

Studies of the Solid-State Thermal Degradation of PVC.

I. Autocatalysis by Hydrogen Chloride

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SYNOPSIS

The thermal degradation of virgin and HCl-treated PVC in powder form, as well as of PVC films of different thicknesses, has been studied as a function of time and temperature. The rate of dehydrochlorination was determined conductimetrically and from the polyene sequence distributions as obtained by UV spectroscopy. Increases in the rate of dehydrochlorination, ranging between 30 and 45%, were observed at all temperatures for the samples pretreated with HCl, while the corresponding activation energies were found to be lower by about 20%. For the PVC films, the rate increased with thickness, i.e., with longer residence time of evolved HCl within the sample. The results offer insight regarding the autocatalytic role of evolved HCl.

INTRODUCTION

The predominant reaction in the thermal degradation of PVC in the solid state is dehydrochlorination to form polyene sequences, with average length of about 10 (Refs. 1–3) and maximum length between 15 and 20.^{4–6} Since this degradation occurs at temperatures well below those at which small molecule model compounds undergo dehydrochlorination, albeit in the gas phase, it is generally thought that defect sites in the chain, such as tertiary and allylic chlorines, have a major role.^{7–9} Indeed, Hjertberg and Sorvik¹⁰ reported correlations between the number of defect sites in PVC and its rate of thermal degradation.

Characteristically, an induction period is seen in the evolution of HCl. This suggests that the reaction involves some form of autocatalysis, and it is commonly held that the evolved HCl acts as the catalyst for the thermal degradation. Consequently, many of the stabilizers that are used are designed to neutralize the acid.¹¹ Clearly, this behavior could also reflect the occurrence of other processes, either

chemical or physical. For example, it is not inconceivable that some process involving realignment of the macromolecules occurs during the induction period.

In spite of the many detailed studies of the thermal degradation of PVC, relatively little is known about the nature of the autocatalysis by HCl in solid PVC and whether it occurs during the “normal” degradation, i.e., in the absence of added HCl. Several reports suggest that there is no autocatalysis by HCl or that it cannot be detected.^{12,13} On the other hand, Hjertberg and Sorvik¹⁴ showed that at 190°C the rate of degradation of bulk PVC, in a nitrogen/HCl atmosphere, increases with HCl concentration. This is in agreement with conclusions of Minsker et al.¹⁵ Martinsson et al.¹⁶ reported that the HCl evolved when PVC degraded is sufficient to catalyze the lengthening of the polyene sequences.

This paper describes studies of the effect of HCl on the thermal degradation of solid-state PVC. Experiments have been made to determine (1) the effect on the rate of degradation of previously exposing the samples, at temperatures above and below the T_g , to an atmosphere of HCl and (2) the effect of film thickness, for films and for PVC-coated solid supports, on the kinetics of degradation. This latter study seeks to determine the effect of HCl diffusion on the rate of degradation.

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EXPERIMENTAL

1. Materials

The poly(vinyl chloride) (PVC) used was an Esso 366 commercial resin, for which the following characteristics were quoted: $\langle M_n \rangle = 46,000$; $\langle M_w \rangle = 83,000$; density = 1.39 g/cm³; $[\eta] = 0.98$ dL/g at 25°C in chlorobenzene. The resin was purified by repeatedly dissolving in freshly distilled (under nitrogen after refluxing over sodium), peroxide-free tetrahydrofuran (THF) and precipitating by addition of cold methanol. After a final wash with methanol, the purified resin was dried in air and then under vacuum. This reprecipitation extracted material of low molecular weight, including resin, so that the final product was free of stabilizer, plasticizers, and other additives. The number of double bonds and the number of labile chlorines per 1000 monomer units were determined by bromination^{17,18} and phenolysis¹⁷⁻¹⁹ to be 2.6 and 1.2, respectively. Studies by ¹³C-NMR, using a Varian XL-300 spectrometer, indicated an essentially atactic polymer with $P_m = 0.45$, as determined from the methine triad sequence distribution.

The solvent 1,2-dichloroethane (EDC) was distilled before use. Hydrogen chloride gas, technical grade, 99.0% purity (Linde-Union Carbide) was used, as received, for treating the PVC prior to degradation.

