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Studies on Polymerization Activities by Soluble Catalysts Based on Compounds of Organotransition Metals and Aluminum Alkyls

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ABSTRACT

Polymerization activities of the soluble Ziegler-type of catalyst systems, $Ti(OR)_4$-$AlEt_3$, $Ti(NEt_2)_4$-$AlMe_3$, and $V(NEt_2)_4$-$AlEt_3$, were investigated. In the catalyst system of $Ti(OR)_4$-$AlEt_3$, formation of two types of Ti(III) compounds, i.e., $Ti(OR)_2Et$ and its bridged complex with aluminum alkyl, was confirmed by IR and ESR measurements. With the addition of donor molecule to the system, it was found that the polymer yield decreased remarkably and that the bridged complex dissociated into a single or uncomplex Ti(III) paramagnetic species. It has been concluded that the bridged structure of Ti(III) species was responsible for the polymerization activity of styrene. Two reaction products of $Ti(NEt_2)_3Me$ and $Al(NEt_2)Me_2$ were found by NMR spectroscopic observation with the $Ti(NEt_2)_4$-$AlMe_3$ catalyst system. From the kinetic study of polymerization of styrene, it was found that $Ti(NEt_2)_3Me$ is an active species. An anionic mechanism was proposed for the styrene polymerization by $Ti(NEt_2)_3Me$. In the polymerization of MMA with the $V(NEt_2)_4$-$AlEt_3$ system, a difference in the tacticity of polymer was found to depend on the polymerization conditions, e.g., Al/V ratio and temperature. From an analysis of the tacticity of the polymer, the presence of two active sites in the propagation process is suggested.

INTRODUCTION

For several years we have been studying the polymerization activities of the soluble Ziegler-type of catalysts. In general, catalysts which are composed of a mixture of a transition metal halide and aluminum alkyl are often heterogeneous systems containing a precipitate. The heterogeneity leads to a difficulty in determining the reaction products in the catalyst system by means of physicochemical methods. This paper summerizes our works on the polymerization activities of the soluble catalysts by using some spectroscopic techniques. The catalyst systems discussed here are $Ti(OR)_4$-$AlEt_3$ [1-3], $Ti(NEt_2)_4$-$AlMe_3$ [4], and $V(NEt_2)_4$-$AlEt_3$ [5, 6].

EXPERIMENTAL

Reagents

$M(NEt_2)_4$ (M = Ti and V) was synthesized by reacting $LiNEt_2$ with MCl_4 by the method employed by Bradley et al. [7].

$Ti(NEt_2)_3Me$ was prepared according to the method of Bürger et al. [8].

$Ti(O$-n-$Bu)_4$ (Nihon Soda Co. Ltd.,) was purified by distillation under vacuum (160°C/2 Torr). $Ti(O$-tert-$Bu)_4$, $Ti(O$-sec-$Bu)_4$, and $Ti(O$-n-$Bu)_3$ were synthesized with the methods reported by Yoshino et al. [9] and Nesmeyanov et al. [10].

$AlEt_3$, $AlMe_3$, $Al(O$-n-$Bu)_3$, and VCl_4 were the commercial pure grade reagents and used without further purification.

$Al(O$-n-$Bu)Et_2$ was synthesized by the reaction of $AlEt_3$ with $Al(O$-n-$Bu)_3$ and distilled under reduced pressure (124 to 129°C/1 Torr).

$Al(NEt_2)R_2$ (R = Me, Et) was synthesized according to the method of Davidson et al. [11].

The purity of the reagents employed in this investigation were ascertained by measurements of their NMR and IR spectra.

Polymerization

All polymerization procedures were carried out under nitrogen atmosphere.

Analyses

The IR spectra were recorded by a Hitachi EPI-2 double-beam spectrophotometer. The spectra were observed by using a 0.203-mm thick cell with KBr windows. Absorption peaks arising from the solvent were compensated for by using a variable thickness cell in the reference beam.

NMR spectra were recorded by a Varian spectrometer (Model A-60) and a JEOL (Model JNM-4H-100) spectrometer.

ESR measurements were carried out with JEOL (Model No. 111, X-band) and Hitachi (Model MES-4002A) instruments.

A Gel Permeation Chromatographer of Waters and Associates (Model GPC 200) was used to analyze the molecular weight distribution of polymethyl methacrylate.

RESULTS AND DISCUSSION

Studies on the Active Complex in the $Ti(OR)_4$-$AlEt_3$ Systems

$Ti(O\text{-}n\text{-}Bu)_4$—$AlEt_3$ System

Polymerization of Styrene. Polymerization reactions were carried out at two different conditions in order to obtain an optimum Al/Ti ratio for polymerization activity. In the first case, the concentration of $AlEt_3$ was varied and that of $Ti(O\text{-}n\text{-}Bu)_4$ was kept constant, and in the second case, $Ti(O\text{-}n\text{-}Bu)_4$ was varied and $AlEt_3$ was kept constant. The polymerization was carried out after 20 min of aging of the catalyst system.

