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Mechanism of Reaction of Poly(vinyl Chloride) with Triethylaluminum

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ABSTRACT

Poly(vinyl chloride) was treated with triethylaluminum in 1,2-dichloroethane solution. Negligibly small amounts of hydrogen chloride are evolved from the modified poly(vinyl chloride) in decomposition at 180°C for 150 min in nitrogen. Quantitative analysis of the rate of dehydrochlorination of the modified polymer gave a calculated activation energy for the alkylation of 8.3 kcal/mole in 1,2-dichloroethane solution; the concentration of the labile chlorines in the original poly(vinyl chloride) was less than 0.25 mole %. Furthermore, the fact that the average polyene length of the modified polymer for the thermal decomposition was much shorter than that of the starting material suggests that the labile chlorines inherent in the polymer exist not only in the chain end but also in the polymer chain.

INTRODUCTION

Poly(vinyl chloride) (PVC) is a widely used plastic material which has found a variety of uses. A serious drawback during processing and in use of PVC, however, is the decomposition accompanied by discoloration of the resin and deterioration of the physical properties. Stabilizers are added to the polymer in order to retard the thermal dehydrochlorination as well as to scavenge the evolved hydrogen chloride, which commonly includes metal compounds, such as lead, calcium, cadmium, barium, and zinc compounds. The disadvantage of such added stabilizers includes their potential toxicity, color, incompatibility, and extractability. The synthesis of thermally stable PVC has been the subject of extensive recent research [1-8].

In a previous paper [1], we have pointed out that PVC prepared with the triethylaluminum-Lewis base-carbon tetrachloride catalyst system shows thermal stability much superior to that of commercial PVC, suggesting that the thermally unstable structures of the polymer react with triethylaluminum to give thermally stable structure on the polymerization process.

Several recent publications have dealt with modifications of PVC by organoaluminum compounds to improve the heat stability of the polymer, i.e., graft modification of PVC with alkylaluminum compounds [2, 3], phenylation of PVC by triphenylaluminum [4], and reaction of PVC with dialkylaluminum halides followed by treatment with low alkanols [5]. Miller [6] and Kennedy [7] have reported that trialkylaluminum easily reacts with halohydrocarbons, in particular, tertiary alkyl halides, to give alkylated hydrocarbons.

In the present investigation, PVC was treated with triethylaluminum in 1,2-dichloroethane solution. The reaction mechanism of triethylaluminum with PVC and the concentration of the labile chlorines in PVC are discussed on the basis of quantitative analysis for the rate of dehydrochlorination of the modified PVC decomposed at 180°C in nitrogen.

EXPERIMENTAL

Materials

All experiments were carried out with commercial PVC (San Arrow Co. Ltd., Japan, $\bar{P}_w = 820$), prepared by suspension polymerization. 1,2-Dichloroethane (EDC) was washed in a separatory funnel with sulfuric acid, pure water, aqueous sodium hydroxide, and pure water in this order, and then dried over calcium hydride, distilled, and stored in argon. 1.4-Dioxane and tetrahydrofuran were dried over lithium aluminum hydride, distilled, and stored under an argon atmosphere. Triethylaluminum (Et_3Al) (Ethyl Corporation, Co. Ltd.) was used without further purification.

Treatment of PVC with Et_3Al

The reaction was carried out in a glass flask with stirrer. PVC was dissolved at 60°C in 40 ml EDC under argon atmosphere. The vessel was maintained at a selected temperature, and the described amounts of Et_3Al in EDC solution were added. After the reaction the product was poured into a methanol-hydrochloric acid mixture, washed several times with methanol, and dried in vacuo at 50°C.

Analysis of PVC Samples

The intrinsic viscosity of polymer was measured in a Ubbelohde type viscometer at 25°C in tetrahydrofuran solution. The molecular weight distribution of polymer was measured at 23°C in tetrahydrofuran solution by using a Waters Type 200 gel-permeation chromatograph. The double bond content of the polymer was determined on the basis of the method proposed by Morikawa [9]. Head-to-head linkages were determined according to the method of Ohtsu [10].