For the studies involving PVC coatings, Chromosorb W, 60/80 mesh (Chromatographic Specialties) was used. Before use, it was heated in a vacuum oven at 200°C to remove volatile impurities, including adsorbed water. To avoid readsorption of water, it was stored under vacuum.

2. Apparatus

The apparatus is shown schematically in Figure 1. The reaction chamber was maintained at constant temperature in a furnace (from a Perkin-Elmer GC, Model 881). The conductance was measured using dipping Pt electrodes and a Model 35 conductance meter (YSI Scientific) interfaced to an Apple II microcomputer, which allowed automatic acquisition and processing of a large number of data points. The interface and data acquisition system were developed especially for this purpose.

The UV-visible spectra were recorded at room temperature, to determine the extent of dehydrochlorination, with samples at a concentration of 4.0

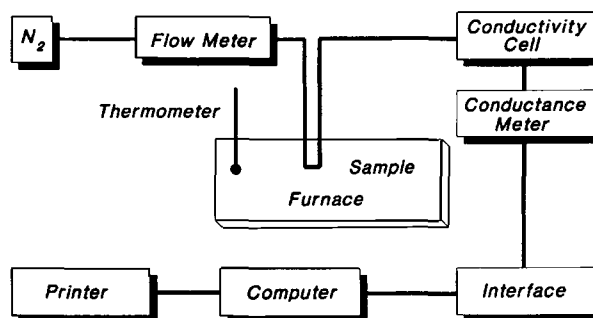


Figure 1 Thermal dehydrochlorination apparatus—schematic diagram.

g/L in freshly distilled, peroxide-free THF, under nitrogen, using a Beckman double-beam spectrometer, Model 25.

3. Method

The PVC samples were degraded, at constant temperature, under a steady flow of nitrogen (60 cc STP/min). For these studies, only the PVC fraction with particle size between 35 and 60 mesh was used. The evolved hydrogen chloride was swept by the nitrogen stream to the conductance cell and was monitored by continuously measuring the conductance of the resulting solution, at 25.0°C.

RESULTS AND DISCUSSION

1. Effect of Added HCl

It is common knowledge that in the thermal degradation of solid PVC an induction period is observed in HCl evolution. Furthermore, the rate of degradation of PVC powders depends to a significant degree on the particle size and sample preparation.^{20,21} These results are consistent with an initial buildup of HCl, within the particles, until the HCl concentration exceeds its solubility in PVC and diffuses to the surroundings. Furthermore, it is entirely reasonable to expect that the dissolved HCl can catalyze the dehydrochlorination process. Indeed, previous work indicates that the rate of degradation of PVC is increased by the presence of HCl in the surrounding nitrogen atmosphere.¹⁴

The following experiments were designed to establish the effect, if any, of dissolving HCl in PVC particles *prior* to degradation: Samples of PVC, in the degradation cell, were exposed to an atmosphere

of hydrogen chloride gas at 25, 100, and 150°C for 30 min. Subsequently, the samples were cooled to room temperature and excess HCl was removed by exhaustive flushing of the cell with nitrogen for about 24 h until conductance measurements showed that no further HCl was being removed.

Figure 2 shows isotherms, in which the percent HCl evolved is plotted as a function of time, for the degradation at 120°C of a sample of PVC pretreated by exposure to HCl at room temperature and for untreated PVC. For the HCl-treated sample, there is little, if any, evidence of an induction period in HCl production and the rate of HCl evolution, i.e., the slope of the isotherm, is clearly higher than for the untreated sample. Although the rate of HCl evolution from the HCl-treated sample decreases somewhat at about 2 h of heating, it persistently exceeds that of the untreated sample for times in excess of 9 h, i.e., accelerated dehydrochlorination continues well beyond the time required for complete desorption of any HCl dissolved in the PVC sample during the pretreatment. Thus, it would seem that the difference is due not only to the HCl produced by desorption. Similar results, although with a

