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Heat Degradation of PVC Stabilized by Treatment with Alkylaluminum Compounds

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ABSTRACT

Thermal degradation of PVC treated with alkylaluminum compounds has been studied. Four PVC samples of different molecular weights have been treated with Me_3Al and Et_3Al , and the dehydrochlorination rates of the polymers were determined at 190 and 220°C under a nitrogen atmosphere. The alkylaluminum-treated low molecular weight samples show marked increase in thermal stability, i. e., slower rate of dehydrochlorination right from the beginning of degradation, whereas with the higher molecular weight samples stabilization becomes pronounced only after a few percent of dehydrochlorination. The color of R_3Al -treated samples was much lighter (yellowish) than those of controls (dark brown) at 1% HCl loss. The average polyene sequence lengths formed during the early

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stages of dehydrochlorination are found to be much shorter with R_3Al -treated PVC than with virgin samples. It appears as though polyene sequences which arose by zipping-initiation from allylic and/or tertiary chlorine sites are longer than those which form by random initiation along the chain. The auto-catalytic (i. e., HCl-catalyzed) dehydrochlorination observed with virgin PVC disappears after treatment with R_3Al . The HCl-catalyzed dehydrochlorination is minimized when thin films are used instead of powdery samples, which may be due to higher rates of HCl diffusion through thin films. Autocatalysis of dehydrochlorination is affected by the concentrations of double bonds and HCl and the length of polyene sequences. Interaction between polyenes and HCl by hydrogen transfer may lead to the re-initiation of unzipping, thus lengthening the polyene sequences.

INTRODUCTION

In the course of our fundamental studies on cationic reactions [1] and PVC degradation [2, 3] we decided to reinvestigate in detail the observation that the thermal stability of poly(vinyl chloride) (PVC) increases noticeably upon treating the resin either in a slurry or in solution by organoaluminum compounds e. g., Me_3Al , Et_3Al , $(C_6H_5)_3Al$ [4-11].

In view of the commercial importance of PVC, a large amount of research has been directed toward the definition and detailed characterization of its microstructure, and ways to improve its inherently low thermal stability. Studies concerning the thermal degradation and stabilization of PVC have recently been reviewed [12-17]. It has been generally accepted that thermal degradation of PVC involves dehydrochlorination by "zipping" off HCl, and results in polyene sequences of different lengths.

The mechanism of initiation and termination of the zipping process is a matter of contention and the source of controversy. The surprisingly low heat stability of PVC was proposed to arise from a variety of "active" or "labile" chlorines in the chain e. g., allylic, tertiary [17], which were viewed as sites for zipping-initiation. Recently it has been postulated that zipping may also initiate at random, including secondary chlorines [2, 18-21]. Zipping termination has been postulated to occur by cyclization [3, 19], irregular structure [18, 22], intermolecular dehydrochlorination [23], and chain transfer [24].

The rates of dehydrochlorination and the shape of the plots of HCl loss versus time are affected by sample morphology and degradation conditions. Decelerating [2, 25] and accelerating rates [26-28]

have been observed. Acceleration was usually attributed to HCl catalysis [26-28]. The subject of autocatalytic dehydrochlorination, particularly in liquid systems, is controversial [12, 29]. During degradation HCl may interact with the polyenes [30] by proton exchange [2] or readdition [2, 31].

Attempts have been made to enhance the thermal stability of PVC by polymerization at low temperatures and/or by use of special initiator systems [32-34] and by post-polymerization treatment with organoaluminum compounds [4-11]. This paper concerns a detailed reinvestigation of the thermal stability of PVC treated in solution with Me_3Al and Et_3Al , in particular the effect of degradation conditions and origin of PVC, including molecular weight, on thermal degradation behavior.

EXPERIMENTAL

Materials

Characteristics of the four suspension PVC samples used are compiled in Table 1. The samples were purified by two precipitations into methanol from tetrahydrofuran (THF) freshly distilled from CaH_2 under nitrogen. The effect of this purification procedure on degradation kinetics is negligible.

Trimethylaluminum and triethylaluminum (Texas Alkyls Co.) were distilled under vacuum and the middle fractions were used. 1,2-Dichloroethane (DCE) (MCB Co.) was purified by treating it with Et_3Al and distilling. Dry grade (Linde) nitrogen was used.

Several poly(vinyl chloride-g-isobutylene) (PVC-g-PIB) samples prepared by grafting isobutylene from G62 (for the meaning of symbols, see Fig. 1) backbones by using Et_2AlCl coinitiator [36] have also been examined.

Treatment of PVC with Me_3Al and Et_3Al

Experiments were carried out in a stainless steel enclosure under a dry nitrogen atmosphere. Treatment of PVC with the alkylaluminums was carried out by using DCE solutions (1.5% PVC in the solvent) in test tubes. Concentrations, temperatures, and times are indicated in the appropriate tables and figures.