Degradation of PVC

The PVC samples were thermally decomposed at 180°C in a stream of pure nitrogen, 50-60 ml/min. The quantity of hydrogen chloride evolved, which was absorbed in water, was read off on a pH meter. PVC films, about 70 μ thick, contained in evacuated thin-walled cells with quartz windows were heated at 150°C. The absorbance of the films was measured in a Hitachi Type 323 spectrometer.

RESULTS AND DISCUSSION

PVC treated with Et_3Al in EDC solution was characterized (Table 1). In the reaction of triethylaluminum with haloalkanes, haloalkanes are reported to undergo alkylation, coupling, and β-elimination; the relative extent of these reactions depends on the experimental conditions [6-7]. In this regard, it should be mentioned that no change in molecular weight was revealed by the intrinsic viscosity and gel-permeation chromatography measurements of the PVC samples treated with Et_3Al, except for sample VX3. In addition, the number of the double bonds of the modified polymer was almost 0.8 per chain as well as that of the starting material, suggesting that no addition of Et_3Al to the double bonds of PVC has occurred.

In the reaction of excess Et_3Al with PVC in EDC solution, therefore, alkylation of PVC predominated, but addition of a small amount of Et_3Al caused dehydrochlorination of PVC.

TABLE 1. Analysis of PVC treated with Et_3Al[a]

Sample	Et_3Al (mmole)	Reaction temp (°C)	Reaction time (hr)	$[\eta]$	$\overline{M}_w/\overline{M}_n$	Rate of dehydrochlorination K_{HCl} (mole HCl/g PVC-min$\times 10^7$)
CM[b]	-	-	-	0.73	2.0	14.6
VX1	0.5	0	2	0.73	2.0	13.5
VX2	3.0	0	1	0.73	2.0	9.3
VX3[c]	0.1	25	1	0.78	2.3	109.5
VX4	0.5	25	2	0.73	2.0	12.0
VX5	0.5	25	6	0.73	2.0	5.9
VX6	1.0	45	2	0.73	2.0	6.4
VX7	3.0	45	2	0.72	2.0	1.3
VX8	0.5	45	4	0.73	2.0	4.2
VX9	0.5	65	1	0.73	2.0	8.8
VX10	0.5	65	2	0.73	2.0	3.3
VX11	2.0	65	1	0.72	2.0	0.9

[a] A 2.0 g portion of PVC was dissolved in 40 ml EDC.
[b] Commercial PVC ($\overline{P}_w = 820$).
[c] Sample was decomposed.

Effect of Et_3Al Concentration

Figure 1 shows the kinetic curves of dehydrochlorination of PVC samples, treated with Et_3Al at 60° C for 2 hr and then decomposed at 180° C in nitrogen, as a function of Et_3Al concentration. The modified PVC exhibits improvement in thermal stability over unmodified PVC. The extent of the improvement increases with the amount of Et_3Al at Et_3Al concentrations more than 0.2 mmole to 32 mmole PVC, but the sample treated with 0.1 mmole Et_3Al leads to increased heat sensitivity (sample VX3 in Table 1); optimum stabilization of the modified PVC is achieved only when Et_3Al is used in high concentrations and at a closely regulated ratio to PVC. These results are the very important in investigating the reaction mechanism of Et_3Al with PVC by analyzing the rate of dehydrochlorination of the modified PVC

