European Polymer Journal, 1968. Vol. 4, pp. 521–535. Pergamon Press. Printed in England.

THE THERMAL DEGRADATION OF POLYVINYLCHLORIDE IN SOLUTION—V.

EFFECT OF DIMETHYLFORMAMIDE AS SOLVENT

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(*Received* 27 *January* 1968)

Abstract—The thermal degradation of polyvinylchloride (PVC) at 12·5 g/l. in dimethylformamide (DMF) has been studied at 130° by following the changes which occur in the u.v. and visible absorption spectra of the solutions. Degradations *in vacuo* and under nitrogen gave similar spectra having broad absorption bands with maxima at 478 mμ, while those carried out in air, or in an atmosphere of oxygen, gave spectra in which the absorbance was at a maximum at around 320–340 mμ, and fell off rapidly with increase in wavelength. A distinct change in spectral pattern was observed when oxygen was admitted to a solution which had been partially degraded *in vacuo*: the effect was not so pronounced when the process was reversed.

During the degradations no hydrogen chloride gas was liberated: it dissolved in the DMF to form a complex which decomposed yielding dimethylamine hydrochloride which was found to be a catalyst for the degradation.

Viscosity measurements on vacuum degraded solutions through which oxygen had been passed for various periods at 70°, indicate that the degradation occurs mainly at the ends of the polymer chains.

In Part IV of this work⁽¹⁾ the thermal degradation of PVC in solution was investigated by following the changes in the absorption spectra of the solutions during the degradation. In most of the solvents used the absorption spectra of the degraded polymer were similar even though there were significant differences in the rate of development of the spectra. In dimethylformamide (DMF) however, not only was the rate of degradation very much greater than with any of the other solvents, but the pattern of absorbance was completely different. A more detailed study of this system has now been undertaken and is reported in this paper.

Because of the very rapid rate of degradation at 178°, it was decided to work at a much lower temperature. 130° was found to give a convenient rate of degradation, and consequently this temperature has been used throughout this work.

Some earlier work⁽²⁻⁴⁾ had been carried out on the thermal degradation of PVC in DMF solution; it had been done in the presence of metal salts which catalysed the reaction. Consequently, the reaction was studied at an even lower temperature, namely 80°.

EXPERIMENTAL

Materials

Polyvinylchloride. (Pevikon KL2) kindly supplied by British Geon Ltd. was purified as follows. The polymer was shaken for 24 hr in peroxide-free tetrahydrofuran to give a 2 per cent solution, and was subsequently precipitated in a large excess of methanol with constant stirring, allowed to stand overnight, filtered, and dried at 50° for 2 days. This procedure was repeated except that the final polymer was dried *in vacuo* for a week at 47°.

Dimethylformamide. (DMF) supplied by May & Baker Ltd. was distilled under reduced pressure before being used.

Acetophenone supplied by Hopkin & Williams Ltd., *paraformaldehyde* and *isoamyl alcohol* supplied by British Drug Houses Ltd. were used without further purification.

High purity nitrogen was supplied by Air Products Ltd., and oxygen by British Oxygen Co. Ltd.

Apparatus

The oil bath used for degradation studies consists of a 4 necked, 5 -l. round-bottomed flask containing silicone oil. External pre-heating is by a 500 W Electrothermal heating mantle, and internal heating by a 100 W fish tank heater. The temperature is controlled to ± 0·50° by a 0–250° contact thermometer via a relay to the fish tank heater. Stirring is achieved by a Gallenkamp variable speed stirrer. The whole unit is lagged with fibre-glass.

Vacuum degradations were carried out in a vapour jacket using *iso*-amyl alcohol as the heating medium (b.pt. 130°) since the cells were too long to be completely immersed in the oil bath. The cell units are shown in Fig. 1(a) and 1(b).

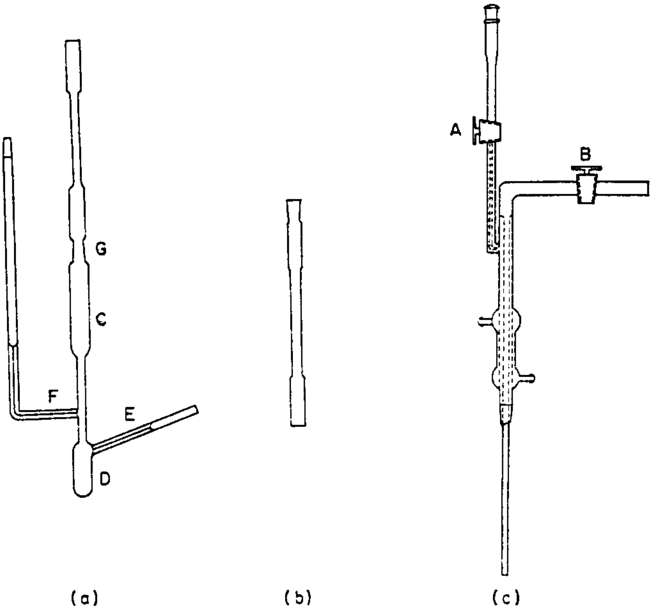


FIG. 1. (a) Vacuum cell; (b) Ordinary cell; (c) Gas delivery unit.

Procedure

Stock solutions of PVC in DMF were made up at a concentration of 12·5 g. $l.^{-1}$, and were allowed to stand overnight. They were then immersed for 30 min in a water thermostat at 60°, and afterwards shaken for a further 30 min.

From the stock solution 3·5 ml was taken, vacuum filtered (porosity 3) and run into the cell through a drawn capillary. For vacuum work, the solution was introduced via the capillary tube which was subsequently sealed off at E, degassed in bulb D (Fig. 1a) by repeated freezing–pumping–thawing cycles, sealed off at F and run into the cell (Fig. 1a).

