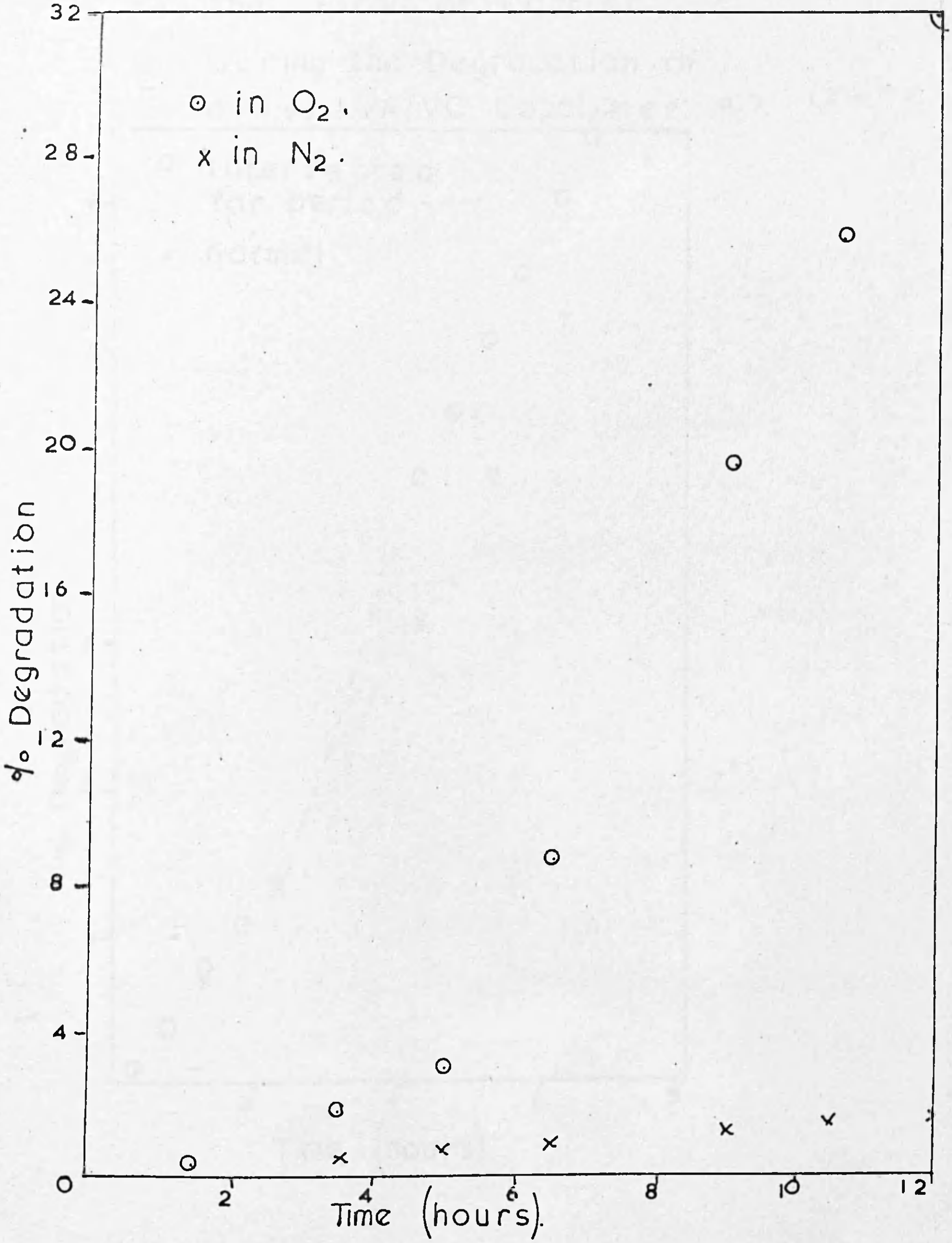
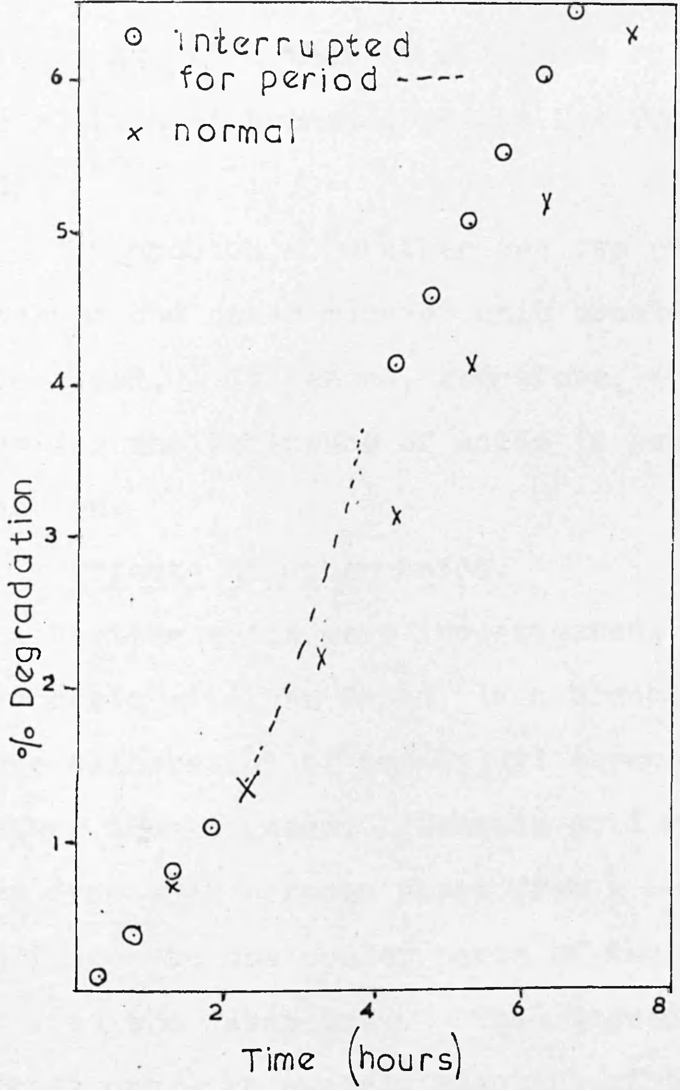


Figure 28 a

Effect of Switching off the Flow of Carrier Gas during the Degradation of a 0·9/1 VA/VC Copolymer. at 180°C



The results obtained in ethyl benzoate gave a strong indication that, in this medium, acetic acid catalysed the degradation of PVA and many of the copolymers and it has been previously suggested (166) that acetic acid catalyses the degradation of PVA but a suggestion that it catalyses only the degradation of branched models for PVA has also been made (167).

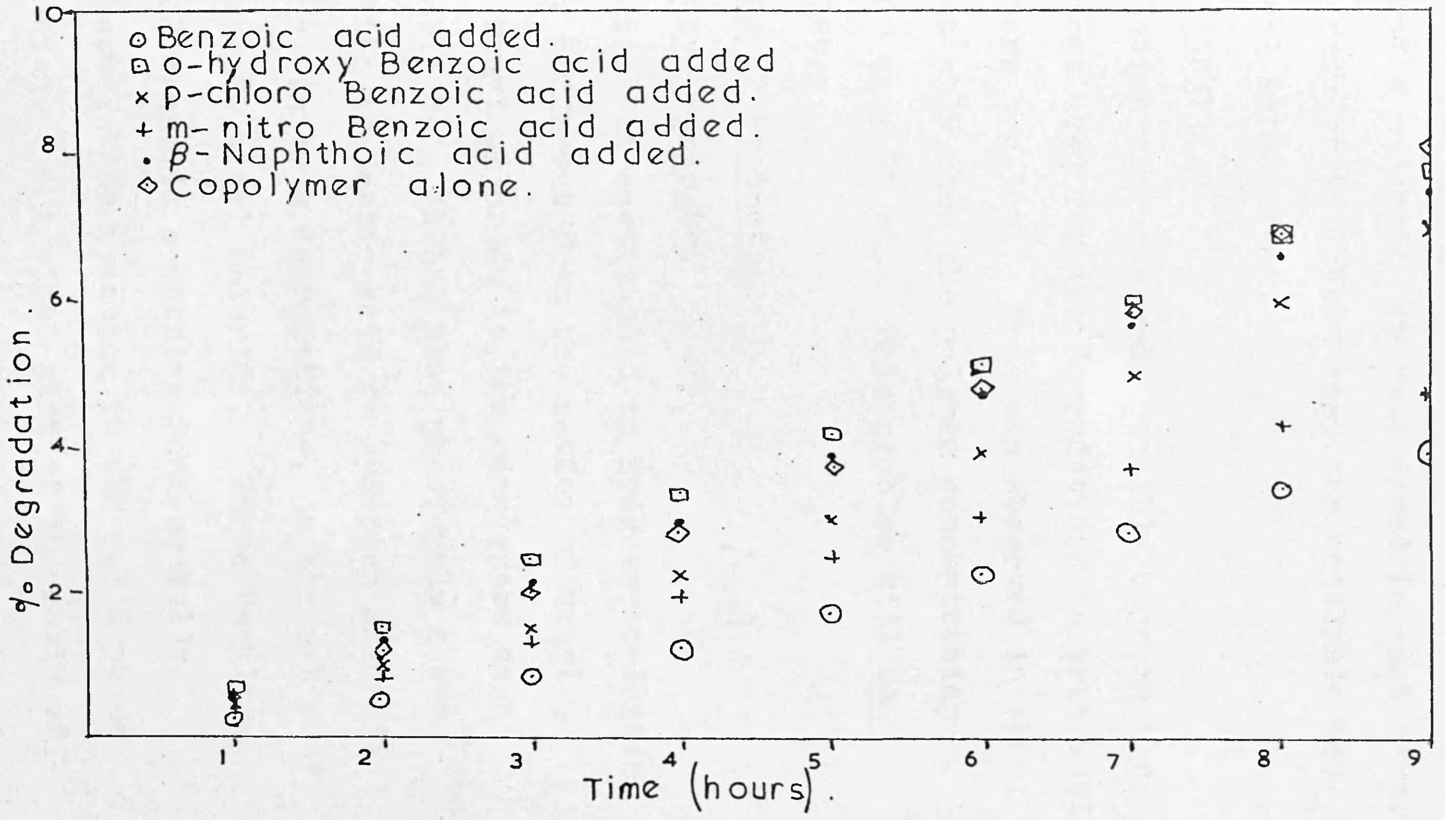
The problem of whether the two products will catalyse the other monomer unit breakdown is still unresolved. It seemed, therefore, worth while to consider the influence of acids in general on the reaction.

E). Effects of Other Acids.

Various acids were investigated. Ortho phosphoric acid was found, in a blank experiment, to cause colouration of tri-toluyl phosphate and was not further investigated. Benzoic acid was found to be free from such effects apart from a tendency to sublime on to the cooler parts of the apparatus, but not into the water trap. When degradations were carried out with a small quantity of benzoic acid added, the effect was as shown in figure 28. This

Figure 28.

Effect of Acids on the Rate of Degradation of a 0·9/1 VA/VC Copolymer at 180°C



effect was repeated with the various acids shown in figure 28 and a reduction in rate found in each case.

These results indicated that the catalysis was not a general acid effect.

F). Crosslinking.

No gelation was observed, possibly because the concentrations used for the degradations in tritoluyl phosphate were too low. Some was observed in ethyl benzoate but only when the polymer concentration exceeded 200 mg / 10 ml. This problem will be discussed later.

2). Ratios of Products.

A). In Ethyl Benzoate.

The ratios of acetic acid to hydrogen chloride were widely different from the ratios of vinyl acetate to vinyl chloride in the copolymers as shown in table 9. It had been previously shown (164) that the ratio of acetic acid to hydrogen chloride was the same, in bulk degradations, as the ratio of vinyl acetate to vinyl chloride. These results, then, showed there is something fundamentally different between the reaction in the solid phase and in solution. A typical plot of the ratio of

TABLE 9.

Copolymer Composition VA/VC	% Degrad.	Ratio Acetic Acid Hydrogen Chloride at 180°C	Theoretical Ratio
1/10	2.696	1.38	0.0986
1/10	7.401	0.685	0.0986
1/10	9.701	0.602	0.0986
0.9/1	7.22	3.19	0.828
0.9/1	21.95	1.56	0.828
0.9/1	38.25	1.00	0.828
25/75	4.35	1.053	0.333
25/75	12.63	1.136	0.333
25/75	21.75	0.641	0.333
60/40	4.00	2.76	1.198
60/40	12.88	1.49	1.198
60/40	27.75	1.42	1.198

acetic acid to hydrogen chloride against time is shown in figure 29 which also shows the mole ratio in the copolymer.

One thing which these investigations did show was that, contrary to expectations, all the hydrogen chloride was not removed from the ethyl benzoate solution and, when PVC was degraded, quite a considerable proportion of the hydrogen chloride had to be extracted from the ethyl benzoate solution.

B). In Tri-toluyl Phosphate.

The values obtained for the ratios of acetic acid to hydrogen chloride are shown in table 10 and typical plots of ratios of products against time, indicating also the mole ratios in the copolymers, are shown in figure 30 (a-d).

These results are another indication that degradation behaviour in tri-toluyl phosphate solutions is very similar to that in bulk and thus it is a good solvent for kinetic work. This is contrary to a claim by Bengough (146) that it is a poor solvent for kinetic work probably because, in his degradations, the nitrogen was blown over the surface of the solution. This procedure could allow the hydrogen

Figure 29.