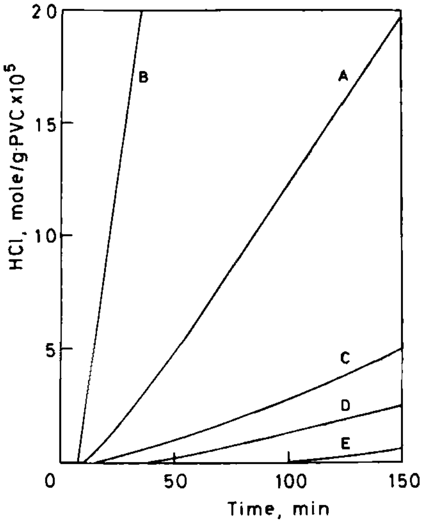


FIG. 1. Thermal decomposition at 180° C in nitrogen of PVC samples treated with Et_3Al: (A) purified commercial PVC; (B) sample VX3; (C) sample VX10; (D) sample VX7; (E) sample VX11 (data from Table 1).

samples. The amount of hydrogen chloride evolved is not necessarily linearly related to the heating time, due to the fact that the induction period depends on the Et_3Al concentration, and so the slope of the plots was regarded as a measure of the thermal stability of the modified polymer.

The rate of dehydrochlorination of the modified PVC is plotted against the Et_3Al concentration in Fig. 2. At relatively low concentrations of Et_3Al, the rate of dehydrochlorination obeys good first-order kinetics to the Et_3Al concentration. Thus, based on the following assumptions, we considered the reaction kinetics of Et_3Al with PVC.

Et_3Al is assumed to react primarily with the labile chlorines in PVC, due to the fact that the rate of dehydrochlorination of the modified polymer decreases with an increase in the reaction time, reaction temperature, and the amount of Et_3Al. Miller [6] and Kennedy [7] have reported that trialkylaluminum reacts with tertiary alkyl halides and allyl chloride compound to give alkylated hydrocarbons much more easily than primary and secondary haloalkanes.

The deleterious effect of the accumulation of Et_2AlCl, generated by the reaction of Et_3Al with PVC, functions to catalyze the rapid degradation of PVC. As shown in Fig. 3, this assumption was based

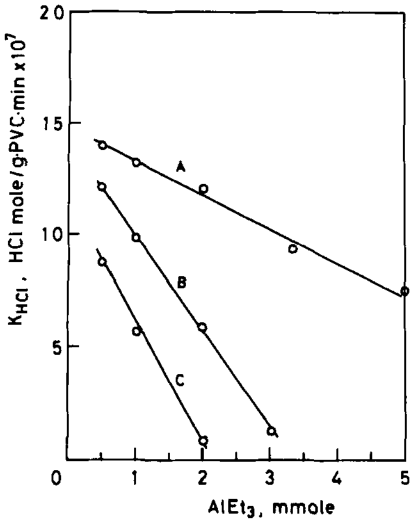


FIG. 2. Rate of dehydrochlorination of PVC treated at various temperatures with Et_3Al and decomposed at 180° C in nitrogen: (A) 0° C; (B) 45° C; (C) 65° C. PVC concentration, 2.0 g/40 ml EDC.

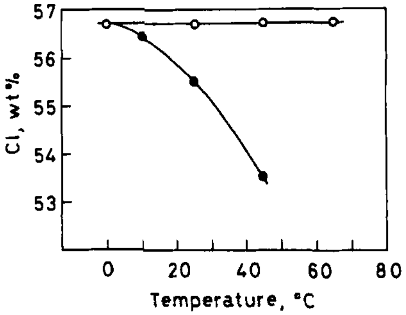
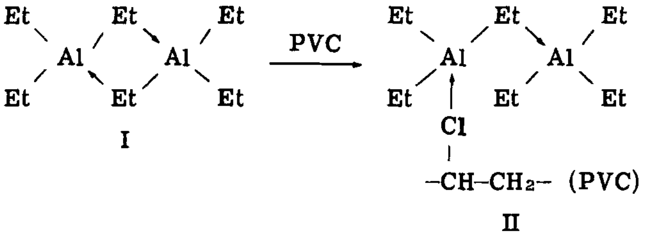


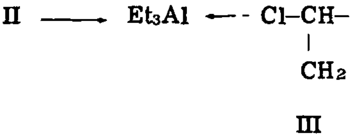
FIG. 3. Chlorine content of PVC samples treated with Et_3Al and Et_2AlCl: (○) Et_3Al; (●) Et_2AlCl. PVC concentration, 2.0 g/40 ml EDC.

on the fact that the chlorine content of PVC samples reacted with Et_3Al at temperatures in the range from 0 to 70° C, was constant, but in the presence of Et_2AlCl, the dehydrochlorination reaction of PVC proceeds vigorously and results in the decrease in the chlorine content of the polymer.