After the desired length of exposure to the alkylaluminums the excess R_3Al was decomposed by the addition of methanol and the tubes were removed from the enclosure. The samples were precipitated with methanol, dissolved in THF, and the aluminum-containing

TABLE I. PVC Samples

Commercial name	Source	Symbol	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$[\eta]_{\text{CHO}}^{25}$ (dl/g)
Geon 103	Goodrich Chemical Co.	G62	62 ^a	114 ^a	-
Ongrovil S470	Borsod Chemical Works, Hungary	H56	55.6	104	1.10
Laboratory sample prepared in the presence of a chain transfer agent	Goodrich Chemical Co.	G34	34 ^b	71 ^b	-
Laboratory sample, prepared in the presence of a chain transfer agent at 85°C	Borsod Chemical Works, Hungary	H14	14.4	24.5	0.33

^aSee Davidson [35].^bData of E. L. Collins, Goodrich Chemical Co.

residues removed by centrifugation for ca. 1/2 hr. During this purification process the reaction products of alkylaluminum and methanol remain in contact with the polymer for some time; this may cause some further reaction influencing the degradation behavior of the polymer. The THF solution was precipitated into methanol, redissolved in THF, filtered, and subsequently reprecipitated three more times from THF into methanol (a total of five precipitations after treatment with R_3Al). Finally the finely powdery products were dried for two days in vacuo at room temperature.

Untreated (control) samples were prepared by subjecting them to the same vigorous purification process except alkylaluminum compounds were not added.

Great care must be exercised to remove aluminum-containing residues from the samples as they may affect the rate of HCl loss. Indeed, R_3Al -treated samples that have not been purified showed much higher initial rates of dehydrochlorination than virgin (untreated) samples.

Attempts have been made to determine the Al content of samples used, however, the quantity of materials that remained after experimentation was insufficient for accurate analysis. Therefore several gram batches of G62 and H14 samples were prepared separately by treating them with 91 mM Et_3Al at 25°C and reprecipitating five times (i. e., G62/ $Et_3Al/91/25$ and H14/ $Et_3Al/91/25$). The Al content of these samples determined by atomic absorption was 0.086 and 0.013%, respectively. The degradation rates of these samples were somewhat higher than those obtained in this research. Since the aluminum compound that arises during the decomposition of Et_3Al with methanol enhances PVC degradation rate (as determined by the use of unpurified samples) the Al contents of the samples examined in this paper must have been lower than those found in the samples prepared only for Al analysis.

Dehydrochlorination Experiments

Experiments were carried out on both powdery samples and thin films. For the experiments with powders, the carefully weighed (ca. 0.02 g) sample was placed into a U-shaped glass tube (6 mm internal diameter) immersed into a thermostatted silicon-oil bath. Before heat degradation, 100 ml/min nitrogen was passed over the sample for at least 30 min at room temperature. Degradation commenced on lowering the U-tube into the bath at 190 or 220°C. The HCl liberated was carried by the nitrogen stream into a conductivity cell containing a known amount of doubly distilled water. The rate of HCl evolution was followed continuously by a chart recorder attached to the conductometer.

Degradation kinetics of thin films were determined similarly. In these experiments films were cast from freshly distilled THF solution on flat-bottomed glass cylinders fitted with inlet and outlet tubes; the latter were extended near the bottom of the cylindrical cell used as reactor. The solvent was slowly evaporated under a flow of nitrogen at room temperature and finally dried in vacuum overnight at room temperature. The thickness of the film was varied by varying the amount of PVC and changing the diameter of the base of the cylindrical cell.

The length of polyene sequences was determined spectroscopically by using a Carey 17 instrument and 2.1 g degraded PVC/liter THF solutions at 0.5 and 1.0 mole % HCl loss. From the UV and visible spectrum of the degraded PVC the concentrations of polyene chains of different lengths were estimated [2, 37]. From the slope of the logarithmic plot of polyene concentration against polyene length (according to geometrical distribution) the value of the average polyene chain length was calculated [2, 18].

RESULTS AND DISCUSSION

Dehydrochlorination Rates of R_3Al -Treated and Untreated PVC

Figure 1 shows the results of degradation experiments carried out with Et_3Al -treated and control samples at $190^\circ C$. It is noteworthy that the four control samples exhibited two kinds of degradation behavior. With the two higher molecular weight industrial samples, G62 and H56, the rate of HCl loss decreases with degradation time; the two lower molecular weight laboratory samples, G34 and H14, exhibit autocatalytic degradation patterns. Their physical appearance was also noticeably different: while the higher molecular weight samples sintered and remained somewhat porous, the low molecular weight materials appeared to have melted and fused during degradation.

