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The Reinitiation Mechanism of HCl Catalysis in PVC Degradation

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Summary

The effect of HCl on the thermal degradation of PVC has been studied. Changes in UV and visible spectra and kinetics of HCl loss indicate that HCl is able to reinitiate the allyl-activated zip elimination by proton exchange with polyenes. Also polyene-consuming secondary reactions are accelerated by HCl.

Introduction

HCl catalysis is one of the most debated questions of PVC degradation. The mechanism of catalysis has not yet been clarified in spite of the large number of papers on the subject. Even the experimental results seem to be controversial.

HCl affects both the rate of HCl loss and the distribution of polyene sequences. Under the conditions of HCl catalysis longer polyenes were observed by some authors (THALLMAIER and BRAUN, 1967; PALMA and CARENZA, 1972; GUPTA et al., in press). In other experiments a shift towards shorter polyenes was reported in the presence of HCl (MORIKAWA, 1968; KELEN et al., 1971). The participation of polyenes in HCl catalysis has been suggested a decade ago (MORIKAWA, 1968; RASUVAEV et al., 1971). The latter authors found that the rate of HCl-catalyzed degradation increased not only with increasing HCl pressure, but also with increasing polyene content (i.e., with the predegradation time).

The interaction of HCl with polyenes of thermally degraded PVC has been studied in detail a few years ago (TÜDŐS and KELEN, 1973). Under the conditions of thermal degradation fast proton exchange of the polyenes was demonstrated using tritium labelled HCl. Recently proton exchange and conversion of shorter polyene sequences to longer ones was observed during trifluoroacetic-acid treatment of chemically degraded PVC (OWEN and PASHA, 1978).

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In this paper we deal with the role of proton exchange in HCl catalysis.

Experimental

Ongrovil S 470 suspension polymerized PVC powder (kindly supplied by Borsod Chemical Works, Hungary) was used. The degradation was carried out with 0.5 g samples in evacuated and sealed h shape ampoules (total volume 4.5 ml) the HCl evolved was frozen out with liquid air.

To remove the last traces of oxygen and other volatile impurities we kept the ampoules at 100°C at 10^{-5} torr vacuum for 30 min before sealing. In several cases the liquid air was removed after a certain period of degradation. After degradation was stopped, HCl was frozen out, absorbed in 45 ml water and measured conductometrically. UV and visible spectra were recorded in 10 g/l tetrahydrofuran solutions. THF was freshly distilled from sodium.

Results and Discussion

The dependence of HCl-loss conversion on experimental conditions and degradation time clearly shows the catalytic effect of HCl (Fig.1).

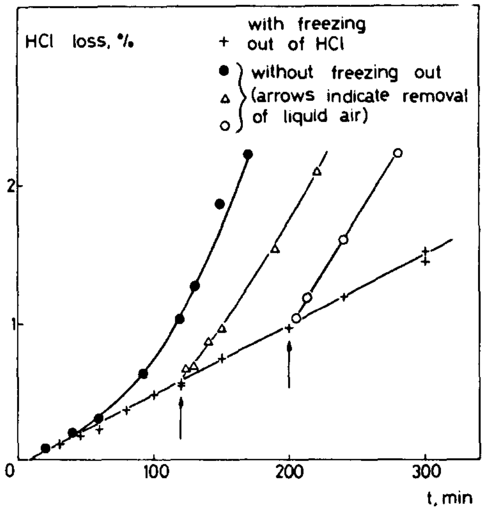


Figure 1. Typical HCl-loss conversion curves at 180°C.

The results obtained in vacuo with freezing out of HCl are identical with those obtained in argon flow. When HCl is removed, polyene distribution shifts slowly towards shorter sequences due to secondary reactions (TÜDŐS et al., 1974). In the presence of HCl the shape of the spectra are markedly dissimilar and the resolution of the peaks corresponding to the individual polyenes diminishes. This is especially pronounced when the HCl is allowed to react with the polyenes of pre-degraded PVC (Fig.2).

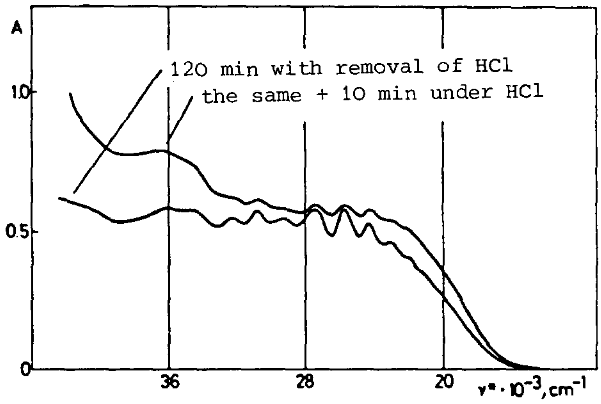


Figure 2. Spectra of PVC samples degraded at 180°C (10 g/l PVC in THF, 0.5 cm cell).

