Polymerization Mechanism of Vinyl Chloride with Trialkylaluminum-Lewis Base Catalyst and Thermal Stability of Poly(vinyl Chloride)

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ABSTRACT

The mechanism of vinyl chloride polymerization by the tri-ethylaluminum-Lewis base-carbon tetrachloride catalyst system and the thermal stability of the resulting polymer were investigated. When the Lewis base is multidentate, the resultant complex with triethylaluminum shows significantly high catalytic activity for radical polymerization of vinyl chloride in the presence of carbon tetrachloride to give a white powder with high molecular weight. Carbon tetrachloride accelerates the rate of polymerization and participates in an initiating process rather than in a propagating step. The thermal stability of the polymer prepared with this catalyst system is much superior to that of commercial poly(vinyl chloride), although the numbers of the double bonds in a chain end and of the head-to-head linkage are similar in both samples, suggesting that the thermally unstable structures of the former react with triethylaluminum to give the thermally stable structure on the polymerization process.

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INTRODUCTION

In the polymerization of vinyl chloride with organometallic compounds nucleophilic compounds are mostly combined with them to prevent the reaction of the initiators with the resulting polymer. Breslow and co-workers [1] have reported that a complex of organo-aluminum compounds with various Lewis bases is an active catalyst for vinyl chloride polymerization and that the polymerization rate is accelerated by carbon tetrachloride (CCl_4). They have also investigated the effect of the organometallic compounds, ligands, and solvents on the polymerization process.

The authors [2] have found that with the use of a multidentate Lewis base as the complexing agent, the trialkylaluminum-Lewis base-CCl_4 catalyst system induces significantly high catalytic activity for vinyl chloride polymerization and also that the thermal stability of the polymer produced is superior to that of commercial poly(vinyl chloride) (PVC) prepared with peroxide catalyst. Akimoto [3] has also reported that complex triethylaluminum ($AlEt_3$) formed with oligo-amine in the presence of CCl_4 shows high catalytic activity for vinyl chloride polymerization. However, no detailed investigation of the initiating process with this complex catalyst and of the structure of the resulting polymer has been attempted.

It is of considerable interest from the viewpoint of organometallic chemistry to investigate the polymerization mechanism of vinyl chloride using $AlEt_3$-CCl_4 catalyst in the presence of multidentate Lewis base. Furthermore, from an industrial viewpoint, vinyl chloride polymerization with this catalyst system is especially interesting in development of thermally stable PVC on the polymerization process.

We report here a study of the mechanism of polymerization of vinyl chloride with $AlEt_3$-multidentate Lewis base-CCl_4 catalyst. The reactions of $AlEt_3$ with CCl_4 and Lewis base have been examined by using NMR spectroscopy, in order to clarify the enhanced catalytic activity. Finally, we consider why the thermal stability of the polymer prepared with this catalyst system is superior to that of commercial PVC.

EXPERIMENTAL

Materials

Methylene chloride, 1,2-dichloroethane, and carbon tetrachloride were washed in a separatory funnel with sulfuric acid, pure water, aqueous sodium hydroxide, and pure water in that order, and then dried over calcium hydride, distilled, and stored in argon. Benzene, 1,4-dioxane, and tetrahydrofuran were dried over lithium aluminum hydride, distilled, and stored over calcium hydride under an argon atmosphere. $AlEt_3$ (Ethyl Corporation, Co. Ltd.) was used without further purification as benzene solution. Vinyl chloride monomer (VC)

was dried by passage through a column filled with calcium chloride. The other chemicals were distilled under reduced pressure.

Polymerization Procedure

All polymerization runs were carried out by using 150-ml sealed glass ampoules, which were placed in the thermostatted bath maintained at 40°C. After the mixture of AlEt₃ and Lewis base was aged at room temperature for 10 min under an argon atmosphere, the ampoule was cooled to -78°C, and CCl₄ was added, and then argon was released and VC was introduced. After all monomer had been distilled into the ampoule, the glass-tube neck was sealed and placed in a water bath. After a predetermined time, the contents of the ampoule were poured into a methanol-hydrogen acid mixture, washed several times with methanol, and dried under vacuum at 50°C.

Analysis of PVC

The molecular weight of PVC was determined by Kobayashi's equation [4]

$$[\eta] = 1.63 \times 10^{-4} M_w^{0.766}$$

at 25°C in tetrahydrofuran solution.

The molecular weight distribution of polymer was measured at 23°C in tetrahydrofuran solution by use of a Waters Type 200 gelpermeation chromatograph.

Proton NMR spectra were obtained on 7-8% solutions of PVC in o-dichlorobenzene at 165°C, and recorded with Varian HR-220 and JEOL-4H-100 spectrometers.

The double bond of polymer was determined on the basis of the method proposed by Morikawa [5].