In both catalyst systems the polymer yield was found to be increased with an increase in Al/Ti ratio up to 1.4, where the polymer yield reached a maximum, thereafter it decreased

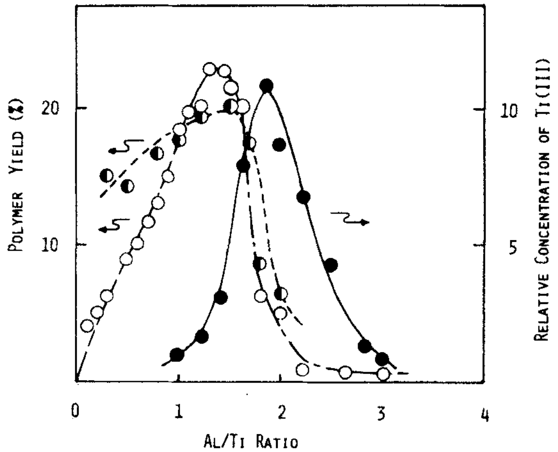
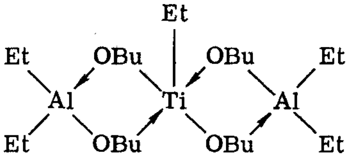


FIG. 1. Variations of polymer yield and relative concentration of Ti(III) species (g = 1.960 and g = 1.962) with Al/Ti molar ratio in the catalyst solution. (○): Concentration of $Ti(O\text{-}n\text{-}Bu)_4$ was kept constant at 1.5×10^{-3} mole and that of $AlEt_3$ was varied. (◐): Concentration of $AlEt_3$ was kept constant at 1.5×10^{-3} mole and that of $Ti(O\text{-}n\text{-}Bu)_4$ was varied. (●): Relative concentration of Ti(III) species determined from the ESR measurement. Polymerization conditions: n-hexane solvent = 10 ml, styrene = 5 ml, temperature = 60°C, time = 20 hr.

rapidly and became negligibly small when the Al/Ti ratio was over 3 (Fig. 1). These results demonstrate that the polymerization activity of the catalyst system depends strongly on the Al/Ti ratios. It was also noted that no polymerization occurred at temperatures below 0°C.

IR and ESR Spectra. With an increase in the Al/Ti ratio, the catalyst solution of n-hexane developed colors from green to reddish-brown. To determine the reaction products between the catalytic components, IR and ESR spectra were observed at the different Al/Ti ratios. When $AlEt_3$ was added to the solution of $Ti(O\text{-}n\text{-}Bu)_4$ in n-hexane, rapid decreases in the band intensities at 1085 and 1120 cm^{-1} (attributable to the Ti—O—C stretching vibration [12]) were observed, and the new bands at 1045 and 1065 cm^{-1} (attributable to the Al—O—C stretching vibration [13]) appeared. The latter new bands were caused from the formation of $Al(O\text{-}n\text{-}Bu)Et_2$. Reliable evidence for this conclusion was provided by the experimental fact that the IR spectrum of $Al(O\text{-}n\text{-}Bu)Et_2$, synthesized independently, was identical with that of the reaction product at a Al/Ti ratio of 3.

The ESR spectra of the catalyst system at different Al/Ti ratios are shown in Fig. 2. A singlet signal with a g-value of 1.960 was observed in the ESR spectra of the green catalyst solution in which Al/Ti ratios were less than 1.2. The singlet signal can be ascribed to a trivalent titanium species [14]. With an increase in the Al/Ti ratios (Al/Ti = 1.4 to 2.4), where the catalyst solution developed a reddish-brown color, the singlet signal changed to a g-value of 1.962, having a hyperfine structure with eleven splittings (a = 2.2 gauss). The hyperfine structure can be caused by a complex (I),



I

as pointed out by Djabiev et al. [15]. The signal having a hyperfine structure with eleven splittings arises from an interaction between the trivalent titanium nucleus and the two aluminum nuclei. No paramagnetic signals were observed at Al/Ti ratios higher than 5. This could be attributed to a further reduction of the valency of titanium to less than 3.

Changes in the relative concentration of the paramagnetic species with a variation in the Al/Ti ratio are shown in Fig. 1. A correlation between the polymer yield versus the Al/Ti ratios and the relative concentration of paramagnetic species versus the Al/Ti ratios was found.

IR and ESR Studies with $Ti(O\text{-}n\text{-}Bu)_3—AlEt_3$ System. $Ti(O\text{-}n\text{-}Bu)_3$ was only slightly soluble in n-hexane. However, when $AlEt_3$ was added successively to $Ti(O\text{-}n\text{-}Bu)_3$ in n-hexane, the color of the mixture changed from green to reddish-brown, similar to that observed in the $Ti(O\text{-}n\text{-}Bu)_4—AlEt_3$ system. In the supernatant part of the reddish-brown solution, the formation of $Al(O\text{-}n\text{-}Bu)Et_2$ was confirmed by the observation of the IR spectrum, and also the paramagnetic signal with eleven hyperfine splittings (g = 1.962, a = 2.2 gauss) was observed by the ESR measurement. These findings were the same as those observed for the $Ti(O\text{-}n\text{-}Bu)_4—AlEt_3$ system.

