

Photochemical Reactions of Polyene Sequences Produced during the Degradation of Poly(vinyl Chloride)

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Synopsis

Photosensitized reactions of tetrahydrofuran (THF) and dichloromethane (DCM) solutions of polyene sequences introduced into poly(vinyl chloride) molecules by chemical degradation have been investigated. The distribution of polyenes produced following further thermal degradation in DCM were shifted toward longer sequences than were observed for the same reaction in THF. Benzophenone-sensitized bleaching of the polyene absorption in aerated THF solutions was characterized by induction periods, but the presence of oxygen had little effect on the same reaction in DCM. The bleaching process seems to involve reaction of the polyenes with the tetrahydrofuranyl radical formed by abstraction of the α -hydrogen from THF by triplet benzophenone. No induction periods were observed for benzoin-sensitized reactions, but the rate of reaction was faster in DCM than in THF. The differences are discussed in terms of the difference in reactivity of the alkyl and alkoxy radicals.

INTRODUCTION

Work directed toward obtaining a more complete understanding of the reasons for the thermal and photochemical instability of poly(vinyl chloride) (PVC) continues unabated. Some slow progress has been made in recent years, but several aspects of the problem remain of which an understanding is far from complete.

It has long been appreciated that the inevitable heterogeneity of polymer samples prepared and purified by a variety of different procedures has been one of the reasons for the apparently contradictory conclusions which have been drawn from the same experiments carried out by different groups of workers. The extent of this particular problem has been recently emphasized further by the development of improved methods for characterizing the various structural features which occur to different extents in the polymer depending on the conditions of the polymerization process. Several such structural variations, which were once thought to be important features of PVC structure, are now thought to be unimportant as sources of instability or to be present at much lower levels than was previously supposed.

A closely related area on which recent work has indicated that more emphasis should be placed is that of making clear just how the rate and extent of degradation should be defined. The three most common methods used are (1) measurement of the rate of HCl evolution, (2) the use of infrared spectroscopy to measure concentrations of oxidation products such as carbonyl or peroxide groups, and (3) the use of ultraviolet and visible spectroscopy to determine the color of PVC, which has been equated with the well-documented polyene se-

quences that are the products of the primary dehydrochlorination process. This latter method of measuring the extent of the degradation process is of particular importance since most of the effort to stabilize PVC has been directed toward preventing thermally or photochemically induced discoloration of the polymer from taking place either during the processing stage or during later outdoor applications. In this context, it is necessary to distinguish between factors that influence the color stability by bringing about changes in the rate of the basic dehydrochlorination reaction and those that allow it to continue unchanged but conceal one of its undesirable effects by inhibiting the formation of color. A closely related aspect concerns the recently discovered toxicity problem associated with vinyl chloride monomer (VCM) and the very low levels of exposure to it which have been set. This emphasizes the need to establish whether VCM is a degradation product, as has been suggested, or whether changes that could allow the escape of residual VCM occur in the polymer during degradation.

In this article we describe some experiments which we have carried out as part of a continuing program to understand more about the nature of the products that are responsible for the color of degraded PVC. They are concerned with the reactions of chemically degraded PVC in various solvents and the relationship between the absorptions concerned and those of thermally degraded PVC.

EXPERIMENTAL

Poly(vinyl chloride) (Breon M110/50), a gift from B.P. Chemicals (International) Ltd., was chemically degraded using minor modifications of the method described by Shindo.¹

Tetrahydrofuran (BDH) was refluxed for 24 hr over calcium hydride, then freshly distilled under pure nitrogen immediately before use.

Dichloromethane (BDH) was distilled once before use.

Other reagents used were of the highest quality available and were used without further purification.

Irradiation: Solutions were irradiated with light from an Osram ME/D medium-pressure mercury lamp passed through a Balzer metal interference filter with maximum (40%) transmission at 340 nm.