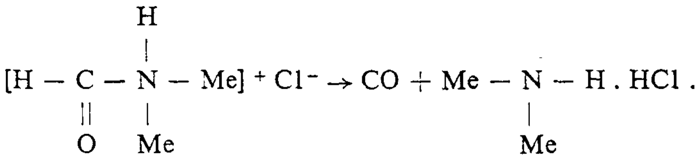
The cells were removed at regular intervals from the oil bath, or vapour jacket, and plunged into iced water to stop the degradation. For work under nitrogen or oxygen, cells (Fig. 1b) together with the apparatus shown in Fig. 1(c) were used, the gas flow rate being approximately 0·4 $l.hr^{-1}$. On removing the unit to record a spectrum, the taps A and B were closed and the condenser hoses were removed; the cell was cooled, dried, and placed in a Perkin–Elmer 137 u.v. spectrophotometer modified slightly to take the long cells. A matched cell containing undegraded polymer solution was placed in the reference beam. When changing from degrading *in vacuo* to an oxygen atmosphere, the cell unit shown in Fig. 1(a) was cut open at C, and the gas delivery unit (Fig. 1c) fitted into the SCB 10 socket G. The procedure mentioned above was then followed.

Because DMF absorbs strongly in the u.v. region, it was not possible to measure the absorption of polymer solutions below 265 mμ.

RESULTS

Hydrogen chloride evolution

Although the polymer solution became brownish in colour quite quickly, no acidity could be detected in the carrier gas which was passed into water to extract any HCl which might have been evolved. No change in pH of the water could be detected even after the degradation had been proceeding for 40 min. This rather unexpected result was later found to be due to the very considerable solubility of HCl in DMF. At a gas pressure of 1 atmosphere, 106 and 93 g HCl dissolve in 100 g DMF at 20° and 40° respectively. Furthermore, at temperatures above 90° the DMF hydrochloride decomposes⁽⁵⁾ giving off carbon monoxide and leaving dimethylamine hydrochloride, according to the equation



$$[\mathrm{H}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{Me}}{|}}{\mathrm{N}}}-\mathrm{Me}]^{+}\mathrm{Cl}^{-}\rightarrow \mathrm{CO}+\mathrm{Me}-\underset{\underset{\mathrm{Me}}{|}}{\mathrm{N}}-\mathrm{H}\,.\,\mathrm{HCl}\,.$$

As the polymer degradation was being studied at 130°, one might expect that the HCl liberated from the polymer would first form DMF hydrochloride which would subsequently decompose to form dimethylamine hydrochloride. As no information was available regarding the rate of this reaction, DMF hydrochloride was prepared by passing anhydrous HCl through DMF at 77°, and then converted to the amine hydrochloride by heating it at 130°. The dimethylamine hydrochloride so formed was characterized by its melting point (171°), and by its derivative⁽⁶⁾ ω,ω′-dimethylaminopropiophenone hydrochloride. This same derivative was also prepared from the residual liquid after degrading a solution of PVC in DMF at 130°. That the derivative was the same in both cases was confirmed both by its melting point (156°) and by its i.r. absorption spectrum shown in Fig. 2. Thus dimethylamine hydrochloride must have been present in the solution after degradation, since DMF, its hydrochloride and dimethylamine are incapable of forming the above derivative.

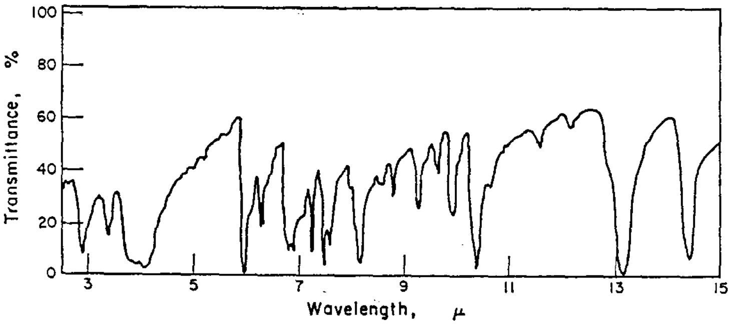


FIG. 2. Infra-red spectrum of ω,ω′-dimethylaminopropiophenone hydrochloride.

Recent experiments⁽⁷⁾ have shown clearly that dimethylamine hydrochloride is a catalyst for the degradation of PVC in DMF solution, but they will be the subject of a later paper in this series.

Absorption spectra

The absorption spectra obtained when degradations are carried out *in vacuo*, and in nitrogen, air and oxygen atmospheres are given in Figs. 3–6 respectively. The first spectrum shown in each figure (i.e. curve a) was taken 10 min after the start of degradation, and subsequent spectra (curves b, c, d, etc.) each differ by 10-min periods of degradation with the exception of curve f of Fig. 4 which corresponds to a period of 5 min degradation after curve e. The most significant difference between the

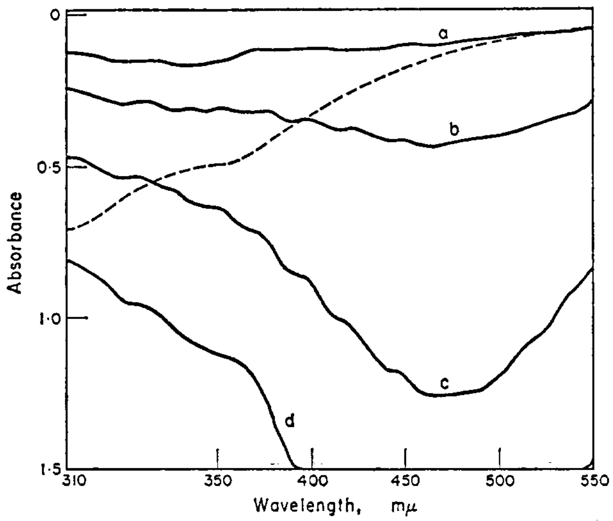


Fig. 3. Absorption spectra of PVC solution in DMF degraded *in vacuo* for (a) 10, (b) 20, (c) 30, and (d) 40 min respectively. Broken line shows the effect on spectrum (c) of passing oxygen through the degraded PVC solution at 70° for 800 min.

