

Catalytic Effect of Hydrogen Chloride on the Degradation of Poly(Vinyl chloride)

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Synopsis

The distribution of polyenes which results from the chemical dehydrochlorination of poly(vinyl chloride) has been studied in dichloromethane (DCM) and tetrahydrofuran (THF) solvents. A higher percentage of longer polyenes is formed in DCM than in THF. On the addition of trifluoroacetic acid to DCM solutions of the polyenes, new species are formed with strong absorptions in the region 500–800 nm. The absorptions are probably due to polyenylic ions formed by protonation of the polyenes, and the interrelated changes in their intensities can be explained by the migration of short polyene sequences along the polymer chain with the formation of longer sequences. The species are extremely photosensitive and are bleached in a few seconds with light from a medium-pressure mercury lamp. The relevance of these experiments to the effect of HCl on the polyene distribution and on the rate of photocrosslinking is discussed.

INTRODUCTION

The catalytic role of hydrogen chloride (HCl) in the degradation of poly(vinyl chloride) (PVC) has for many years been a matter of considerable importance to technologists concerned with the commercial fabrication of the polymer because it has a direct relevance to the choice of stabilizers used to minimize the effects of the thermal degradation which takes place during the processing stage. As HCl is a primary degradation product, its autocatalytic effect on the subsequent reaction has long been suggested. Although the failure of some workers to find such an effect led to some uncertainty for a while,^{1,2} there is now overwhelming evidence that it does occur both in the presence and absence of oxygen.^{3–5} It has proved difficult to design and conduct experiments that would show conclusively which of the mechanistic processes (i.e. initiation, propagation, or termination) is most affected by HCl, but some recent work by Sorvik has shown that in atmospheres containing 10% HCl, the rate of propagation is increased,⁵ which is in agreement with the conclusions drawn by Minsker.⁴ In atmospheres containing higher proportions of HCl, the rate of initiation also appears to be affected possibly by the increased rate of formation of a cyclic transition state which catalyzes the random elimination of HCl.

Braun³ has made a spectrophotometric study of the polyene sequences formed in the thermal degradation of PVC powder and has concluded that the distribution of polyene sequence lengths shifts to shorter sequences with increasing temperature as well as with increasing time of degradation but that the effects are opposite for PVC films. In a similar study of thermal degradation at 190°C in a nitrogen atmosphere containing 10% HCl, Sorvik⁵ noted a marked shift of average sequence lengths to higher values with increasing conversion but concluded that termination owing to crosslinking is unaffected by HCl except insofar

as it is related to the increase in the dehydrochlorination rate. Marks,⁶ on the other hand, showed that the amount of insoluble material, and therefore presumably the amount of crosslinking, was related to the amount of HCl present.

Some authors^{7,8} have concluded that the presence of some degree of unsaturation is a prerequisite for HCl catalysis so that the details of the mechanism, the polyene sequence distribution, and the extent of crosslinking are interrelated. We now show that the situation may be even further complicated by the occurrence of photo and dark reactions of carbonium ions formed by protonation of the polyenes.

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, Read, and Stein.⁹

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

Dichloromethane (BDH) was distilled once before use.

Trifluoroacetic acid (BDH), reagent grade, was used without further purification.

Irradiation: Solutions were irradiated with the full visible spectrum of light from an Osram ME/D medium pressure mercury lamp.

RESULTS

PVC (Breon M100/50) was degraded chemically by the method described by Shindo.⁹ After thorough washing with water and drying, samples, 0.1 g, were extracted at 0–5°C with dichloromethane (DCM) or tetrahydrofuran (THF). A sample of the resulting solution was placed in the cell compartment of a spectrophotometer, and the absorption was measured at various time intervals. Figures 1 (in DCM) and 2 (in THF) show that the course of the reaction was different in the two solvents. In the case of THF the polyene distribution was similar to that found by several workers^{2,10} in thermally or photochemically

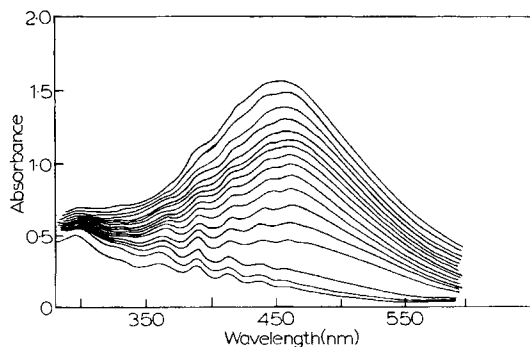


Fig. 1. Changes in the absorption spectra at 35°C of DCM solutions of chemically degraded PVC with time. Increasing absorbances correspond to 0, 10, 20, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 150, 170, 200, and 230 min.

