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The Stabilizing Effect of Allyl Chloride Copolymer Units on the Thermal Degradation of Poly(vinyl Chloride)

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ABSTRACT

The rate of dehydrochlorination at 190° C of vinyl chloride/allyl chloride copolymers decreases with increasing content of allyl chloride. In agreement with the hypothesis that this is due to the blocking action of the CH_2Cl side groups, copolymer samples degraded at 170° C give a UV spectrum showing a greater preponderance of short polyene sequences than is found for the vinyl chloride homopolymer.

INTRODUCTION

When it was thought that chain branch points in poly(vinyl chloride) occurred as a result of intramolecular transfer reactions, tertiary chlorine atoms were suggested as sources of thermal instability [1]. Correlation between branch frequency and susceptibility to dehydrochlorination was found with copolymers of vinyl chloride and

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2-chloropropene [2]. Evidence for tertiary chlorine in vinyl chloride homopolymer was lacking, however, and it is now well recognized [3, 4] that most of the branches in PVC are chloromethyl groups and these are linked to a CH group in the main chain. Although recent work has not shown a correlation between chloromethyl content and thermal instability [5] this matter is not regarded as settled and the availability of copolymers containing relatively large amounts of chloromethyl groups introduced by copolymerizing vinyl chloride with allyl chloride has allowed us to investigate this matter further.

EXPERIMENTAL

Allyl chloride obtained from BDH Ltd. was dried over calcium chloride and distilled; the fraction boiling at 45-46°C was collected and stored under nitrogen. Analar 1,2-dichloroethane was used as a solvent for the copolymerization without further purification. Vinyl chloride monomer was kindly given to us by BP Chemicals Ltd. It was dried by passing the gas through a tube of magnesium perchlorate. The dried monomer was outgassed on the vacuum line. The first third was distilled away and the second third was used. The final third was discarded. Tributyltin hydride used for the reduction of the copolymer samples was made by reduction of tributyltin oxide with polymethyl hydrosiloxane [6, 7]. Benzoyl peroxide used as polymerization initiator and azoisobutyronitrile used as a free radical source for the reduction of the polymer samples were commercial samples and were purified by recrystallization from solution.

Copolymerization

The copolymers were prepared in 1,2-dichloroethane solution as described previously [7] except that benzoyl peroxide (0.06 mol/L) was used instead of azoisobutyronitrile. Allyl chloride concentrations between 0.66 and 1.66 mol/L and vinyl chloride (4.5 mol/L) were used and the copolymerization was carried out at 60° C. The polymer recovered at about 10% conversion was precipitated into methanol and purified from the initiator fragments by further precipitations into methanol from deperoxidized tetrahydrofuran solutions. The copolymers were dried in a vacuum dessicator before use.

Copolymer Composition

The polymer samples were reduced with tributyltin hydride in 2-methyltetrahydrofuran solution according to the method of Starnes et al. [8]. The ratio of allyl chloride to vinyl chloride in the copolymer was determined from the intensity of the methyl group absorption band at 1378 cm^{-1} using a high molecular weight Rigidex wedge in the reference beam to compensate for the CH_2 absorptions [7].

Rates of Dehydrochlorination

The dehydrochlorination rates were determined on 50 mg samples of powdered copolymer under nitrogen at 190°C. Hydrochloric acid evolved was drawn by a stream of preheated nitrogen into the cell of an automatic titrimeter. The rate of HCl evolution was obtained by a sodium hydroxide titration using this system. We are indebted to BP Chemicals Ltd. who allowed us to use their apparatus for these rate determinations.

UV Visible Analysis of Degraded Samples

The UV visible spectra of copolymer samples degraded in vacuum at 170°C for 2 h were recorded in THF solutions (less than 1% w/v) using a Perkin-Elmer 402 UV Spectrophotometer. Samples degraded at 190°C in vacuum were insoluble in tetrahydrofuran.