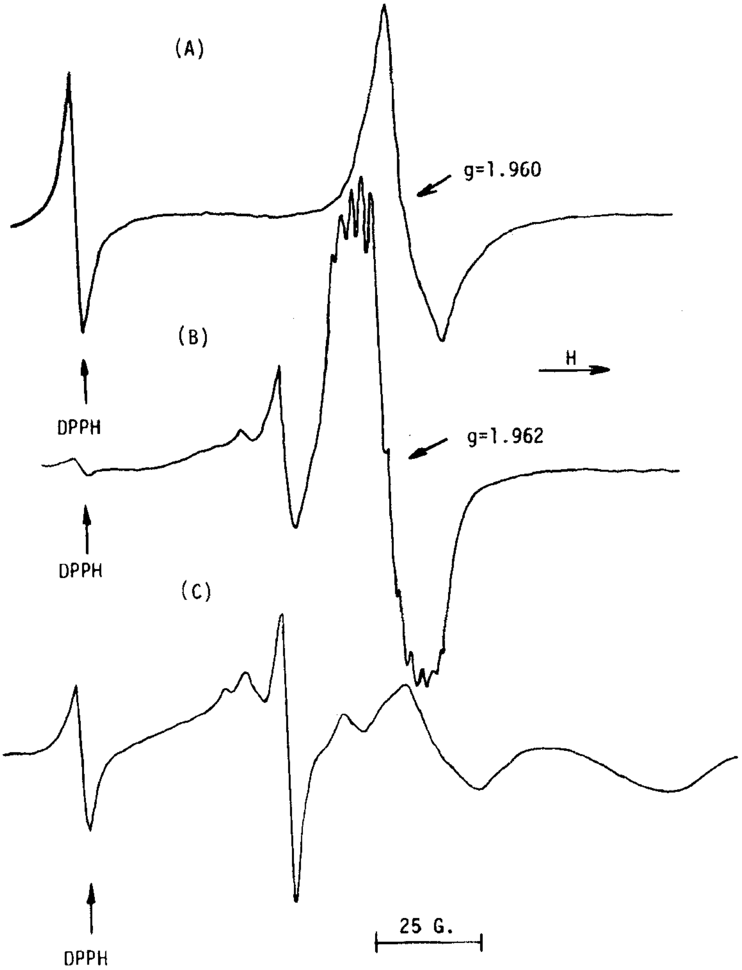


FIG. 2. ESR spectra of $Ti(O\text{-}n\text{-}Bu)_4-AlEt_3$ system in n-hexane. $[Ti(O\text{-}nBu)_4] = 0.05$ mole/liter. (A) $Al/Ti = 0.5$, (B) $Al/Ti = 1.5$, and (C) $Al/Ti = 3.0$.

The polymerization of styrene with the $Ti(O\text{-}n\text{-}Bu)_3-AlEt_3$ system was also carried out. The single component, $Ti(O\text{-}n\text{-}Bu)_3$ or $AlEt_3$, was not active for the polymerization of styrene, However, the $Ti(O\text{-}n\text{-}Bu)_3-AlEt_3$ catalyst solution yielding a reddish-brown color gave a maximum activity for the polymerization of styrene in 10% polymer yield.

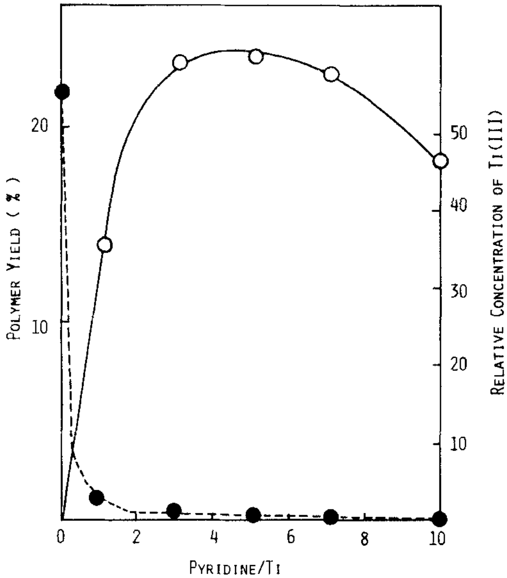


FIG. 3. Variations of polymer yield and relative concentration of Ti(III) species (singlet signal at g = 1.960) against pyridine/Ti molar ratio. (●): Polymer yield. (○): Relative concentration of Ti(III) species determined from the ESR measurement. Polymerization conditions: n-hexane solvent = 10 ml, styrene = 5 ml, temperature = 60°C, time = 20 hr, Al/Ti = 1.5, [$Ti(O\text{-}n\text{-}Bu)_4$] = 2×10^{-4} mole.

The above experimental findings lead us to conclude that the complex of a trivalent titanium species with 2 moles of $Al(O\text{-}n\text{-}Bu)Et_2$ having the eleven hyperfine splittings may be responsible for the polymerization of styrene.

Effects of Electron Donor on Paramagnetic Species and Polymerization Activities. In order to determine the structure of active species in the $Ti(O\text{-}n\text{-}Bu)_4$—$AlEt_3$ system, changes in the polymerization activity and ESR spectra of the catalyst solution in the presence of a electron donor, pyridine, were examined.

In the case of the $Ti(O\text{-}n\text{-}Bu)_4$—$AlEt_3$—pyridine system (Al/Ti = 1.5), as shown in Fig. 3, the polymer yield decreased remarkably with an increase in the pyridine/Ti ratio over 1.0. The bridged structure of the paramagnetic trivalent titanium species with two aluminum nuclei (g = 1.962) dissociated into a single paramagnetic trivalent titanium species (g = 1.960) at a pyridine/Ti ratio of 1.0.

This was confirmed by the disappearance of the ESR signal having the eleven hyperfine splittings with the addition of pyridine to the catalyst solution. The relative intensity of the signal arose from the single or uncomplexed trivalent titanium species ($g = 1.960$), increased with an increase in the pyridine/Ti ratio, and reached to a maximum at a pyridine/Ti ratio of 3.0.

$Ti(O\text{-}tert\text{-}Bu)_4$—$AlEt_3$ System

Polymerization. Polymer yield was dependent on the Al/Ti ratios, with optimum activity at an Al/Ti ratio of ~1.0. When the Al/Ti ratio was higher than 3, no polymerization occurred. Polymerization activity of the $Ti(O\text{-}tert\text{-}Bu)_4$—$AlEt_3$ catalyst system for styrene was found to be twice that of the $Ti(O\text{-}n\text{-}Bu)_4$—$AlEt_3$ catalyst system.

ESR Spectra. ESR spectra of the $Ti(O\text{-}tert\text{-}Bu)_4$—$AlEt_3$ catalyst system are shown in Fig. 4. At an Al/Ti ratio of 0.5, a singlet signal was observed at $g = 1.960$. In the case of an Al/Ti ratio of 1.5, a hyperfine structure with six splittings was found, with a coupling constant of ~3.5 gauss. The hyperfine structure may arise from an interaction between a trivalent titanium nucleus and an aluminum nucleus ($I = 5/2$). The signal with the eleven hyperfine splittings could not be detected at any Al/Ti ratio employed in the catalyst system.