The rates of dehydrochlorination at 1% HCl loss have been calculated from the curves in Fig. 1 and similar data and are compiled in Tables 2-4. As shown by the data in Table 2, treatment with Et_3Al did not significantly affect the rates of dehydrochlorination at 1% HCl loss of the two higher molecular weight samples.

In contrast to the higher molecular weight samples the degradation rate at 1% HCl loss of which did not change upon treatment with Et_3Al , the lower molecular weight materials after exposure to Et_3Al (Fig. 1 and Table 2) and Me_3Al (Fig. 2 and Table 3) showed significantly reduced dehydrochlorination rates. The rates of dehydrochlorination

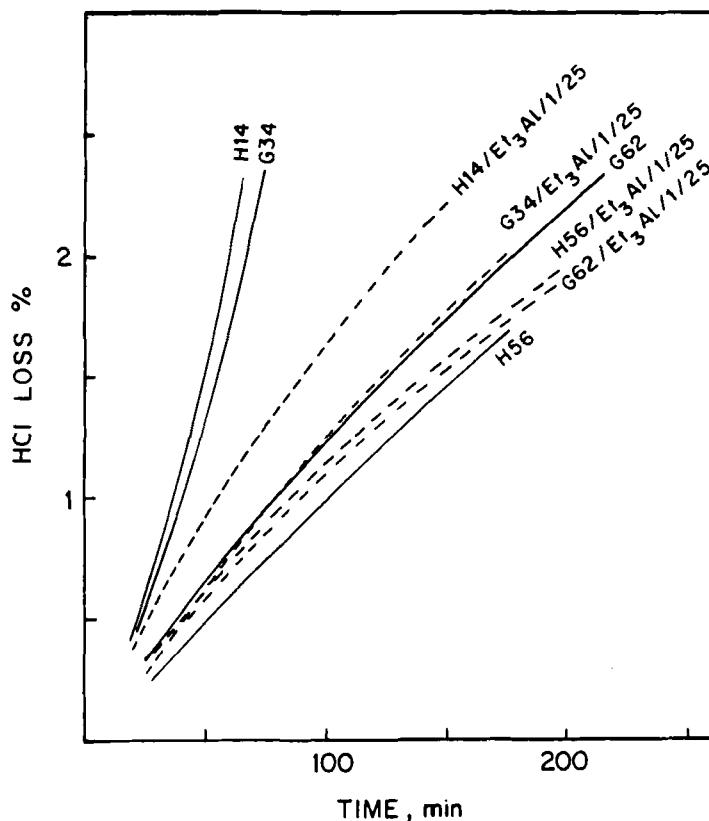


FIG. 1. Dehydrochlorination of untreated and Et_3Al -treated PVC powders at 190°C . Key: symbol of sample/nature of alkylaluminum/alkylaluminum concentration (in mM)/temperature of treatment. For example: H14/ Et_3Al /1/25 indicates a H14 sample treated with Et_3Al , the concentration of which was 1 mM , at 25°C .

at 1% HCl loss of these samples were lower by a factor of 2-3 than those of the controls.

In line with these findings, as shown by the data in Table 4, the rates of dehydrochlorination of a series of PVC-g-PIB copolymers prepared by using a G62 backbone and Et_2AlCl coinitiator [35] were somewhat lower than that of the control (relatively high molecular weight PVC).

TABLE 2. Rate of Dehydrochlorination at 1% HCl Loss of Et₃Al-Treated PVC Samples

Et ₃ Al concn (mM)	Et ₃ Al (mole/mole monomer unit)	Temp (°C) ^a	Dehydrochlorination rate (w × 10 ⁵) ^b			
			G62	H56	G34	H14
91	0.38	25	9.4	8.2	9.9	13.7
91	0.38	-30	12.3	10.9	15.9	15.7
20	0.083	25	12.1	8.9	12.1	17.3
20	0.083	-30	13.9	6.8	11.5	14.5
5	0.021	25	9.8	10.9	12.2	19.5
5	0.021	-30	12.4	11.3	13.4	14.4
1	0.0042	25	9.9	9.9	12.7	16.1
1	0.0042	-30	12.6	8.7	11.5	14.6
Control ^c	-		11.2	9.6	33.3	37.2

^aTemperature of Et₃Al treatment (1 hr).

^bMeasured at 190°C; dimension: (mole HCl/mole monomer unit)/min.

^cAverage of at least two determinations.

TABLE 3. Rate of Dehydrochlorination at 1% HCl Loss of the Lowest Molecular Weight (H14) PVC Sample Treated with Me₃Al

Me ₃ Al concn (mM)	Me ₃ Al (mole/mole monomer unit)	Temp (°C) ^a	Dehydrochlorination rate (w × 10 ⁵) ^b
50	0.21	25	10.6
50	0.21	-30	13.2
5	0.021	25	14.2
5	0.021	-30	13.6
0.5	0.0021	25	17.1
0.5	0.0021	-30	19.5
Control ^c	-		37.2

^aTemperature of Me₃Al treatment (1 hr).