RESULTS

Extraction of Chemically Degraded PVC

Samples (0.2 g) of chemically degraded PVC were stirred for 1 hr in cooled (2–5°C) dichloromethane (DCM) (100 ml) through which nitrogen was bubbled. The solution was allowed to warm to room temperature and was then filtered; next, the absorption spectrum was measured (Fig. 1). A diluted (DCM) solution was placed in the thermostatted cell compartment of a spectrophotometer and the spectrum was measured at 10- to 15-min intervals. The results showing a typical series of spectra in DCM are given in Figure 2. As the intensity of the absorption increased, the initial absorbance, which was typical of a sequence of polyenes of different lengths, was gradually replaced by a broad absorption centered at about 462 nm in the early stages and gradually changing to shorter wavelengths (~440 nm) as the reaction progressed. During this time, there was

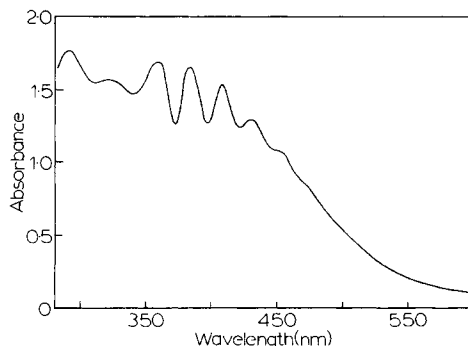


Fig. 1. Absorption spectrum of the solution obtained by extracting chemically degraded PVC (0.15 g) with dichloromethane (DCM) (100 ml) for 1 hr at 0–5°C under nitrogen.

very little change in absorbance in the ultraviolet region between 325 and 225 nm. The experiment was repeated at various temperatures in the range 35–50°C and showed a temperature dependence which corresponded to an apparent energy of activation of $85.5 \pm 2.0 \text{ kJ mole}^{-1}$.

When the same experiment was repeated using THF or cyclohexanone as solvent, the increase in absorbance which occurred was different from the DCM case. In both solvents, the absorption at all wavelengths increased at about the same rate with no indication of the development of the broad maximum at 440 nm. Figure 3 shows the data for cyclohexanone solvent which is of the same form as that in THF. Good first-order kinetic plots were obtained for the reaction and gave a value of $5.2 \times 10^{-3} \text{ min}^{-1}$ at 45°C for the pseudo-first-order rate constant (k^1) and corresponded to an activation energy of $43.2 \text{ kJ mole}^{-1}$.

Photolysis of Polyene Sequences

Direct Reaction

Irradiation (340 nm) of THF solutions of the polyene sequences produced an initial fairly rapid change in absorbance over the whole wavelength range which reduced the absorbances by about 25% and was followed by a slower reaction extending over a longer period. Curve a, Figure 4 shows the decrease in ab-

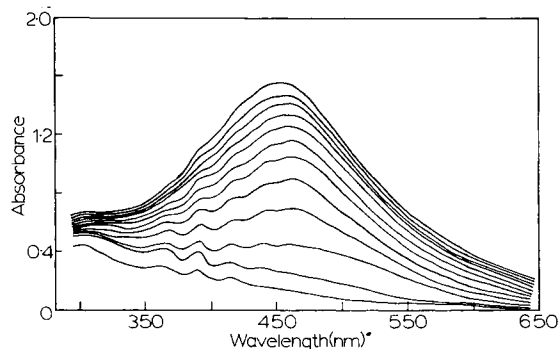


Fig. 2. Increase with time of the absorption of the DCM solution of chemically degraded PVC described in Fig. 1 (diluted $\times 6$) at 35°C. Increasing absorptions correspond to 20-min intervals from 0 to 220 min.

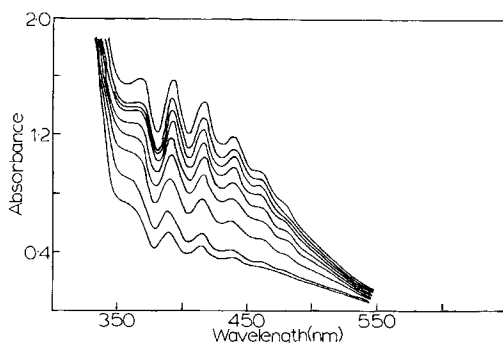


Fig. 3. Increase with time of the absorption of a cyclohexanone solution of chemically degraded PVC extracted as for Fig. 1, then thermostatted at 35°C. Increasing absorptions correspond to 0, 30, 75, 105, 135, 165, 195, 225, and 300 min.

sorbance at 406 nm, a wavelength where absorbances would be due only to polyenes and be unaffected when sensitizers were added.