Typical Plot of Ratio of Acetic Acid to Hydrogen Chloride in Products from Degradation of a 0·9/1 Copolymer in Ethyl Benzoate Solution. at 180°C

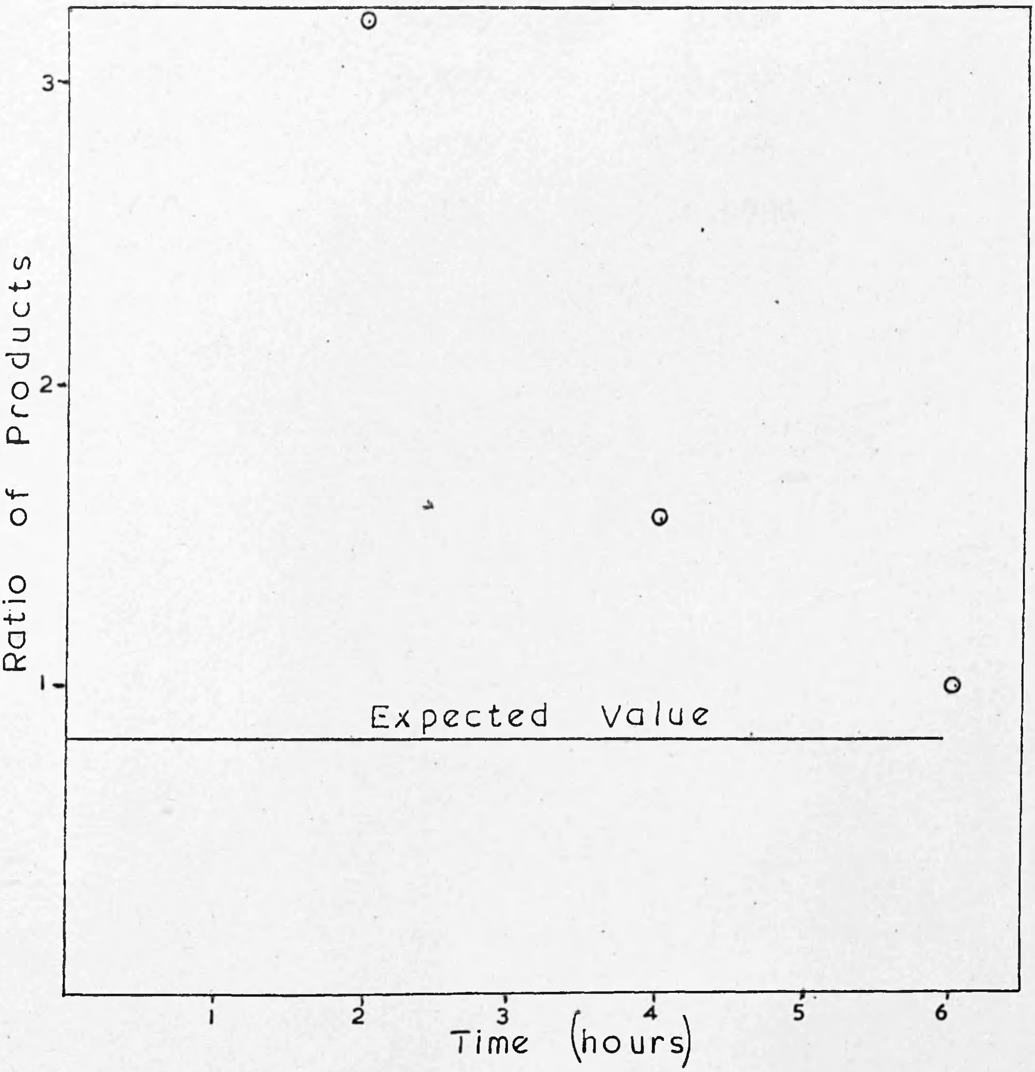


TABLE 10.

Copolymer Composition VA/VC	Ratio Of Products.	
	Observed at 180°C	Expected
0.9/1	0.865	0.828
25/75	0.307	0.333
60/40	1.074	1.198
1/10	0.11	0.0986

Figure 30a.

Plot of Ratio of Acetic Acid to Hydrogen Chloride from the Degradation of a 60/40 VA VC Copolymer in Tri-toluyl Phosphate Solution. at 180°C

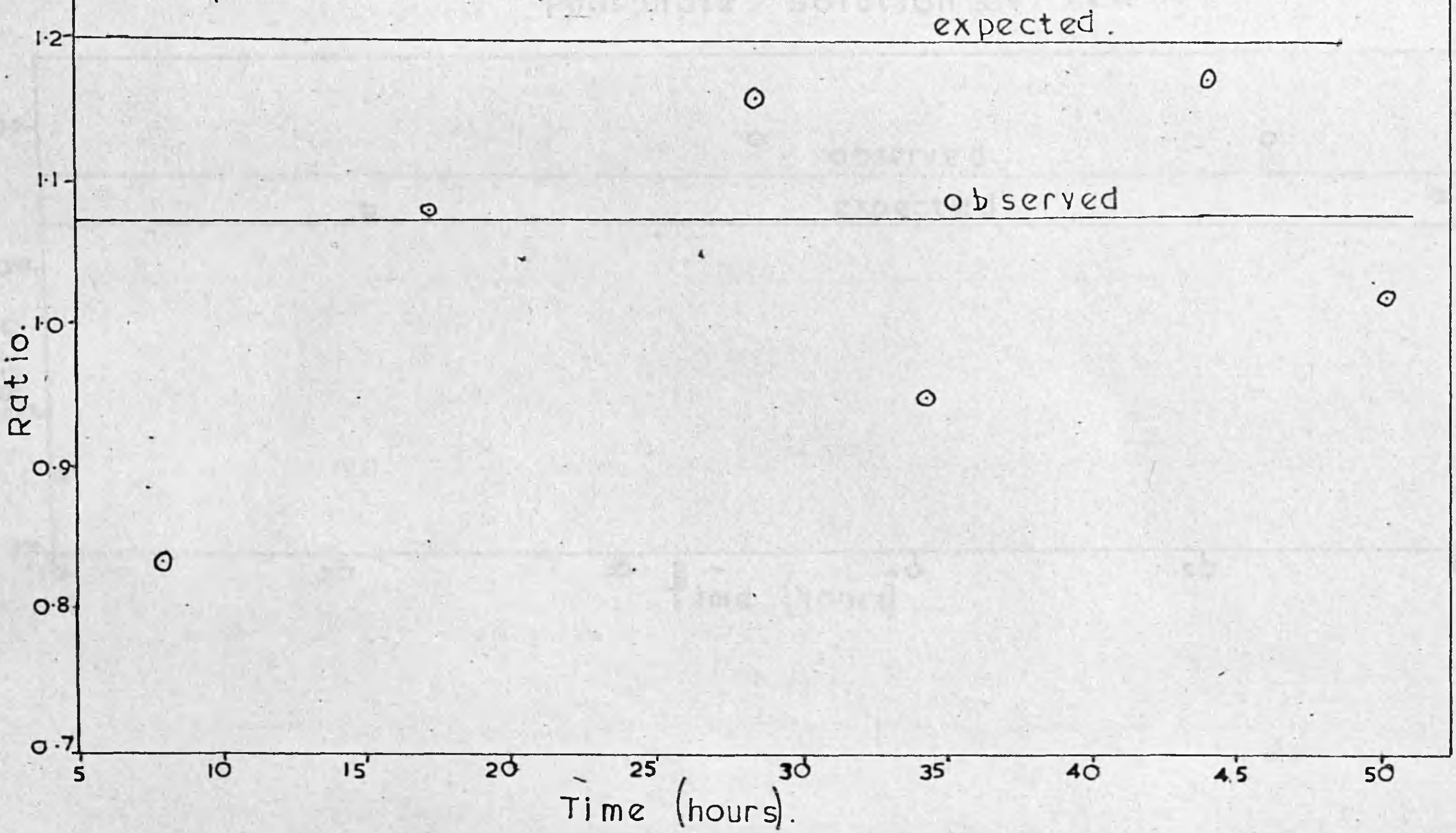


Figure 30b.

Plot of Ratio of Acetic Acid to Hydrogen Chloride from the Degradation of a 0·9/1 VA/VC Copolymer in Tri-toluyl Phosphate Solution at 180 °C

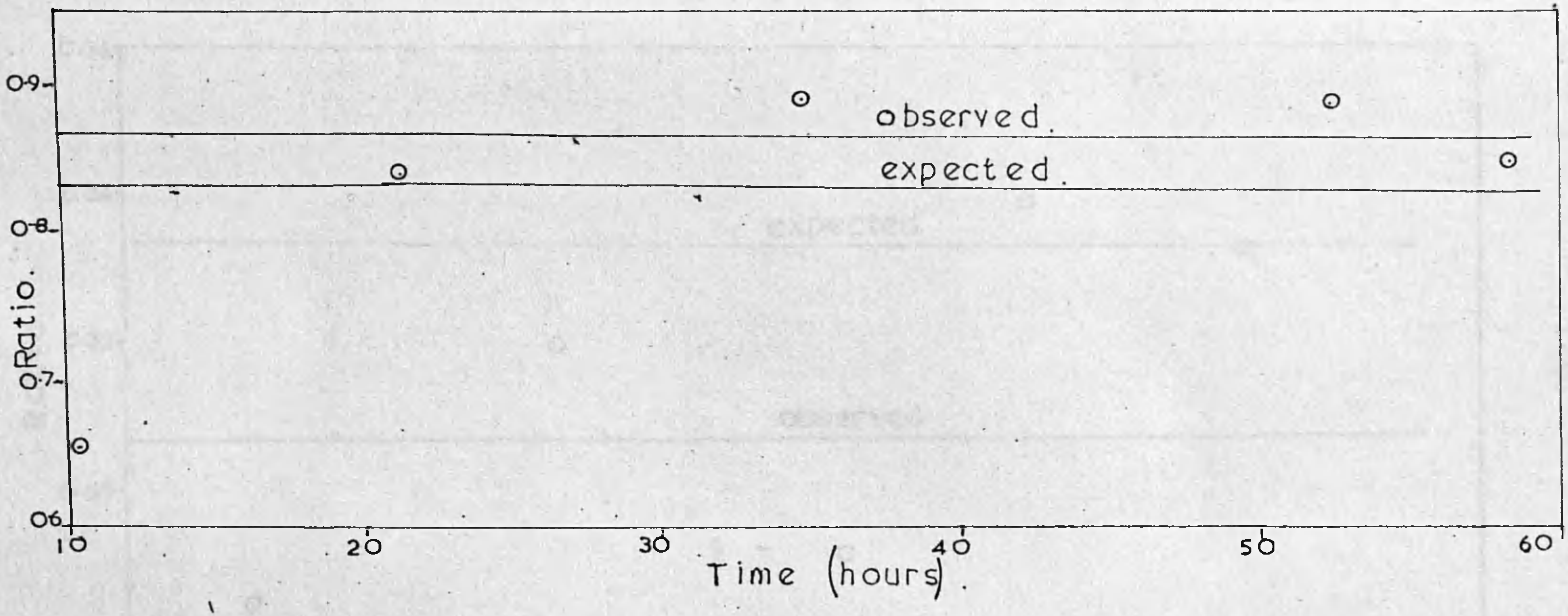


Figure 30c.

Plot of Ratio of Acetic Acid to Hydrogen Chloride from the Degradation of a 25/75 VA/VC Copolymer in Tri-toluyl Phosphate Solution. at 180°C