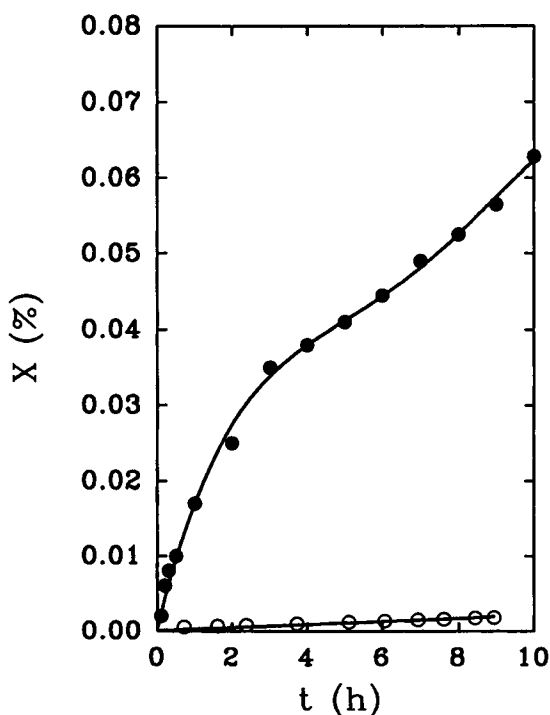


Figure 2 Degree of dehydrochlorination, X , as a function of time for the degradation, at 120°C, of HCl-treated and untreated PVC: (○) untreated PVC; (●) HCl-treated PVC.

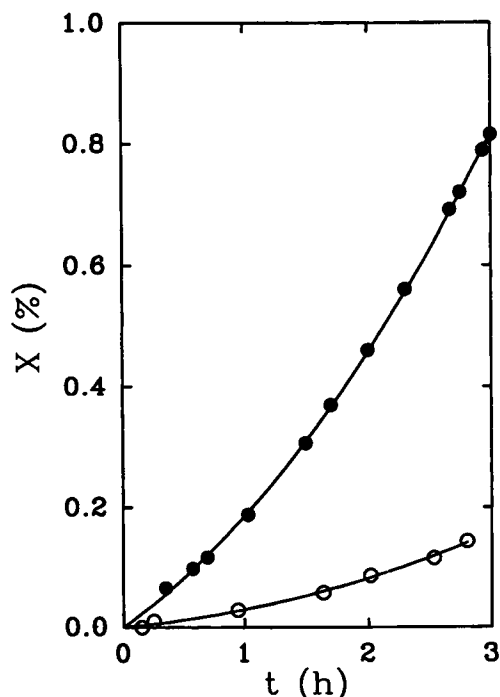


Figure 3 Degree of dehydrochlorination, X , as a function of time for the degradation, at 150°C, of HCl-treated and untreated PVC: (○) untreated PVC; (●) HCl-treated PVC.

smaller difference in rates, are obtained when the degradation occurs at 150 and 190°C (Figs. 3 and 4).

In keeping with previous studies, the thermal degradation process may be assumed to be first order so that rate constants, k , can be calculated from the linear portions of the isotherms. The results, given in Figure 5, indicate that an increase of 30–45% in k is obtained at all degradation temperatures when PVC is treated with HCl prior to degradation. Activation energies, obtained from Arrhenius plots, were 100 kJ/mol for virgin PVC and 81 kJ/mol for HCl-treated PVC, i.e., the activation energy for dehydrochlorination was found to be lower by about 20% for the HCl-treated PVC, strongly suggesting a catalytic role for the HCl. Amer and Shapiro²² showed, in a previous study, that an increase in the rate of PVC degradation is obtained also for samples in an HCl-containing atmosphere. On the other hand, the activation energies given for the dehydrochlorination of the virgin PVC and for the process in the HCl-containing atmosphere were 103 and 114 kJ/mol, respectively, which is inconsistent with a catalytic role for HCl. However, Amer and Shapiro considered the difference between the two activation