^bMeasured at 190°C; dimension: (mole HCl/mole monomer unit)/min.

^cAverage of two determinations.

TABLE 4. Rate of Dehydrochlorination at 1% HCl of Poly(vinyl Chloride-g-Isobutylene)^a

Conditions of grafting				
Temp (°C)	Time (min)	Et ₂ AlCl concn (mM)	PIB in graft (wt %)	Dehydrochlorination rate (w × 10 ⁵) ^b
-70	15	16	1.8	10.3
-70	45	16	9.5	7.8
-50	51	40	32.6	9.3
-30	12	40	42.2	9.8
Control ^c				11.2

^aSamples prepared by using Geon 103 PVC (G62) and Et₂AlCl [35].

^bMeasured at 190°C, rates corrected for PIB content; dimension: (mole HCl/mole VC monomer unit)/min.

^cAverage of two determinations.

Color Differences Between R₃Al-Treated and Control Samples

After heat-degradation experiments, i. e., after heating the finely powdery samples in a stream of dry nitrogen to 190°C for 150-200 min, the samples were inspected. It was quite apparent that treatment with alkylaluminums caused important differences in their physical appearance: At the same level of dehydrochlorination, i. e., at 1% HCl loss, the R₃Al-treated samples were greenish-yellow or pale-yellow while the controls were dark-brown. As illustrated in Fig. 3, the UV and visible spectra of the R₃Al-treated samples showed much lower absorptions in the visible region than the controls.

Reduction of Polyene Sequence Length by R₃Al Treatment in Heat-Degraded PVC

It was decided to characterize further the discoloration phenomenon described above. Consequently a detailed examination of polyene sequence lengths of R₃Al-treated and untreated heat-degraded samples was undertaken. Significantly, it was discovered that the average lengths of polyene sequences formed upon heating PVC were much shorter for R₃Al-treated samples than those for untreated PVC.

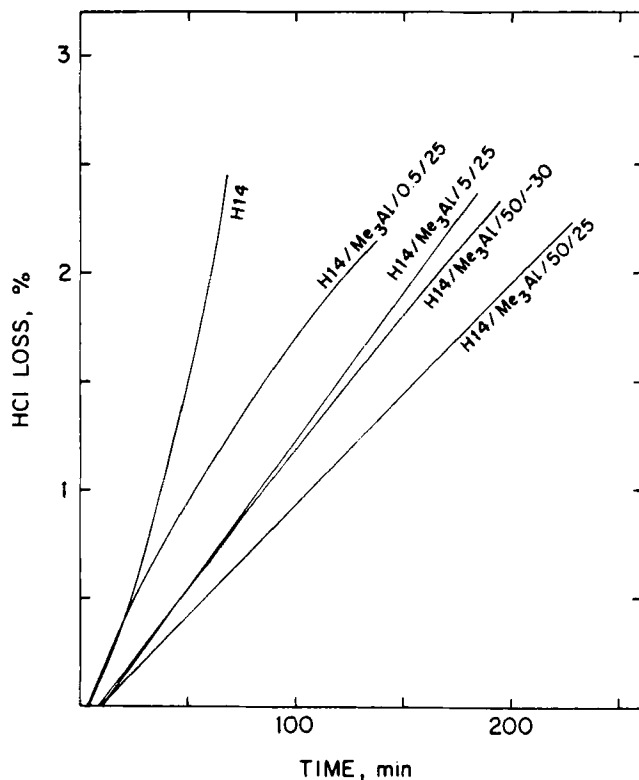


FIG. 2. Degradation of Me₃Al-treated and control H14 sample at 190°C. For key, see Fig. 1.

Table 5 shows representative data according to which the average polyene sequence length \bar{n} determined by geometric distribution [2] at the same level (0.5%) of HCl loss is markedly shorter for R₃Al-treated G34 and H14 samples than for corresponding controls. For example, while \bar{n} is 6.2 for untreated G34 PVC, it is reduced to around 3.0 with Et₃Al or Me₃Al treated samples.