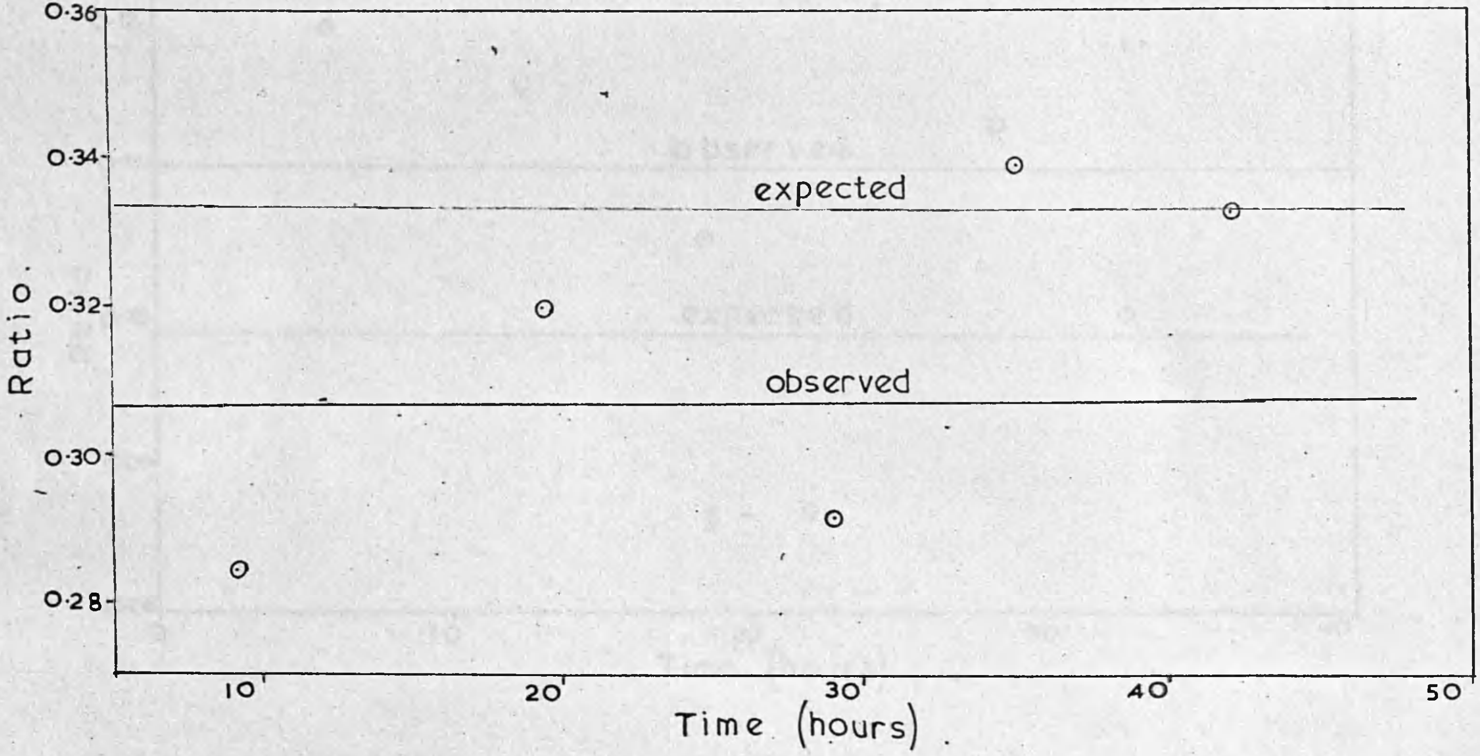
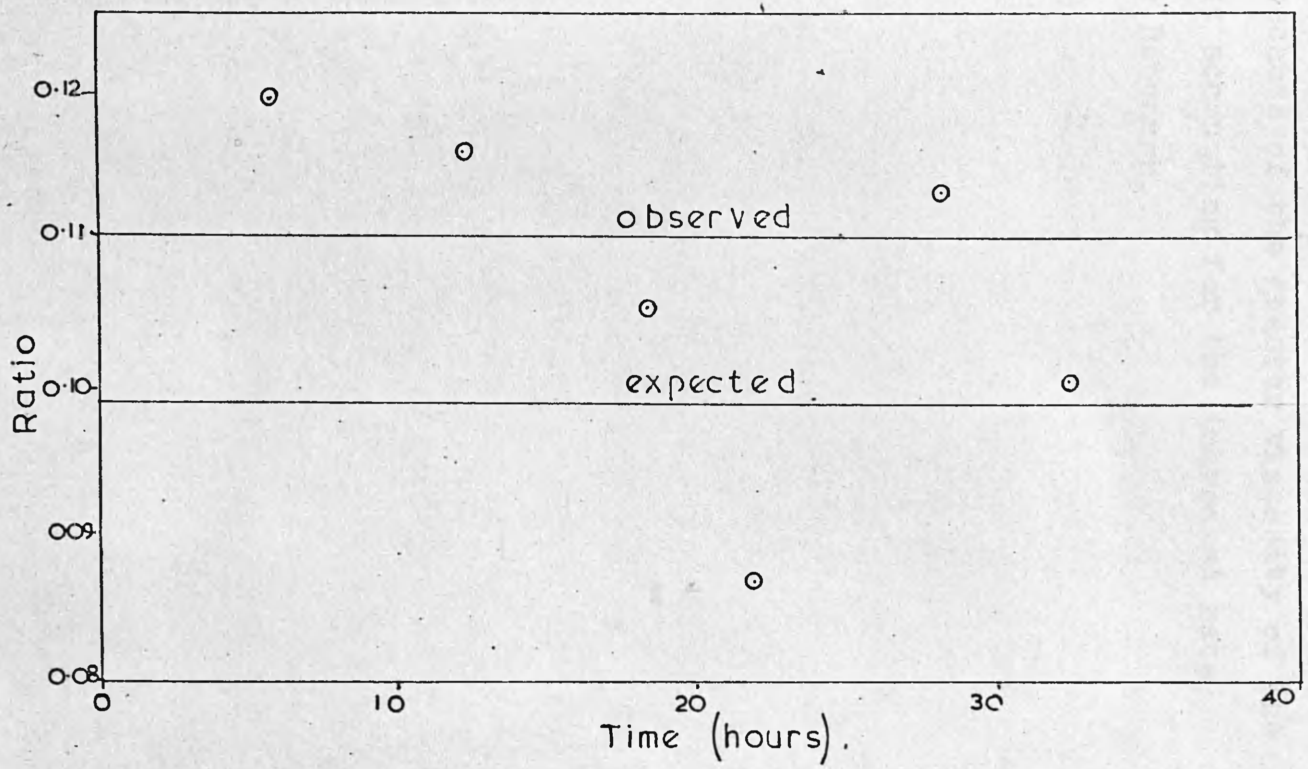


Figure 30d.

Plot of Ratio of Acetic Acid to Hydrogen Chloride from the Degradation of a 1/10 VA/VC Copolymer in Tri-toluyl Phosphate Solution. at 180°C.



chloride concentration to build up in tri-toluyl phosphate to a greater extent than it does in ethyl benzoate, because of the greater viscosity of the former, thus accounting for the increased rate observed by Bengough.

CHAPTER VI.

Colour Development.

1). Comparison of Spectra.

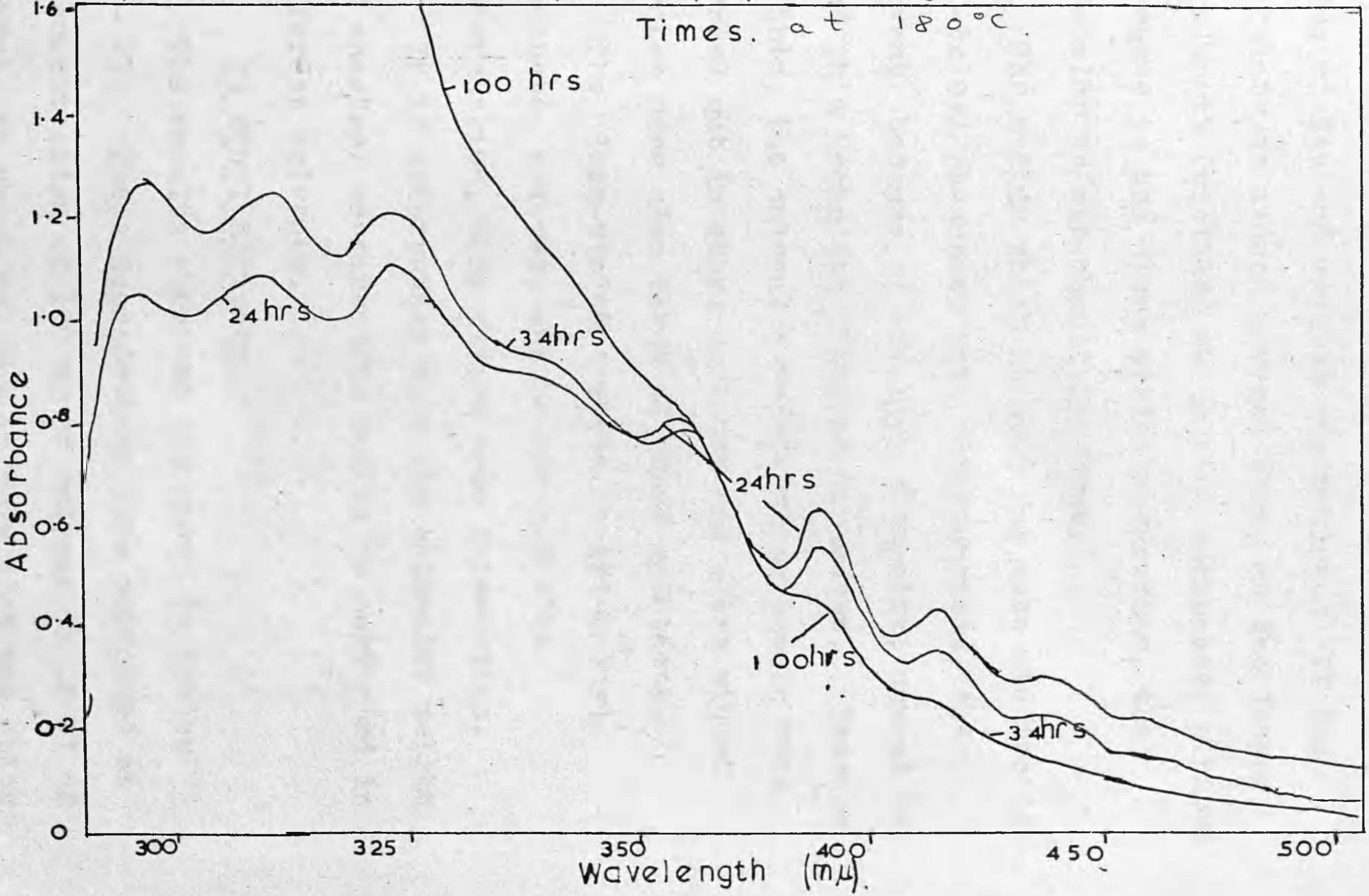
Because of the uncertainty about extinction coefficients, concentrations of polyene sequences could not be obtained in a satisfactory manner. It was therefore decided at an early stage merely to compare the spectra of the degraded polymer solutions by measuring the peak heights and the wavelengths of the absorption maxima.

As shown in figure 20 (page 104) and 31, the absorption at long wavelengths (which corresponds to longer polyene sequences) at first increases with time and then, at a later stage, decreases. This means that the actual number of longer polyene sequences is reduced. This phenomenon could be accounted for by crosslinking by a Diels Alder type of reaction involving a long polyene sequence and either a single carbon-carbon double bond or another polyene sequence.

This postulate may be checked by measurement of molecular weight and it was decided to examine the relationship between molecular weight and

Figure 31.

Spectra of a 60/40 VA/VC Copolymer Degraded for Different Times. at 180°C.



ultra violet and visible absorption. If the postulate is indeed correct then, as the longer wavelength (visible) absorption decreases, without decrease in the ultra violet absorption, the molecular weight should increase.

The medium which is best for rate studies is tri-toluyl phosphate but, unfortunately, this solvent, because of its high viscosity, cannot be used in a Mechrolab Membrane Osmometer. Because of this, the molecular weight measurements were carried out in ethyl benzoate and ultra violet spectra were also taken of these solutions.

The ultra-violet spectra in tri-toluyl phosphate, however, can be matched with % degradation, thus giving more information.

It is unfortunate that the molecular weight and spectral measurements had to be performed in different solvents.

A). <u>In Ethyl Benzoate.</u>

The results obtained are shown in tables 11 - 21. These degradations were performed at a concentration of 100 mg. of polymer in 10 ml. of solvent, at which gelling is very slow but which

TABLE 11.

Spectra and Molecular Weights of Degraded PVA. at 180°C

Wavelength	340	360	390	410	430	460	475	505	
				Absorbance					
Time of Degradation (hours)									Molecular Weight
0	-	-	-	-	-	-	-	-	745,000
1	0.160	0.190	0.160	0.140	0.120	0.090	0.075	0.060	603,000
2	0.450	0.490	0.470	0.415	0.360	0.300	0.240	0.140	684,000
3	0.930	0.940	0.880	0.750	0.625	0.505	0.390	0.240	281,000
4	0.855	0.820	0.685	0.525	0.390	0.270	0.200	0.120	507,000
5	0.790	0.765	0.665	0.500	0.370	0.270	0.195	0.125	496,000

TABLE 12.

Spectra and Molecular Weights of a Degraded 100/1 VA/VC Copolymer. at 180°C

Wavelength	340	360	390	410	430	460	475	505	
				Absorbance					
Time of Degradation (hours)									Molecular Weight.
0	-	-	-	-	-	-	-	-	64,400
1	0.260	0.260	0.245	0.200	0.160	0.120	0.090	0.060	74,900
2	0.560	0.605	0.580	0.500	0.410	0.340	0.260	0.200	84,300
3	0.920	0.930	0.840	0.700	0.505	0.435	0.340	0.250	62,600
4	1.490	1.320	0.990	0.730	0.500	0.360	0.260	0.180	75,400
5	1.140	0.050	0.840	0.640	0.460	0.340	0.260	0.195	64,200
6	2.100	1.820	1.310	0.940	0.700	0.510	0.410	0.310	72,500

TABLE 13.

Spectra and Molecular Weights of a Degraded 19/1 VA/VC Copolymer. at 180°C

Wavelength	340	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight
0	–	–	–	–	–	–	–	90,500
1	0.360	0.410	0.410	0.370	0.330	0.280	0.230	89,000
2	0.900	0.910	0.885	0.825	0.735	0.630	0.490	68,500
3	1.370	1.420	1.260	1.100	0.925	0.780	0.620	98,000
4	–	–	–	2.000	1.580	1.240	0.930	88,300
¼ conc.	0.860	0.790	0.665					
5	2.100	1.900	1.470	1.170	0.915	0.730	0.570	105,000
6	–	–	–	–	1.600	1.240	0.920	91,600
¼ conc.	1.660	1.390	1.000	0.750				

TABLE 14.

Spectra and Molecular Weights of a Degraded 10/1 VA/VC Copolymer at 180°C.

Wavelength	340	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight.
0	-	-	-	-	-	-	-	179,000
1	0.530	0.520	0.430	0.340	0.280	0.225	0.180	185,000
2	-	-	2.680	2.860	2.880	2.680	2.280	275,000
3	1.230	1.210	1.020	0.790	0.590	0.420	0.300	211,000
4	-	-	-	-	-	1.800	1.280	130,000
¼ conc.	1.300	1.190	0.970	0.790	0.620			
5	1.440	1.360	1.100	0.825	0.620	0.445	0.340	128,000
6	1.560	1.280	1.000	0.790	0.6	1.590	1.220	118,000

TABLE 15.

Spectra and Molecular Weights of a Degraded 15/25 VA/VC Copolymer.at 180°C.

Wavelength	340	365	380	412	437	460	480	
	Absorbance							
Time of Degradation (hours)								Molecular Weight
0	-	-	-	-	-	-	-	69,800
1	0.795	0.800	0.690	0.550	0.440	0.380	0.300	89,000
2	-	-	-	2.880	2.780	2.470	2.100	76,000
3	1.500	2.280	1.820	1.350	0.960	0.730	0.570	86,300
4	-	-	2.600	2.870	2.630	2.170	1.750	84,000
5	-	2.700	1.990	1.330	1.020	0.820	0.665	72,300
6	3.650	3.100	2.460	2.700	2.400	1.900	1.450	66,600

TABLE 16.

Spectra and Molecular Weights of a Degraded 60/40 VA/VC Copolymer. at 180°C

Wavelength	340	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight
0	-	-	-	-	-	-	-	37,000
1	1.340	1.255	1.090	0.940	0.820	0.700	0.590	34,300
2	2.470	2.270	1.780	1.420	1.120	0.910	0.760	36,000
3	-	-	2.460	2.030	1.580	1.240	1.010	41,000
4	-	-	2.380	1.830	1.440	1.130	0.930	40,200
5	-	-	2.405	1.840	1.400	1.090	0.885	45,000
6	-	-	2.590	2.040	1.520	1.200	0.980	44,300

TABLE 17.