Changes in the relative intensity arising from the paramagnetic species with a variation of the Al/Ti ratio were found to be similar to those of the $Ti(O\text{-}n\text{-}Bu)_4$—$AlEt_3$ system (see Fig. 1).

Effect of Electron Donor. With the addition of pyridine to the catalyst solution (Al/Ti = 1.5), a rapid decrease in the polymer yield was noted, and also the signal with six hyperfine splittings disappeared and changed into a signal with a g-value of 1.960, which was caused by the single or uncomplexed trivalent titanium species.

Conclusion. The active species for the polymerization of styrene in these catalyst system is considered to be the bridged complexes of a trivalent titanium species with 1 or 2 moles of $Al(OR)Et_2$. This can be concluded from the following experimental facts: 1) In the catalyst system where a maximum activity for the polymerization of styrene is noted, the ESR signals attributable to these complexes are observed; 2) with the addition of an electron donor, pyridine, a remarkable decrease in polymerization activity is found accompanying the dissociation of bridged complexes into a single or uncomplexed trivalent titanium species. The reaction scheme producing the active species may be considered to be as in Scheme 1.

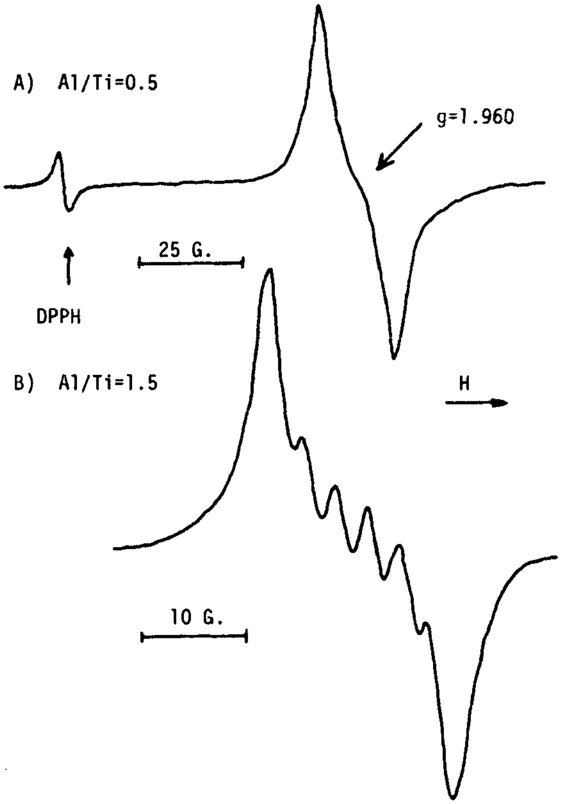


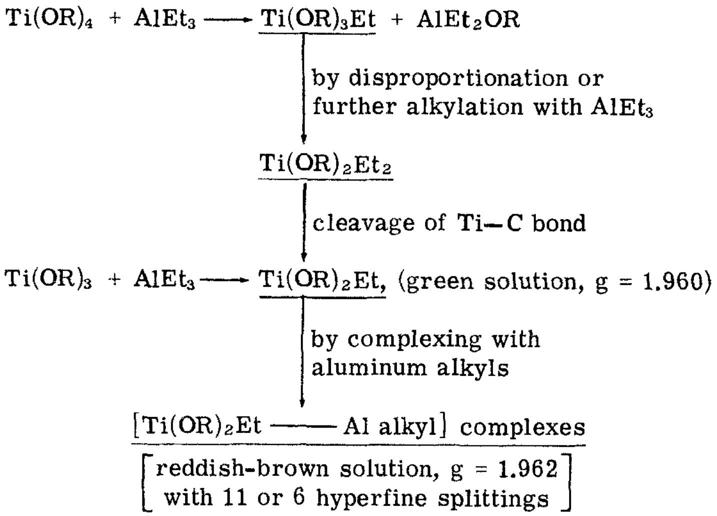
FIG. 4. ESR spectra of Ti(O-tert-Bu)$_4$—AlEt$_3$ system in n-hexane. [Ti(O-tert-Bu)$_4$] = 0.05 mole/liter.

NMR Studies on Ti(NEt$_2$)$_4$-AlMe$_3$ System and Its Polymerization Activity

In this study, an active species in the Ti(NEt$_2$)$_4$-AlMe$_3$ system for the polymerization of styrene was examined by NMR measurement.

Polymerization and NMR Measurement of Catalyst Solution

As shown in Fig. 6, the polymerization activity for styrene was found to depend on the Al/Ti ratio with an optimum activity at a



SCHEME 1. Sequence of reactions

ratio of 1.5. When the Al/Ti ratio was beyond 4, no polymer was obtained. Even with an addition of DPPH, the polymerization of styrene was not inhibited. This evidence suggests that no radical initiation occurred in the catalyst system.

NMR measurements at the various Al/Ti ratios were carried out to determine a structure of the active species. From the NMR observations the two reaction products in the catalyst system were confirmed to be $Ti(NEt_2)_3Me$ and $Al(NEt_2)Me_2$ (Fig. 5). The relative concentration of $Ti(NEt_2)_3Me$ came to a maximum at an Al/Ti ratio of about 1.5, as shown in Fig. 6. This concentration dependence on the Al/Ti ratios is well correlated with the variation of the polymerization activity against the Al/Ti ratio. The peak at τ = 9.52 ppm attributed to the methyl protons in the Ti—Me linkage of $Ti(NEt_2)_3Me$ disappeared as the polymerization progressed.

It may be concluded that $Ti(NEt_2)_3Me$ plays a major role for the polymerization of styrene. The polymerization of styrene was, then, carried out by using $Ti(NEt_2)_3Me$ only.