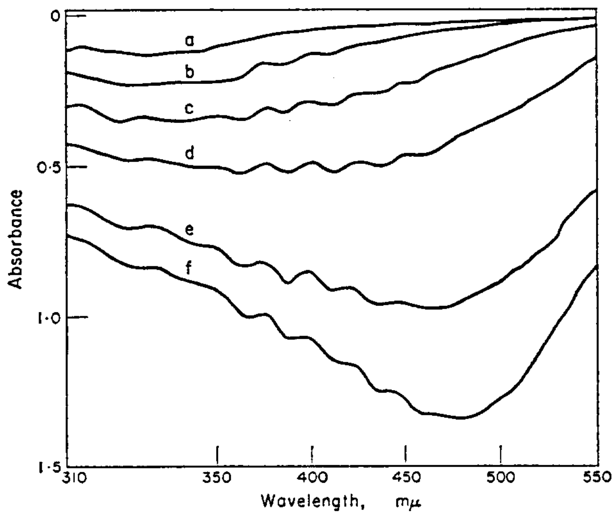


Fig. 4. Absorption spectra of PVC solution in DMF degraded under nitrogen at 130° for (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 55 min.

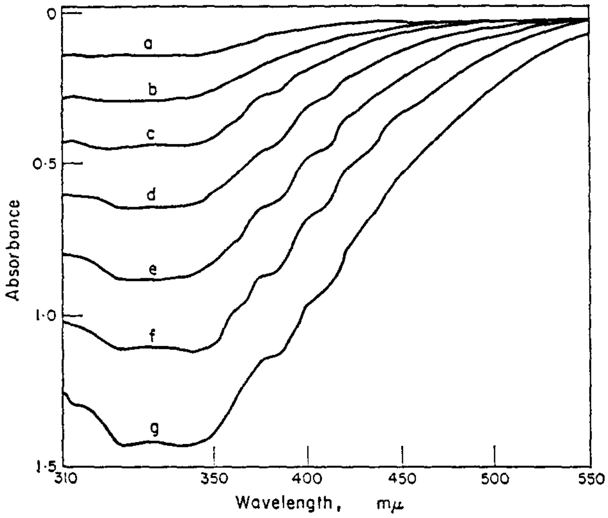


FIG. 5. Absorption spectra of PVC solution in DMF degraded in air at 130° for (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, and (g) 70 min.

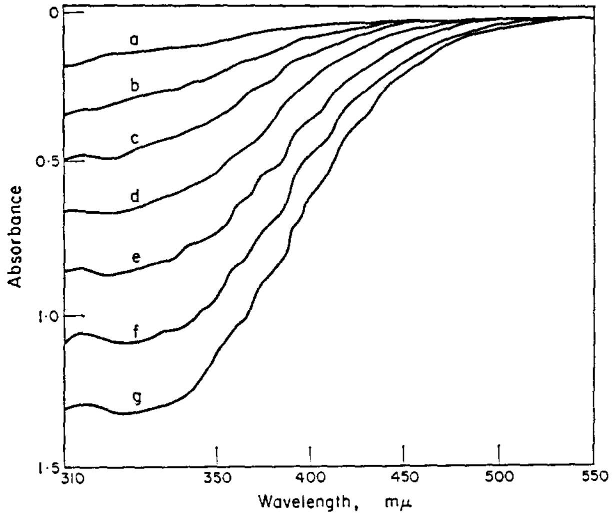


FIG. 6. Absorption spectra of PVC solution in DMF degraded under oxygen at 130° for (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, and (g) 70 min.

results for the various atmospheres is that the spectra obtained from degradations carried out *in vacuo* or under nitrogen contain a broad absorption band which has a maximum at 478 mμ whereas those performed in air or in oxygen have no such band. The absorbance in the last two cases decreases gradually with increase in the absorption wavelength.

The main difference between the spectra obtained for degradations *in vacuo* and in nitrogen are that the rate of increase in absorbance in the former is very much greater than in the latter, and that the broad absorption band at 478 mμ begins to develop very much earlier in the former system. The band can be observed after only 20 min of degradation *in vacuo* compared with 50 min for degradations under nitrogen. This latter difference could be explained if the PVC solution degraded under nitrogen contained some dissolved oxygen since the presence of the latter would tend to lower the absorbance at the longer wavelengths. To test this point, oxygen-free nitrogen was passed through the polymer solution for approximately 16 hr before the solution was degraded at 130°. The spectra thus obtained (given in Fig. 7) are of a type intermediate between those given in Fig. 3 and 4, and show that the absorption band at 478 mμ developed after a period of from 30 to 40 min of degradation. The rate of increase in absorbance is still however considerably lower than for degradations carried out *in vacuo*.