Spectra and Molecular Weights of a Degraded 09/1 VA/VC Copolymer. at 180°C

Wavelength	340	365	380	412	437	460	480	
			Absorbance					
Time of Degradation (hours)								Molecular Weight.
0	-	-	-	-	-	-	-	47,600
1	1.480	1.530	1.355	1.215	1.050	0.830	0.750	55,500
2	2.600	2.430	2.490	2.450	2.240	1.980	1.680	54,000
3	2.470	2.120	1.505	1.160	0.970	0.780	0.640	58,500
4	-	-	2.490	2.340	2.000	1.600	1.350	67,500
5	-	-	2.080	1.800	1.400	1.100	0.920	68,300
6	-	-	2.560	2.470	2.100	1.650	1.380	65,000

TABLE 18.

Spectra and Molecular Weights of a Degraded 25/75 VA/VC Copolymer. at 180°C

Wavelength	340	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight.
0	-	-	-	-	-	-	-	24,800
1	0.035	0.020	0.010	-	-	-	-	36,200
2	1.420	1.280	0.990	0.760	0.620	0.490	0.390	39,800
3	1.880	1.630	1.220	0.920	0.760	0.635	0.525	36,800
4	2.360	1.920	1.410	1.000	0.780	0.635	0.515	43,400
5	1.950	1.600	1.180	0.820	0.680	0.560	0.440	41,500
6	2.510	2.000	1.530	0.960	0.720	0.570	0.450	57,100

TABLE 19.

Spectra and Molecular Weights of a Degraded 1/10 VA/VC Copolymer. at 180°C.

Wavelength	345	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight
0	-	-	-	-	-	-	-	21,800
1	0.200	0.160	0.120	0.080	0.060	0.040	0.025	31,200
2	0.700	0.660	0.480	0.360	0.290	0.220	0.165	33,200
3	0.655	0.580	0.400	0.280	0.220	0.160	0.125	32,400
4	1.450	1.270	0.940	0.670	0.550	0.430	0.355	45,000
5	1.910	1.500	1.200	0.820	0.680	0.550	0.450	41,000
6	2.070	1.620	1.300	0.940	0.760	0.650	0.520	45,300

TABLE 20.

Spectra and Molecular Weights of a Degraded 1/100 VA/VC Copolymer. at 180°C

Wavelength	345	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight.
0	-	-	-	-	-	-	-	34,800
1	0.205	0.285	0.240	0.155	0.120	0.080	0.050	55,000
2	0.460	0.415	0.300	0.200	0.140	0.105	0.075	44,600
3	0.630	0.560	0.370	0.260	0.200	0.140	0.110	60,000
4	0.780	0.670	0.540	0.400	0.325	0.260	0.220	54,700
5	0.730	0.640	0.470	0.360	0.250	0.180	0.140	66,500
6	1.260	0.940	0.760	0.580	0.470	0.380	0.320	83,000

TABLE 21.

Spectra and Molecular Weights of Degraded PVC. at 180°C.

Wavelength	345	365	380	412	437	460	480	
				Absorbance				
Time of Degradation (hours)								Molecular Weight
0	-	-	-	-	-	-	-	40,600
1	0.160	0.140	0.125	0.095	0.070	0.060	0.040	55,400
2	0.270	0.300	0.260	0.190	0.145	0.105	0.085	61,100
3	0.300	0.265	0.220	0.160	0.120	0.095	0.070	62,500
4	0.500	0.450	0.370	0.270	0.200	0.155	0.130	66,800
5	0.415	0.370	0.310	0.215	0.160	0.125	0.105	61,600
6	0.570	0.490	0.390	0.290	0.225	0.180	0.150	58,000

is optimum for molecular weight measurements. The ultra-violet spectra do not support any firm conclusions but, if they are closely examined, here and there examples are seen of the drop in absorbance at high wavelengths with increased extent of reaction.

The molecular weight measurements do show, however, that the molecular weights increase continuously with the extent of reaction.

B). In Tri-toluyl phosphate.

A typical spectrum is shown in figure 32 and a typical series of spectra, obtained for the same polymer for different times of degradation, is shown in figure 31. This illustrates a very decided drop in absorbance at long wavelengths with increased extent of reaction.

The spectra obtained, in this case, could be related to percentage degradation and thus to the actual amount of acid produced. The spectra are recorded against percentage degradation in tables 22 - 32. These show that there is a definite drop in absorbance at longer wavelengths, with increased percentage degradation. The

Figure 32.

Typical Spectrum of a 1/10 VA VC Copolymer
Degraded for 25 hours. at 180 °C.

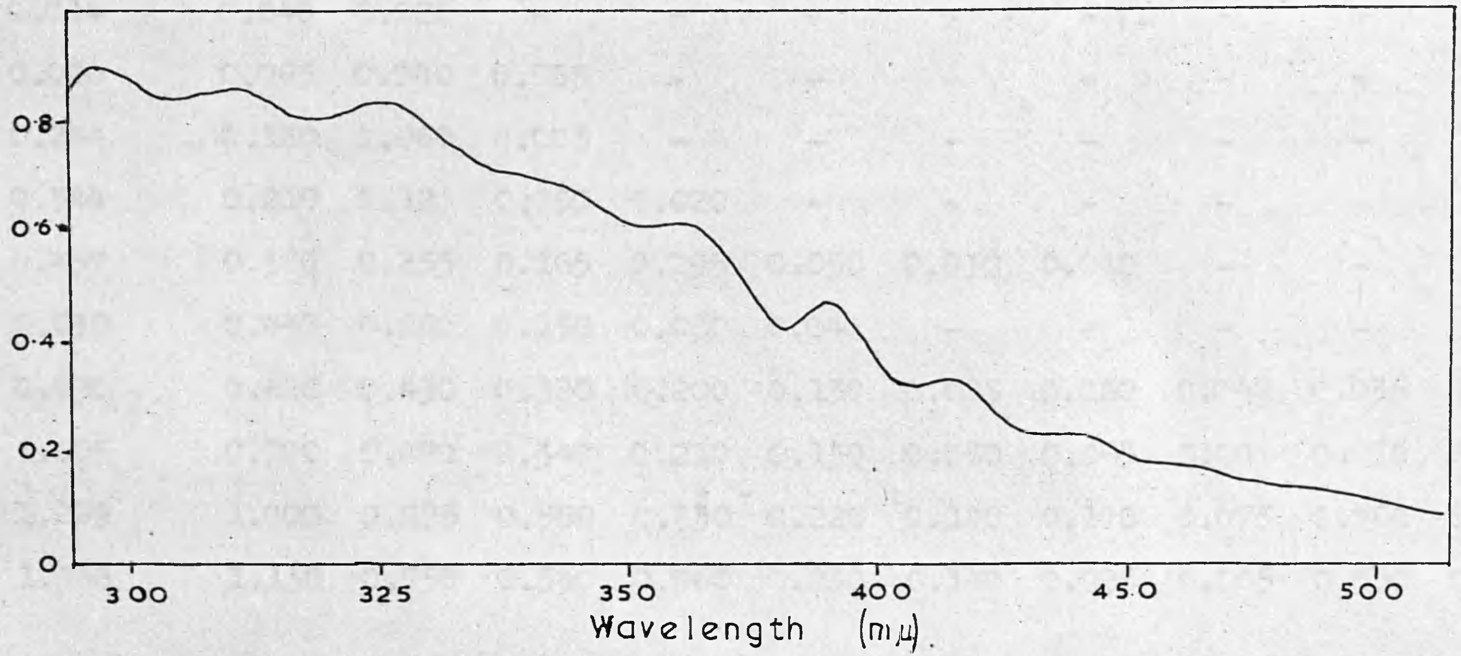


TABLE 22.

U.V. Development in PVA. at 180°C

Wavelength →	295	310	322	340	360	390	415	440	460	480
% degrad. ↓				Absorbance						
0.014	0.040	0.020	-	-	-	-	-	-	-	-
0.020	0.065	0.040	0.005	-	-	-	-	-	-	-
0.244	0.120	0.060	0.005	-	-	-	-	-	-	-
0.344	0.210	0.120	0.050	0.020	-	-	-	-	-	-
0.457	0.380	0.255	0.165	0.095	0.050	0.030	0.010	-	-	-
0.630	0.440	0.260	0.150	0.080	0.040	-	-	-	-	-
0.790	0.620	0.430	0.320	0.200	0.130	0.085	0.060	0.040	0.035	0.030
1.005	0.700	0.470	0.340	0.210	0.130	0.080	0.065	0.040	0.030	0.020
1.299	1.000	0.675	0.580	0.330	0.220	0.140	0.100	0.075	0.060	0.045
1.366	1.130	0.750	0.530	0.360	0.230	0.140	0.095	0.065	0.050	0.030

TABLE 23.

U.V. Development in a 100/1 VA/VC Copolymer. at 180°C.

Wavelength →	295	310	322	340	360	390	415	440	460
% degrad. ↓	Absorbance								
0.0556	0.08	–	–	–	–	–	–	–	–
0.0804	0.095	–	–	–	–	–	–	–	–
0.5134	0.20	–	–	–	–	0.015	–	–	–
1.0019	0.36	0.260	0.165	0.095	0.080	0.06	0.045	0.03	0.025
5.5002	1.2	0.850	0.640	0.450	0.340	0.23	0.165	0.120	0.105

TABLE 24.

U.V. Development in a 19/1 VA/VC Copolymer. at 180°C.

Absorbance

Wavelength → % degrad ↓	295	310	322	340	360	390	415	440	460	480
0.1125	0.040	0.020	–	–	–	–	–	–	–	–
0.1849	0.110	0.080	0.040	0.015	–	–	–	–	–	–
0.3908	0.180	0.125	0.085	0.025	0.015	0.010	0.005	–	–	–
1.3008	0.360	0.255	0.175	0.100	0.070	0.050	0.035	0.020	0.010	0.005
1.795	0.540	0.400	0.285	0.200	0.150	0.120	0.085	0.060	0.045	0.030
3.527	0.840	0.640	0.500	0.370	0.280	0.200	0.135	0.100	0.070	0.055
4.701	1.045	0.800	0.650	0.495	0.380	0.260	0.180	0.135	0.100	0.080
6.133	1.390	1.080	0.890	0.685	0.540	0.360	0.245	0.170	0.130	0.100
7.359	1.610	1.280	1.060	0.800	0.645	0.410	0.275	0.180	0.140	0.105
8.562	1.950	1.550	1.300	1.000	0.780	0.490	0.320	0.220	0.160	0.120
8.748	2.030	1.620	1.365	1.020	0.780	0.495	0.315	0.210	0.145	0.110

TABLE 25.

U.V. Development in a 10/1 VA/VC Copolymer. at 180°C

Wavelength →	295	310	325	340	360	390	415	440	460	480
					Absorbance					
% degrad ↓										
0.1629	0.090	0.080	0.050	0.020	0.015	0.010	-	-	-	-
0.419	0.120	0.090	0.050	0.015	-	-	-	-	-	-
0.971	0.190	0.150	0.090	0.055	0.045	0.040	0.030	0.015	0.005	-
2.731	0.460	0.410	0.345	0.270	0.220	0.185	0.135	0.100	0.080	0.065
4.041	0.670	0.625	0.540	0.425	0.360	0.295	0.220	0.160	0.120	0.090
7.271	1.200	1.120	1.015	0.805	0.675	0.485	0.335	0.230	0.160	0.125
9.024	1.500	1.400	1.260	0.980	0.810	0.580	0.400	0.280	0.200	0.155
11.194	1.995	1.855	1.655	1.290	1.040	0.695	0.460	0.320	0.225	0.170
12.824	2.240	2.110	1.910	1.445	1.140	0.735	0.480	0.325	0.235	0.180
14.29	2.500	2.400	2.170	1.640	1.280	0.785	0.500	0.330	0.240	0.170
14.85	2.610	2.540	2.240	1.680	1.280	0.800	0.505	0.340	0.235	0.170

TABLE 26.

U.V. Development in a 75/25 VA/VC Copolymer. at 180°C.

Wavelength →	295	310	325	340	360	390	415	440	460	480
% degrad. ↓				Absorbance						
0.386	0.01	0.01	-	-	-	-	-	-	-	-
0.8	0.075	0.05	0.01	-	-	-	-	-	-	-
1.214	0.14	0.1	0.055	0.02	0.005	-	-	-	-	-
3.274	0.44	0.42	0.34	0.26	0.225	0.175	0.13	0.105	0.08	-
5.120	0.725	0.67	0.575	0.46	0.39	0.305	0.230	0.170	0.130	-
10.03	-	1.385	1.295	1.045	0.885	0.640	0.450	0.320	0.260	0.210
13.09	-	-	1.800	1.360	1.190	0.820	0.550	0.385	0.295	0.235
16.89	-	-	-	1.715	1.430	0.920	0.585	0.400	0.300	0.230
19.82	-	-	-	-	1.585	1.020	0.665	0.445	0.325	0.255
23.60	-	-	-	-	1.730	1.040	0.640	0.415	0.295	0.210
24.49	-	-	-	-	1.760	1.055	0.660	0.440	0.310	0.240

TABLE 27.

Ü.V. Development in a 60/40 VA/VC Copolymer. at 180°C.

Wavelength →	295	310	325	340	360	390	415	440	460	480
% degrad ↓					Absorbance					
1.44	0.620	0.600	0.570	0.415	0.380	0.385	0.375	0.370	0.365	0.350
3.64	0.890	0.900	0.860	0.660	0.625	0.595	0.520	0.450	0.395	0.350
7.67	1.370	1.440	1.420	1.140	1.060	0.960	0.790	0.640	0.540	0.450
13.97	–	–	–	–	–	2.680	2.860	2.920	2.820	2.560
¼ conc.	1.260	1.250	1.260	1.100	1.100					
30.07	–	–	–	–	–	2.105	1.555	1.100	0.860	0.690
¼ conc.	1.580	1.530	1.510	1.220	1.040					
42.4	–	–	–	–	–	1.910	1.270	0.860	0.640	0.480
¼ conc.	1.580	1.500	1.410	1.080	0.880					
49.88	–	–	–	–	–	1.845	1.206	0.780	0.550	0.390
¼ conc.	1.850	1.690	1.560	1.170	0.920					
56.33	–	–	–	–	–	1.740	1.080	0.780	0.550	0.390
¼ conc.	2.080	2.000	1.805	1.300	1.020					
61.61	–	–	–	–	–	1.660	1.005	0.620	0.390	0.265
¼ conc.	2.400	2.240	2.020	1.450	1.080					
66.06	–	–	–	–	–	1.570	0.930	0.560	0.350	0.230
¼ conc.	2.120	1.940	1.640	1.180	0.880					
67.28	–	–	–	–	–	1.540	0.910	0.550	0.340	0.220
¼ conc.	2.100	1.920	1.615	1.170	0.860					

TABLE 28.