RESULTS AND DISCUSSION

Figure 1 shows the course of HCl evolution from two of the copolymer samples compared with that of a homopolymer. It will be noticed that the copolymers show a more rapid initial evolution of HCl than the homopolymer but at about the 1% decomposition level the rate of HCl evolution from the copolymers is less than from the homopolymer. Taking this as an index of the instability of the polymers, Fig. 2 shows that even less than 1% of allyl chloride in the copolymer causes a 30% drop in the dehydrochlorination rate. This is followed by a more gradual but steady drop in decomposition rate over the whole range of composition studied. From time to time it has been suggested that polymer endgroups are a source of instability and hence low molecular weight polymers could be less stable than high molecular weight ones. Table 1 shows the number-average and weight-average molecular weights of the copolymer samples. The molecular weight drops rapidly as the amount of allyl chloride increases and so, if polymer endgroups were a source of instability, we would expect the polymers with high allyl chloride content to be the least stable. This is not the case.

Abbås and Sörvik [8] have suggested that chloromethyl side groups in PVC can act as termination points for dehydrochlorination. If this were so the length of the runs of conjugated double bonds in the degraded polymer should be decreased by the allyl chloride comonomer units. The UV spectra in Fig. 3 show this to be the case but the main

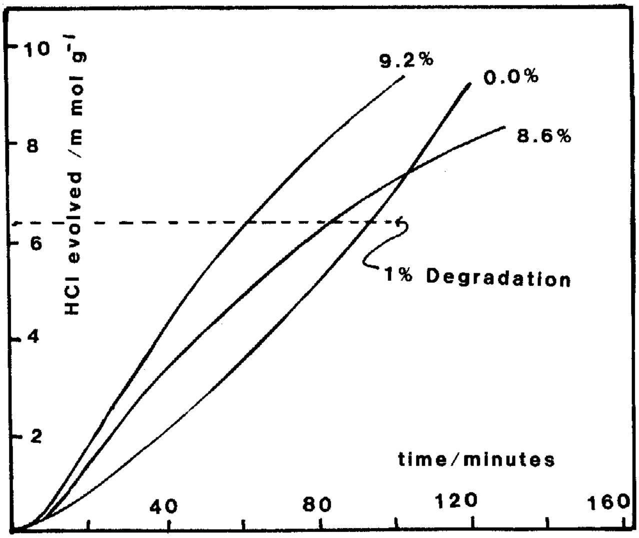
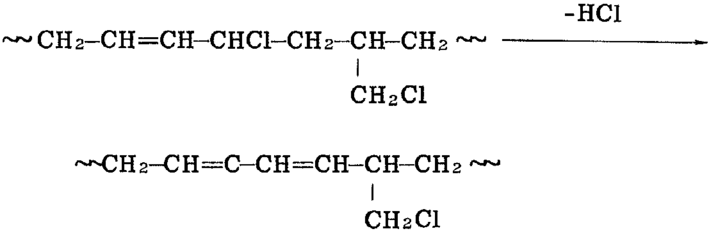


FIG. 1. Degradation kinetics of copolymers at 190°C. Allyl chloride percent indicated.

effect is a considerable increase in pairs of double bonds shown by the absorption at 230 nm. It is surprising that the relatively small amount (less than 1%) of allyl chloride comonomer should cause a large increase in the number of pairs of double bonds. This could only occur if the blocking action of the chloromethyl groups is four carbon atoms away from a preexisting double bond in the structure:



$$\sim CH_2-CH=CH-CHCl-CH_2-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-CH_2\sim \xrightarrow{-HCl}$$

$$\sim CH_2-CH=C-CH=CH-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-CH_2\sim \qquad (1)$$

The presence of this structure in the copolymers could account for the peculiar shape of the HCl evolution plots in Fig. 1. Here, an initially high rate of evolution is very quickly followed by a rate which is less than that of the homopolymer. The initially high rate would be due to the preexisting double bonds but this would only lead