The head-to-head linkage of PVC was determined according to the method of Ohtsu [6].

Degradation of PVC

Thermogravimetry data were obtained by using a Rigaku Denki thermogravimetric analyzer on 15 mg samples in air. The heating rate was 10°C/min.

The rate of dehydrochlorination of PVC samples, which were thermally decomposed at 180°C in nitrogen, was investigated by the method described in the previous paper [7].

PVC films, 70 μm thick, were heated at 150°C in evacuated thin-walled quartz cell unit windows. The absorbance of the films was measured in a Hitachi Type 323 spectrometer.

Treatment of PVC with AlEt₃

Reaction was carried out in a glass flask with stirrer. A 2.0-g portion of commercial PVC (San Arrow Co. Ltd., P_w = 820) was dissolved at 60°C in 40 ml in 1,2-dichloroethane under argon atmosphere. The vessel was maintained at 40°C, and described amounts of AlEt₃ were added. After 2 hr the product was poured into a methanol-hydrochloric acid mixture, washed several times with methanol, and dried under vacuum at 50°C.

RESULTS AND DISCUSSION

Polymerization Mechanism

Vinyl chloride is smoothly polymerized in bulk by the AlEt₃-ethers or esters-CCl₄ catalyst system to give a white precipitate. Figure 1 shows the effect of CCl₄ concentration on polymerization conversion
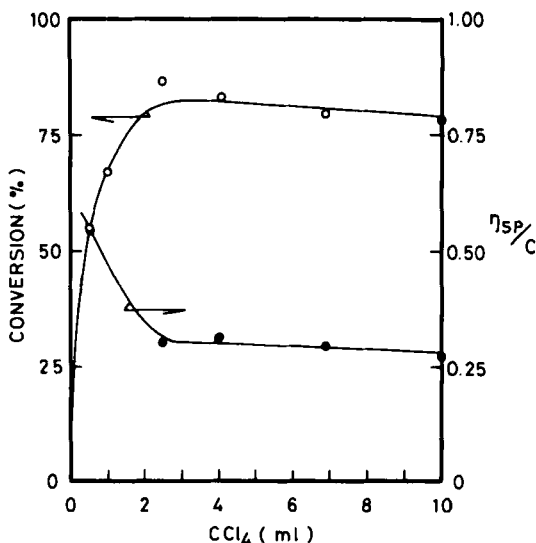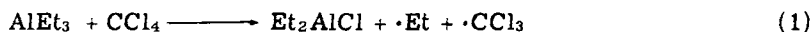

FIG. 1. Effect of CCl₄ concentration on (○) polymerization conversion and (●) reduced viscosity of PVC as 0.1% tetrahydrofuran solutions. Vinyl chloride (21 g) was polymerized at 40°C for 3 hr with AlEt₃ (4.0 mmole)-tetraethyleneglycol dimethyl ether (4.0 mmole) complex.

and molecular weight of PVC. The polymer yield increases with the quantity of CCl_4 and reaches a maximum at addition of 2.5 ml CCl_4 (about 26 mmole). On the other hand the reduced viscosity decreases at the first stage of carbon tetrachloride addition and becomes independent of CCl_4 concentration at concentrations above 2.5 ml which the polymer yield levels off. The polymer yield decreases markedly when chloroform or methyl chloride is used instead of CCl_4.

Acceleration of the rate of polymerization by CCl_4 has been reported on the polymerization of vinyl chloride with $Ti(OBu)_4$-$EtAlCl_2$ [8] and $AlEt_3$-CuCl [9] complexes, in which CCl_4 participates in the initiating process rather than in a propagating reaction.

In order to clarify the initiation mechanism of the $AlEt_3$-CCl_4 complex, the reaction of $AlEt_3$ with CCl_4 was investigated with the aid of NMR spectroscopy, and the results are given in Fig. 2 (the peak of methylene chloride protons was used as an internal reference). Peaks a and c were assigned to the methylene and methyl protons, respectively, of the starting triethylaluminum. Peaks b and d were assigned to the methylene and methyl protons, respectively, of Et_2AlCl. At room temperature $AlEt_3$ reacts smoothly with CCl_4 to give Et_2AlCl and by-products such as ethane, ethylene, ethyl chloride, and 1,1,1-trichloropropane. The fact that the amount of Et_2AlCl is independent of the CCl_4 concentration above 3 times the molar quantity (Fig. 2B and 2C) corresponds nearly to the dependence of the polymer yield on the CCl_4 concentration in Fig. 1. Et_2AlCl can also react with CCl_4 to give $EtAlCl_2$, but the reaction rate of Et_2AlCl with CCl_4 is about one-fifth of that of $AlEt_3$ with CCl_4.