A number of hypotheses were examined to explain this surprising observation, however, none of them seem to be entirely satisfactory. Reduced rates of dehydrochlorination of R₃Al-treated samples necessarily lead to longer degradation times to reach the same level of HCl loss as in the controls, and one may surmise that during extended degradation times, secondary reactions may occur which would shorten the length of average polyene sequences. However,

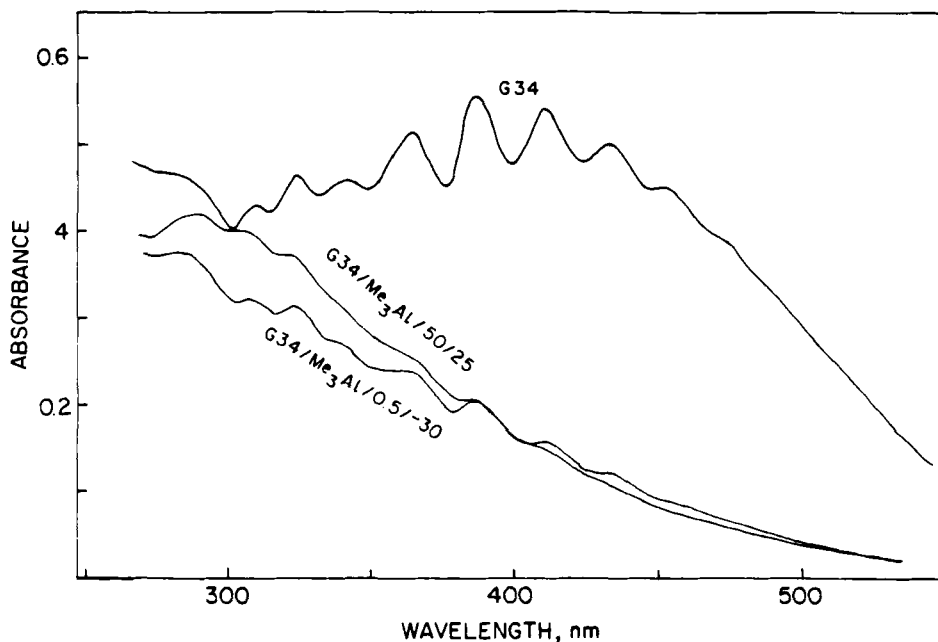


FIG. 3. UV and visible spectra of degraded G34 samples. Degradation up to 0.5% HCl loss at 190°C; 2.1 g/liter PVC in THF in 2 cm cuvet. For key, see Fig. 1.

this assumption cannot be correct, because the reduction of polyene sequence lengths upon prolonged degradation time was found to be much less than that obtained upon treatment with alkylaluminum. Thus experimentally we found that by almost doubling the degradation time, i. e., increasing HCl loss from 0.5 to 1.0%, the average polyene sequence length decreased very little, i. e., from 6.2 to 5.8 on the untreated H14 sample.

To account for the short polyene sequences one may also assume that alkylaluminum compounds substitute not only the active chlorines in PVC but also some secondary chlorines and that thus R_3Al -treatment may create terminating-sites for zipping dehydrochlorination. That alkylaluminums are able to react, albeit slowly, with secondary chlorines, has been described [10, 38, 39]. This possibility was explored by determining the chlorine contents of samples treated with highest R_3Al concentrations (91 mM Et_3Al and 50 mM Me_3Al) used in these studies and those of control samples. According to our findings, the

TABLE 5. Effect of R_3Al -Treatment on PVC

Sample	\bar{n}^a	$W_0 \times 10^{3b}$	$W_m \times 10^{3b}$	$S \times 10^3 c$
G62	3.4	1.35	0.64	13.0
H56	4.5	1.18	0.85	16.6
G34	6.2	2.30	-	54.0
H14	6.3	2.62	-	40.7
G62/ Et_3Al /91/25	-	0.98	0.36	0
H56/ Et_3Al /91/25	-	0.85	0.35	0.2
G34/ Et_3Al /91/25	2.9	1.25	0.22	0
G34/ Et_3Al /1/25	3.3	1.38	0.37	1.0
H14/ Et_3Al /91/25	2.9	1.28	0.46	0.5
H14/ Me_3Al /50/25	2.8	1.37	0.64	0.7
H14/ Me_3Al /0.5/-30	3.2	2.22	0.94	2.8
G62/ Et_2AlCl /16/-70 ^d	3.6	0.92	0.55	0

^a Average polyene sequence length at 0.5% HCl loss at 190°C.

^b W_0 = Initial rate; W_m = minimum rate at 220°C; dimension: (mole HCl/mole VC monomer unit)/min.

^c Slope of rate vs. HCl loss curves during the accelerating period of dehydrochlorination at 220°C, dimension: min^{-1} .

^d PVC-g-1.8% PIB, rates corrected for PIB content.

chlorine contents decreased only 0.9% and 1.3% upon Et_3Al and Me_3Al treatment, respectively. This chlorine loss is far too small to account for the drastic reduction in average polyene sequence lengths.