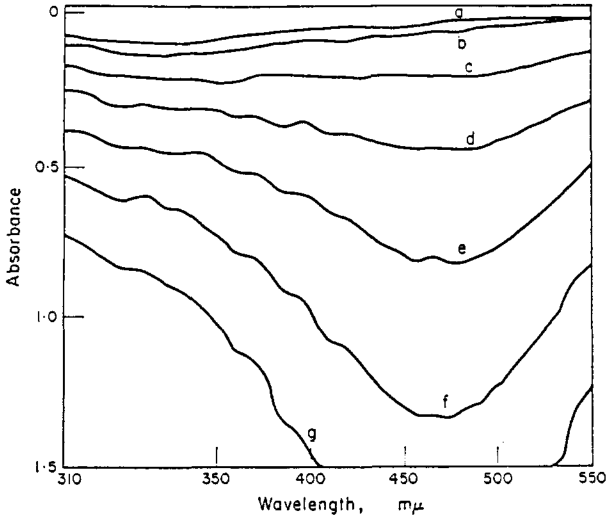


FIG. 7. Absorption spectra of a DMF solution of PVC flushed with oxygen-free nitrogen for 16 hr and subsequently degraded under nitrogen at 130° for (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, and (g) 70 min.

A more quantitative estimate of the differences between the spectra obtained for degradations under nitrogen and oxygen can be seen from Figs. 8 and 9 in which the changes in absorbance at 325, 386, 434, and 478 mμ are plotted against time. For degradations in a nitrogen atmosphere, the absorbance initially is greater at the shorter wavelengths but after about 30 min (point P in Fig. 8) it becomes greater the longer the wavelength. Similar results were obtained for degradations *in vacuo*, the main difference being that the change-over point P occurred earlier after only 10 min of degradation. In oxygen and in air, however, there is no change-over region, and the absorbance continues to be greater the lower the wavelength of absorption as can be seen in Fig. 9.

One of the chief differences between the absorbance against time plots obtained in this work and those found in earlier work$^{(1)}$ is that they are autocatalytic in character over the range studied, whereas with the solvents previously examined the absorbance frequently became nearly constant, i.e. independent of time and conversion after it had attained a value of about 1–1·5. This difference in behaviour may be partly due to

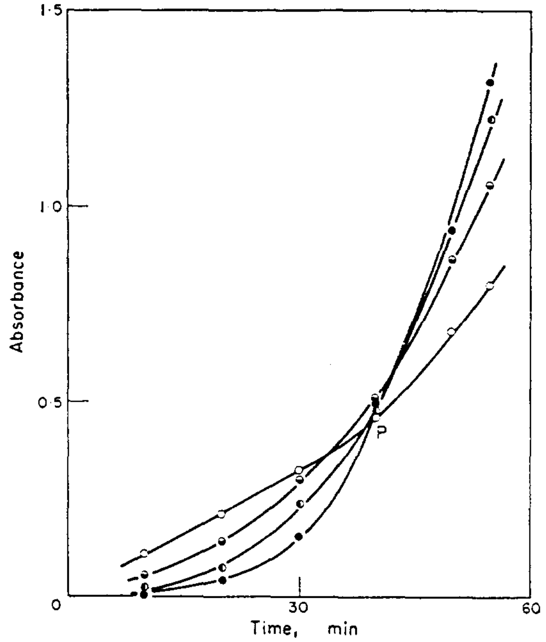


Fig. 8. Effect of time of degradation under nitrogen at 130° on the absorbance of a DMF solution of PVC at various wavelengths.

○ = 325; ◒ = 386; ◑ = 434; ● = 478 mμ.

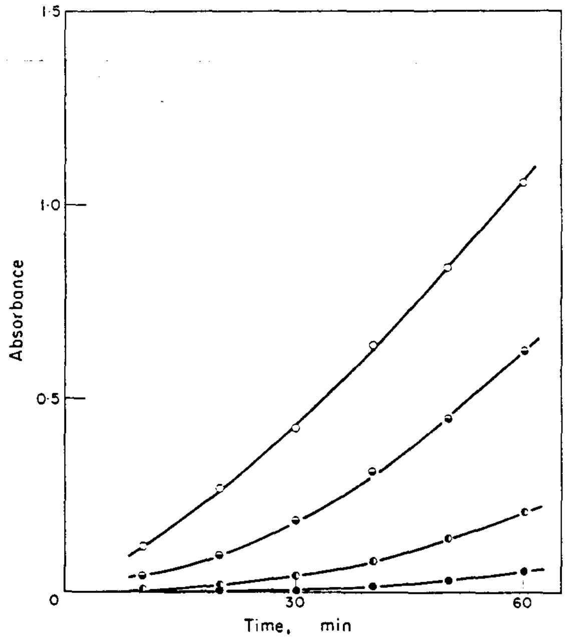


Fig. 9. Effect of time of degradation under oxygen at 130° on the absorbance of a DMF solution of PVC at various wavelengths.

○ = 325; ◒ = 386; ◑ = 434; ● = 478 mμ.

the autocatalytic nature of the degradation in DMF solution since dimethylamine hydrochloride formed during the degradation is a catalyst, and also because the wavelengths studied in this work are mainly longer than in the earlier work.

Using the Lewis and Calvin relationship(8) which relates the wavelength of the absorption band to the number of conjugated double bonds in the polyene sequence, it appears that degradations under nitrogen or *in vacuo* give rise to relatively long polyene sequences of around 13–16 conjugated double bonds (absorption wavelength 478 mμ) whereas most of the polyene structures obtained for degradations in oxygen or in air contain no more than about 4–5 conjugated double bonds. These shorter polyene structures might arise in two ways. Firstly oxygen might prevent the formation of the longer polyene structures by reacting in some way with the intermediate structures in the dehydrochlorination process. It may for example react with the hydrogen on the $>CH_2$ groups adjacent to the carbon–carbon double bonds, forming hydroperoxide groups which may react further and result in chain scission. Alternatively, the longer polyene sequences may be formed initially, but may be so readily oxidized at the temperature of degradation that their concentration in the system becomes negligible.