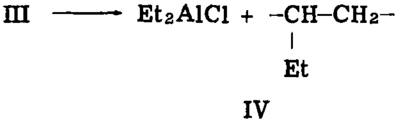
The reaction of Et_3Al with PVC is assumed to obey the mechanism shown in Eqs. (1)-(4).



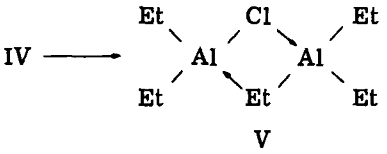
(1)



$$\mathrm{II} \longrightarrow \mathrm{Et_3Al} \leftarrow \mathrm{Cl{-}}\underset{\displaystyle \mathrm{CH_2}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}} \qquad \mathrm{III} \tag{2}$$



$$\mathrm{III} \longrightarrow \mathrm{Et_2AlCl} + \mathrm{{-}}\underset{\displaystyle \mathrm{Et}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}} \qquad \mathrm{IV} \tag{3}$$



(4)

The processes in Eqs. (1)-(3) have been proposed by J. P. Kennedy and co-workers in the reactions of trimethylaluminum with tert-butyl halides [7] and of triphenylaluminum with PVC [4]. Et_2AlCl produced in Eq. (4) is dimeric in the liquid state and in solution, in similar to Et_3Al, which is assumed to be complex (V) under the condition of $Et_3Al/Et_2AlCl \geqq 1$. In addition, attack of complex V on PVC is assumed to be significantly slower than that of complex I on PVC. This assumption was verified by the results in Table 2; i.e., in the conditions of $Et_2AlCl/Et_3Al \geqq 1$, the polymer decomposes as soon as the mixture of Et_3Al and Et_2AlCl is added to the reaction system, and at high temperatures PVC treated with dilute Et_3Al solution starts to discolor gradually with increasing the reaction time.

Furthermore, the next experimental evidence may justify the above assumption. When Et_3Al is present at 24°C in a free state, Et_3Al is

TABLE 2. Effect of Mixture of Et_3Al and Et_2AlCl on the Thermal Stability of Modified PVC Samples

Et_3Al (mmole)	Et_2AlCl (mmole)	Reaction temp (°C)	Reaction time (min)	K_{HCl} (mole HCl/ g PVC-min × 10^7)
1.0	0.7	45	60	14.0
1.0	0.7	65	60	12.1
1.0	0.8	10	120	-[c]
1.0	0.8	25	60	-
1.0	1.0	25	30	-
1.0	1.0	65	10	-
1.0	1.5	25	5	-
1.0	1.5	65	5	-

[a] A 2.5 g portion of PVC was dissolved in 40 ml EDC.
[b] Rate of dehydrochlorination.
[c] Sample was decomposed.

dimeric, and an exchange reaction of ethyl groups of Et_3Al in both bridging and terminal positions occurs at a sufficiently high rate, and so only one type of signal of Et_3Al should be observed in the NMR spectrum as shown in Fig. 4A. In addition, Et_3Al mixed with Et_2AlCl forms a dimeric complex, not only with Et_3Al but also with Et_2AlCl, to give one type of signal of ethyl groups due to the high rate of exchange reaction of ethyl groups, and the internal chemical shift between the methyl and the methylene positions of the mixture of Et_3Al and Et_2AlCl is expected to correspond to the weight mean value of the complex in Et_3Al and Et_2AlCl as shown in Fig. 4B. Addition of excess dioxane with Lewis basicity to the mixture of Et_3Al and Et_2AlCl, however, breaks these dimers to give a stable complex of dioxane with Et_3Al and Et_2AlCl, respectively, and so two types of ethyl groups should be observed in Fig. 4C.