Reactions Sensitized by Benzophenone

The addition of benzophenone to solutions of polyenes in THF followed by irradiation at 340 nm caused a rapid reaction of the polyenes (Fig. 5) after an initial induction period which depended on the benzophenone concentration (curves b–d, Fig. 4). A degassed solution of polyenes and benzophenone in THF reacted even faster (curve c, Fig. 4) with only a suggestion of an induction period. The rate of reaction was 1.9 times faster than that of the same but aerated solution. A comparison of the sum of the absorbances of separate solutions of polyenes and of benzophenone with mixtures of the two reagents at the same concentrations gave no firm indication of any ground-state interaction.

When the same experiments were carried out using DCM solvent immediately after extraction of the polyenes and before the absorbance with a maximum at 440 nm had time to develop, the overall pattern of absorbance changes was the same but the time scale differed. In the presence of oxygen, the decrease began immediately and continued with a slight acceleration (curve a, Fig. 6). Outgassed solutions behaved in much the same way, but the maximum rate attained was about 50% faster (curve b, Fig. 6). In both of the solvents studied, the reaction

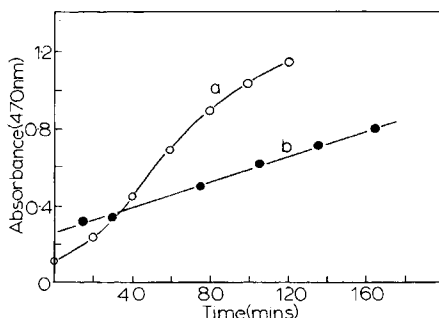


Fig. 4. Changes in absorbance with time of irradiation (340 nm) of THF solutions of chemically degraded PVC containing benzophenone. Benzophenone concentrations (a) 0; (b) $5 \times 10^{-3}M$; (c) $10^{-2}M$; (d) $5 \times 10^{-2}M$; (e) $5 \times 10^{-2}M$ (degassed).

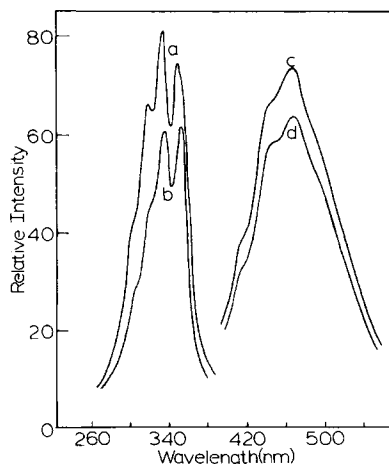


Fig. 5. Changes in absorption spectrum with time of irradiation (340 nm) for a THF solution of chemically degraded PVC containing benzophenone ($5 \times 10^{-2}M$). Decreasing absorptions correspond to irradiation at 0, 60, 120, 150, 180, 210, 240, 270, 300, and 330 sec.

was quenched by the addition of naphthalene to the system. Experiments carried out in DCM after the absorbance at 440 nm had been allowed to develop gave essentially the same results.

Reactions Sensitized by Benzoin

Reactions of THF or DCM solutions of the polyenes sensitized by benzoin ($5 \times 10^{-2}M$) underwent changes in absorbance over the whole wavelength range which were similar to those described for the benzophenone-sensitized reaction. Figure 7 shows that the rate of reaction was greater in DCM solvent than in THF. No induction periods were observed in the benzoin-sensitized systems, nor was there any acceleration in rate. Addition of naphthalene to the solutions produced no quenching of the reaction.