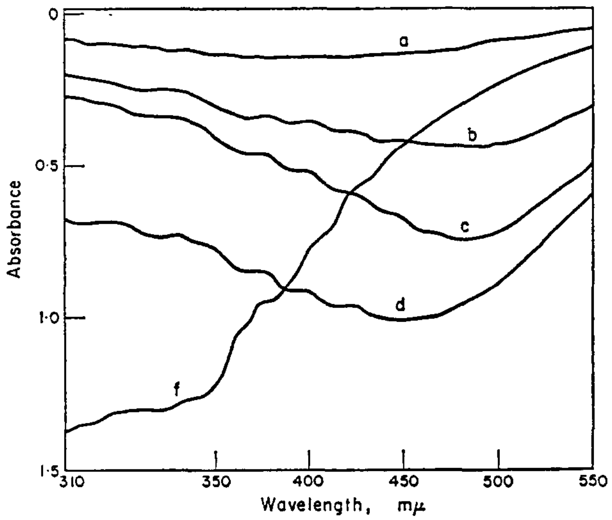


Fig. 10. Absorption spectra of a DMF solution of PVC degraded at 130° *in vacuo* for (a) 10, (b) 20, (c) 25 min, (c) being followed by degradation in an atmosphere of oxygen for (e) 10 and (f) 30 min.

That the latter process is possible is clearly demonstrated by the spectra in Fig. 10 which show the effect of introducing oxygen to a system which has been partly degraded *in vacuo*. Curves a, b, and c correspond to degradation *in vacuo* while curves d and f show the effect of subsequent degradation in an atmosphere of oxygen. It will be seen that the absorption band at 478 mμ formed *in vacuo* rapidly disappears after the introduction of oxygen, presumably due to the rapid oxidation of the polyene sequences. This change in absorbance pattern is very readily seen from Fig. 11 which shows the change in absorbance at 325, 386, 434, and 478 mμ with time of degradation. In the period from 10 to 25 min (i.e. while degradation *in vacuo* was taking place) the absorbance measurements were greater for the longer wavelengths. Oxygen was introduced after 25 min of degradation *in vacuo*, and after a further 15 min of degradation in oxygen the absorbances at the four wavelengths were equal. Further periods of degradation in oxygen resulted in a decrease in the absorbance at 478 and 434 mμ and an increase in the absorbance at 325 and to a lesser extent at 386 mμ.

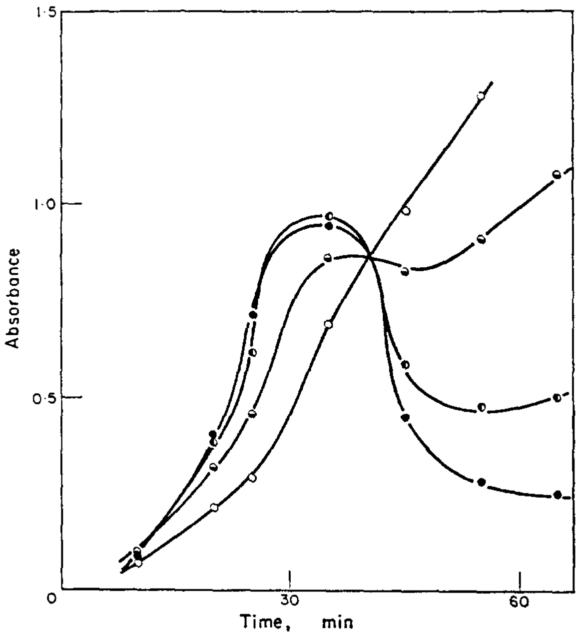


FIG. 11. Effect of time of degradation on the absorbance of a DMF solution of PVC degraded for 25 min *in vacuo* and subsequently for 40 min in oxygen.
○ = 325; ⊖ = 386; ◐ = 434; ● = 478 mμ.

The effect on the absorption spectra of degrading the polymer solution first in oxygen and then continuing the degradation *in vacuo* is rather less striking. The results for such an experiment are given in Fig. 12. Curves a, b, and c represent the absorption spectra obtained for 10-, 20-, and 30-min periods of degradation in an oxygen atmosphere, while curves d, e, and f are the spectra obtained for subsequent periods of degradation *in vacuo* of 10, 20, and 30 min respectively. Clearly the absorbance at longer wavelengths increases markedly following the removal of oxygen from the system, and the overall maximum absorbance tends to move from ~310 mμ to ~360 mμ. If the degradation had been carried out for a sufficiently long period, it may well have moved to ~478 mμ. However, it was not possible to follow the degradation for longer periods with our experimental arrangement.

Oxidation at 70° of degraded polymer

The oxidation of polyene structures would be expected to result in chain scission processes. Thus if polyene structures were formed somewhere in the middle region of polymer chains, their oxidation would result in an appreciable change in the weight

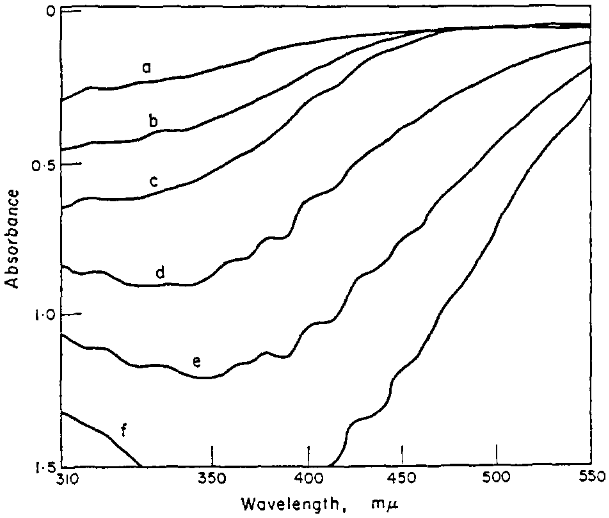


FIG. 12. Absorption spectra of a DMF solution of PVC degraded at 130° in oxygen for (a) 10, (b) 20, and (c) 30 min respectively, (c) being followed by degradation *in vacuo* for (d) 10, (e) 20 and (f) 30 min respectively.

average molecular weight of the polymer. If, however, the polyene structures were situated at the ends of the polymer molecules, their removal following oxidation would have little effect on the weight average molecular weight of the polymer.