These chlorine loss data and those reported earlier [9] for a similar experiment in which PVC was treated with Et_3Al , are within what is considered to be experimental variation. On the basis of their chlorine loss data the earlier authors proposed that PVC may contain as much as 2-3 mole % labile chlorines. In contrast to this estimate, Caraculacu et al. [40] and Berens [41], using different techniques, concluded that the level of active chlorines in PVC is much less i. e., of the order of 0.2 mole %. The latter estimate is probably correct since the earlier authors [9] neglected to consider the possibility of chlorine losses due to interaction between secondary chlorines in PVC and Et_3Al . The finding that the rate of HCl loss remains essentially unaffected by an almost 100 fold change in Et_3Al

concentration (from 0.0042 to 0.38 Et_3Al /monomer unit) also supports the lower value. (cf. Table 2).

The shortening of the average polyene sequence length could be explained by assuming, that the average length of zips initiated at random is shorter than of those initiated at labile sites, as the alkylaluminum treatment removes active chlorines from the polymer. Most likely a combination of factors affects average polyene lengths including the effect of traces of aluminum compounds remaining in the resin even after several reprecipitations.

Further experiments would be necessary to elucidate the reduced polyene sequence lengths observed at 0.5% HCl loss with alkylaluminum-treated samples. For example, a detailed kinetic analysis of polyene formation from the beginning of degradation might be of interest.

Disappearance of Autocatalytic Dehydrochlorination Kinetics of PVC Upon Treatment with R_3Al

Closer inspection of the kinetic curves in Figs. 1 and 2 reveals a pronounced acceleration of dehydrochlorination in the two low molecular weight control samples, G34 and H14, which disappears in the corresponding R_3Al -treated materials. This change in dehydrochlorination mechanism interested us greatly and additional investigations were carried out to further characterize the phenomenon.

Autocatalytic PVC dehydrochlorination has been described and discussed by previous investigators who also noted that the phenomenon becomes more pronounced with increasing temperatures [26-28]. In line with this information we have raised the temperature of our degradation experiments from 190°C to 220°C to maximize the effect of R_3Al on autocatalysis, should there be any.

The results of a representative set of experiments with Et_3Al and Me_3Al are shown in Fig. 4 (for the symbols used consult legend of Fig. 1). Indeed, the effect of treatment with these alkylaluminums on the degradation kinetics is unmistakable. While the control samples all show more or less pronounced accelerating dehydrochlorination commencing at 2-8% HCl loss, the R_3Al -treated materials either do not exhibit such behavior or the effect is very slight.

The difference in behavior of these materials is more dramatically illustrated in Fig. 5, which shows the first derivative of HCl-loss/time curves as a function of HCl-loss. From the latter plots we have obtained numerical values for the initial and minimum rates, W_0 and W_m , respectively, and for the slopes S of the lines in the region of autocatalysis i. e., above 2-8% HCl loss, a measure of the autocatalytic effect. The data are compiled in Table 5. Evidently, the initial and minimum rates as well as the S values of the controls are higher than

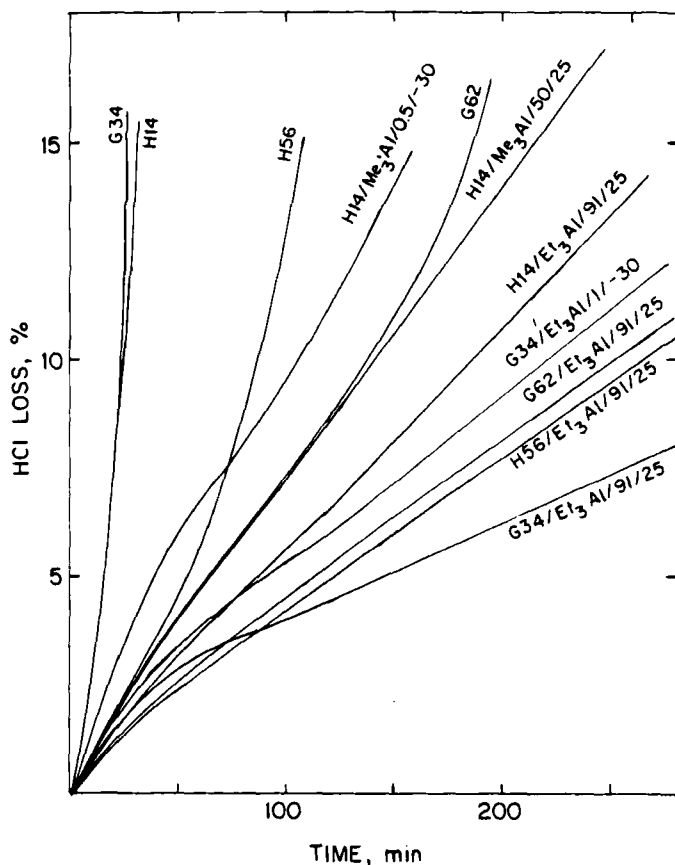


FIG. 4. Dehydrochlorination of Et_3Al and Me_3Al treated and untreated PVC powders at 220°C . For key, see Fig. 1.

those of the R_3Al -treated samples. Indeed, the S values clearly indicate the essential disappearance of autocatalytic dehydrochlorination in all R_3Al -treated materials.