On the basis of the above assumption, the following equations were established.

$$[PVC]_0 + 2\,[Et_3Al] = [PVC]_s + [PVC]_n + [Et_3Al + Et_2AlCl] \tag{5}$$

$$[PVC]_0 = [PVC]_s + [PVC]_n \tag{6}$$

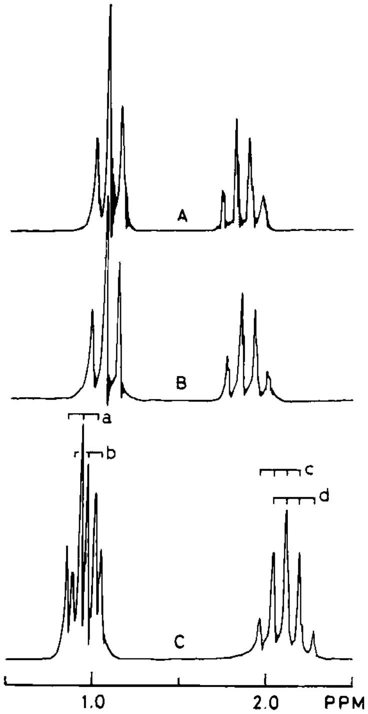


FIG. 4. The 100-MHz NMR spectra of (A) Et_3Al, (B) a mixture of Et_3Al and Et_2AlCl in equimolar solutions and (C) addition of excess dioxane to mixture of Et_3Al and Et_2AlCl, respectively. a and b are the methyl protons of Et_3Al and Et_2AlCl, respectively; c and d are the methylene protons of Et_3Al and Et_2AlCl, respectively.

where $[PVC]_0$, $[PVC]_s$, and $[PVC]_n$ are the concentrations of the starting polymer, of the modified PVC, and of the unreacted PVC, respectively.

Here, we defined the fraction of the labile chlorines inherent in the starting polymer, α. If the concentration of Et_3Al is larger than $2\alpha[PVC]_0$, the amount of the stabilized polymer at the ambient reaction time t, is expressed as follows:

$$[PVC]_s = K[PVC]_0[Et_3Al]t \tag{7}$$

where K is the rate constant.

Substituting the above expression for $[\mathrm{PVC}]_s$ into Eq. (6) yields the Eq. (8):

$$([\mathrm{PVC}]_0 - [\mathrm{PVC}]_n)/[\mathrm{PVC}]_0 = K[\mathrm{Et_3Al}]t \tag{8}$$

As shown in Fig. 2, the rate of dehydrochlorination of the modified polymer decreases with an increase in the amount of Et_3Al, and evolution of hydrogen chloride from well stabilized PVC is negligible on heating at 180°C for 150 min in nitrogen. Accordingly when the rates of dehydrochlorination of the starting polymer and of the unreacted PVC are expressed by K_{HCl}^0 and K_{HCl}, respectively, the molar ratio of the unreacted PVC to the starting polymer is represented by Eq. (9):

$$[\mathrm{PVC}]_n/[\mathrm{PVC}]_0 = K_{HCl}/K_{HCl}^0 \tag{9}$$

Substituting in Eq. (8) yields

$$(K_{HCl}^0 - K_{HCl})/K_{HCl}^0 = k[\mathrm{Et_3Al}]t \tag{10}$$

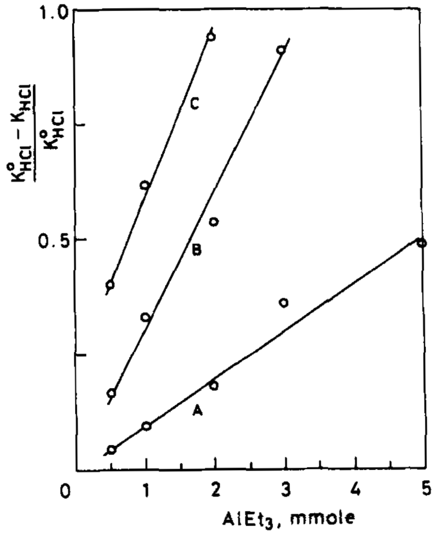


FIG. 5. Plot of $(K_{HCl}^0 - K_{HCl})/K_{HCl}$ against the Et_3Al concentration with reaction at various temperatures: (A) 0°C; (B) 45°C; (C) 65°C.