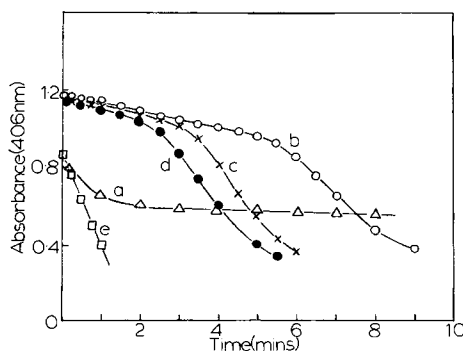


Fig. 6. Changes in absorbance (406 nm) with time of irradiation (340 nm) for (a) aerated and (b) degassed DCM solutions of chemically degraded PVC containing benzophenone ($5 \times 10^{-2}M$).

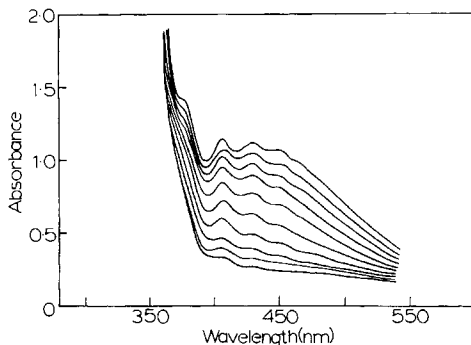


Fig. 7. Changes in absorbance (406 nm) with time of irradiation (340 nm) for (a) degassed THF solutions and (b) degassed DCM solutions of chemically degraded PVC containing benzoin ($5 \times 10^{-2}M$).

Reactions Sensitized by Azoisobutyronitrile (AIBN)

Reactions of THF or DCM solutions of polyenes sensitized by AIBN followed the same pattern as those sensitized by benzoin except that the difference between the two solvents was even more marked. The rate of photolysis was about 40 times faster in DCM than in THF.

DISCUSSION

The changes in absorption that take place when chemically degraded PVC (CPVC) is thermostated at temperatures in the range 20–50°C are markedly dependent on the solvent. In THF the polyene distribution that is formed is “normal” in the sense that it resembles that observed by many workers when PVC is thermally degraded at higher temperatures.^{2–5} The absorption of DCM solutions, however, is different and corresponds to a distribution that contains a preponderance of long ($n = 11–13$) polyenes. This latter type of distribution has been observed previously by other authors when PVC was degraded at 130°C in dimethylformamide⁶ (DMF) and in films cast from the same solvent.⁷ In both cases a specific polymer solvent interaction was suggested to explain the catalytic effect of DMF, although in the case of the reaction in solution, the high solubility of HCl, together with the decomposition of DMF hydrochloride and formation of the catalytic dimethylamine, was a complicating factor. No evidence of any difference in the ground-state interaction among our CPVC and the two solvents studied was apparent from an examination of the absorption and fluorescence spectra. The work of Palma and Carenza⁸ has shown that it is the removal of HCl from the degrading polymer or its retention which determines the kind of polyene distribution that is produced and that a constant length distribution is observed as long as HCl is removed. Their value for the activation energy (92 kJ mole⁻¹) for $n = 11$ polyenes is in good agreement with our value in DCM where the most abundant polyene length is also about 11–12 polyenes. Our experiments in DCM produce almost the same distribution as those mentioned in DMF,^{6,7} and although a cyclic transition state between the degrading PVC chain and a molecule of DCM could be envisaged which is analogous to that suggested⁶ in the DMF case, it seems likely that the differences can be explained more simply by a different extent of catalysis by HCl. Figure 8 shows a more rapid increase

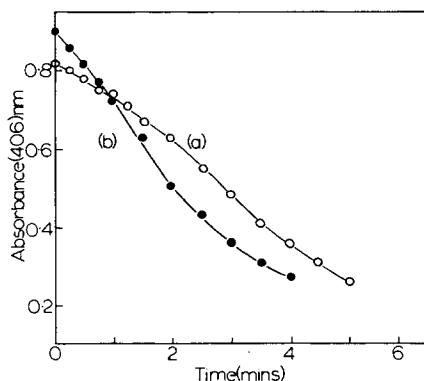
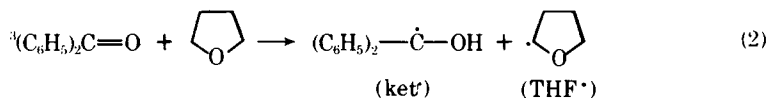
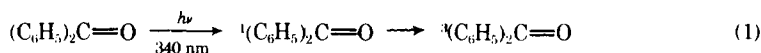


Fig. 8. Changes in absorbance (470 nm) with time for (a) the DCM solution of Fig. 2 and (b) the THF solution of Fig. 3.