U.V. Development in a 0.9/1 VA/VC Copolymer. at 180 °C.

Wavelength → % degrad ↓	295	310	325	340	360	390	415	440	460	480
	Absorbance									
0.806	0.270	0.270	0.250	0.200	0.190	0.200	0.190	0.200	0.205	0.200
2.8	0.500	0.500	0.480	0.400	0.395	0.390	0.355	0.320	0.295	0.260
6.64	1.080	1.140	1.160	1.010	1.030	1.000	0.880	0.770	0.680	0.580
15.68	2.550	2.910	2.950	2.480	2.340	1.810	1.390	1.015	0.800	0.660
21.76	–	–	–	2.990	2.840	1.950	1.430	0.995	0.760	0.610
33.25 ¼ conc.	– 1.490	– 1.460	– 1.420	– 1.100	– 0.925	1.995	1.400	0.915	0.660	0.590
40.4 ¼ conc.	– 1.800	– 1.740	– 1.660	– 1.250	– 1.015	1.910	1.215	0.745	0.495	0.340
51.26 ¼ conc	– 1.600	– 1.500	– 1.400	– 1.145	– 0.820	1.860	1.160	0.700	0.460	0.305
56.76 ¼ conc.	– 1.980	– 1.870	– 1.680	– 1.240	– 0.945	1.805	1.090	0.650	0.390	0.260
61.47 ¼ conc.	– 2.200	– 2.080	– 1.840	– 1.300	– 0.990	1.720	1.020	0.590	0.350	0.210
62.96 ¼ conc.	– 2.310	– 2.140	– 1.920	– 1.340	– 1.010	1.640	0.960	0.560	0.320	0.190

TABLE 29.

U.V. Development in a 25/75 VA/VC Copolymer. at 180°C.

Wavelength →	295	310	325	340	360	390	415	440	460	430
% degrad ↓	Absorbance									
0.794	0.240	0.230	0.220	0.180	0.180	0.170	0.165	0.170	0.170	0.165
2.589	0.670	0.680	0.695	0.650	0.695	0.705	0.680	0.630	0.585	0.535
7.179	-	1.720	1.780	1.620	1.680	1.580	1.440	1.260	1.115	0.960
16.48	-	-	-	-	-	2.120	1.865	1.445	1.210	1.020
21.99	-	-	-	-	-	2.170	1.800	1.440	1.190	0.990
34.09	-	-	-	-	-	2.170	1.760	1.360	1.100	0.900
41.56	-	-	-	-	-	2.100	1.635	1.215	0.950	0.760
49.31	-	-	-	-	-	1.965	1.500	1.060	0.800	0.620
54.92	-	-	-	-	-	1.960	1.455	0.990	0.720	0.530
60.21	-	-	-	-	-	1.880	1.365	0.900	0.630	0.470
62.04	-	-	-	-	-	1.870	1.360	0.880	0.620	0.440

TABLE 30.

U.V. Development in a 1/10 VA/VC Copolymer. at 180°C.

Wavelength →	295	310	325	340	360	390	415	440	460	480
% degrad ↓				Absorbance						
1.642	0.575	0.550	0.530	0.480	0.495	0.485	0.425	0.365	0.320	0.270
2.172	0.930	0.885	0.870	0.805	0.770	0.730	0.625	0.520	0.440	0.370
5.362	1.515	1.475	1.460	1.295	1.220	1.045	0.850	0.690	0.565	0.470
14.01 ¼ conc.	– 0.870	– 0.840	– 0.810	– 0.680	– 0.600	1.565	1.150	0.850	0.670	0.560
17.94 ¼ conc.	– 1.130	– 1.060	– 1.010	– 0.835	– 0.720	1.660 0.540	1.205 0.380	0.875 0.270	0.790 0.200	0.560
30.52 ¼ conc.	– 1.10	– 1.00	– 0.920	– 0.740	– 0.600	1.800	1.240	0.860	0.640	0.500
35.6 ¼ conc.	– 1.700	– 1.545	– 1.420	– 1.10	– 0.860	1.820	1.245	0.850	0.620	0.460
40.63 ¼ conc.	– 2.035	– 1.905	– 1.660	– 1.280	– 1.000	1.850	1.255	0.830	0.595	0.440
44.34 ¼ conc.	– 2.280	– 2.160	– 1.925	– 1.400	– 1.060	1.840	1.230	0.790	0.560	0.400
47.92 ¼ conc.	– 2.380	– 2.240	– 2.010	– 1.520	– 1.10	1.840	1.230	0.780	0.550	0.390
48.61 ¼ conc.	– 2.520	– 2.420	– 2.140	– 1.550	– 1.190	1.880 0.680	1.270 0.420	0.800	0.590	0.405

TABLE 31.

U.V. Development in a 1/100 VA/VC Copolymer. at 180°C.

Wavelength → % degrad. ↓	295	310	325	340	360	390	415	440	460	480
					Absorbance					
0.294	0.400	0.380	0.360	0.310	0.275	0.260	0.220	0.180	0.145	0.120
0.915	0.535	0.500	0.470	0.400	0.360	0.320	0.245	0.190	0.140	0.105
1.815	0.780	0.705	0.640	0.555	0.465	0.375	0.280	0.200	0.150	0.110
4.130	1.310	1.210	1.080	0.910	0.740	0.540	0.370	0.260	0.180	0.140
5.226	1.520	1.400	1.240	1.000	0.810	0.570	0.385	0.265	0.190	0.145
8.491	2.040	1.860	1.620	1.250	0.950	0.640	0.420	0.380	0.200	0.145
10.369	2.245	2.120	1.850	1.420	1.020	0.665	0.425	0.270	0.180	0.125
12.104 ¼ conc.	– 0.880	– 0.800	– 0.700	1.560	1.200	0.725	0.460	0.290	0.200	0.135
13.517 ¼ conc.	– 0.750	– 0.650	– 0.560	1.770	1.260	0.750	0.460	0.280	0.180	0.120
14.903 ¼ conc.	– 0.665	– 0.590	– 0.500	1.990	1.500	0.880	0.580	0.375	0.280	0.195
15.214 ¼ conc.	– 1.110	– 0.970	– 0.830	1.900	1.350	0.870	0.560	0.370	0.265	0.190

TABLE 32.

U.V. Development in PVC. at 180 °C.

Wavelength → % degrad. ↓	295	310	325	340	360	390	415	440	460	480
					Absorbance					
0.1351	0.260	0.240	0.235	0.210	0.220	0.205	0.195	0.175	0.160	0.125
0.770	0.520	0.490	0.460	0.420	0.390	0.330	0.280	0.235	0.185	0.140
3.70	-	1.240	1.120	0.940	0.745	0.520	0.360	0.260	0.200	0.140
4.502	1.590	1.450	1.290	1.060	0.840	0.630	0.450	0.335	0.260	0.210
6.342	2.030	1.800	1.570	1.250	0.950	0.640	0.440	0.310	0.230	0.185
7.316	2.170	1.950	1.620	1.300	0.940	0.610	0.390	0.260	0.180	0.130
8.456	2.410	2.160	1.840	1.440	1.040	0.640	0.405	0.265	0.190	0.140
8.990	2.530	2.290	1.960	1.520	1.060	0.685	0.440	0.315	0.230	0.160
10.299	2.840	2.610	2.210	1.600	1.200	0.765	0.510	0.350	0.250	0.190
10.57	2.860	2.580	2.185	1.600	1.210	0.720	0.465	0.300	0.220	0.155

absorbances at the particular wavelengths at which the maxima occur were then plotted against percentage degradation (an example is shown in figure 33) and thus the absorbance at each wavelength at certain percentage degradations was found. The values found by this method are shown in tables 33 (a -d). Tables 33c and 33d show the visible region of the spectrum and it is noticeable that, initially, PVC is much more discoloured, at the same percentage degradation, than is PVA or any of the copolymers. There appear to be two minima in colour formation, occurring at 10% VA and 10% VC. This relation is of extreme interest but discussion of it will be reserved until later.

At the low wavelength end of the ultra violet region (shown in Tables 33a and 33b) PVA is beginning to absorb more strongly than PVC. This would suggest that PVA initially has very short chains of conjugated carbon-carbon double bonds but many of them are present. PVC seems to have a greater proportion of longer conjugated sequences.

Figure 33.

Plot of Absorbance at Peak Maxima against % Degradation for a 75/25 VA/VC Copolymer. at 180°C

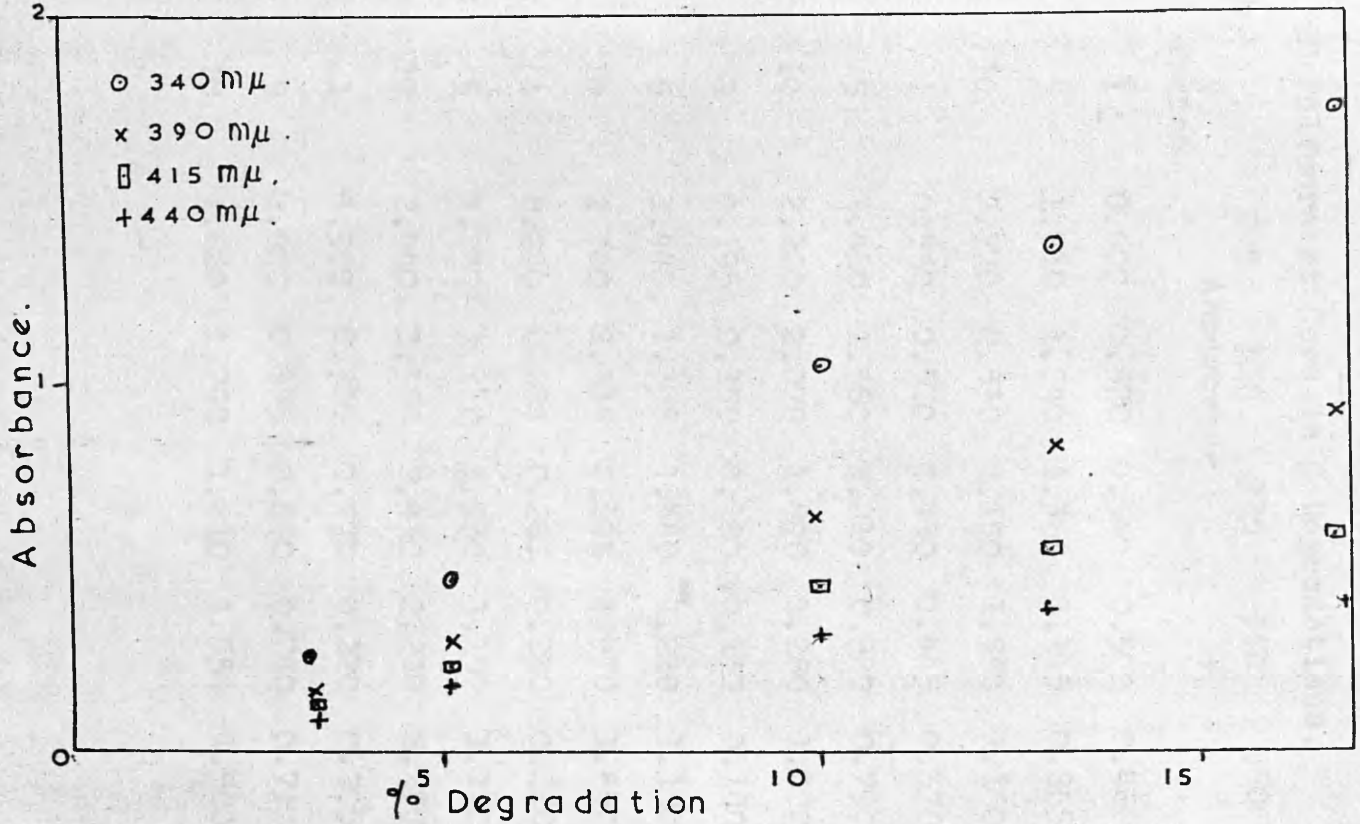


TABLE 33 a.

Spectra of Polymers at Certain % Degradations.

Wavelength		295	310	325	340	360
Polymer	% degrad.	Absorbance				
PVC	1	0.600	0.570	0.540	0.500	0.460
PVC	5	1.710	1.540	1.365	1.115	0.865
PVC	10	2.770	2.530	2.150	1.580	1.160
1VA/100VC	1	0.560	0.520	0.480	0.445	0.370
1VA/100VC	5	1.480	1.360	1.210	0.980	0.790
1VA/100VC	10	2.200	2.070	1.800	1.280	1.000
1VA/10VC	1	0.195	0.180	0.180	0.130	0.180
1VA/10VC	5	1.440	1.395	1.380	1.220	1.150
1VA/10VC	10	2.340	2.315	2.295	1.970	1.850
25VA/75VC	1	0.280	0.280	0.260	0.230	0.220
25VA/75VC	5	1.260	1.210	1.250	1.150	1.170
25VA/75VC	10	2.440	2.360	2.450	2.210	2.270
0.9VA/1VC	1	0.300	0.300	0.270	0.220	0.205
0.9VA/1VC	5	0.820	0.855	0.860	0.740	0.750
0.9VA/1VC	10	1.620	1.790	1.810	1.550	1.500

TABLE 33 b.

Spectra of Polymers at Certain % Degradations.