A detailed inspection of the data in Fig. 4, or more conveniently in Fig. 5, shows that the untreated H56 sample exhibited decreasing rate initially, but turned accelerating at about 2% HCl loss. The G62 sample had a higher initial rate, reached at about 4% HCl loss a lower steady state rate, and at about 8% HCl loss turned autocatalytic. In comparison, the G62 sample degraded at 190°C for an

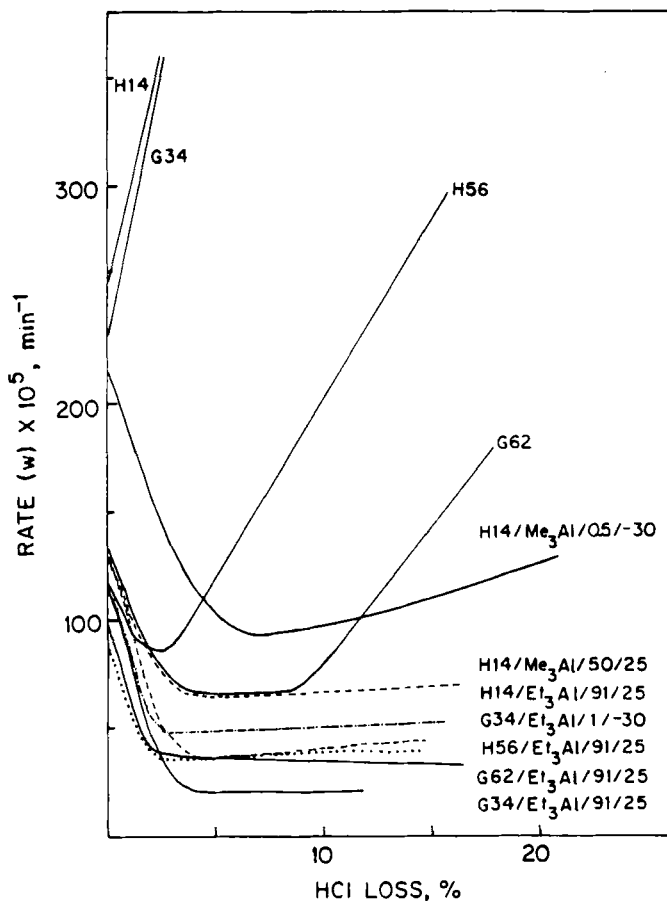


FIG. 5. Dependence of dehydrochlorination rate on percent HCl loss at 220°C. For key, see Fig. 1.

exceptionally long time to reach high conversion and showed decreasing rate up to 4%, but then the rate remained practically constant until the end of the experiment (17%) (Fig. 6). The alkylaluminum-treated samples showed, even at 220°C, no or only slight acceleration. At this high temperature the initial rates of all alkylaluminum-treated samples are lower than those of the corresponding controls.

In this context we may consider earlier observations on the effect of alkylaluminum used for grafting on PVC. Thame et al. [9] observed

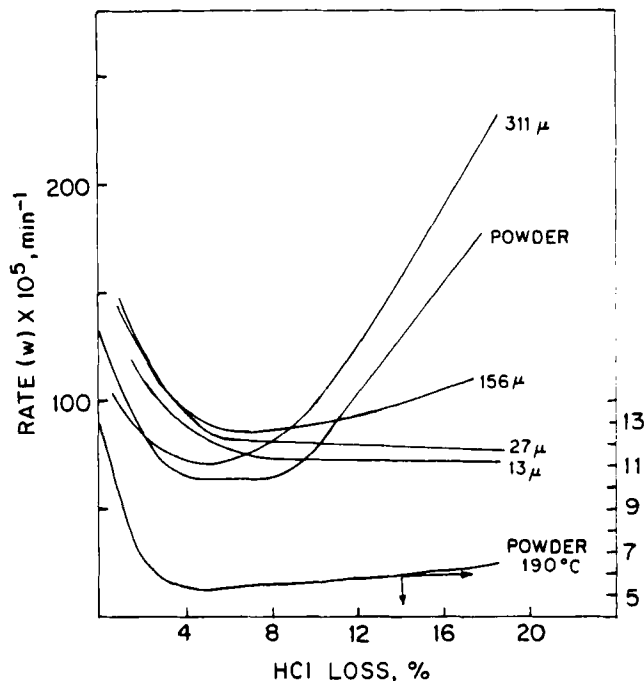


FIG. 6. Effect of film thickness on dehydrochlorination of untreated G62 at 220°C. Approximate film thickness in μm .