TABLE 3. Effect of the Et_3Al Concentration on the Thermal Stability of PVC[a]

Et_3Al (mmole)	Reaction temp (°C)	Reaction time (min)	K_{HCl} (mole HCl/g PVC-min × 10^7)
0.5	65	120	1.5
0.4	0	180	14.2
0.4	65	60	11.0
0.3	0	80	-[b]
0.3	45	25	-
0.3	65	10	-
0.2	0	50	-
0.2	65	5	-

[a] A 3.75 g portion of PVC was dissolved in 40 ml EDC.
[b] Samples were decomposed.

By using Eq. (10), $(K_{HCl}{}^0 - K_{HCl})/K_{HCl}{}^0$ was plotted against the Et_3Al concentration in Fig. 5, in which two functions are in a linear relationship.

Equation (10) is inapplicable to the rate of dehydrochlorination of PVC treated with dilute Et_3Al concentration, because the modified PVC starts to decompose with the progress of reaction under the deleterious effect of Et_2AlCl when the concentration of Et_2AlCl accumulated is more than that of Et_3Al. Accordingly, the rate of dehydrochlorination of the modified PVC (K_{HCl}) becomes much larger than that of the starting polymer ($K_{HCl}{}^0$). The reaction time at which the modified polymer starts to decompose and show discoloration was investigated as a function of Et_3Al concentration and reaction temperature. The results are summarized in Table 3. At relatively low temperatures the modified PVC difficultly decomposes even at very low cencentrations of Et_3Al.

Regardless of reaction temperature, however, it can be assumed that addition of Et_3Al at levels below 0.5 mmole to 60 mmole of PVC induces decomposition of PVC. Therefore, assuming the formation of complex V in the reaction of Et_3Al with PVC, the amount of the labile chlorines present in the initial PVC may be estimated to be about 0.25%, which is much smaller than the level predicted by Thame [2]. This discrepancy probably is due to the differences in the species of the starting polymer, of the reaction medium, and of the method of analysis of the modified PVC. This estimated value, however, is assumed to be highly accurate as the following experimental evidences show.

Addition of 1.0 mmole Et_3Al and 0.8 mmole Et_2AlCl to 40 mmole PVC induces the decomposition of the polymer, but addition of 1.0 mmole Et_3Al and 0.7 mmole Et_2AlCl gives the stabilized polymer, as shown in Table 2. Thus, assuming the equimolar complex formation of Et_3Al and Et_2AlCl, the amount of Et_2AlCl produced in the reaction of Et_3Al with PVC is deduced to be below 0.1 mmole, i.e., the probable level of the labile chlorines in PVC is below 0.25 mole % of the total chlorines.

The suspension-polymerized PVC used in this experiment contains only 2.0 double bonds and about 6-7 head-to-head linkages per 1000 monomeric units [11], of which the latter is assumed to be unreactive to Et_3Al due to the fact that no attack of Et_3Al was observed to chlorinated polybutadiene, is a model compound for head-to-head PVC. The number of branches varies between 4 and 18 per 1000 carbon atoms, depending on the conditions of polymerization [12-15], but the experimental results of the determination of branches and of the