Solutions of PVC in DMF were therefore degraded at 130° for 30 min *in vacuo*, and then oxygen was bubbled through the solution at 70° for varying periods of time. At this temperature further degradation is restricted but oxidation of the polyene structure still occurs fairly readily, as can be seen from the change in absorption spectrum shown by the dotted line in Fig. 3. Curve c is the absorption spectrum of the sample of degraded polymer before oxygen is bubbled through it, while the dotted line shows the final spectrum obtained after passing oxygen through the solution for 800 min. The intrinsic viscosity of the polymer, before degradation, after degradation and after oxidation for various periods is shown in Table 1. The slight decrease in the intrinsic viscosity from 0·92 to 0·87 $dl.g^{-1}$ resulting from the degradation *in*

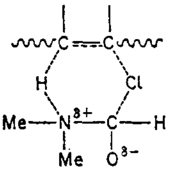
TABLE 1. CHANGES IN THE INTRINSIC VISCOSITY OF PVC WITH CONDITIONS OF DEGRADATION

Time of degradation *in vacuo* in DMF solution at 130° (min)	Time of subsequent oxygen treatment at 70° (min)	[η] value ($dl.g^{-1}$)
0	0	0·92
0	900	0·88
30	0	0·87
30	176	0·862
30	380	0·855
30	800	0·835

vacuo indicates that there is a small amount of random chain scission taking place during the degradation. The decrease in intrinsic viscosity following oxidation at 70° is also very small and not significantly different from that found when oxygen is passed through undegraded PVC solution at 70°. In the latter case a change in intrinsic viscosity from 0·92 to 0·88 dl.g^{-1} occurred when oxygen was passed through a PVC solution at 70° for 900 min. Since spectral changes following oxidation at 70° indicate that the polyene structure is being destroyed presumably by chain scission reactions following oxidation, it would appear that the majority of the polyene sequences are situated near the ends of the polymer chains.

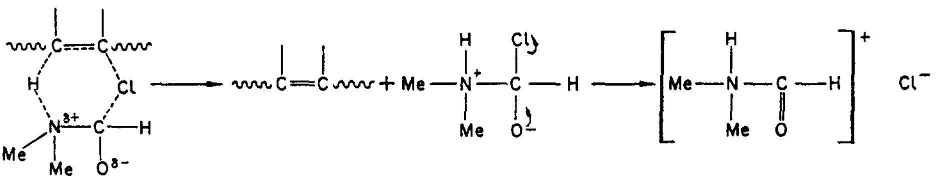
DISCUSSION

The rate of degradation of PVC in DMF is clearly very much greater than in tritoluylphosphate, benzophenone, ethyl benzoate, dioctylphthalate, benzyl alcohol, or dichloronaphthalene all of which were studied previously.(1) This difference may be due to an interaction between the solvent and the polymer. This view is supported by the fact that although the solubility parameters(9) for PVC and DMF are very different in value (9·6 and 12·1 respectively) and on this basis one might expect DMF to be a non-solvent for the polymer, DMF is in fact a reasonably good solvent for PVC. This association between solvent and polymer might involve the cyclic structure (I).



(I)

which is similar to the transition state suggested by Kornbloom(10) to explain the dehydrobromination of alkyl bromides in DMF. Such an intermediate would facilitate dehydrochlorination since it would not only lower the bond energies of the carbon–hydrogen and carbon–chlorine bonds, but would also cause the polymer–solvent associated regions of the molecule to be in a *cis*-conformation which would facilitate the elimination of hydrogen chloride. The latter may well be eliminated as dimethylformamide hydrochloride rather than as the free acid.



Furthermore, it has been demonstrated that at 130° dimethylformamide hydrochloride is converted into dimethylamine hydrochloride which is a catalyst(7) for the dehydrochlorination. Both these effects may contribute to the ease of degradation in DMF, but presumably the catalytic effect will be less important in the very early stages of degradation.

This difference in mechanism of degradation might also be responsible for the difference in the type of spectra obtained when degradation is carried out in DMF solution compared with other solvents previously studied.(1) When DMF is used as solvent, polyene structures consisting of around 13 conjugated double bonds appear to be formed in greatest concentration (absorption maximum at 478 mμ) although because each polyene structure gives rise to several absorption bands, overlapping occurs, and the overall absorption maximum observed does not necessarily correspond to the predominant band of the polyene present in the greatest concentration. However, the type of absorption spectra obtained does indicate that longer conjugated sequences occur when PVC is degraded in DMF solution than in the other solvents previously studied,(1) and that the distribution of polyene structures would fit in with a relatively rapid dehydrochlorination along the polymer chain following the start of degradation. This is in contrast to the relatively slow stepwise elimination of HCl indicated by degradation work in other solvents.(1) Solvent–polymer interaction as discussed above is probably responsible for this difference.