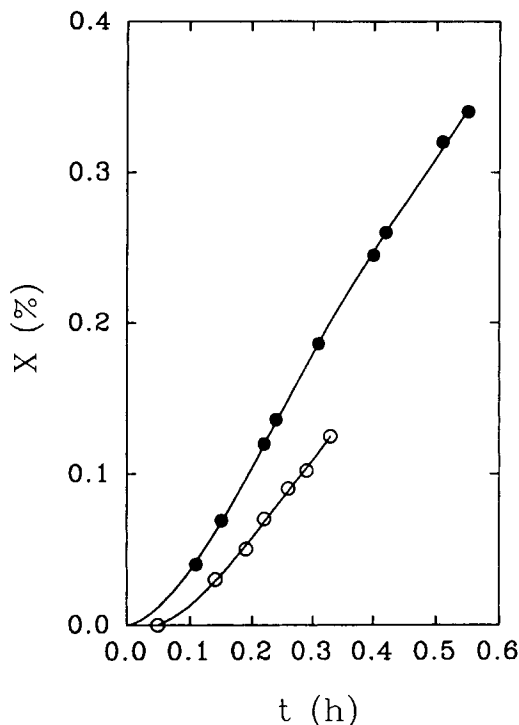


Figure 4 Degree of dehydrochlorination, X , as a function of time for the degradation, at 190°C , of HCl-treated and untreated PVC: (○) untreated PVC; (●) HCl-treated PVC.

energies to be insignificant, essentially within experimental error of each other.

In the experiments described above, HCl evolution is considered to be a measure of degree of dehydrochlorination. However, since HCl is also released by desorption from the sample, a direct measure of the extent of degradation is desirable. In the process of dehydrochlorination, sequences of conjugated double bonds of various lengths are known to form,¹⁻³ which are directly related in number to the extent of the reaction. These are amenable to quantitative measurement by UV-visible spectrophotometry.²³

The UV-visible spectra of virgin PVC and of HCl-treated PVC degraded at 120°C for 9 h are shown in Figure 6. For identical heating times, the degree of degradation of the HCl-treated sample clearly is higher as reflected by the higher absorbances obtained for samples having the same concentration. At the same time, simple ocular inspection revealed that the HCl-treated resin turned light yellow while the untreated resin remained almost colorless. Both of these observations are direct evidence of the

greater extent of degradation in the HCl-treated resin.

The concentration of polyene sequences, C_n , is given by

$$C_n = A/(\epsilon_{\lambda} \cdot d) \quad (1)$$

where A is the absorbance at wavelength λ , ϵ_{λ} is the extinction coefficient, and d is the path length of the cell. According to a method developed by Popov and Smirnov,²⁴ the extinction coefficients, ϵ_{λ} , can be calculated by

$$\epsilon_{\lambda} = 10,000 + [20,000(n - 1)] \quad (2)$$

where n is the polyene sequence length. The mol fraction of polyene sequences containing n conjugated double bonds can be determined from C_n as

$$N_n = C_n/C \quad (3)$$

where C is the concentration of vinyl chloride repeat units, in mol/liter. Similarly, the mol fractions of

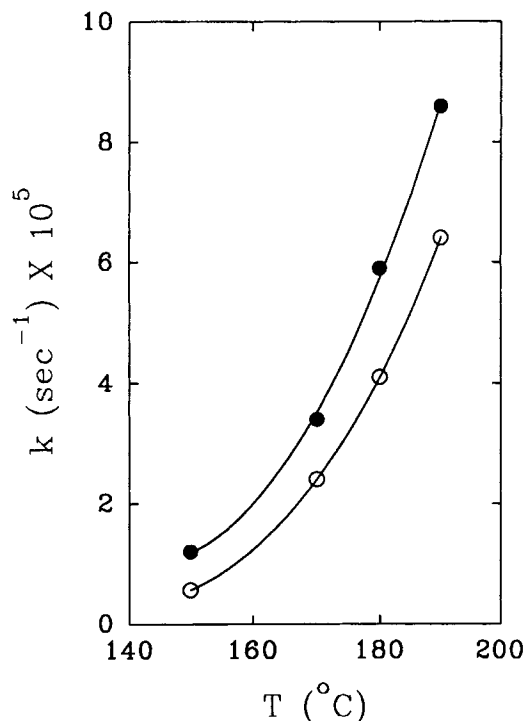


Figure 5 First-order rate constants, k , for the dehydrochlorination of PVC and HCl-treated PVC as a function of degradation temperature: (○) untreated PVC; (●) HCl-treated PVC.