This evidence suggests that in the reaction with CCl_4, $AlEt_3$ produces initiating radicals according to the mechanism proposed by Breslow et al. [1].

$$AlEt_3 + CCl_4 \longrightarrow Et_2AlCl + \cdot Et + \cdot CCl_3 \qquad (1)$$

$$\cdot Et + CCl_4 \longrightarrow EtCl + \cdot CCl_3 \qquad (2)$$

In dilute concentration of CCl_4, the overall rate of polymerization is first order and square-root order with respect to the VC and CCl_4 concentrations, respectively:

$$R_p = K[VC]^{1.0}[CCl_4]^{0.5}[AlEt_3]^{\alpha} \qquad (3)$$

where R_p is the overall rate of polymerization, K is a constant, and α is 0.7-1.2.

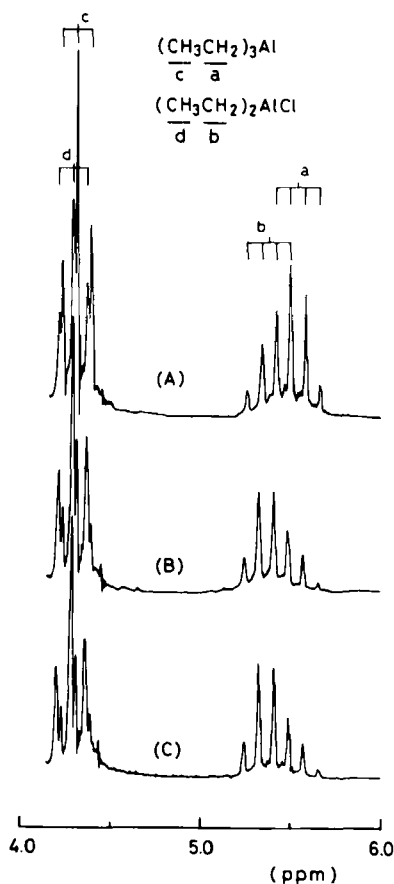As Fig. 3 shows, the exponent α decreases gradually with an

FIG. 2.   100-MHz NMR spectra of AlEt₃ reacted with CCl₄ at 24°C for 24 hr in methylene chloride solution with 5 mmole AlEt₃ and (A) 5 mmole CCl₄; (B) 15 mmole CCl₄; (C) 30 mmole CCl₄.

increase in AlEt₃ concentration and then approaches more closely to the constant value (0.7) at higher concentration. This behavior conflicts with the kinetic characteristics of vinyl chloride polymerization with the AlEt₃-amine-CCl₄ catalyst system [3], for which the initial overall rate of polymerization is square-root order with respect to the AlEt₃ concentration. This difference seems likely to be attributable to the fact that AlEt₃ complexed with ethers or esters reacts not only with CCl₄ to give the initiating radicals but also with the resulting polymer.
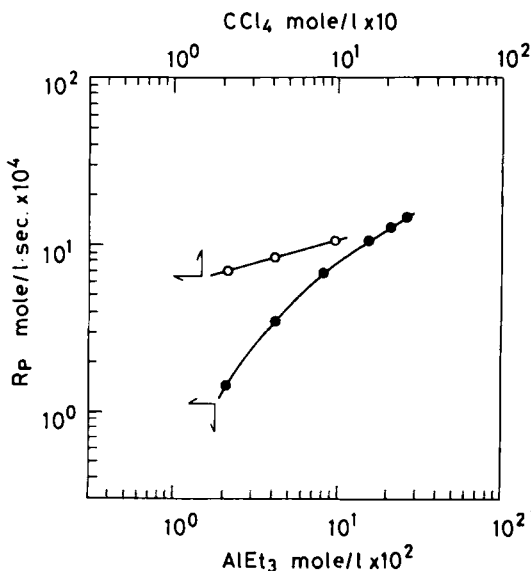
FIG. 3. Overall rate of polymerization R_p as a function of $AlEt_3$ and CCl_4 concentrations: (●) $AlEt_3$; (○) CCl_4.

Effect of Lewis Base

In the polymerization of vinyl chloride with $AlEt_3$-Lewis base-CCl_4 catalyst, the complexing agent has a large effect on polymerization process. Table 1 shows the effect of Lewis base on polymerization conversion. With Lewis bases such as ethers and esters, the polymer obtained is a white powder, whereas with amines the product is slightly colored and the molecular weight of the polymer is lowered independent of polymerization time and initiator concentration.