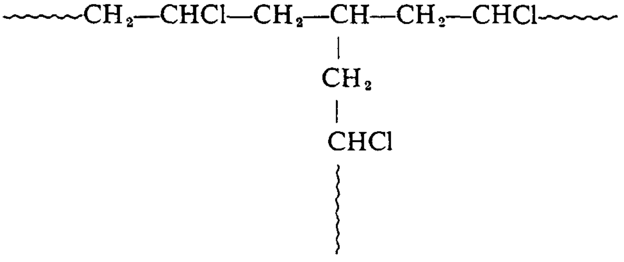
The much longer polyene sequences obtained when degradations are carried out in DMF compared with other solvents could also possibly be due to the difference in the temperature of degradation. There is some evidence(11) from degradations of PVC films at temperatures below 130° that very much longer conjugated polyene sequences are obtained at this temperature than at temperatures in the region of 170–200°. There is some indication that the least stable polymer molecules tend to degrade very slowly(11, 12) at temperatures around 100° or even lower, and that it is this limited fraction of the polymer which gives rise to the long polyene sequences in the degraded polymer.

The main difference observed when a solution of PVC in DMF is degraded *in vacuo*, in nitrogen, in air or in oxygen, is that in the last two cases (i.e. when oxygen is present) the colour of the solution after degradation is a lime green compared with a reddish brown in the former two cases. This difference in colour is clearly demonstrated by the difference in the type of spectra obtained in the presence and absence of oxygen. When oxygen is present, the absorbance is a maximum in the region 320–350 mμ but falls off rapidly with increase in wavelength being only about 20 per cent of its maximum value at a wavelength of 450 mμ. This fall-off in absorbance with increase in wavelength is very much more marked than that obtained previously for degradations in other solvents,(1) and is also different in that the sub-maxima expected in polyene systems containing 4–8 double bonds are not clearly resolved. It is quite possible that the spectra obtained from degradations in oxygen are not due to the presence of short polyene sequences but result from the presence of carbonyl groups in conjugation with one or more carbon–carbon double bonds.

It would appear from experiments in which degradation was first carried out in vacuum or nitrogen, and subsequently continued in oxygen that the oxidation process is significantly more rapid at 130° than the process leading to long conjugated polyene structures. In fact the oxidation reaction proceeds at a significant rate even at 70°, whereas the rate of polyene formation is too low to be measured at this temperature. Precisely what happens when degradation is carried out in oxygen is not known, but even if long chain polyenes are produced under such conditions they will be very rapidly removed by oxidation.

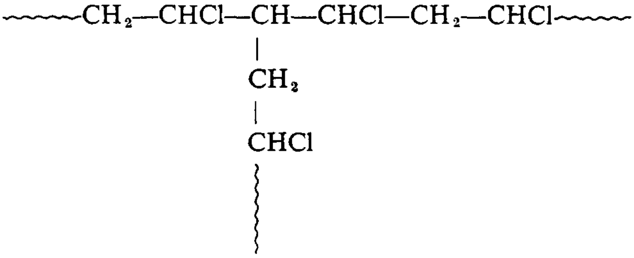
The relatively slight change in intrinsic viscosity observed when degraded polymer is oxidized at 70° indicates that either oxidation is occurring by addition of oxygen to the polyene structures without any accompanying chain scission, or alternatively that the polyene structures are situated near the ends of the polymer chains so that there is little change in weight average molecular weight even after chain scission has occurred. The latter view is thought to be the more likely explanation.

One difficulty encountered in PVC degradation in general is to explain why the polyene structures formed during degradation do not normally contain on average more than about 16 conjugated double bond sequences. If oxygen is present, or if free radicals are involved in the degradation processes, it is possible that these sequences are limited in length by their reaction with such species. However, even in the present work when oxygen is excluded, and when the reaction is carried out at low temperatures and is unlikely to be a free radical process, the lengths of the conjugated polyene sequences are still on average not greater than about 16 double bonds. To explain this, it is necessary to put forward some structural abnormality which would prevent the continuation of the conjugated sequence. In an earlier paper(1) it was suggested that pendant —CH_2Cl groups might be formed during polymerization in the same way that pendant —CH_3 groups are produced in the polymerization of ethylene. Such groups would interrupt the alternation of H and Cl atoms attached to carbon atoms of the main backbone, and hence interrupt the conjugation when HCl is eliminated from the polymer. Alternative structures which would interrupt the above-mentioned sequence could be formed by chain transfer reactions with polymer during polymerization. These reactions may be either inter-molecular reactions with 'dead' polymer molecules, or intramolecular ('back-biting') reactions resulting in branch points along the polymer chain. The structure of the polymer at these branch points will probably be as shown in either II, III, or IV. Structure II arises from a chain transfer reaction involving the abstraction of a chlorine atom from a >CHCl group in the polymer molecule. Such a reaction seems to be quite likely to occur from polarity considerations, although perhaps a little less likely than hydrogen abstraction on steric grounds. If such reactions do occur then they lead to a branch point with no chlorine atoms attached to any of the adjacent carbon atoms. Clearly such a structure would be an effective stop to a polyene sequence in the degraded polymer.



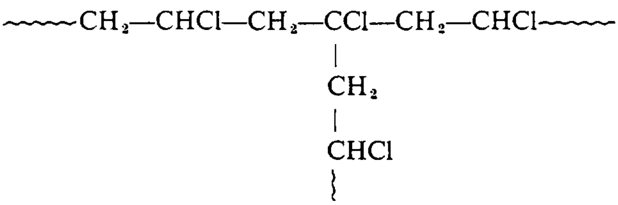
$$\begin{array}{c} \sim\sim CH_2{-}CHCl{-}CH_2{-}CH{-}CH_2{-}CHCl\sim\sim \\ | \\ CH_2 \\ | \\ CHCl \\ \wr \end{array}$$

(II)



$$\begin{array}{c} \sim\sim CH_2{-}CHCl{-}CH{-}CHCl{-}CH_2{-}CHCl\sim\sim \\ | \\ CH_2 \\ | \\ CHCl \\ \wr \end{array}$$