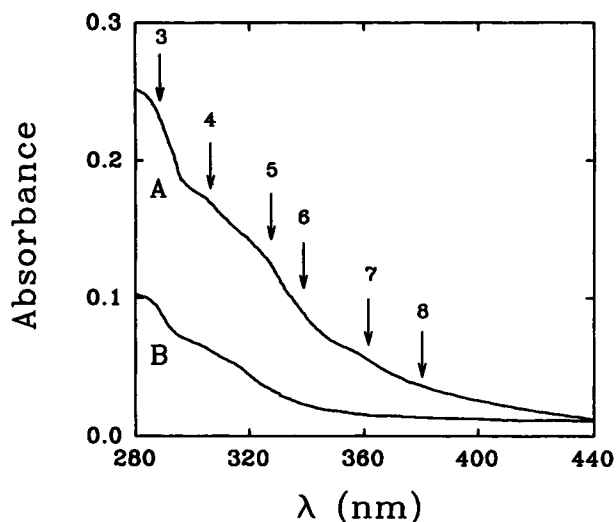


Figure 6 UV-visible spectra of (A) HCl-treated and (B) untreated PVC, degraded at 120°C for 9 h. The arrows indicate the wavelength of maximum absorption of a conjugated sequence containing the number of double bonds shown above the arrows.

polyene sequences and of double bonds, N_T and N_D , respectively, are given by

$$N_T = \sum N_n \quad (4)$$

$$N_D = \sum n \cdot N_n \quad (5)$$

Then, the average length of conjugated double bonds, $\langle n \rangle$, is simply given by N_D/N_T . The results of these calculations are given in Tables I and II. In every case, for identical degradation conditions, the values of N_n , N_T , and N_D obtained for the HCl-treated PVC are higher than for the untreated sample. For example, at 120°C, the extent of dehydrochlorination as given by the mol fraction of double bonds, N_D , was determined to be 2.5 times greater for the HCl-treated resin. This offers unequivocal evidence that the increased rate of HCl

Table I Mol Fraction, N_n , of Polyene Sequences for HCl-treated and Untreated PVC, Degraded at 120°C

Sample	N_3	N_4	N_5	N_6 ($\times 10^5$)	N_7	N_8
PVC	2.7	1.4	0.99	0.54	0.29	0.12
PVC/HCl	6.1	4.6	2.4	1.4	0.60	0.25

Table II Total Mol Fraction of Polyene Sequences, N_T ; Mol Fraction of Double Bonds, N_D ; and Average Polyene Sequence Length, $\langle n \rangle$, for HCl-treated and Untreated PVC, Degraded at 120°C

Sample	$N_T \times 10^5$	$N_D \times 10^4$	$\langle n \rangle$
PVC	6.0	2.5	4.2
PVC/HCl	15	6.3	4.2

evolution is not due to desorption alone but also to a higher rate of dehydrochlorination.

The persistently higher rate of HCl evolution for the treated resin suggests that the dissolved HCl somehow affects the initiation of the degradation process. This hypothesis was tested by performing the pretreatment of the PVC samples with HCl at three different temperatures for the same length of time, namely, 30 min. The assumption was that the increase in the pretreatment temperature would result in the creation of a greater number of labile sites, especially at the highest temperature, 150°C—

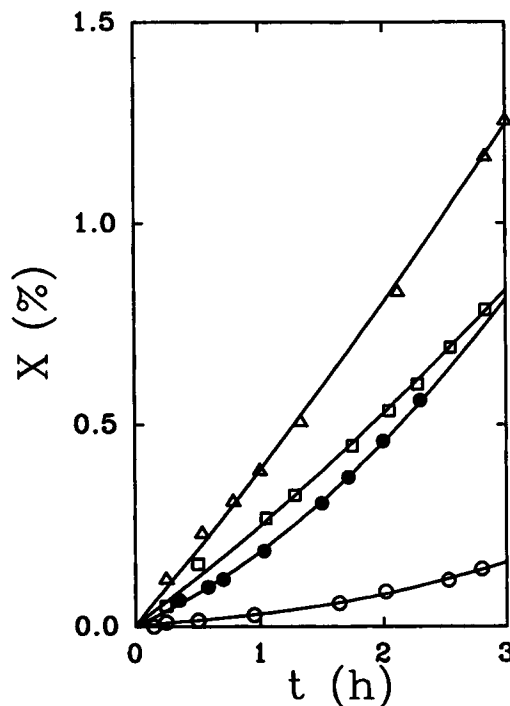


Figure 7 Degree of dehydrochlorination, X , as a function of time for the degradation, at 150°C, of PVC pretreated with HCl at various temperatures: (O) untreated PVC; (●) pretreated 25°C; (□) pretreated 100°C; (Δ) pretreated 150°C.