To facilitate comparison of the numerous spectra taken under different degradation conditions the ratio of absorbances at $\nu^* = 20\ 000$ and $28\ 000$ cm^{-1} (A_{20}/A_{28}) as well as the ratio at $\nu^* = 36\ 000$ and $28\ 000$ cm^{-1} (A_{36}/A_{28}) are plotted against degradation time (Fig.3). A_{20} corresponds to 12-13, A_{28} to 5-6 and A_{36} to 3 conjugated double bonds in the polyene; thus A_{20}/A_{28} is a measure of the concentration of long polyenes and A_{36}/A_{28} the concentration of short polyenes relative to medium ones.

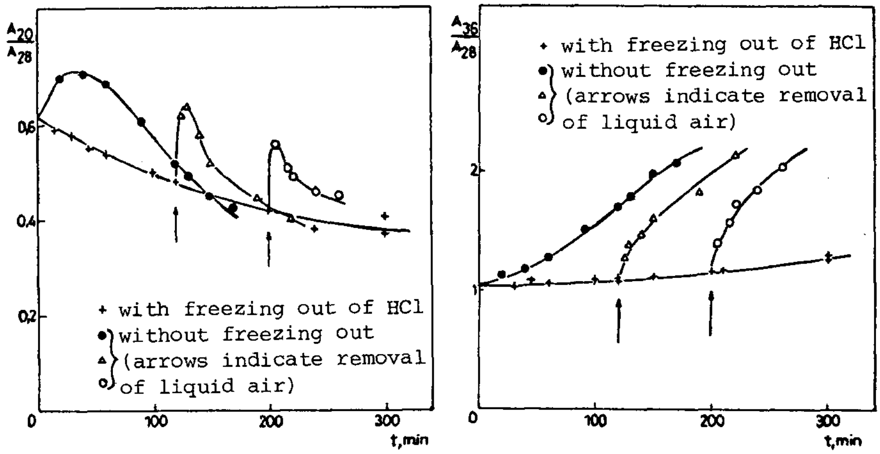
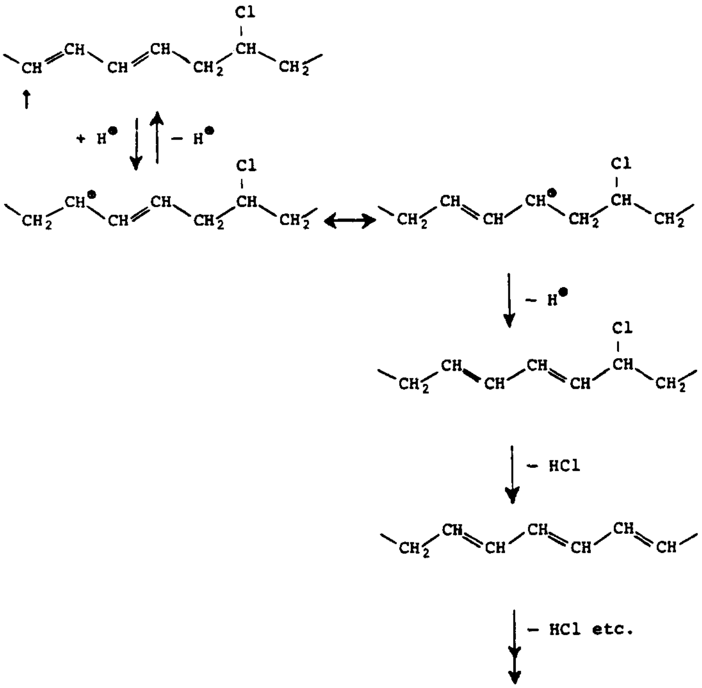


Figure 3. The ratio of absorbances at the indicated wavenumbers for PVC samples degraded at 180°C.

During degradation with the removal of HCl, the ratio A_{20}/A_{28} slowly decreases, due to polyene-consuming secondary reactions (TÜDŐS et al., 1974). In the presence of HCl, however, a sharp increase in A_{20}/A_{28} is observed indicating the formation of longer polyenes.

In explaining the experimental results we must take into account that the pure thermal degradation of PVC involves relatively slow initiation, allyl-activated zip-elimination of HCl, and termination of unzipping (BRAUN, 1971; TÜDŐS and KELEN, 1973). In the presence of HCl and other acids, proton exchange may lead to the migration of the polyene, and a chlorine atom becomes allyl-activated. Then reinitiation of allyl-activated zip-elimination occurs:



The newly formed double bonds are conjugated with the original polyene, so that the average polyene length increases. Reinitiation of earlier terminated polyenes is not the sole effect of HCl. As shown in Fig.3, after the sudden increase the A_{20}/A_{28} ratio decreases faster in presence of HCl than in vacuum, and at the same time a rapid increase in the A_{36}/A_{28} ratio occurs. These observations indicate that the polyene consuming secondary reactions are accelerated by HCl as well.

The reinitiation mechanism and the simultaneous acceleration of secondary reactions by HCl clarify the apparent controversy that the average polyene length may increase or decrease in the presence of HCl. In some cases polyene growth by reinitiation was predominant while under other conditions the effect of HCl catalyzed secondary reactions was more pronounced.

In addition to the above two effects, HCl may influence PVC degradation in other ways, e.g., by catalyzing primary HCl loss.

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