Figure 4 shows the relation between polymerization conversion and electron-donating power [10] of Lewis bases such as ethers and esters in Table 1. An increase in the basicity of the ligand induces an increase in the conversion to the polymer. When the ligand Lewis base is bidentate, such as γ-butyrolactone and ethyl acetate, the conversion increases slightly even if the basicity of the ligand is small. In addition, complexing agents such as $H_2N(CH_2CH_2NH)_{n-1}H$ and

$CH_3(OCH_2CH_2)_{n-1}OCH_3$ which are multidentate show high catalytic activity regardless of their basicity. In particular, compounds with more than three functional groups greatly accelerate the rate of polymerization (see Table 1). This result indicates that the rate of polymerization

TABLE 1. Effect of Lewis Base on Polymerization Conversion[a]

Lewis base	Conversion (%)	Electron-donating power $\Delta\nu_0$ (cm^{-1})
-	0.5	0
Furan	1.2	4
Anisole	1.8	26
Ethyl vinyl ether	1.3	33
Ethyl acetate	6.6	39
Epichlorohydrin	3.4	45
Propylene oxide	6.1	59
γ-Butyrolactone	14.2	66
1,2-Dimethoxyethane	17.2	71
Diisopropyl ether	7.9	75
1,4-Dioxane	6.2	77
Diethyl ether	9.5	78
Tetrahydrofuran	16.2	90
Triethylamine	1.5	238
Ethylenediamine	9.8	-
Diethylenetriamine	46.2	-
Triethylenetetramine	40.5	-
Tetraethylenepentamine	42.4	-
Pentaethylenehexamine	50.4	-
Diethyleneglycol dimethyl ether	64.7	-
Triethyleneglycol dimethyl ether	67.0	-
Tetraethyleneglycol dimethyl ether	76.3	-

[a]Solution of 21 g of vinyl chloride in 10 ml of CCl$_4$ for 3 hr. AlEt$_3$/Lewis base = 1/1, AlEt$_3$ = 4.0 mmole.

depends on the coordination number of the Lewis base rather than its basicity. A similar effect has been reported for the polymerization of ethylene by AlEt$_3$-γ-butyrolactone-peroxide catalyst [11], of methyl methacrylate with AlEt$_3$-bidentate amine complex [12], and of vinyl chloride with AlEt$_3$-multidentate amine-CCl$_4$ catalyst [3].
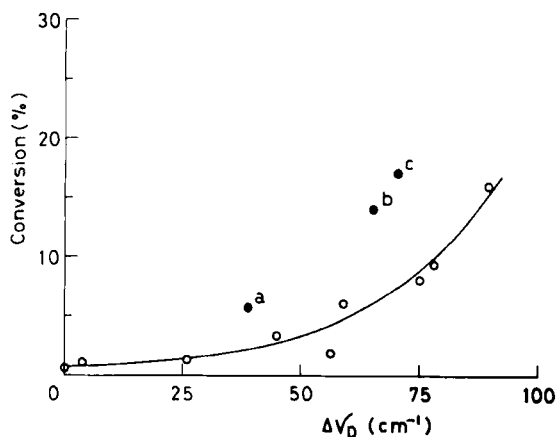
FIG. 4. Relation between polymerization conversion and electron-donating power [10] of Lewis base: (a) ethyl acetate; (b) γ-butyrolactone; (c) 1,2-dimethoxyethane.

The complexing reaction of $AlEt_3$ with various kinds of ethers was investigated by using NMR spectroscopy. When $AlEt_3$ is present at 24°C in a free state together with the complex bound to ether, a ligand exchange reaction occurs at sufficiently high rate, and so only one type of $AlEt_3$ signals should be observed. The internal chemical shift between the methyl and the methylene protons of $AlEt_3$ is expected to correspond to the fractional populations of the complex and the component in a free state.