Wavelength		295	310	325	340	360
Polymer	% degrad.	Absorbance				
60VA/40VC	1	0.570	0.520	0.490	0.350	0.320
60VA/40VC	5	1.060	1.090	1.010	0.840	0.760
60VA/40VC	10	1.660	1.750	1.570	1.400	1.320
75VA/25VC	1	0.100	0.075	0.030	-	-
75VA/25VC	5	0.720	0.665	0.570	0.455	0.385
75VA/25VC	10	-	1.385	1.295	1.045	0.885
10VA/1VC	1	0.190	0.160	0.100	0.065	0.050
10VA/1VC	5	0.820	0.770	0.670	0.530	0.450
10VA/1VC	10	1.720	1.610	1.440	1.150	0.910
19VA/1VC	1	0.300	0.160	0.120	0.060	0.050
19VA/1VC	5	1.120	0.850	0.700	0.535	0.410
100VA/1VC	1	0.360	0.260	0.165	0.095	0.080
100VA/1VC	5	1.100	0.800	0.590	0.410	0.310
PVA	1	0.690	0.470	0.340	0.210	0.130

TABLE 33 c.

Spectra of Polymers at Certain % Degradations.

Wavelength Polymer	% degrad.	390	415	440	460	480
			Absorbance			
PVC	1	0.400	0.320	0.250	0.180	0.140
PVC	5	0.635	0.440	0.330	0.250	0.200
PVC	10	0.740	0.490	0.340	0.230	0.180
1VA/100VC	1	0.340	0.250	0.190	0.140	0.100
1VA/100VC	5	0.560	0.380	0.265	0.190	0.140
1VA/100VC	10	0.660	0.430	0.270	0.185	0.120
1VA/10VC	1	0.205	0.260	0.260	0.220	0.195
1VA/10VC	5	1.000	0.810	0.660	0.540	0.450
1VA/10VC	10	1.320	1.000	0.775	0.610	0.520
25VA/75VC	1	0.235	0.230	0.205	0.200	0.200
25VA/75VC	5	1.160	1.060	0.960	0.860	0.750
25VA/75VC	10	1.740	1.570	1.310	1.140	0.970
0.9VA/1VC	1	0.210	0.210	0.205	0.200	0.195
0.9VA/1VC	5	0.720	0.650	0.570	0.510	0.435
0.9VA/1VC	10	1.290	1.050	0.850	0.720	0.600

TABLE 33 d.

Spectra of Polymers at Certain % Degradations.

Wavelength		390	415	440	460	480
Polymer	% degrad.	Absorbance				
60VA/40VC	1	0.320	0.310	0.330	0.320	0.340
60VA/40VC	5	0.710	0.610	0.520	0.440	0.380
60VA/40VC	10	1.160	0.940	0.770	0.590	0.500
75VA/25VC	5	0.300	0.225	0.165	0.125	-
75VA/25VC	10	0.640	0.450	0.320	0.260	0.210
10VA/1VC	1	0.030	0.025	0.020	0.010	0.005
10VA/1VC	5	0.350	0.245	0.170	0.120	0.090
10VA/1VC	10	0.650	0.430	0.300	0.210	0.180
19VA/1VC	1	0.040	0.030	0.020	0.010	0.005
19VA/1VC	5	0.280	0.190	0.140	0.100	0.080
100VA/1VC	1	0.060	0.045	0.030	0.025	-
100VA/1VC	5	0.210	0.155	0.110	0.100	-
PVA	1	0.080	0.070	0.040	0.030	0.020

Table 34 shows the percentage degradation at which the absorption at 440$m\mu$ of the various copolymers begins to decrease. These suggest that there are competing reactions, one of which varies with copolymer composition and the other which is invariant.

Table 22 shows that PVA is very slow to absorb in the visible region (above 380$m\mu$) but quick to absorb in the ultra-violet region. It is also quick to lower the visible absorption, possibly by crosslinking, and it is thus a more useful material than PVC, with respect to discolouration, but it may have a tendency to crosslink very early on in the degradation, thus affecting the physical properties.

The copolymers are more slow to absorb in the visible region than PVC and thus, for use where discolouration is a disadvantage, these might be useful substitutes for PVC, although they are more unstable, with respect to loss of acid, than PVC.

2). Measurement of Spectra.

Many methods have been proposed for quantitative examination of spectra of degraded PVC

TABLE 34.

Polymer VA/VC	% Degradation at which decrease in absorption at 440 mμ begins. at 180°C.
PVA	1.3
19/1	8.6
75/25	25
60/40	25
0.9/1	37
25/75	18
1/10	18
1/100	14
PVC	10

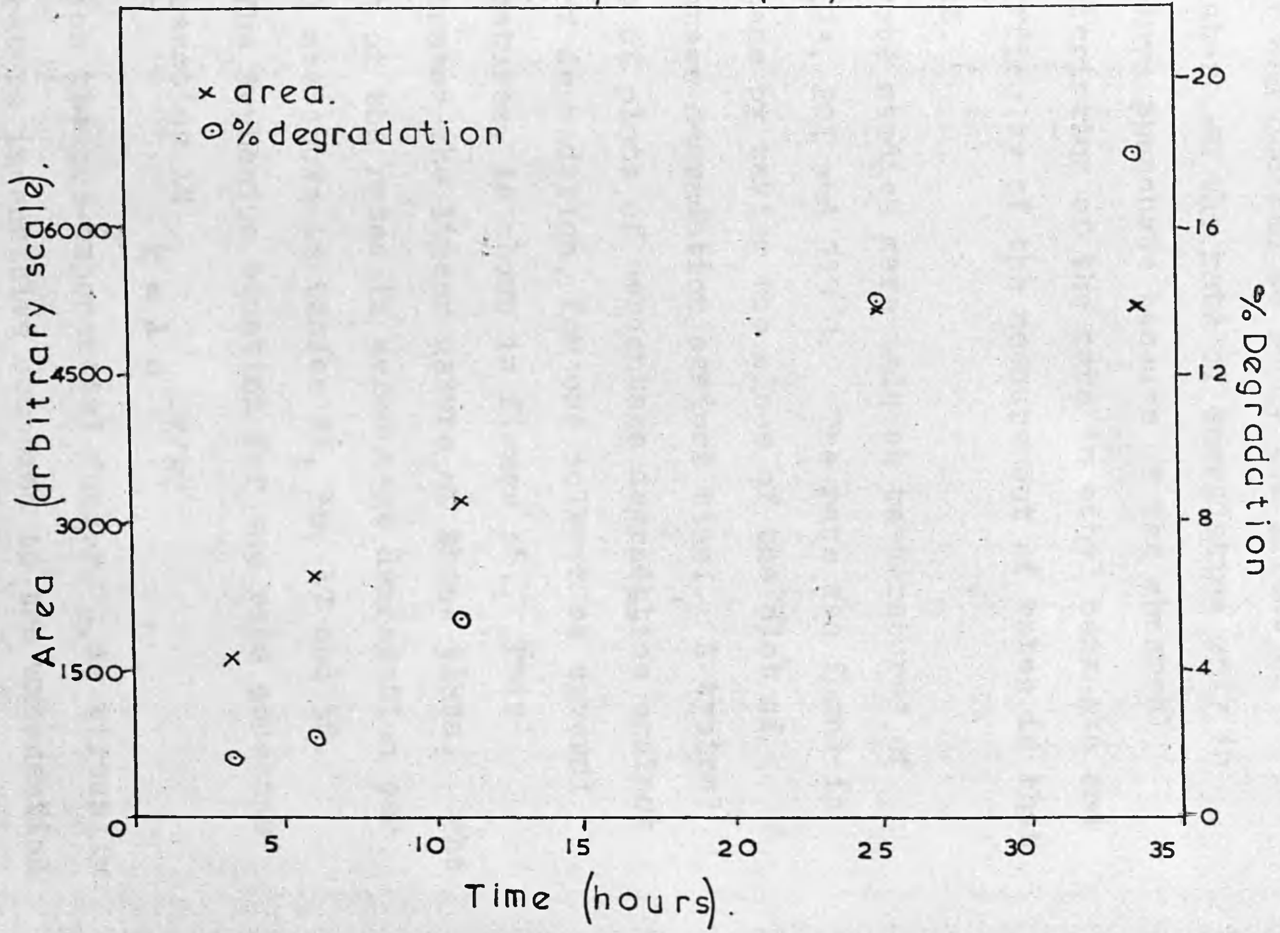
but these have mostly been rather unsuccessful. The most recent method is that of Geddes (111) who showed that it gave good agreement with his own results. This method involved integration of the spectrum from 360mμ to 670mμ and plotting the area, on an arbitrary scale, against time of degradation. This plot followed closely the plot of percentage degradation against time of degradation.

A plot for a 1/10 VA/VC copolymer is shown in figure 34. This shows that there are well-marked differences between the two relationships. The absorbance is clearly arrested after a certain percentage degradation and this could be caused by crosslinking.

Before any further conclusions may be drawn from these results, complete characterisation of the spectra with respect to model polyenes, is necessary. This will doubtless involve very complex calculations probably necessitating the use of a computer.

Figure 34.

Plots of Area under the Absorption Spectra and % Degradation against Time for a 1/10 VA/VC Copolymer. at 180°C.



CHAPTER V11.

The effect of Temperature on the Rate of the Reaction.

It was decided to study the effect of temperature on the rate of degradation only in tri-toluyl phosphate because of the abnormal characteristics of the rate in ethyl benzoate and the difficulty of the measurement of rates in that solvent.

Rate studies were made at temperatures of 180, 193, 201 and 215°C. The rate was found in each case by taking the slope of the plot of percentage degradation against time. A typical series of plots of percentage degradation against time of degradation, for one polymer at several temperatures, is shown in figure 35. This illustrates the linear nature of these plots. The values of the rates in percentage degradation per second are shown in tables 35, 36, 37 and 38.

The Arrhenius equation for the rate constant of a reaction is

$$k = A\ e^{-E/RT}$$

in which the pre-exponential factor, A, is virtually temperature insensitive compared to the exponential

Figure 35.

Typical Series of Plots of % Degradation against Time at Different Temperatures for a 25/75 VA/VC Copolymer.

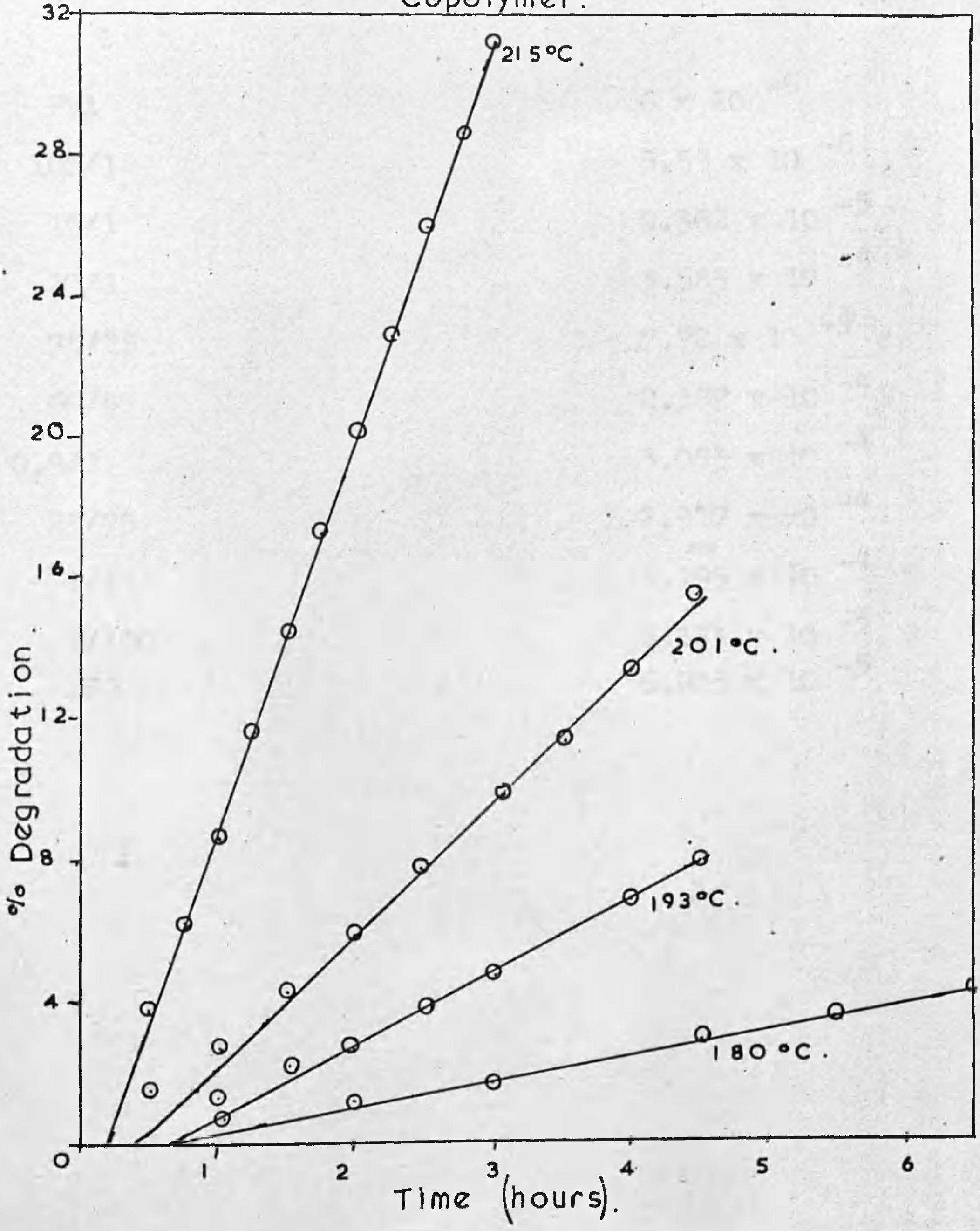


TABLE 35.

Rate of Reaction at 180°C

Polymer VA/VC	Rate % degrad. / sec.
PVA	6×10^{-6}
100/1	5.55×10^{-6}
19/1	2.362×10^{-5}
10/1	3.583×10^{-5}
75/25	7.22×10^{-5}
60/40	2.187×10^{-4}
0.9/1	3.083×10^{-4}
25/75	2.917×10^{-4}
1/10	1.195×10^{-4}
1/100	6.333×10^{-5}
PVC	6.805×10^{-5}

TABLE 36.