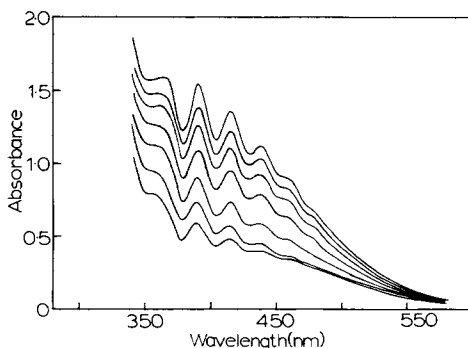


Fig. 2. Changes in the absorption spectra at 32°C of THF solutions of chemically degraded PVC with time. Increasing absorbances correspond to 0, 75, 120, 190, 240, 285, and 370 min.

degraded samples of PVC. In DCM solvent, however, the distribution was shifted in the direction of longer polyenes and resembled that found by Bengough and Grant¹¹ for PVC degraded at 150°C in dimethylformamide (DMF) and by Smirnov and Grachev¹² for PVC films cast from the same solvent where a large proportion of the polyene lengths are in the region $n = 11-13$. In both cases, a specific polymer-solvent interaction was thought to be the reason for the increased ease of dehydrochlorination which resulted in the longer polyene sequences. Palma and Carenza¹³ have shown that both kinds of distribution can be obtained depending on whether the HCl evolved was rigorously removed or allowed to remain. The effect of adding small amounts of other solvents to the solution formed by extraction of the degraded PVC with DCM was investigated. The relative rate of growth of the absorbance at 450 nm was increased by CBr_4 and decreased by CCl_4 , with CH_3CN , cyclohexanone, and THF having smaller effects (Fig. 3).

When DCM solutions of the polyenes which had been prepared as described previously were added to DCM solutions of trifluoroacetic acid (TFA), new species were formed which had strong absorptions in the region 500-850 nm. Figure 4 shows some typical spectra for such a solution (a) immediately after

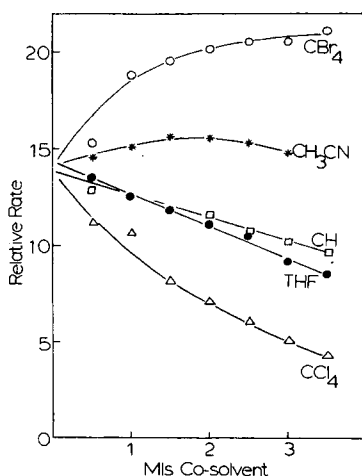


Fig. 3. Effect of added cosolvents on the relative rate of increase of the absorbance at 450 nm for DCM solutions of chemically degraded PVC. Total volume in each case was 6 ml.

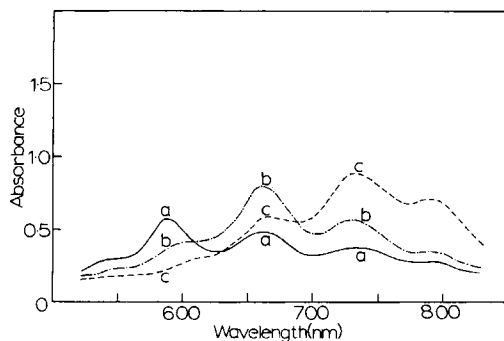


Fig. 4. Absorption spectra of DCM solutions of chemically degraded PVC containing TFA (0.1M) (a) after mixing, (b) after 20 min, and (c) after 200 min.

mixing, (b) after a further 20 min, and (c) after 200 min. In spectrum (a), clearly defined maxima are visible at 590, 660, 730, and 790 nm, the intensities of which change with time in a way that indicates that they are interrelated (Fig. 5). As A_{590} decreases, A_{660} increases until it in turn begins to decrease and is replaced by A_{730} , which finally gives way to A_{790} . The obviously large overlap of the adjacent maxima makes detailed kinetic analysis difficult, but some qualitative conclusions can be drawn. Figure 6 shows the effect of varying the TFA concentration on the rate of change of the absorbance at 790 nm. Similar changes are observed at the other wavelengths which correspond to the absorption maxima. These data are summarized in Figures 7 and 8, which show the maximum absorbance reached and the maximum rate of increase of absorbance for each wavelength at which an absorbance maximum occurs for different TFA concentration. When these experiments using TFA were repeated using chloroform or *ortho*-dichlorobenzene solvent instead of DCM, similar results were obtained with only small differences in the positions and relative intensities of the absorption maxima.