The 220-MHz NMR spectra of $AlEt_3$ complexed with tetraethylene-glycol dimethyl ether (TEG) in toluene solutions at -50°C are given in Fig. 5. At -50°C, the peaks of the complexed and free $AlEt_3$ are resolved because of a slow exchange reaction. At a small TEG/$AlEt_3$ ratio, the methyl protons of $AlEt_3$ show two triplets and a broad peak, of which the latter decreases with the increase of TEG/$AlEt_3$. The broad peak was assigned to the free $AlEt_3$ in both bridging and terminal positions due to the slow exchange of ethyl groups. $AlEt_3$ complexed with TEG, different from that with monodentate ethers, shows two types of signals; the internal chemical shifts between the methyl and the methylene protons of $AlEt_3$ are 1.15 and 1.28 ppm, of which the latter increases with an increase in the TEG/$AlEt_3$ ratio. The electronegativities of aluminum atoms of peaks a and b obtained on the basis of Narashimhan's equation [13] were 1.28 and 1.36, respectively; that is, the coordination of a Lewis base to $AlEt_3$ reduces the electronegativities of the aluminum atom and increases the ionic character of the aluminum-carbon bond. On the other hand, the
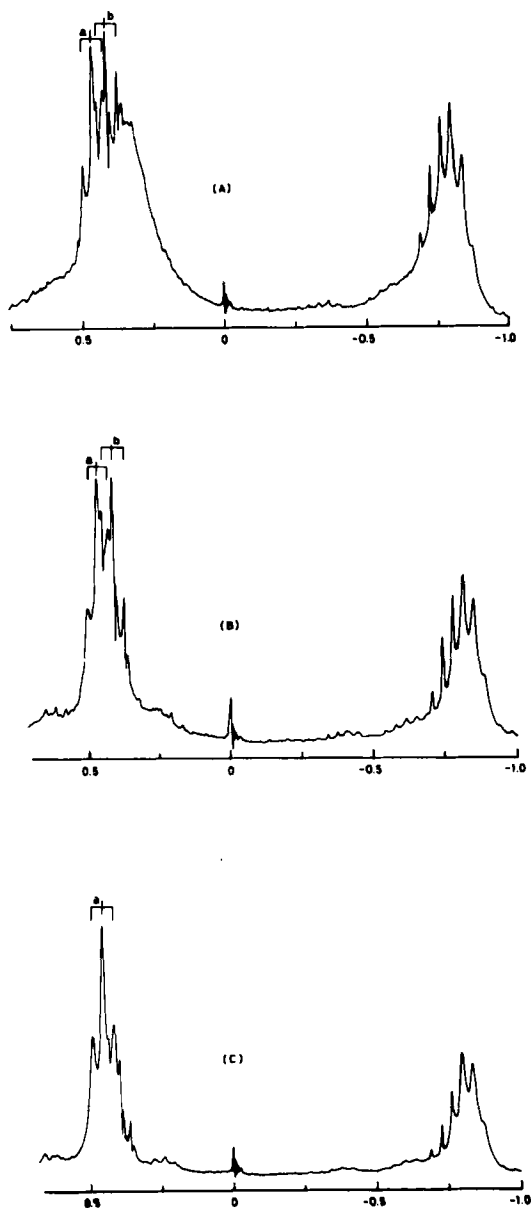
FIG. 5. 220-MHz NMR spectra of AlEt₃ complexed with TEG in toluene at -50°C and various TEG/AlEt₃ molar ratios: (A) 0.12; (B) 0.16; (C) 0.20.
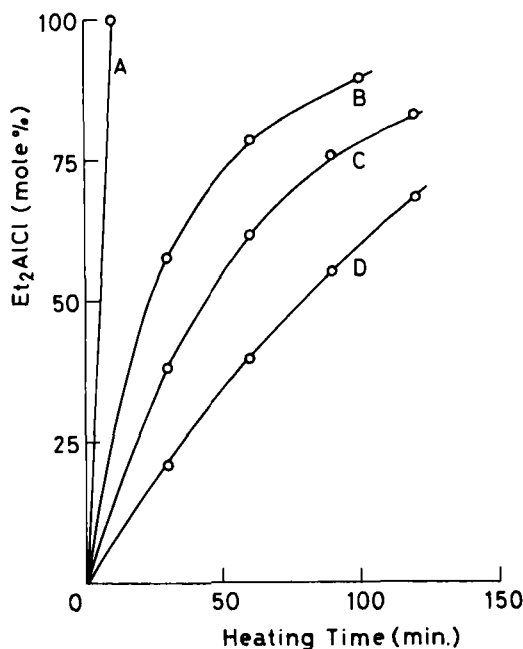
FIG. 6. Relative reactivity of AlEt₃ with CCl₄ in various ethers: (A) none; (B) diisopropyl ether; (C) tetrahydrofuran; (D) tetraethylene-glycol dimethyl ether (TEG).

electronegativity of the aluminum atom in the AlEt₃ complexed with isopropyl ether was 1.21. Thus, the ionic character of the ethyl group of the AlEt₃ complexed with TEG, which is a multidentate Lewis base, increased more than that of the ethyl group complexed with mono-dentate ethers.

Ikeda [12] and Thile [14] have proved that AlEt₃ reacts with bi-dentate amine compounds to give a five-coordinated complex in which the ionic character of the ethyl group in the Al-Et bond is more highly increased.

The ligand Lewis base not only prevents the polymer degradation which occurs with the initiator but also moderates the reaction of AlEt₃ with CCl₄ [1]. The reaction of AlEt₃ with CCl₄ in the presence of ethers was investigated by NMR spectroscopy at 65°C in benzene solution in a similar manner as described in Fig. 2. Experimental details of these reactions are given in Fig. 6, in which AlEt₃ and ligand concentrations were 0.5 mole/liter and 1.0 mole/liter, respec-tively. It can be seen that uncomplexed AlEt₃ reacts very quickly

with CCl_4 to give Et_2AlCl but the addition of ethers decreases the amount of the product. The larger the basicity of the ligand, the smaller the amount of Et_2AlCl becomes. In particular, more remarkable is the fact that the multidentate complex agent (TEG) strongly moderates the reaction of $AlEt_3$ with CCl_4. This result seems likely to correspond closely with the fact that the $AlEt_3$-multidentate ligand complex in the presence of CCl_4 shows high catalytic activity for vinyl chloride polymerization.