Rate of Reaction at 193°C.

Polymer VA/VC	Rate % degrad. / sec.
PVA	$3.667. \times 10^{-5}$
100/1	5.988×10^{-5}
19/1	8.022×10^{-5}
10/1	1.167×10^{-4}
75/25	1.972×10^{-4}
60/40	5.888×10^{-4}
0.9/1	7.167×10^{-4}
25/75	5.805×10^{-4}
1/10	3.333×10^{-4}
PVC	2.333×10^{-4}

TABLE 37.

Rate of Reaction at 201°C

Polymer VA/VC	Rate % degrad. / sec.
PVA	5.388×10^{-5}
100/1	7.862×10^{-5}
19/1	1.419×10^{-4}
10/1	2.355×10^{-4}
75/25	3.708×10^{-4}
60/40	9.667×10^{-4}
0.9/1	1.170×10^{-3}
25/75	1.154×10^{-3}
1/10	6.461×10^{-4}
1/100	2.638×10^{-4}
PVC	3.583×10^{-4}

TABLE 38.

Rate of Reaction at 215°C

Polymer VA/VC	Rate % degrad. / sec.
PVA	1.217×10^{-4}
100/1	2.208×10^{-4}
19/1	4.5×10^{-4}
10/1	7.778×10^{-4}
75/25	1.375×10^{-3}
60/40	2.672×10^{-3}
0.9/1	4.3×10^{-3}
25/75	3.588×10^{-3}
1/10	1.771×10^{-3}
1/100	8.112×10^{-4}
PVC	8.388×10^{-4}

term. E is the energy of activation, R is the gas constant and T is the temperature in degrees absolute.

If logarithms of this expression are taken,

$$\ln k = \ln A - \frac{E}{RT}$$

which is

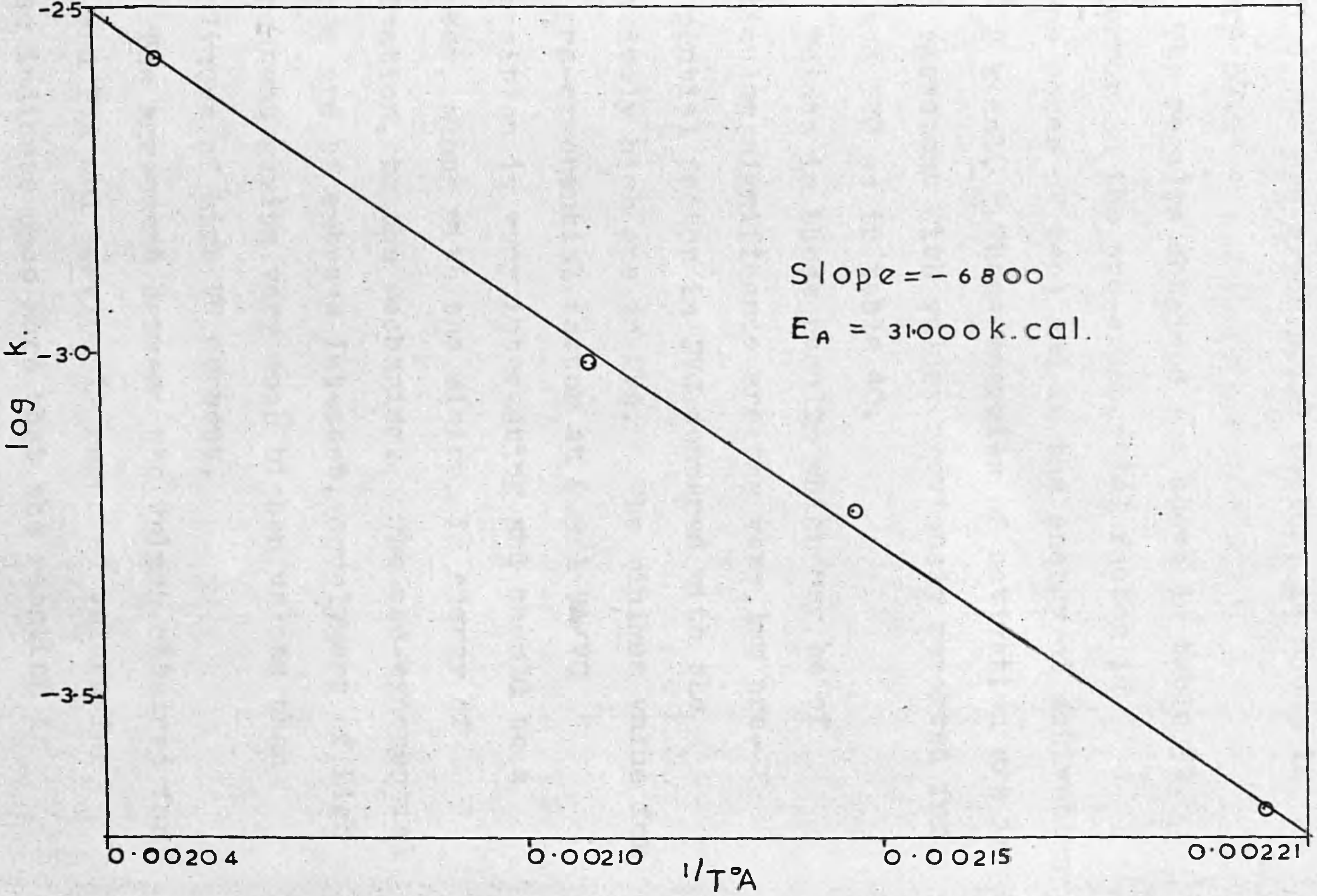
$$\log k = \log A - \frac{E}{2.303\ RT}$$

Thus, if the logarithm of the rate constant is plotted against the reciprocal of the absolute temperature, the slope of the line is $- \frac{E}{2.303\ R}$ and the intercept on the log (rate constant) axis is log A. Thus the energy of activation and the pre-exponential factor may be found. Strictly, k is the rate constant but, if only T is varied, the rate can be used instead of the rate constant, assuming that the order of reaction remains constant throughout the temperature range studied. In this case, while strictly correct values of the energy of activation are obtained, it should be noted that the pre-exponential factors are at best only relative and certainly do not represent precise A values.

A typical energy of activation plot is shown in figure 36 and the same plot on a reduced scale,

Figure 36.

Typical Plot of log k against 1/T°A to Obtain Energy of Activation for a 60/40 VA VC Copolymer.



to find the pre-exponential factor, is shown in figure 37.

The results obtained are shown in table 39. The error in the pre-exponential factor is ± (one power of ten) and in the energy of activation is ± 2 k cal. These energies of activation are in good agreement with values previously reported for PVA and PVC as in table 40.

Points in these results which may be of particular significance are the very low pre-exponential factor in PVC compared with the relatively high one in PVA. The minimum value for the pre-exponential factor at 0.9/1 VA/VC composition is very interesting and should be a pointer, along with the minimum in energy of activation, to the mechanism. The pre-exponential values are of extreme interest, copolymers of high VA content giving very much higher values than copolymers of high VC content.

The agreement between the values obtained for PVC and PVA and previously reported values for these indicate once more that the reaction in tri-toluyl phosphate is of the same type as, and is

Figure 37.

Typical Plot of log k against $1/T$ to Obtain Pre-exponential Factor for a 60/40 VA/VC Copolymer.

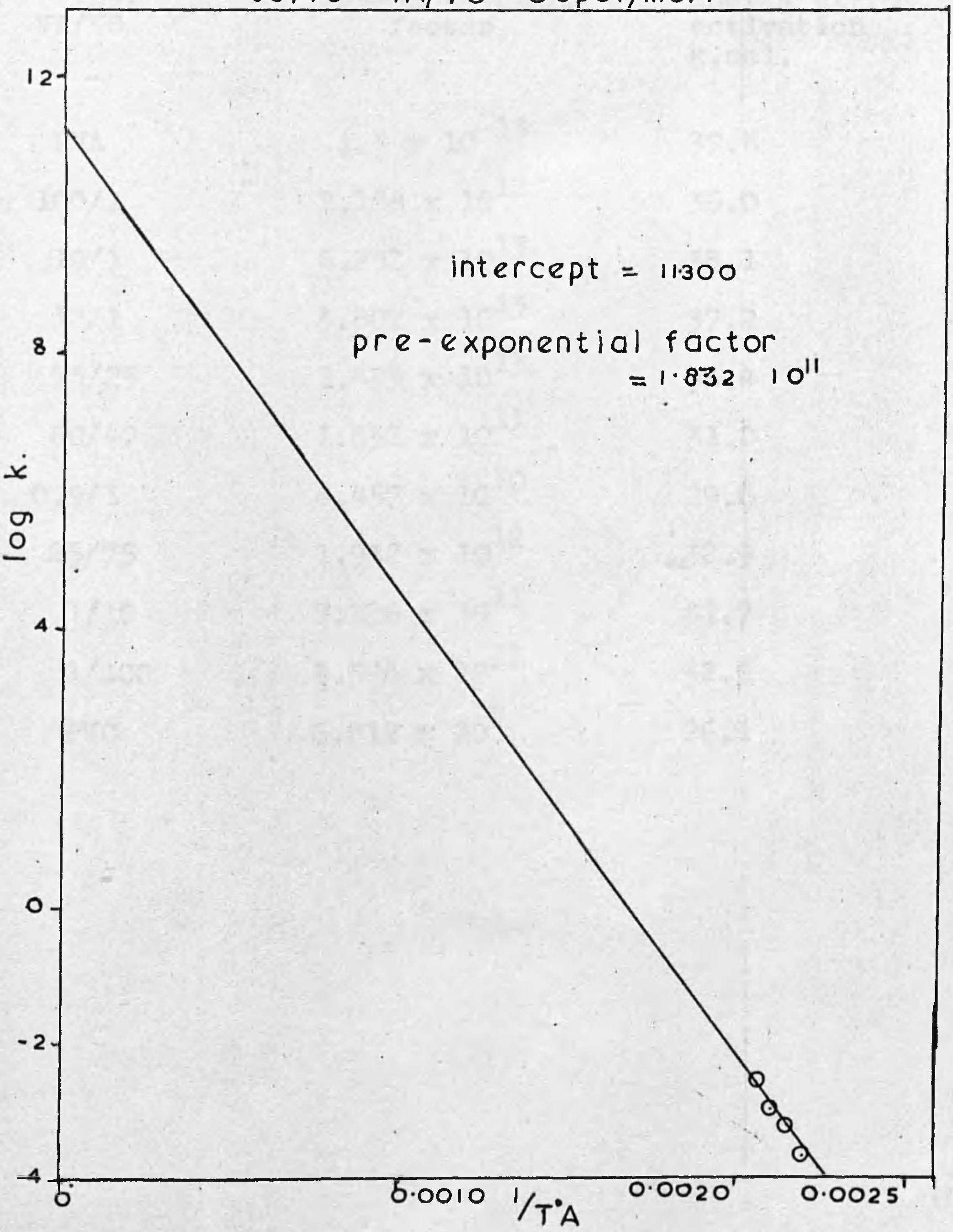


Table 39.

Polymer VA/VC	Pre-exponential factor	Energy of activation k.cal.
PVA	1.3×10^{13}	37.6
100/1	2.188×10^{12}	36.0
19/1	6.252×10^{13}	38.1
10/1	3.802×10^{13}	37.2
75/25	1.435×10^{13}	35.4
60/40	1.832×10^{11}	31.0
0.9/1	6.457×10^{10}	29.6
25/75	1.932×10^{12}	32.9
1/10	7.226×10^{11}	31.7
1/100	3.524×10^{11}	32.6
PVC	6.012×10^{8}	26.1

Table 40.

Polymer	Energy of activation k. cal/mole.	Reference.
PVA	36.7	149
PVA	37.6	present
PVC	29	40
PVC	22.8 (solution)	26
PVC	22.5	25
PVC	28	168
PVC	33	50
PVC	26	10
PVC	30 (solution)	146
PVC	26 (solution)	present

indeed very similar to, the reaction in the solid phase.

Full discussion of these results will be reserved until the next chapter.

CHAPTER VIII.

DISCUSSION.

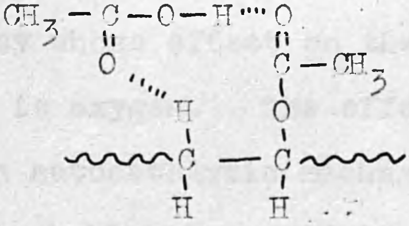
The experimental results obtained using the Thermal Volatilisation Analysis (T.V.A.) technique showed the relative stability of the different copolymers, but gave no information about the main products or their ratios or the energies of activation for degradation. This technique is an extremely useful tool for qualitative study and product control since a high degree of reproducibility may be obtained.

Unfortunately, T.V.A. is not very likely to become a highly useful quantitative technique but there are some limited possibilities for it in this direction.

Similarly, T.G.A. is unlikely to be useful for quantitative work on PVC but it can again be used qualitatively. An improvement of great value would be to combine these two techniques. The combination would add infinitely to the usefulness of T.G.A. and it is possible that all products and energies of activation may be found from one or, at the most, two runs.

The effects of three agents upon the degradation behaviour of the polymers are of interest. The first agent is ethyl benzoate which was found to interfere quite strongly with the degradation. The first reason which might be suggested for this is ester exchange with the polymer but this is unlikely as the reactants and the conditions are not those normally considered necessary for this type of reaction. The second suggestion is that hydrolysis of the ethyl benzoate by the degradation products, especially acetic acid, might occur, since it is PVA which is most affected. This is most unlikely, especially in the light of later findings, chapter V , that the product of this reaction, benzoic acid, actually inhibits the degradation. The reason for this inhibition has still to be found.

The third possible explanation for the effect of ethyl benzoate is that, although the ethyl benzoate itself plays no direct part, the acetic acid, which remains in the reaction solution, catalyses the degradation and causes the autocatalytic behaviour observed. This is quite feasible in the light of the charge separation mechanism for the decomposition of PVA (169) where the rate would increase if the dielectric constant of the medium were increased. This would happen if acetic acid were added to ethyl benzoate.