Polymerization of Styrene by $Ti(NEt_2)_3Me$ [16]

A kinetic study of the polymerization of styrene with $Ti(NEt_2)_3Me$ itself was carried out. Variations of the rate of polymerization against the concentrations of catalyst and styrene were examined.

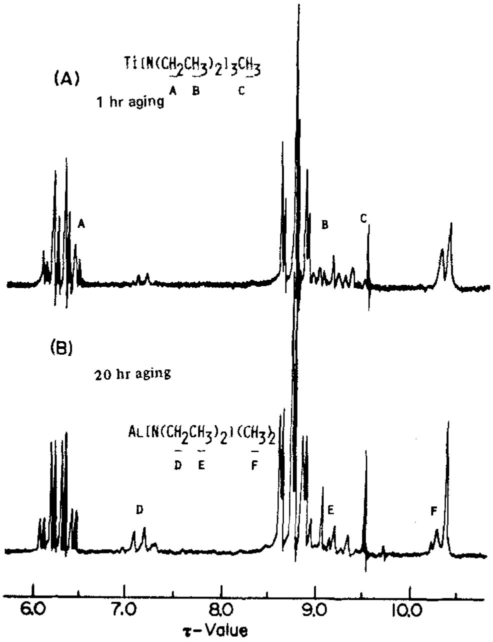


FIG. 5. NMR spectra of $Ti(NEt_2)_4$-$AlMe_3$ system at Al/Ti molar ratio of 1.0. $[Ti(NEt_2)_4] = 6 \times 10^{-2}$ mole/liter benzene.

It was found that the polymer yield was proportional to the degree of polymerization. This suggests that the polymerization reaction of the catalyst is not caused by a radical mechanism (Fig. 7).

The rate of polymerization was found to be proportional to the first-order of $Ti(NEt_2)_3Me$ concentration and to the second-order of styrene concentration (Figs. 8 and 9).

The activation energy determined from the relationship between the logarithum of the rate of polymerization and the reciprocal of absolute temperature was found to be 9.56 kcal/mole. An ionic mechanism is proposed by the above kinetical investigations. In this case, an insertion reaction of monomer to the Ti—Me bond of $Ti(NEt_2)_3Me$ may be anticipated, because the peak at $\tau = 9.52$ ppm arising from the Ti—Me protons disappears with the addition of monomer.

With the addition of benzoquinone (an inhibitor for radical polymerization) to the catalyst, no inhibitive effect was found

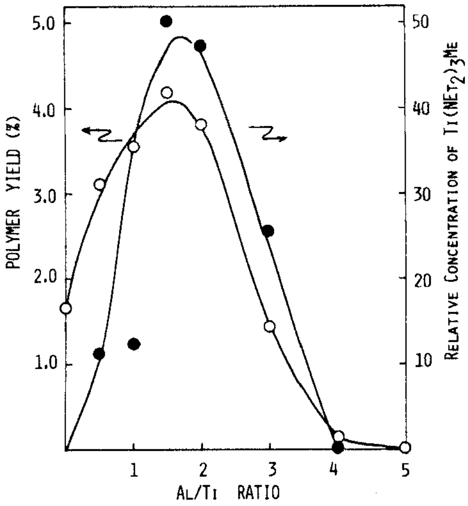


FIG. 6. Variations of polymer yield and relative concentration of $Ti(NEt_2)_3Me$ with Al/Ti molar ratio in the catalyst solution. (○): Polymer yield. (●): Relative concentration of $Ti(NEt_2)_3Me$ determined from the NMR measurement. Polymerization conditions: benzene = 5 ml, styrene = 5 ml, temperature = 60°C, time = 20 hr, $[Ti(NEt_2)_4] = 1 \times 10^{-3}$ mole.

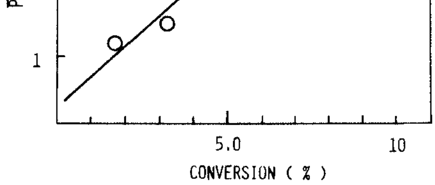


FIG. 7. Degree of polymerization against polymer yield. Polymerization conditions: toluene = 9 ml, styrene = 10 ml, temperature = 60°C, time = 2, 4, 8, and 24 hr, $[Ti(NEt_2)_3ME] = 5 \times 10^{-3}$ mole.

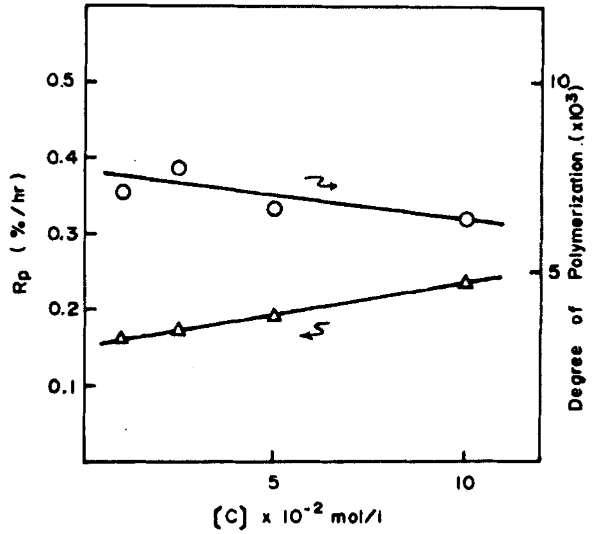


FIG. 8. Rate of polymerization and degree of polymerization against the catalyst concentration. Polymerization conditions: toluene = 10 ml, styrene = 4.4 mole, time = 6 hr, temperature = 60°C.