Characterization of PVC

Microstructures of PVC prepared with $AlEt_3$-TEG-CCl_4 catalyst and of commercial PVC (suspension, peroxide catalyst) were investigated, and the results are given in Tables 2 and 3.

The molecular weight distribution $(\overline{M}_w/\overline{M}_n)$ of PVC obtained by this catalyst system is about 2.0, independent of polymerization temperature, in accordance with that of commercial PVC polymerized with radical initiator. Furthermore the dyad tacticity of this polymer which was obtained from the 100-MHz NMR spectrum coincides closely with that of conventional PVC. The triad tacticities of this polymer, obtained from the 220-MHz NMR spectra, show the adequacy of Bernoullian statistics in describing the mechanism for stereo-chemical propagation.

Polymers synthesized with a small amount of CCl_4 to $AlEt_3$ ligand have numbers of double bonds nearly equal to that of commercial PVC and show no absorption band ascribed to the $-CCl_3$ group in the infrared spectra. By contrast, in the infrared spectra of polymer prepared with $AlEt_3$-TEG complex in a large amount of CCl_4, two absorption bands were observed at 770 cm^{-1} and 790 cm^{-1}, the latter of which is assigned to the $-CCl_3$ group [8]. The band at 770 cm^{-1} has been obscure, but may be assigned to the $-CHCl_2$ structure produced by a chain transfer of the propagating species with the quantity of CCl_4 and with decreasing number of unsaturated chain ends.

$$-CH_2-CHCl\cdot + CCl_4 \longrightarrow -CH_2-CHCl_2 + \cdot CCl_3 \qquad (4)$$
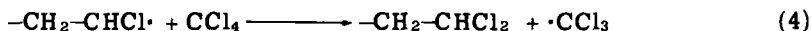
These results indicate that in a small amount of CCl_4 a chain transfer to monomer is the predominant molecular termination process, but with a large amount of CCl_4 the $-CHCl_2$ and the $-CCl_3$ structures (end groups) produced by a chain transfer to CCl_4 increases with the quantity of CCl_4.

The amount of head-to-head arrangements in this polymer is nearly equal to that of commercial PVC which is half as much as the value reported by Shimizu and Ohtsu [6] and decreases with decreasing

TABLE 2. Analysis of PVC Samples[a]

Sample	Polym. temp. (°C)	P_w	$\overline{M}_w/\overline{M}_n$[c]	Dyad[d] s	Double bond Chain	Head-to-head linkage 1000 Monomeric units
T1	30	1090	2.10	0.59	0.55	5.5
T2	40	930	2.05	0.58	0.65	6.2
T3	50	780	2.00	0.58	0.67	7.2
CM[b]	-	1020	2.00	0.58	0.67	7.5

[a]Bulk polymerization of 25g of vinyl chloride for 3.0 hr; $AlEt_3$ = 1.0 mmole; $AlEt_3/TEG/CCl_4$ = 1/1/1.
[b]Commercial PVC.
[c]Obtained from GPC.
[d]Syndiotactic dyad placement was obtained from the 100-MHz NMR spectra.

TABLE 3. Analysis of PVC Samples[a]

Sample	CCl$_4$ (mmole)	P$_w$	Infrared analysis[b]		Double bond
			$\dfrac{D_{790}}{D_{1434}}$	$\dfrac{D_{770}}{D_{1434}}$	$\dfrac{\text{Double bond}}{\text{Chain}}$
T4	42	336	0.08	0.09	0.16
T5	62	184	0.14	0.13	0.14
T6	83	139	0.14	0.14	0.14
T7	125	139	0.14	0.15	0.13

[a]Vinyl chloride, 16 g; 1.0 hr; 40°C; AlEt$_3$ = 2.0 mmole; AlEt$_3$/TEG = 1/1.

[b]The absorption band at 1434 cm^{-1} is assigned to the CH$_2$ bending vibration.

polymerization temperature. Consequently, the head-to-head linkage of PVC is assumed to be affected by the polymerization temperature rather than the kinds of radical-initiating catalysts [15].

Thermal Stability of PVC

The thermal stability of PVC polymerized with AlEt$_3$-TEG-CCl$_4$ catalyst was compared with that of commercial PVC.