This postulate is supported by results in tri-toluyl phosphate which showed that the two acidic degradation products catalysed the degradation. This again could be by an increase in the dielectric constant and this would favour a charge separation mechanism. It is difficult to see how these products could increase the rate of a radical reaction but it is known that hydrogen chloride causes the breakdown of peroxides (100). The question arises as to whether there are sufficient hydroperoxides present in the polymer to cause the changes noted and this appears to be unlikely.

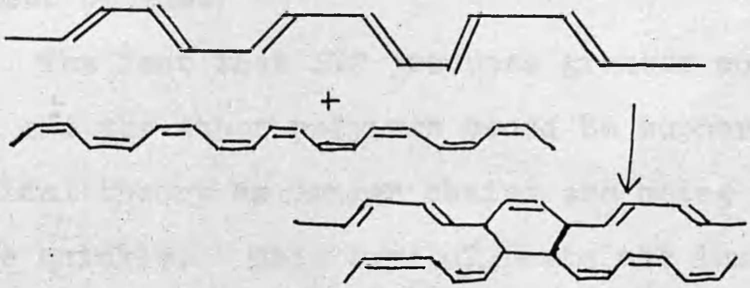
The rate is increased when the products are allowed to build up but it returns to the uncatalysed rate thereafter. One explanation for this is that the rate of initiation is increased by the degradation products and thus there are more propagating chains.

The final agency whose effect on the rate is to be discussed, is oxygen. The effect of oxygen is to give an autocatalytic mechanism. The reason for this is probably that oxidation of double bonds occurs to give reactivation of these sites at the end of long conjugated polyene sequences, which are no longer capable of propagating. There is less colour formation in oxygen than in nitrogen and the molecular weight drops (4,26). Thus, the attack is in the body of the chain and probably in the central parts of polyene sequences to give structures capable of propagation and transfer. It is possible, therefore, that oxygen acts as a transfer agent.

It was shown in a number of ways that minimum stability occurs in the copolymer range between

50% VC and 75% VC and it is noticeable that this is the composition at which there is the greatest likelihood of one VA unit having two VC units adjacent to it without it being in a block of VC units i.e. the most random structure will occur.

It was noted, chapter Vl, that the heights of peaks, in the long wavelength portion of the spectra of the degraded co-polymer, began to decrease after a certain amount of degradation, dependant upon the composition of the copolymer. This reduction was associated with an increase in molecular weight. This could be caused by the condensation of a long polyene chain with another one or with a carbon-carbon double bond, in a Diels Alder or other polyene condensation reaction.



This would give a centre capable of propagation in four directions, because the conjugation length has been reduced, in at least one part. There will thus be an increase in rate as has been noted by other workers (5). Such a reaction would also give the type of structure which would be ideal for breakdown to benzene and other aromatic compounds which are found in the volatile products at degradation temperatures above 250°C. This cross-linking mechanism also has support in that it was shown by Bengough (6) that the cross-linking reaction is non-radical.

It was also noted that there are two minima in colour production, at 10% VC and 10% VA. It is possible that these polymers produce more propagating chains but, for a set percentage acid loss, they will produce less colour by depropagating to a lesser extent.

The fact that PVC produces greater colour than PVA and the other polymers could be support for the radical theory as longer chains are being produced more quickly. This type of postulate immediately requires that the copolymers degrade by an ionic or charge separation mechanism, which is not necessarily the case.

This phenomenon shown by PVC could also be attributable to a production of fewer initiation sites.

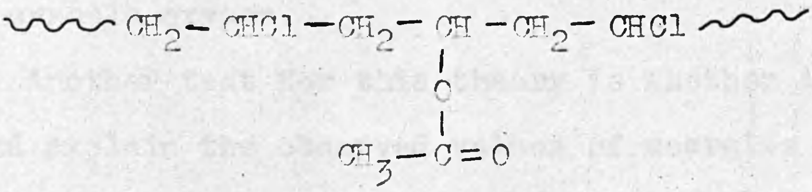
Any future work on the colouration of these polymers will require very sensitive ultra-violet and visible spectral measurements.

The energies of activation, chapter V11, for PVC and PVA are very similar to values previously obtained and this indicates that solution effects are not changing the kinetics of the degradation with respect to those in the solid. The increase in rate of dehydrochlorination in tri-toluyl phosphate reported by Bengough (146) may be caused by the build up of rate-accelerating hydrogen chloride in the tri-toluyl phosphate to a greater extent than in ethyl benzoate. When nitrogen is blown through the solution, this feature is removed. This could also account for the high energy of activation found by Bengough (146) when using tri-toluyl phosphate. No previous work has been carried out on the energies of activation of the copolymers.

The energies of activation found do not show a great variation throughout the range although there is a trend upwards from PVC to PVA. The apparent minimum at a 0.9/1 copolymer may be associated in some way with the minimum in stability which is observed in this area of composition. In many cases the highest temperature rate is out of line with the rest as the products here are coming off very rapidly and may not be swept out as efficiently as at lower temperatures and thus the rate and the energy of activation would be increased.

The pre-exponential values give little additional information about the mechanism of the reaction but the relatively large values may be an indication that a chain reaction is involved.

The many, varied pieces of evidence discussed above make the postulation of a mechanism very difficult. However, if the relative stability of the various copolymers is taken as the most vital fact, the degradation could occur by activation of VA units by adjacent VC units.



$$\sim\sim CH_2-CHCl-CH_2-\underset{\substack{|\\ O\\ |\\ CH_3-C=O}}{CH}-CH_2-CHCl\sim\sim$$

The chlorine atom will have an electron-withdrawing effect on the adjacent methylenic carbon-hydrogen bonds. This will activate these hydrogen atoms for reaction with the acetate group by a charge separation process as postulated by Grassie (169) for PVA. . This would produce a carbon-carbon double bond in the chain.

Support for this postulate is found in the fact that acetic acid tends to be preferentially removed in the first stages of the reaction, chapter V 2 A. fig. 29.

The double bond formed in this way could activate an adjacent VC unit by allylic activation, if this unit will decompose by a charge separation or ionic mechanism.

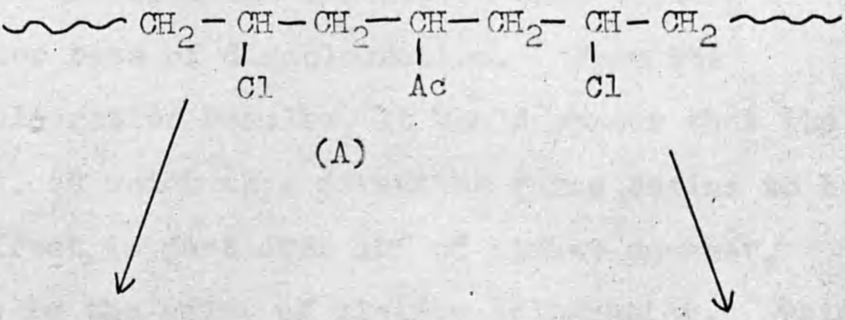
An alternative mode of action of the double bond is by being a secondary initiation point, incapable in itself of initiation but capable of initiation after activation by some other agent, for example oxygen.

Another test for this theory is whether it could explain the observed values of energies of activation. It could be because there is a distinct possibility that an ionic or unimolecular mechanism for breakdown can be imposed upon the VC unit and thus, in this case, the radical portion could well be suppressed.

Because of the activation of the VA unit, the expected minimum in energy of activation would be between 50% and 75% VC, at which compositions the likelihood of a VA unit being flanked by VC units, is greatest, without being in a block of VC units.

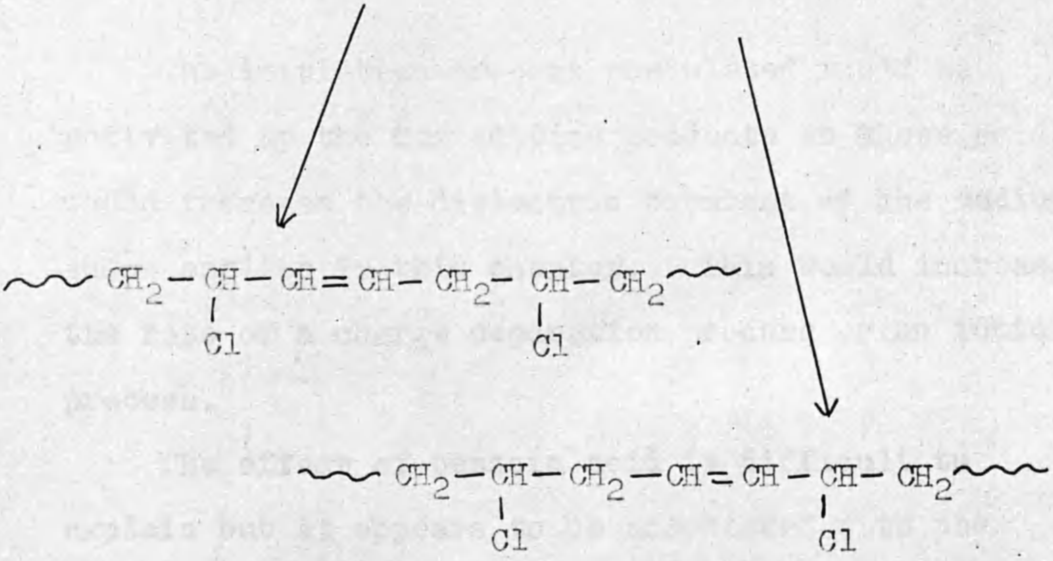
If this proposed mechanism is correct, there will obviously be many more points of initiation in the copolymers than in the homopolymers. There is certainly allylic activation in PVA but, in this case, it probably constitutes all the initiation through unsaturated terminal structures and there is far less initiation in PVA, as evidenced by its reluctance to degrade. Thus, in these copolymers, one would expect many more possible points of initiation than in PVA. In all cases, however, the degradation will build up slowly as the activation from one carbon-carbon double bond will be much less than that from two conjugated carbon-carbon double bonds.

The colouration observed is also explicable by this mechanism. As the number of initiation sites increases, the discolouration, at a given percentage loss of acid, will be less. The structure A may lose acetic acid by either of the routes shown, which are equivalent. The products formed will reduce the possibilities for long polyene sequences if two subsequent VA units liberate acid in the two different directions.



$$\sim CH_2-\underset{Cl}{CH}-CH_2-\underset{Ac}{CH}-CH_2-\underset{Cl}{CH}-CH_2\sim$$

(A)



$$\sim\sim CH_2-\underset{|\atop Cl}{CH}-CH=CH-CH_2-\underset{|\atop Cl}{CH}-CH_2\sim\sim$$

$$\sim\sim CH_2-\underset{|\atop Cl}{CH}-CH_2-CH=CH-\underset{|\atop Cl}{CH}-CH_2\sim\sim$$

The number of blockages will increase as the number of VA or VC units is increased but some directive effect would be expected to come into play when the initiation sites are close enough together. This effect will tend to remove the randomness from the initiation thus causing a greater rate of discolouration. From the discolouration results, it would appear that the point, at which this directing force begins to have an effect, is just over 10% of either monomer, which is the point of minimum colouration. This means that there is a directive effect if the initiation sites are less than 10 monomer units apart.

The initiation process postulated would be activated by the degradation products as these acids would increase the dielectric constant of the medium, shown earlier in this chapter. This would increase the rate of a charge separation process or an ionic process.

The effect of benzoic acid is difficult to explain but it appears to be associated with the hydroxyl group of the acid. This could merely be by some addition reaction with the products of the reaction.

The mechanism could account for oxygen catalysis by oxidation of the carbon-carbon double bonds formed in the postulated initiation step. This would give peroxide structures which could give chain scission and thus degradation in two directions could occur. This work has not been successful in finally establishing the mechanism of degradation of PVC. However, the results obtained and the mechanism postulated for the degradation of the copolymers both suggest a possible explanation for the difficulty found in elucidating the mechanism of degradation of PVC. This is that the VC unit may be induced, dependant upon it environment, to lose hydrgoen chloride by a radical or ionic mechanism and it is possible that, in PVC degradation, these two mechanisms operate simultaneously.

The factors described in the introduction suggest many possible modes of future investigation. The first of these is the obvious value of electron spin resonance (E.S.R.) investigations in thermally degrading PVC to determine if radicals are present and, if radicals are found, to determine their number. This number could be compared with the number of propagating chains calculated from kinetics or from ultra violet measurements to determine if all the propagating chains involve radicals. This would have to be done at different temperatures and on different polymers to give conclusive results. It would, however, finally prove or disprove the existence of radicals in thermally degrading PVC. If radicals were found, it would confirm that they participate in at least one part of the degradation process but, if they were not found, it would mean that they do not participate at all. It is really of no value to perform E.S.R. measurements on material already thermally degraded as radicals could combine to destroy each other or unsaturated structures could react with oxygen to give radicals during the period between degradation and E.S.R. measurement. This would give totally misleading results.

The next problem is the determination of the polyene chain length and this necessitates a very thorough investigation of the spectra of all individual polyenes of length 2 to 25. Thus spectra of all individual and all possible mixtures of polyenes must be examined to determine extinction coefficients and the wavelengths of the maxima. Because of the effect of substituents on the spectra, four polyenes must be prepared and examined for each chain length.

Thus, the only way that colouration could be tackled in a quantitative way would be very arduous and, possibly for this reason, many workers have used relationships which are satisfactory only for their own requirements, as already discussed in chapter 1.

From a commercial point of view, the problem of inhibiting colouration is clearly one of reducing the polyene sequence length so that the polymer will absorb in the ultra-violet region of the spectrum.

The relationship of the polymerisation initiator to the degradation process may be determinable by the use of radiotracer techniques. These studies may give an insight into the initiation sites for degradation.

The work using N.M.R., described in chapter 111 could be extended to the use of a 220 Mc/s machine which could possibly separate the isotactic, syndiotactic and atactic contributions and perhaps indicate some influence on degradation. Another possible development is the application of a rapid measurement of percentage VA in the copolymers to industrial process control.

From the results obtained, it would appear that a polymer containing about 10% VA would be the most resistant to discolouration.

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