(III)



$$\sim\!\sim\mathrm{CH_2{-}CHCl{-}CH_2{-}\underset{\substack{|\\ CH_2\\ |\\ CHCl\\ \wr}}{CCl}{-}CH_2{-}CHCl}\sim\!\sim \tag{IV}$$

Structure (III) arises from a chain transfer reaction in which a hydrogen atom is abstracted from one of the $>CH_2$ groups in the polymer chain. Such a structure would allow dehydrochlorination to continue in one direction beyond the branch point, but not in the direction of the polymer growth which occurred following the chain transfer reaction. If chain transfer were to occur mainly by 'back-biting' with 5- or 6-membered ring transition states, then propagation of the conjugation through the branch point would normally only continue for two or three double bonds, i.e. to the end of the short branched chain formed in the transfer reaction.

Hydrogen abstraction from a $>$CHCl group would lead to structure (IV), which would in no way prevent propagation of the polyene structure throughout the molecule.

It will be apparent from the above discussion that branch points in the polymer chain could offer an explanation for the relatively short lengths of the polyene sequences obtained on degrading the polymer. There is a fair amount of evidence in the literature both from kinetic(13) and from structural(14–16) measurements that branching does occur in PVC. Unfortunately, this evidence is not sufficiently quantitative to enable a correlation to be made between the number of branch points and the lengths of the polyene sequences obtained when the polymer is degraded.

Acknowledgements—The authors wish to thank the Science Research Council for a grant for equipment, the Cross Trust for a maintenance grant to G.F.G., and Professor P. D. Ritchie for his continued interest in the work.

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Résumé—On a étudié la dégradation thermique du poly(chlorure de vinyle) (PCV) en solution à 12·5g/l. dans le diméthylformamide (DMF) en suivant les modifications des spectres d'absortion u.v. et visible des solutions. Par dégradation sous vide et sous azote on obtient des spectres semblables avec des bandes d'absorption étalées, possédant des maximums à 478 mμ tandis qu'à l'air, ou en atmosphère d'oxygène, les spectres obtenus possèdent un maximum d'absorption à 320–340 mμ et l'absorption diminue rapidement aux longueurs d'onde plus grandes. On observe une modification très nette de la forme du spectre lorsqu'on introduit de l'oxygène dans une solution qui avait été partiellement dégradée sous vide, si au contraire on opère en sens inverse on n'observe pas d'effet aussi prononcé. Aucun dégagement d'acide chlorhydrique ne se produit au cours de la dégradation; ce gaz se dissout dans le DMF pour former un complexe qui se décompose ensuite en donnant du chlorhydrate de diméthylamine. Ce dernier composé catalyse la dégradation. Des mesures de viscosité ont été effectuées sur des solutions dégradées sous vide et soumises à un barbotage d'oxygène à 70°. On a pu en déduire que la dégradation se produit principalement en bout de chaîne.

Sommario—E' stata studiata la degradazione a 130° del polivinilcloruro (PVC) in dimetilformamide (DMF) alla concentrazione di 12·5 g/l. seguendo le variazioni degli spettri di assorbimento nell'u.v. e nel visibile delle soluzioni. Per degradazioni sotto vuoto e in atmosfera di azoto si hanno spettri simili con una larga banda di assorbimento con un massimo a 478 mμ mentre per degradazione all'aria o in atmosfera di ossigeno si ottengono spettri in cui l'assorbanza presenta un massimo a 320–340 mμ e diminuisce rapidamente con l'aumentare della lunghezza d'onda. Una netta variazione dello spettro si osserva nel caso in cui si manda ossigeno in una soluzione già parzialmente degradata sotto vuoto:tale effetto non è così notevole se si inverte il processo. Durante la degradazione non si sviluppa acido cloridrico gassoso: esso infatti si scioglie in DMF formando un complesso che per decomposizione dà cloridrato di dimetilammina che funziona da catalizzatore per la degradazione. Le misure di viscosità su soluzioni degradate sottovuoto nelle quali è stato fatto passare O_2 per tempi diversi a 70°, indicano che la degradazione avviene principalmente agli estremi della catena polimerica.

Zusammenfassung—Der thermische Abbau von Polyvinylchlorid (PCV) wurde bei 130° und einer Konzentration von 12·5 g/l. in Dimethylformamid (DMF) untersucht und die Veränderungen in den Lösungen an Hand der U.V.- und sichtbaren Absorptionsspektren verfolgt. Abbauversuche im Vakuum und unter Stickstoff gaben ähnliche Spektren mit breiten Absorptionsbanden, deren Maxima bei 478 mμ lagen, während bei Abbauversuchen an Luft oder in Sauerstoffatmosphäre Spektren mit einer maximalen Absorption um 320–340 mμ und einem raschen Abfall mit zunehmender Wellenlänge erhalten wurden. Eine deutliche Veränderung im spektralen Verhalten wurde beobachtet, wenn zu einer Lösung, die im Vakuum teilweise abgebaut war, Sauerstoff zugegeben wurde; wenn der Prozess umgekehrt durchgeführt wurde, war der Effekt weniger ausgeprägt. Während des Abbaus wurde kein Chlorwasserstoffgas freigesetzt; es löste sich in DMF unter Bildung eines Komplexes auf, der sich unter Bildung von Dimethylamin-hydrochlorid zersetzte, letztere erwies sich als Katalysator für den Abbau. Viskositätsmessungen an im Vakuum angebauten Lösungen, in die für unterschiedliche Zeiten bei 70° Sauerstoff eingeleitet worden war, ergaben Hinweise darauf, daß der Abbau hauptsächlich an den Enden der Polymerketten erfolgt.