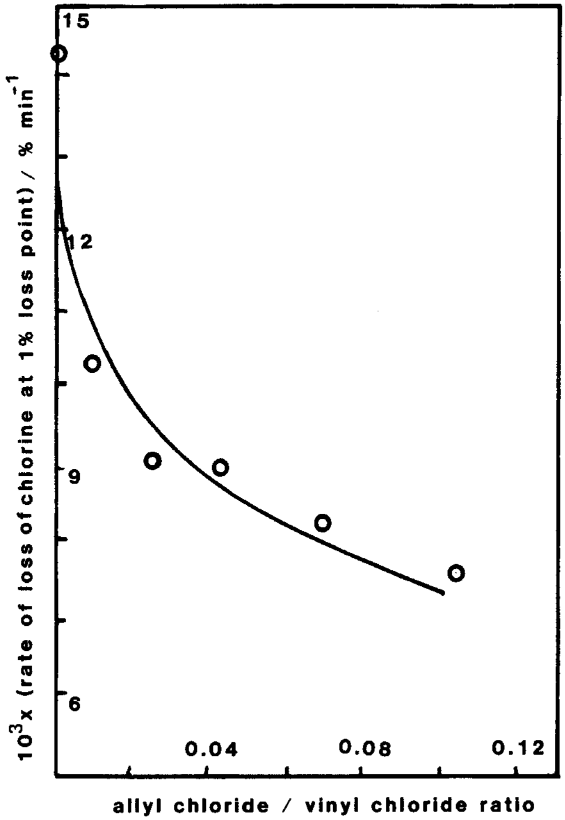
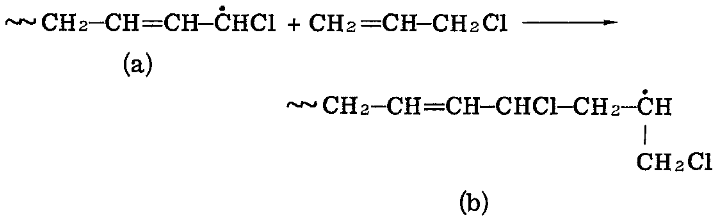


FIG. 2. Dehydrochlorination rate.

to the evolution of one HCl molecule before the blocking action of the CH_2Cl group came into effect.

It is not clear why a structure of this kind should arise in the copolymers but one possibility is that the radical (a) can be formed



$$\underset{\text{(a)}}{\sim\!\sim CH_2{-}CH{=}CH{-}\dot{C}HCl} + CH_2{=}CH{-}CH_2Cl \longrightarrow \underset{\text{(b)}}{\sim\!\sim CH_2{-}CH{=}CH{-}CHCl{-}CH_2{-}\underset{\displaystyle CH_2Cl}{\overset{\bullet}{C}H}} \tag{2}$$

TABLE 1. Molecular Weights of Vinyl Chloride/Allyl Chloride Copolymer

Copolymer composition		Molecular weight	
$CH_2Cl/1000C$	[A]/[M]%	$10^{-4}\ \overline{M}_n$	$10^{-4}\ \overline{M}_w$
2.60	0.00	3.33	7.16
4.40	0.78	2.61	4.85
11.57	2.40	-	-
20.04	4.20	1.04	1.83
41.22	8.90	0.76	1.25
47.26	10.40	0.64	1.12