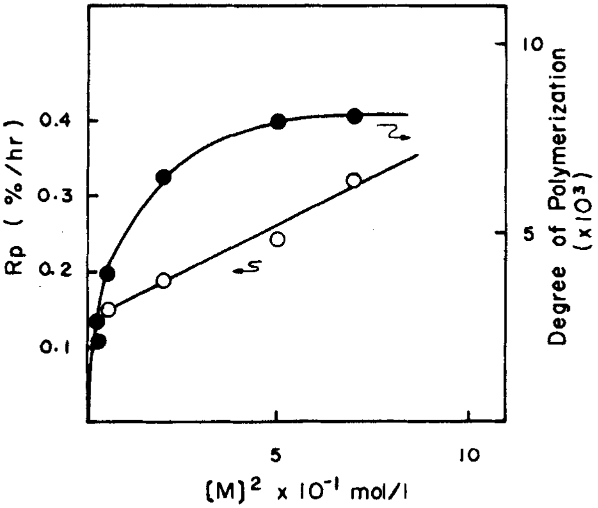


FIG. 9. Rate of polymerization and degree of polymerization against the monomer concentration. Polymerization conditions: $[Ti(NEt_2)_3Me]$ = 1×10^{-3} mole, time = 6 hr, temperature 60°C, toluene solvent, (○) R_p, (●) D_p.

for the polymerization of styrene. Moreover, in the polymerization of isobutyl vinyl ether by the catalyst, no polymer was obtained. These experimental facts suggest that $Ti(NEt_2)_3Me$ initiates the polymerization of styrene by an anionic mechanism.

By assuming a complex formation between styrene and the catalyst in the initiation step, it is possible to deduce the rate law [17]:

$$\mathrm{C} + \mathrm{M} \xrightarrow{K} (\mathrm{CM}) \qquad \text{(rapid equilibrium)}$$

$$(\mathrm{CM}) + \mathrm{M} \xrightarrow{k} (\mathrm{CM}) + \text{polymer} \qquad \text{(slow)}$$

where C is the catalyst, M is a styrene molecule, and (CM) is the styrene-catalyst complex. Then the rate of polymerization can be written as

$$-dM/kt = k[(CM)][M] \tag{1}$$

and

$$K = [(CM)]/\{[C] - [(CM)]\}[M] \tag{2}$$

Solving Eq. (2),

$$[(CM)] = \frac{K[C][M]}{1 + K[M]} \tag{3}$$

Substituting Eq. (3) for the rate Eq. (1) yields

$$-dM/dt = kK[M]^2[C]/\{1 + K[M]\} \simeq kK[M]^2[C] \quad \text{(when } K[M] \text{ is negligibly small)} \tag{4}$$

This rate equation agrees with the experimental facts. Therefore, the assumption of complex formation prior to polymerization may be supported.

Conclusion

The active species in the $Ti(NEt_2)_4$-$AlMe_3$ system for the polymerization of styrene is confirmed as $Ti(NEt_2)_3Me$. Kinetic investigation of polymerization by using $Ti(NEt_2)_3Me$ shows that the rate of polymerization is proportional to the first order of $Ti(NEt_2)_3Me$ and to the second order of styrene concentration.

Polymerization of MMA with $V(NEt_2)_4$-$AlEt_3$ Catalyst System and Tacticity of Polymers

Several studies have been reported on olefin polymerization with the $V(NEt_2)_4$-$AlEt_3$ catalyst system [18-21]. However, no work has been carried out on the polymerization of polar vinyl monomers using this catalyst system. In our studies on the polymerization of methyl methacrylate (MMA), it was found that the tacticities of polymer change depend upon the polymerization conditions, i.e., the polymerization temperature and the Al/V ratios in the catalyst system. Although the catalytic mechanism giving the different tacticities for PMMA is not understood, in this section we present our experimental findings on the polymerization of MMA.

Polymerization

Figure 10 shows the effects of polymerization temperatures and Al/V ratios in the catalyst system for polymer yield. It is clear that the $V(NEt_2)_4$-$AlEt_3$ catalyst system is active for the polymerization of MMA at the lower temperature of -78°C and in the region of higher Al/V ratios beyond 3.

From the observation of the NMR spectra of the catalyst solution, the formation of $Al(NEt_2)Et_2$ was confirmed at higher Al/V ratios. Since it has been reported [22] that $Al(NPh_2)Et_2$ initiates an anionic polymerization of MMA, we have tried the polymerization of MMA with $Al(NEt_2)Et_2$ at -78°C for 20 hr, but no polymer was obtained. It is concluded that $Al(NEt_2)Et_2$ shows no activity for polymerization in the catalyst system $V(NEt_2)_4$-$AlEt_3$.

The effect of aging of the catalyst for polymerization activity was also examined. After the aging of the catalyst solution (Al/V = 5.0) at 70°C for the prescribed time, the catalyst solution was cooled to -78°C, monomer was added slowly, and then polymerization was carried out for 20 hr at this temperature. The catalyst solution aged for 0.5 hr gave the polymer in 94% yield, and that aged for 24 hr gave the polymer in 92% yield. It is noted that the catalyst

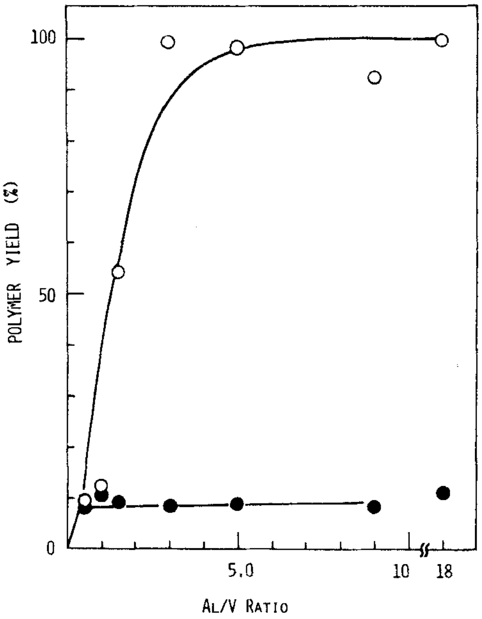


FIG. 10. Variation of polymer yield against Al/V molar ratio in the catalyst solution at the different temperatures. (○): 20 hr at -78°C. (●): 20 hr at 60°C. Polymerization conditions: toluene = 10 ml, MMA = 5 ml, $[V(NEt_2)_4] = 5 \times 10^{-4}$ mole.

system holds its polymerization activity even after a long aging time. As judged by the above experimental findings, a radical mechanism may be excluded from consideration.