On exposure to various forms of energy, PVC liberates hydrogen chloride, and the loss of hydrogen chloride results in the formation of conjugated polyene structures which account of the development of color; in particular, PVC decomposed at temperatures of the glass transition temperature leaves a highly colored product [16]. Figure 7 shows the UV spectra of PVC samples degraded at 150°C under vacuum. The spectrum of commercial PVC consists of major peaks in the shortwave part of the visible region assignable to polyene segments over 10 double bonds in conjugation. On the other hand, sample T1, whose molecular weight and tactic placements are similar to those of commercial PVC, gives rise to an increasingly blue shift of the UV absorption bands of the conjugated double bond and a low absorption intensity with progress of dehydrochlorination, suggesting that the dehydrochlorination occurs with difficulty and the conjugated polyene segments are relatively short.
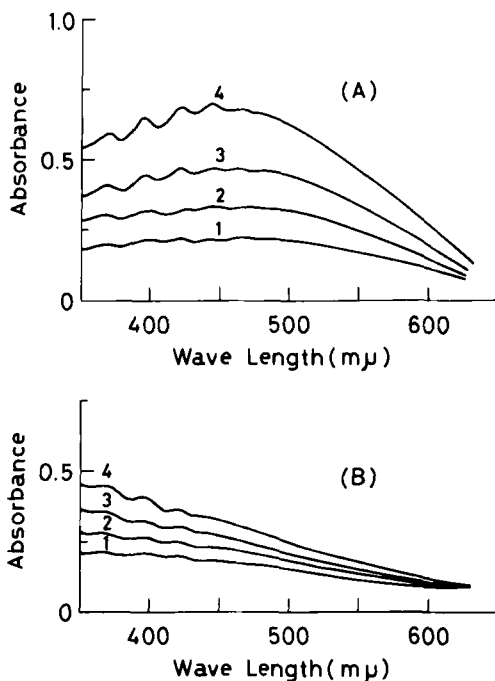
FIG. 7. UV spectra of PVC samples decomposed at 150°C under vacuum: (A) commercial PVC; (B) sample T1.

Thermogravimetry of PVC samples programmed at a heating rate of 10°C/min in air is illustrated in Fig. 8. On heating to a temperature in excess of 200°C, a first-stage weight loss of about 2-3% is observed, and a major loss ensues above 270°C, corresponding to the evolution of hydrogen chloride. The decomposition temperatures of samples T1 and T3 are nearly identical with that of commercial PVC, but the former decompose more slowly with an increase in temperature than the latter. The fact that the decomposition temperature at a major loss of sample T3 is shifted about 10-20°C to high temperatures although its molecular weight is low compared with that of purified commercial PVC suggests that the thermally unstable structures in sample T3 are converted into thermally stable structures on polymerization.

The sites for the initiation reaction have been assumed to be the inherent weak links in the polymer chain, such as tertiary chloride [17, 18] and allyl chloride [17, 19]. However, the kinetics of decomposition at the first stage of dehydrochlorination in Fig. 8 was not
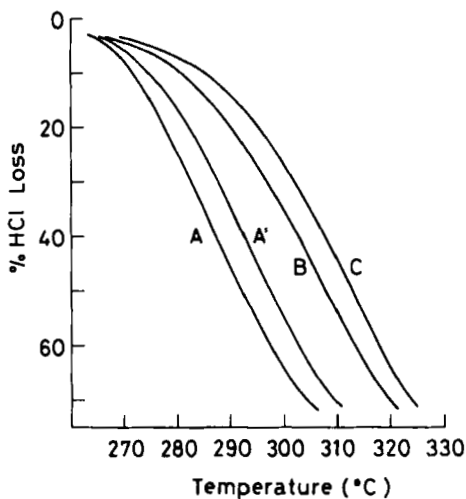
FIG. 8. Thermogravimetry of PVC samples: (A) commercial PVC; (A') purified commercial PVC; (B) sample T3; (C) sample T1.
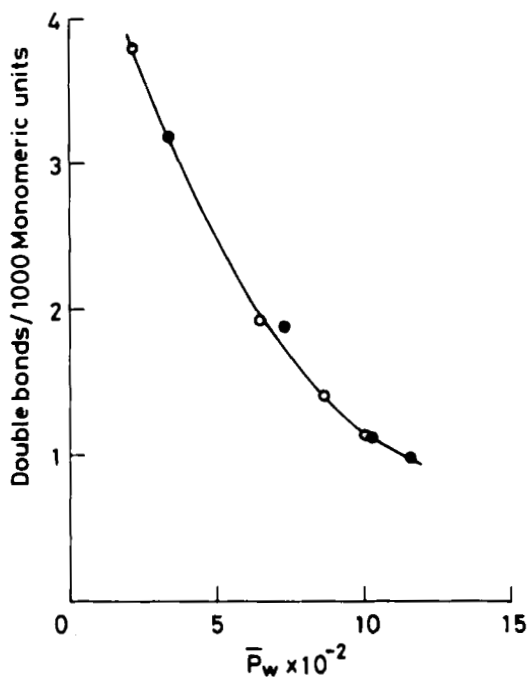