which is above the T_g of the resin and in the temperature regime where thermal degradation becomes quite rapid. Indeed, the results given in Figure 7 show a significantly higher rate of degradation for the sample that was pretreated with HCl at 150°C. One explanation for these results is that the absorbed HCl in pretreated PVC resin causes the formation of additional labile sites that are responsible, at least in part, for the observed higher degradation rate.

To further consider the effects due to partial degradation during pretreatment, a series of experiments was made in the following manner: A PVC sample was heated for several hours at 150°C, and HCl elimination was monitored to establish the rate of degradation. Two other PVC samples were heated at 150°C under flowing nitrogen for periods of 1 and 3 h, respectively, and then cooled to room temperature while the flow of nitrogen continued for a period of at least 24 h, after which no further release of HCl could be detected by conductimetry. Subsequent measurements of the rate of dehydrochlorination, at 150°C, show that the rate of HCl production for these samples is increased by the prior thermal treatment (Fig. 8). Furthermore, there is

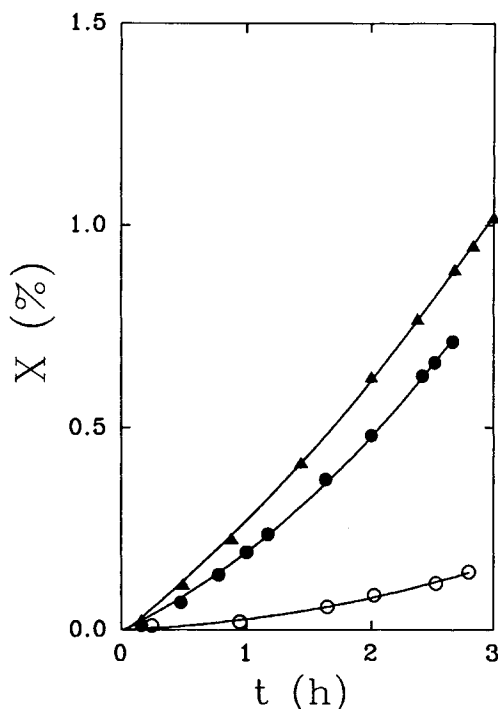


Figure 8 Degree of dehydrochlorination, X , as a function of time for the degradation, at 150°C, of PVC predegraded for different lengths of time at 150°C: (○) untreated PVC; (●) predegraded 1 h; (▲) predegraded 3 h.

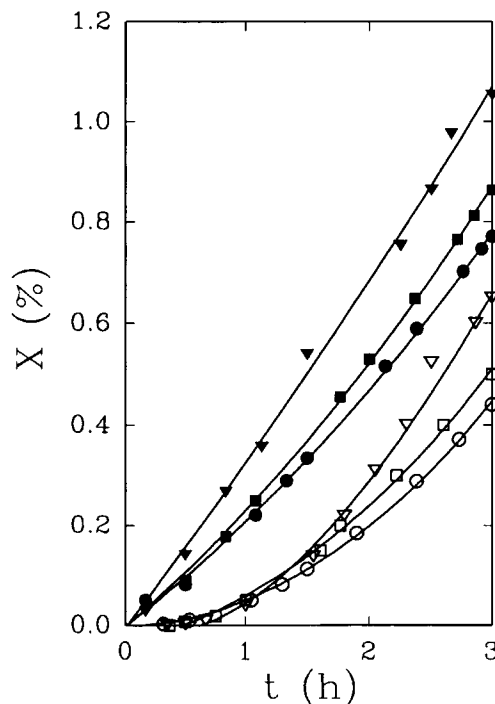


Figure 9 Degree of dehydrochlorination, X , as a function of time, for the degradation, at 150°C, of PVC films (○) 0.08, (□) 0.22, and (▽) 1.02 mm thickness and predegraded PVC films (●) 0.08; (■) 0.22, and (▼) 1.02 mm thickness.