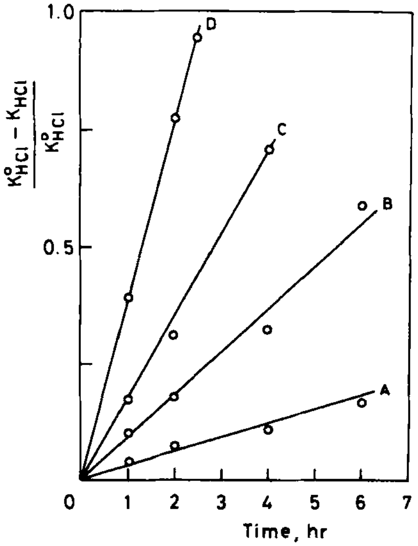


FIG. 6. Relation between $(K_{HCl}^0 - K_{HCl})/K_{HCl}^0$ and reaction time at various reaction temperatures: (A) 0°C; (B) 25°C; (C) 45°C; (D) 65°C.

thermal degradation of PVC have indicated negligibly small amount of tertiary chlorine atoms in PVC [16-18].

Effect of Temperature

The rate of dehydrochlorination of the modified PVC was plotted against the reaction time as a function of the reaction temperature in Fig. 6.

The logarithmic values of $(K_{HCl}^0 - K_{HCl})/K_{HCl}^0$ versus 1/T gave a straight line, the slope of which allowed calculation of the overall activation energy. The apparent activation energy of the reaction of Et_3Al with PVC in EDC solution was 8.3 kcal/mole, which is slightly lower than that (10 kcal/mole) in the reaction of trimethylaluminum with tert-butyl chloride in methyl chloride solution as reported by Kennedy [7]. This difference is probably due to the difference in the ratio chemical species: solvent, organoaluminum compound, and reactant.

Polyene Distribution

Films of the modified PVC were decomposed at 150° C in nitrogen.

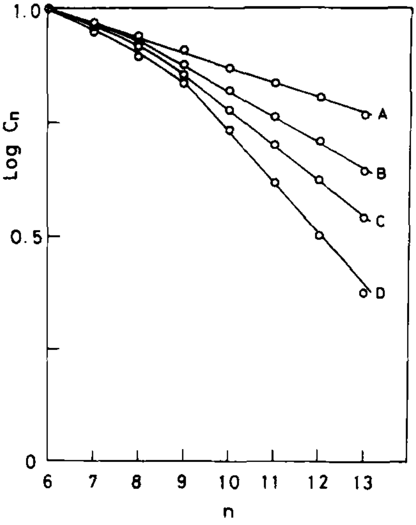


FIG. 7. Logarithm of concentrations of polyenes C_n vs. polyene length: (A) commercial PVC; (B) sample VX4; (C) sample VX8; (D) sample VX11 (data from Table 1).

TABLE 4. Average Polyene Length of the Modified PVC Samples[a]

Et_3Al (mmole)	Reaction temp (°C)	Reaction time (hr)	Average polyene length $\bar{n}$
-	-	-	14.3
0.5	25	2.0	8.5
0.5	45	2.0	5.9
1.0	65	2.0	4.8
2.0	65	1.0	4.3

[a] A 2.0 g portion of PVC was dissolved in 40 ml EDC.

Figure 7 shows the logarithmic concentration of polyenes against their length, and with sequences more than eight double bonds, gives a straight line whose slope allows calculation of the average polyene length [19]:

$$\log C_n \propto (n - 1) \log k \tag{11}$$

$$\bar{n} = 1/(1 - k) \tag{12}$$

where C_n is the concentration of a polyene of length n, k is the propagation probability of polyene, and $\bar{n}$ is the average length of polyene. The results were listed in Table 4.

In the unreacted PVC, there is a good linearity between the length of polyene sequences, n = 5-13, and the logarithm of polyene concentrations, whereas in the modified PVC the polyene length with sequences more than 8 or 9 conjugated double bonds lies on a single straight line when plotted against the logarithm of concentration of polyenes. In addition, the modified PVC gives the exceedingly thermal stability for decomposition, and short polyenes. These evidences may suggest that the labile chlorines in PVC to react with Et_3Al exist not only at the chain end but also in the polymer chain.

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