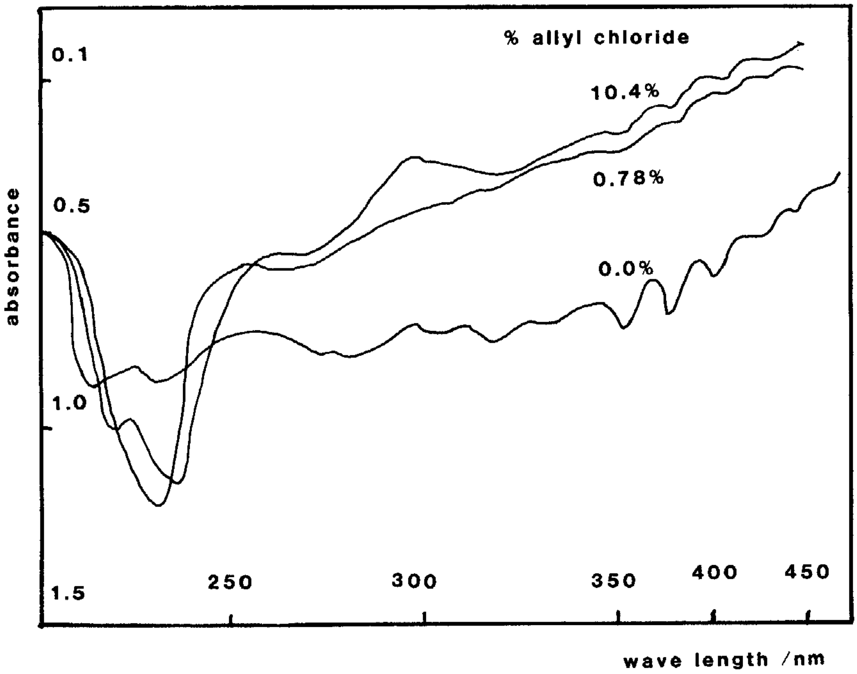


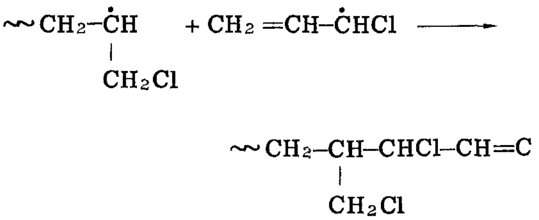
FIG. 3. UV spectra of polymers degraded at 170°C.

during the polymerization and this then adds on to an allyl chloride monomer unit to give the required (b) structure. It is not easy to see how such a radical could arise, but the radical formed by transfer to allyl chloride has the structure

$$CH_2{=}CH{-}\dot{C}H\,Cl \longleftrightarrow \dot{C}H_2{-}CH{=}CH\,Cl \qquad (3)$$

The resonance stabilization of this radical is thought to render it inoperative as a polymerization initiator. Nevertheless, if a small proportion of these radicals does start off polymerization chains by adding on allyl chloride monomer, a structure similar to that shown in Eq. (2) could arise, but with the double bond at the beginning of the chain.

More likely reactions of the allyl chloride radical would be the termination reactions:

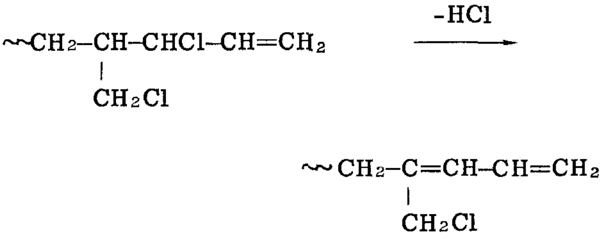


$$\sim\!\sim CH_2{-}\underset{\substack{|\\ CH_2Cl}}{\dot{C}H} + CH_2{=}CH{-}\dot{C}HCl \longrightarrow \sim\!\sim CH_2{-}\underset{\substack{|\\ CH_2Cl}}{CH}{-}CHCl{-}CH{=}C \qquad (4)$$

or

$$\sim\!\sim CH_2{-}\dot{C}HCl + CH_2{=}CH{-}\dot{C}HCl \longrightarrow \sim\!\sim CH_2{-}CHCl{-}CHCl{-}CH{=}CH_2 \qquad (5)$$

Pairs of double bonds could then be formed by the reactions



$$\sim\!\sim CH_2{-}\underset{\substack{|\\ CH_2Cl}}{CH}{-}CHCl{-}CH{=}CH_2 \xrightarrow{-HCl} \sim\!\sim CH_2{-}\underset{\substack{|\\ CH_2Cl}}{C}{=}CH{-}CH{=}CH_2 \qquad (6)$$

or

$$\sim\!\sim CH_2{-}CHCl{-}CHCl{-}CH{=}CH_2 \xrightarrow{-HCl} \sim\!\sim CH_2{-}CCl{=}CH{-}CH{=}CH_2 \qquad (7)$$

Further loss of HCl is prevented by the CH_2 group.

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