little, if any, indication of an induction period in HCl production from the samples with thermal pretreatment. The increased rate of HCl evolution, on heating, can be attributed to (1) the production of labile sites, such as double-bond sequences or free radicals, during pretreatment that persists until the heating is resumed; (2) the production of HCl that remains in the sample, either in a "trapped" or dissolved form so that it is not removed until heating is resumed; or (3) some form of annealing, such as that reported in a DSC study by Teh et al.,²⁵ that results in a rearrangement of the macromolecular PVC chains to a conformation that favors dehydrochlorination. Comparison of the results in Figures 7 and 8 shows that at no time does the rate of degradation of the heat-pretreated samples attain that of the sample pretreated by exposure to HCl. Thus, although annealing appears to contribute to an increased rate of dehydrochlorination, catalysis by HCl is an important factor.

2. Degradation of PVC Films

All the experiments described up to this point were made with PVC powder having a certain range of

Table III First-order Dehydrochlorination Rate Constants for PVC Coated onto Chromosorb W in the Temperature Range 150–190°C

Sample	% PVC	Film Thickness (nm)	k_{150}	k_{170}	k_{180}	k_{190}	E_a (kJ/mole)
CR1	16.0	128	0.042	0.23	0.43	0.81	123
CR2	26.6	213	0.071	0.41	0.81	1.4	144
CR3	32.8	262	0.15	0.75	1.2	2.1	109
Bulk PVC	100.0	—	0.57	2.4	4.1	6.4	100

particle sizes. To further study the effect on the degradation rate of the residence time of the HCl in a sample, i.e., the time HCl remains in contact with the PVC before it diffuses out of the sample, similar experiments were conducted using PVC films of various thicknesses. Films were cast from 5% solutions of the purified resin in 1,2-dichloroethane, which was allowed to evaporate slowly over a period of 48 h. The films were dried in a vacuum oven for 15 days at room temperature. The results, shown in Figure 9, indicate that the rate of dehydrochlori-

nation of even the thinnest film (0.08 mm) greatly exceeds that of the powder samples. Furthermore, the rate of HCl evolution increases with film thickness. This can be explained by noting that in thicker films the HCl produced takes longer to diffuse out of the sample; thus, the autocatalysis is more effective in these films.

When these experiments were repeated with partially degraded films, i.e., films that had been heated at 150°C for 3 h, cooled to room temperature, and flushed with nitrogen for 24 h, the behavior was similar to that observed for the predegraded powder samples.

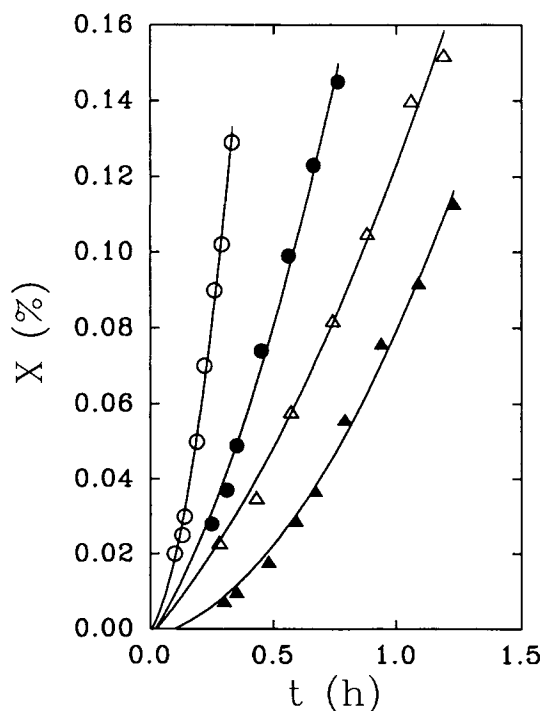


Figure 10 Degree of dehydrochlorination, X , at 190°C, for PVC coated onto Chromosorb W as a function of degradation time: (○) bulk PVC; (●) CR3, (△) CR2; (▲) CR1.

3. Degradation of PVC Coated onto Chromosorb

It follows from the above discussion that the degradation rate should decrease if the rate of escape of HCl out of the degrading polymer were to be increased. One way to verify this is to use much thinner samples than the films described above. Such films, several orders of magnitude thinner, were made by coating PVC onto the surface of Chromosorb W, a silanized diatomaceous earth.