Tacticity of Polymer

The effects of the polymerization temperature and the Al/V ratio for the triad tacticity of polymers are shown in Fig. 11. In the region of Al/V ratios beyond 3, the tacticity of the polymer is constant and does not depend on the Al/V ratios. In this region, however, the tacticity of the polymer depends on the polymerization temperature, and the syndiotactic polymer is obtained at -78°C. Evidently, according to Fig. 11, the tacticity of polymer prepared at 60°C does not depend strongly on the Al/V ratio. In the polymerization at -78°C, however, the tacticity of the polymer prepared at a Al/V ratio of 0.5 is remarkably different from that prepared at higher Al/V ratios, i.e., an isotactic-rich polymer is obtained.

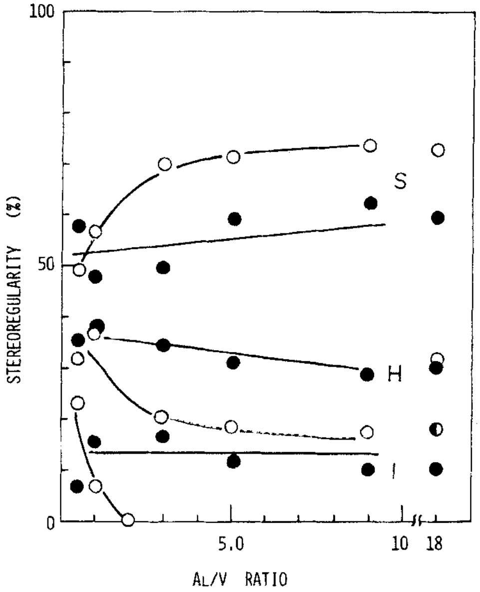


FIG. 11. Variation of triad tacticity of PMMA obtained at the different temperatures against Al/V molar ratio in the catalyst solution. Polymerization conditions are same as for Fig. 10. (○): At -78°C. (●): At 60°C.

As Fig. 12 shows, the propagation steps which yield polymer at -78°C and at Al/V ratios greater than 1, follow Bernoullian statistics, whereas the polymer prepared at a Al/V ratio of 0.5 deviates from Bernoullian statistics (denoted by the arrowheads in the figure). The polymers prepared at a Al/V ratio of 0.5 is supposed to be a stereoblock type of tacticity because the normalized probabilities of isotactic and heterotactic triad are larger in the former and smaller in the latter than those expected from Bernoullian statistics. Regardless of the Al/V ratio, the propagation steps yielding polymer at 60°C follow Bernoullian statistics.

By taking account of the molecular weight distribution described in the next section, the different propagation steps which yield polymers can be suggested to depend on the polymerization conditions.

Molecular Weight Distribution of Polymer

The molecular weight distribution (MWD) of polymers was measured by gel permeation chromatography. As Fig. 13 shows,

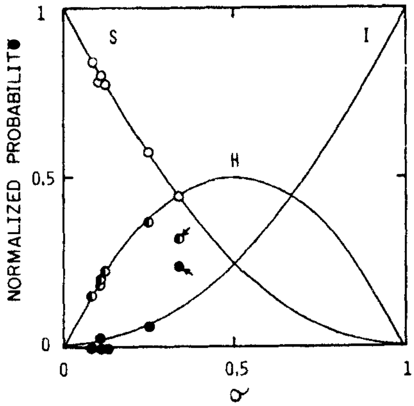


FIG. 12. Stereoregularity of PMMA prepared at -78°C and at different Al/V molar ratios. The triads are syndiotactic (○), heterotactic (◐), and isotactic (●).

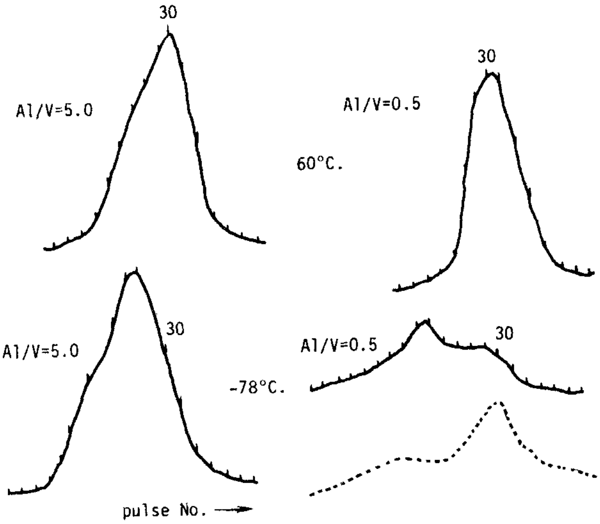


FIG. 13. Molecular weight distributions of PMMA prepared with $V(NEt_2)_4$-$AlEt_3$ system. (- -) $V(NEt_2)_4$-$AlEt_3$-PPh_3 system, Al/V = 0.5, PPh_3/V = 2.0.

there was no remarkable difference in the MWD's among the polymers prepared at 60°C and Al/V = 0.5, at 60°C and Al/V = 5.0, and at -78°C and Al/V = 5.0. In this case the MWD curves had a single peak.

However, the polymer prepared at -78°C and Al/V = 0.5 had at least two peaks in the MWD curve. This suggests that a polymerization mechanism giving polymer at the lower temperature and the lower Al/V ratio may not be simple one.