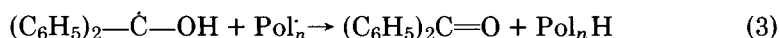
in absorbance at 470 nm (corresponding to an $n = 11$ polyene) for DCM than for THF solutions, whereas similar plots of the absorbance at 390 nm ($n = 7$ polyene) showed the same rate of increase.

THF Solutions of CPVC Containing Benzophenone

The benzophenone photosensitized bleaching of the polyene absorption in THF probably begins with the formation of the ketyl radical [eqs. (1) and (2)] since the rate constant for hydrogen abstraction from THF ($3 \pm 1 \times 10^6 M^{-1} \text{sec}^{-1}$) (ref. 9) is almost the same as for abstraction from propanol-2 ($1.3 \times 10^6 M^{-1} \text{sec}^{-1}$) (ref. 10):



The abstraction of the α -hydrogen atom is also well established in the radical catalyzed thermal oxidation of aliphatic and cyclic ethers.¹¹ Both of the radicals produced are potentially able to react with the polyenes, but the evidence seems to implicate THF \cdot as the most effective since Hutchinson¹² has shown that ket \cdot radicals terminate the free radical polymerization of methyl methacrylate, possibly by hydrogen transfer to growing polymer (Pol) $_n$:

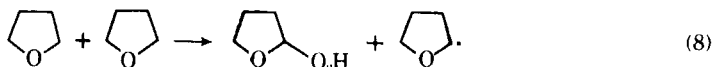
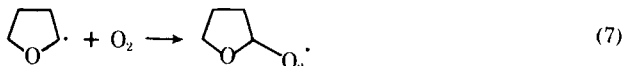
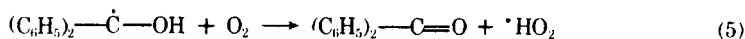


while significant initiation takes place only above 40°C.¹³ THF \cdot radicals on the other hand initiate the polymerization thus¹⁴:

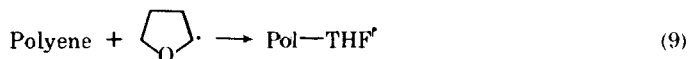


The induction period that is observed in the presence of oxygen, the length of which depends on the benzophenone concentration, can also be explained on this basis. As well as being an efficient quencher for triplet benzophenone,

oxygen can react with both radical species in the following way:



The induction periods occur because dissolved oxygen is consumed by reactions (5) and (7) and THF \cdot is able to react with the polyenes only when the concentration has been reduced sufficiently to make reaction (7) unimportant. The concentrations of benzophenone used are such that the absorption of light and therefore the stationary concentration of ket \cdot radicals are of the right order. Bleaching of polyenes absorption by reaction with THF \cdot may be written as

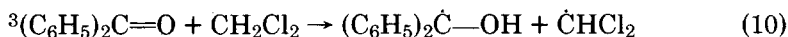


Daniels¹⁵ has investigated the reaction of THF α -hydroperoxide with polyenes, but the very fast rate in the absence of oxygen indicates that this process is unimportant in our system.

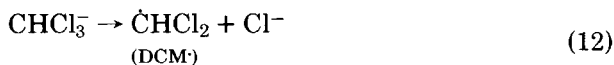
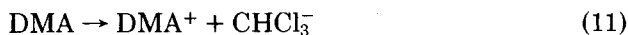
The suggestion that THF \cdot radicals add to the polyenes receives support from the several accounts of free radical alkylation of aliphatic and cyclic ethers¹⁶ and in particular from the ketone sensitized formation of 1:1 adducts of THF with olefins or α,β unsaturated esters¹⁷. The decyclization of the THF \cdot radicals has also been shown to be important¹⁸ but at higher temperatures than those used in our experiments.