a significant lowering of dehydrochlorination rates of alkylaluminum-treated samples compared to those of untreated ones; however, later it has been reported [10, 11] that the difference is rather small and sometimes inconsistent. Fundamental differences between the experimental procedures used by the above authors may explain these discrepancies. While the former authors' main emphasis was on the results of dehydrochlorination rates obtained at a much higher temperature (270°C) and at higher conversions ($> 10\%$) the latter workers reported their results obtained at lower temperatures (170, 190°C) and at lower conversion range ($< 0.5\%$). Our results, which show that the higher the conversion and temperature the larger the difference between the dehydrochlorination rates of treated and untreated samples (mainly because of the disappearance of autocatalysis in the treated samples), can bridge the gap.

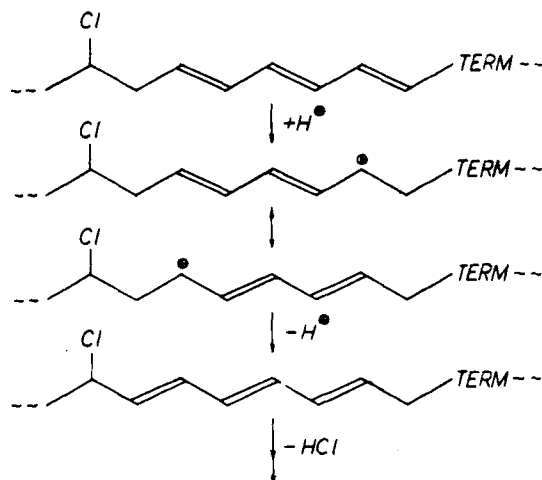
HCl Catalysis and Thin Film Studies

The catalytic effect of HCl on PVC dehydrochlorination has been widely reported [26-28]. There are also reports concerning HCl-polyene interaction to cause catalytic dehydrochlorination of model compounds [31] and PVC [30]. Dependence of autocatalysis on diffusion rate of HCl has been reported, [27, 42]. Comparison of the data in Table 5 shows close correlation between polyene length and autocatalytic behavior. If acceleration of HCl loss requires the presence of a critical concentration of both long polyene chains and HCl in the polymer matrix, then catalyzed dehydrochlorination would not occur even at high concentrations of HCl with low average polyene chain length. Similarly, the acceleration would also be absent if the rate of HCl evolution is slow so that the concentration of HCl in the polymer matrix cannot reach the critical level due to diffusion. Even at higher rates, if the particle size or film thickness is low enough so that the diffusion rate of HCl is highly competitive with the rate of evolution of HCl, there should also not be any acceleration. A combination of these reasons may explain the disappearance of acceleration with aluminumalkyl treated samples. To verify the last statement, a series of experiments with films of various thickness of the same PVC sample (G62) were made. The results are shown in Fig. 6, which plots the rate of dehydrochlorination as a function of percent dehydrochlorination. Evidently the extent of autocatalysis increases with increasing film thickness, and with very thin films (13 and 27 μm) acceleration completely vanishes.

It is difficult to explain the sudden onset of acceleration in a range where HCl evolution tends to decrease without assuming the participation of polyenes in this process (Figs. 5 and 6). Considering differences in the rate of increase of polyene contents in different samples, they will reach critical conditions for the onset of acceleration at different stages of degradation.

Several mechanisms for HCl catalysis have been developed [12, 26-30], but the role of polyenes remains obscure. HCl catalysis may involve reactivation of polyenes by protonation-deprotonation. Irrespective of the chemistry of zipping termination, at one end of the polyene sequence will arise a terminating group (TERM) and at the beginning of it a $\sim\text{CHCl}-\text{CH}_2-\text{CH}=\text{CH}\sim$ group. The conjugated polyene system may be isomerized by protonation-deprotonation and thus secondary chlorines may be transformed into allylic chlorines. The new allylic chlorine at the end of a long conjugated polyene sequence could then resume further zipping. This proposition is illustrated in Eq. (1). Proton exchange should occur more readily with longer polyenes, thus explaining the correlation between autocatalytic dehydrochlorination and polyene length (Table 5).

This mechanism is supported by data of Tüdös and Kelen [2], who



found that fast proton exchange occurs between tritium-labeled HCl and polyenes and that the tritium content can only be partially re-exchanged to protons, i. e., a certain portion of the tritium becomes permanently bound to PVC. If polyene shift and zipping re-initiation (i. e., polyene growth) involve a polyene which contains a tritium on the first carbon of the polyene sequence, then this tritium atom will become permanently attached to the polymer and will find itself in the middle of a polyene sequence.

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