These films were prepared in the following manner: A weighed amount of purified PVC was dissolved in freshly distilled, peroxide-free THF and then a given amount of previously degassed Chromosorb W was added to the solution. After stirring for 4 h under a nitrogen atmosphere, excess THF was removed by rotary evaporation. The samples were stored under vacuum. The amount of PVC coated onto Chromosorb was determined by ashing. The composition of the samples is given in Table III. Higher concentrations were unattainable by this method without significantly changing the particle size of the final sample. The resulting PVC coatings ranged between 64 and 354 nm in thickness.

Plots of percent HCl evolved at 190°C as a function of time are given for the different samples in

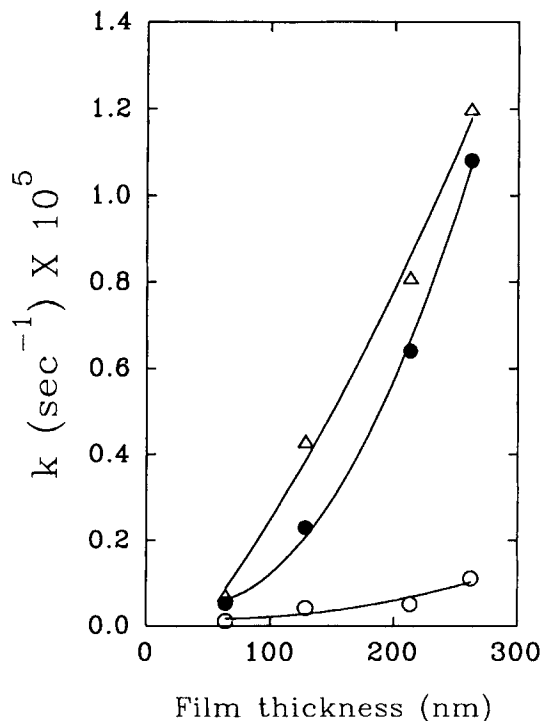


Figure 11 First-order dehydrochlorination rate constants, k , as a function of film thickness, for the degradation at various temperatures of PVC adsorbed onto Chromosorb W: (○) 150°C; (●) 170°C; (△) 180°C.

Figure 10. The rate of HCl evolution is seen to decrease with decreasing PVC layer thickness. The results for other experiments at 150, 170, and 180°C are given in Table III, but, being very similar, are not shown graphically.

The first-order dehydrochlorination rate constants, k , obtained from the linear portion of these curves, are given in Table III. At a given temperature, a decrease in k is obtained with decreasing PVC layer thickness (Fig. 11). As in the case of the PVC films mentioned earlier, the decrease in k is attributable to a shorter residence time of the evolved HCl within the thinner PVC layers. The E_a values (Table III) are generally higher than those obtained for the bulk PVC, in agreement with the conclusions reached earlier that decreasing the amount of HCl in the degradation medium increases the activation energy due to a diminution of the catalytic effect.

CONCLUSIONS

The results indicate clearly that autocatalysis by HCl is an integral feature of the solid-state thermal

degradation of PVC. This is evidenced by increased rates and lower activation energies for the dehydrochlorination of samples presaturated with HCl. Furthermore, decreases in sample thickness, in the case of films that favor diffusion of evolved HCl out of the sample, lowered the rate of reaction, as would be predicted. The experiments involving the treatment of the PVC resin with HCl prior to degradation clearly establish the catalytic role of added HCl. However, as indicated by the experiments conducted with PVC coated onto a solid substrate, HCl autocatalysis occurs as well in the absence of added HCl, i.e., during the normal degradation process.

The absence of an appreciable induction period when thermal degradation is resumed after removal of evolved HCl must reflect significant changes in the physical state of the PVC resin. The annealing appears to alter the physical state of the PVC such that HCl diffusion is hindered, hence, a higher steady-state concentration of HCl in the degradation medium that, in turn, results in a concomitant increase in autocatalysis. However, it is also possible that the annealing results in rearrangements of the macromolecules to conformations that favor the degradation. Thus, the induction period that accompanies the thermal degradation of PVC reflects the buildup of the HCl concentration, within the sample, as well as annealing processes that favor degradation.

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