DCM Solutions of CPVC Containing Benzophenone

Reactions in DCM photosensitized by benzophenone also involves hydrogen abstraction from the solvent to form a pair of radicals:



Some of the reactions of DCM \cdot following production of the radical during the photolysis of dimethylaniline (DMA) in chloroform have been documented by Latowski¹⁹



The differences between THF and DCM in our experiments lie mainly in the effects of oxygen and may be explained by the different reactivity toward oxygen by the two radicals THF \cdot and DCM \cdot or the relative stabilities of THFOO \cdot and DCMOO \cdot . If DCM \cdot reacts more rapidly with the polyenes than with oxygen, this accounts for the small effect which oxygen has on the rate. The difference in reactivity of alkyl and alkoxy radicals is also indicated by the ability of benzo-

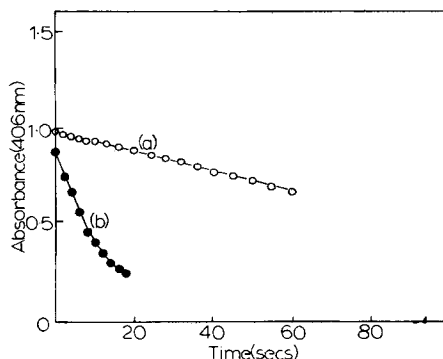
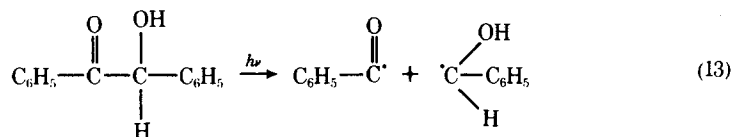


Fig. 9. Fluorescence excitation (a) and (b) ($\lambda_{\text{emission}} = 450 \text{ nm}$) and emission (c) and (d) ($\lambda_{\text{excitation}} = 340 \text{ nm}$) spectra of THF (a) and (c) and DCM (b) and (d) solutions of chemically degraded PVC.

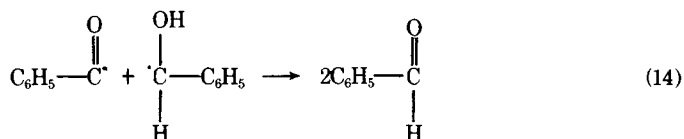
phenone solutions in toluene, but the inability of benzophenone solutions in THF, to initiate the polymerization of vinyl acetate (VA). Further evidence for the inability of α -alkoxy radicals to add to VA is seen in the failure of that monomer to copolymerize with alkyl vinyl ethers by a free radical mechanism.

THF and DCM Solutions Containing Benzoin

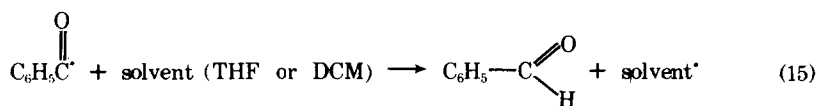
The mechanism of the sensitizing action of benzoin is different from that of benzophenone and involves an α -cleavage with the formation of a radical pair:



The quantum yield of formation of benzaldehyde, the major product following steady-state irradiation in benzene solution, is 0.41 (ref. 20), and its formation involves transfer of the hydroxyl hydrogen from the hydroxybenzyl radical to the benzoyl radical²¹:



The more minor products are benzil and benzpinacol, and the rate constants for their formation have been measured by Kuhlmann.²² Addition to dienes or styrene to the system reduces the yield of benzil and benzaldehyde but not that of pinacol, and it seems therefore that the benzoyl radical is the most reactive. Our results in THF and DCM can easily be interpreted by considering the greater hydrogen-donating ability of both these solvents relative to benzene. The more reactive benzoyl radical can be reduced as shown:



and the results in degassed THF and DCM explained as before by the relative reactivity of THF[•] and DCM[•].

THF and DCM Solutions Containing AIBN

Only preliminary experiments were carried out using this sensitizer, but the fact that the reaction is 40 times faster in DCM than in THF suggests that the same kind of arguments apply as in the benzoin case.

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