In all the solvents studied, the species responsible for the color with TFA were extremely photosensitive and were bleached in a few seconds when irradiated with unfiltered light from a medium-pressure mercury lamp (Fig. 9).

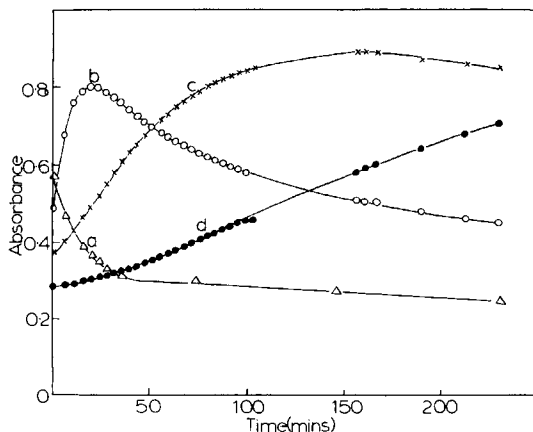


Fig. 5. Changes in the absorbance at (a) 590, (b) 660, (c) 730, and (d) 790 nm for DCM solutions of chemically degraded PVC containing TFA (0.3M).

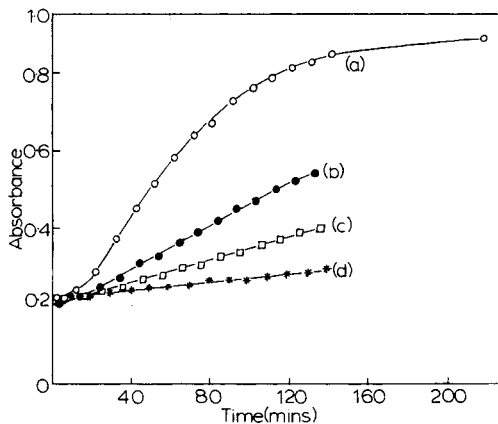


Fig. 6. Effect of changing TFA concentration on the rate of increase in absorbance at 790 nm for DCM solutions of chemically degraded PVC: (a) 0.1M; (b) 0.2M; (c) 0.3M; (d) 0.5M.

DISCUSSION

The striking difference between the polyene distributions in DCM and in THF and the formation of the polyene-TFA interaction in DCM but not in THF may have some relevance to the role of HCl in the degradation of PVC. An exami-

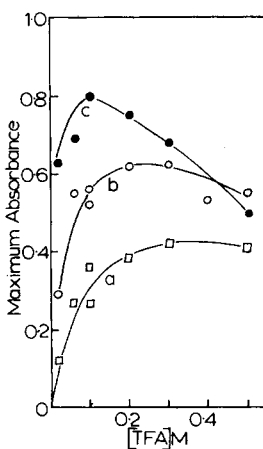


Fig. 7. Variation of maximum absorbances reached at (a) 590, (b) 660, and (c) 730 nm with TFA concentration of DCM solutions of chemically degraded PVC.

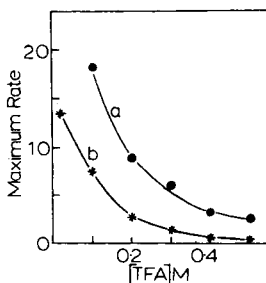
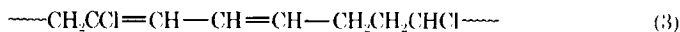
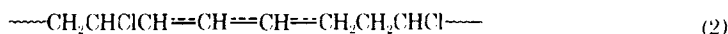
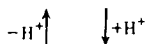
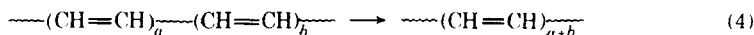


Fig. 8. Variation of the maximum rate of increase in absorbance at (a) 730 and (b) 790 nm with TFA concentration for DCM solutions of chemically degraded PVC.

nation of polyene distributions found by various workers for PVC degraded thermally or photochemically under different conditions shows clearly that the efficiency with which HCl is removed as the reaction progresses is a critical factor. The distributions we observe in THF and in DCM seem to represent the extremes that would result from complete removal or complete retention, respectively, of evolved HCl. The difficulty of distinguishing whether initiation, propagation, or termination are most affected by HCl has already been mentioned, and it now appears that for systems in which the HCl is not removed, the migration of short polyene sequences along the polymer chain may be another complicating factor. The formation of long sequences by the accumulation of short ones may occur following the establishment of a prototropic equilibrium and migration of polyenes along the polymer chain as described in eqs. (1)–(3):

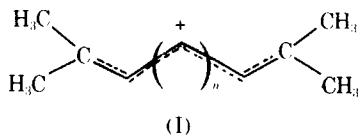


The overall result would be

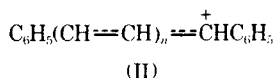


the rate of which would depend on the proximity of the two sequences in the polymer.