Effects of PPh_3-Addition to the Catalyst System

In Table 1 are shown the effects of PPh_3 addition to the catalyst system on the tacticities of polymers.

In spite of the addition of PPh_3, no effect was observed for the triad tacticities of polymers prepared under the polymerization conditions (at -78°C, Al/V = 5.0) following Bernoullian statistics. Other polymerization conditions (at -78°C, Al/V = 0.5) deviated from Bernoullian statistics, and the isotactic content was greatly diminished by the addition of PPh_3. As shown in Fig. 14, the value of triad tacticities of polymer prepared at -78°C and Al/V = 0.5 in the presence of PPh_3 fit Bernoullian statistics. The addition of PPh_3 also affected the MWD of polymer. As shown by the dotted

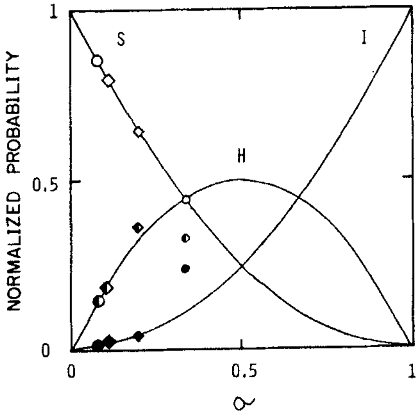


FIG. 14. Effect of the addition of PPh_3 on the triad tacticities of PMMA. (○), (◯), (◇), and (◇) are sample numbers 1, 2, 3, and 4, respectively, as listed in Table 1.

TABLE 1. Effects of Addition of PPh_3 on the Triad Tacticities of Polymers[a]

No.	Al/V	PPh_3/V	Polymerization temperature (°C)	Conversion (%)	Triad tacticity		
					I	H	S
1	0.5	0	-78	10.7	0.24	0.32	0.44
2	0.5	2.0	-78	7.6	0.01	0.14	0.85
3	5.0	0	-78	98.5	0.03	0.18	0.79
4	5.0	2.0	-78	62.0	0.02	0.23	0.75

[a] Polymerization condition: $[V(NEt_2)_4] = 5 \times 10^{-4}$ mole, MMA = 5 ml, polymerization time = 20 hr, toluene = 20 ml.

curve in Fig. 13, the addition of PPh_3 induced a remarkable decrease in the peak intensity on the higher side of the molecular weight for the polymer prepared at -78°C and $Al/V = 0.5$

Conclusion

Two types of the propagation steps can be assumed for the polymerization of MMA with the $V(NEt_2)_4$-$AlEt_3$ system. One is a process which follows Bernoullian statistics. The other process proceeds at a lower temperature and a lower Al/V ratio, and it deviates from Bernoullian statistics. The active site causing the latter process is poisoned by the addition of PPh_3, and the propagation step proceeds in the former process.

REFERENCES

[1] M. Takeda, K. Iimura, Y. Nozawa, M. Hisatome, and N. Koide, J. Polym. Sci., C, 23, 741 (1968).
[2] M. Takeda, K. Iimura, and N. Koide, Kogyo Kagaku Zasshi, 71, 563 (1968).
[3] N. Koide, K. Iimura, and M. Takeda, Ibid., 73, 1038 (1970).
[4] N. Koide, K. Iimura, and M. Takeda, J. Polym. Sci., Polym. Chem. Ed., 11, 3161 (1973).
[5] N. Koide, T. Akita, K. Iimura, and M. Takeda, Paper Presented at the 22nd Annual Meeting of the Society of Polymer Science, Japan, May 1973.
[6] N. Koide, T. Akita, K. Iimura, and M. Takeda, Paper Presented at the 23rd Annual Meeting of the Society of Polymer Science, Japan, June 1974.
[7] D. C. Bradley and I. M. Thomas, J. Chem. Soc., 1960, 3857.
[8] H. Bürger and H. J. Neese, J. Organometal Chem., 20, 129 (1969).
[9] T. Yoshino, I. Kijima, Y. Masuda, and I. Sugiyama, Kogyo Kagaku Zasshi, 62, 77 (1959).
[10] A. N. Nesmeyanov, O. V. Nogina, and R. Kh. Freidlina, Chem. Abstr., 48, 9254 (1954).
[11] N. Davidson and H. C. Brown, J. Amer. Chem. Soc., 64, 316 (1942).
[12] T. Takaya, T. Yoshimoto, and Y. Mashiko, Kogyo Kagaku Zasshi, 60, 1382 (1957).
[13] T. Ishino and S. Minami, Kagaku no Ryoiki, 11, 656 (1957).

[14] P. E. M. Allen, J. K. Brown, and R. M. S. Obaid, Trans. Faraday Soc., 85, 1808 (1963).
[15] T. S. Djabiev, R. D. Sabirova, and A. E. Shilov, Kinet. Katal., 5, 441 (1964).
[16] N. Koide, T. Asahi, K. Iimura, and M. Takeda, Paper Presented at the 23rd Annual Meeting of the Society of Polymer Science, Japan, June 1974.
[17] N. G. Gaylord, T. K. Kwei, and H. F. Mark, J. Polym. Sci., 42, 417 (1960).
[18] A. Mazzei, S. Cucinella, and W. Marioni, Chim. Ind. (Milan), 51, 374 (1969).
[19] S. Cucinella and A. Mazzei, Ibid., 53, 653 (1971).
[20] S. Cucinella and A. Mazzei, Ibid., 53, 749 (1971).
[21] C. Busetto and N. Palladion, Ibid., 53, 934 (1971).
[22] S. Murahashi, H. Yuki, K. Hatada, T. Niki, and T. Obokata, Kobunshi Kagaku, 24, 309 (1967).