FIG. 9. Relation between double bonds and degree of molecular weight of fractionated PVC samples: ($\circ$) sample T3; ($\bullet$) commercial PVC.
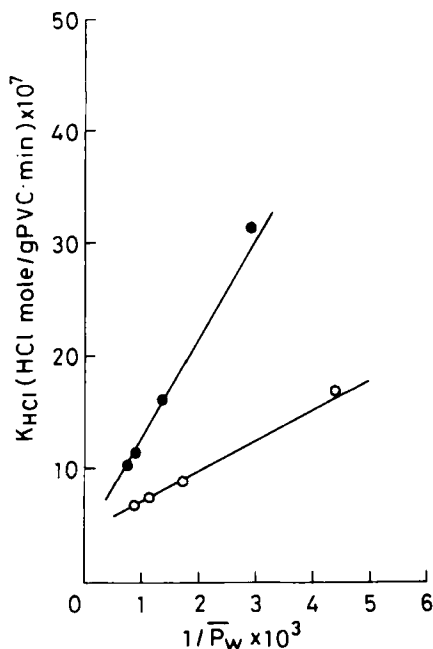
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FIG. 10. Rate of dehydrochlorination of PVC samples degraded at 180°C in nitrogen with degree of polymerization: (○) sample T3; (●) commercial PVC.

determined quantitatively owing to some scatter of their base lines. Thus the kinetic curves for thermal dehydrochlorination of PVC samples fractionated with tetrahydrofuran-H_2O were investigated at 180°C in nitrogen.

Double bonds of fractionated samples of commercial PVC and sample T3 are plotted in Fig. 9 as a function of molecular weight. The fact that the double bonds of commercial PVC and sample T3 decrease with an increase of molecular weight indicates that the double bonds in these polymers exist mainly in the polymer chain end. The relation of the double bond concentration and molecular weight of these samples gives one curve, but the rate of dehydrochlorination of these two samples at 180°C in nitrogen are significantly different.

As Fig. 10 shows, the dehydrochlorination of sample T3 and commercial PVC starts mainly from the end groups due to the fact that the rate of dehydrochlorination is proportional to the reciprocal of molecular weight. More remarkable is the fact that fractions of
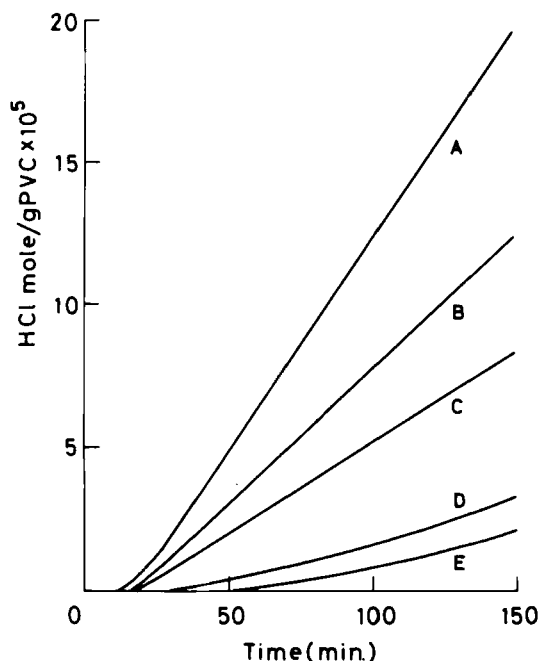
FIG. 11. Thermal decomposition at 180°C in nitrogen of PVC
samples treated with AlEt₃: (A) purified commercial PVC; (B)
AlEt₃ = 0.5 mmole; (C) AlEt₃ = 1.0 mmole; (D) AlEt₃ = 2.0 mmole;
(E) AlEt₃ = 5.0 mmole.

sample T3 are thermally more stable than those of commercial PVC,
although the concentrations of the head-to-head arrangement and the
double bond in the chain end are equal in both samples. Miller [20]
and Kennedy [21] have reported that trialkylaluminum easily reacts
with halohydrocarbons, in particular, tertiary alkyl halides, to give
alkylated hydrocarbons. More recently Kennedy [22] has pointed
out that PVC phenylated by triphenylaluminum in carbon sulfide
slurry shows improved heat stability.

Figure 11 shows the kinetic curves for dehydrochlorination of PVC
treated with AlEt₃ in 1,2-dichloroethane solution at 40°C for 2 hr.
The thermal stability of modified PVC increases significantly with
the concentration of AlEt₃. Under these reaction conditions, side
reactions such as chain scission and crosslinking did not occur, as
the double bond concentration and molecular weight of modified PVC
remains unaltered as do those of the starting polymer.

These data may suggest that AlEt₃ reacts with labile structures

in the polymer to give thermally stable –C–Et structure, and the inherent structures of PVC prepared with AlEt$_3$-Lewis base-CCl$_4$ catalyst were converted –C–Et structures on polymerization; that is, AlEt$_3$ reacts not only with CCl$_4$ to give the initiating radicals but also with the labile structures of the resulting polymer to produce thermally stable PVC.

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