The most likely lengths of the polyenylic cations responsible for the maxima at 590, 660, 730, and 790 nm can best be inferred by reference to the data of Sorenson,¹⁴ who has defined an empirical relationship [$\lambda_{\max} = (330.5 + 65.5n)$ nm] for ions of type I. A similar relationship



[$\lambda_{\max} = (420 + 67n)$ nm] has been established by Hafner¹⁵ for ions of type II:



In each case, the absorption maxima for individual members of the series are separated from each other by about 65 nm, which is also the separation between successive maxima in our systems. Precise identification is made more difficult by the fact that the exact positions of the maxima are solvent dependent and are shifted hypsochromically as the solvent polarity is decreased. In addition, it

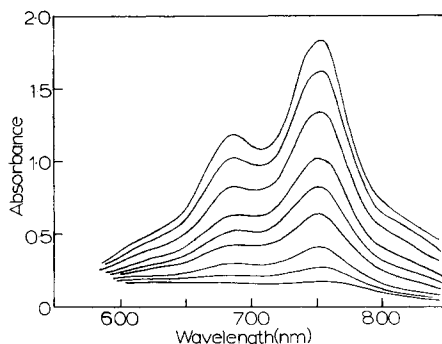
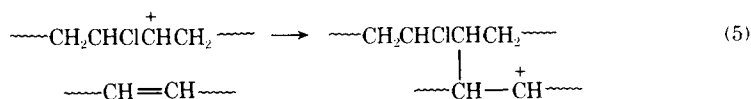


Fig. 9. Photobleaching of absorbance in the region 600–800 nm for *o*-dichlorobenzene solutions of chemically degraded PVC containing TFA. Decreasing absorbances correspond to irradiation for 0, 7, 17, 30, 40, 50, 70, 90, and 120 sec.

is probable that each absorbance has a shoulder on the short wavelength side of the maximum. Application of Sorenson's data would associate the peaks at 590, 660, 730, and 790 nm with ions derived from pentaenes, hexaenes, heptaenes, and octaenes, respectively, and interconversion of A_{590} to A_{660} , A_{660} to A_{730} , and so on corresponds to increase in the length of the ions by one unit in each case. Wasserman¹⁶ has also studied polyenylic cations derived by protonation of various polyenes but the reliability of his spectral data has been questioned¹⁴ because of the high reactivity of the species concerned.

The data of Figures 7 and 8 which describe the effects of varying TFA concentrations on the absorbance maxima and the maximum rates of increase of absorbance enables us to draw some semiquantitative conclusions. As the TFA concentration is increased, the value of the absorbance maximum reached increases to a maximum value, then begins to decrease (Fig. 7). The value of the extinction coefficients for the various ions is not significantly different,¹⁷ so changes in absorbance probably reflect relative concentrations. For A_{660} the maximum is reached at lower TFA concentration and decreases faster than that for A_{590} . For A_{730} the maximum is reached at even lower TFA concentration and decreases even faster. It seems that the lower the TFA concentration, the fewer the polyenes protonated initially and the higher the tendency for migration to occur. This explains why maximum rates of increase of absorbance owing to the higher ions (730 and 790 nm) occur at low TFA concentrations and why maximum concentrations of large ions are formed.

The extreme photosensitivity of these species is similar to that found by Sorenson¹⁴ for analogous but nonpolymeric species in strongly acid media. In those cases, the principal photochemical reaction occurring was a 1,5-cyclization with exclusive formation of five-membered rings, even though the formation of seven and nine-membered rings was possible. The rates were controlled to a large extent by steric factors operating in the ions. These steric factors may be even more critical in our systems where the ions are relatively short segments in long polymer chains. Interpolymer reactions of the type shown which lead to crosslinks may also be important:



The results emphasize the important role played by HCl as a catalyst for the dehydrochlorination process not only in influencing the distribution of polyene sequences which result from the primary part of the degradation process, but also in affecting the photochemical crosslinking reactions of the polyenylic cations.

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Received June 15, 1979

Accepted November 30, 1979