Polymerization of Propylene with $TiCl_3$–$AlEt_2Cl$–Trilauryltrithiophosphite Catalyst

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Synopsis

$AlEt_3Cl$ was modified with TLTTP (trilauryltrithiophosphite) in the catalyst system consisting of $TiCl_3$ and $AlEt_2Cl$. The effects of TLTTP on the polymerization of propylene were studied in comparison with those of alkyl homologues of TLTTP. The catalytic behavior of the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system in the polymerization of propylene was also studied in comparison with that of the $TiCl_3$–$AlEt_2Cl$ catalyst system. In the study of the effect of various alkylthiophosphites added, it is found that the bulkiness of the alkyl group affects the rate of propylene polymerization and the stereoregularity of the resultant polymers. The $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system gave different catalytic behavior in the propylene polymerization from that of the unmodified conventional catalyst system ($TiCl_3$–$AlEt_2Cl$). These effects of TLTTP were considered to be due to the bulkiness of the alkyl groups attached to the phosphorous atom and the higher reactivity to $TiCl_3$ of the modified $AlEt_2Cl$ than of the unmodified $AlEt_2Cl$.

INTRODUCTION

Many studies[1–3] have been carried out on the polymerization of propylene with $TiCl_3$–aluminum alkyl–third component catalysts. Most of the third components are electron donors such as ethers or amines. These donors usually form a complex with $TiCl_3$ or aluminum alkyls. In ternary component catalyst systems,[4] it has been suggested that there exists an equilibrium among the active centers in the $TiCl_3$, aluminum alkyls, and donors. When the equilibrium shifts to the complex formation, the rate of polymerization usually decreases. However, it has been recently reported[5] that the complex between polymeric donors and $AlEt_2Cl$ enhanced the rate of propylene polymerization. In this study we would like to report the effects of trialkylthiophosphites on propylene polymerization, and also the catalytic behavior of the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system in comparison with the unmodified conventional binary catalyst system.

EXPERIMENTAL

Titanium trichloride was $TiCl_3$(AA) grade from Toyo Stauffer Chemical Co. Diethyl aluminum chloride from Texas Alkyl Co. was used as the *n*-heptane solution (2 mmol/mL). *n*-Heptane was dried over CaH_2 and used after distillation. Propylene was used after passage through a column of 3A-molecular sieves. The reagents used are shown in Table I.

Propylene Polymerization. *n*-Heptane (280 mL) was added to a separable flask (500 mL) fitted with a stirrer and a condenser under a nitrogen atmosphere. Propylene was then introduced under atmospheric pressure. After the tem-

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TABLE I
Trialkyltrithiophosphites

Trialkyltrithiophosphites	Abbreviation	Note
Triethyltrithiophosphite	TETTP	Prepared by the reaction of PCl_3 with ethyl mercaptan[6]
Tripropyltrithiophosphite	TPTTP	Prepared by the reaction of PCl_3 with propyl mercaptan
Tributyltrithiophosphite	TBTTP	Prepared by the reaction of PCl_3 with butyl mercaptan[6]
Triphenyltrithiophosphite	TPHTTP	Prepared by the reaction of PCl_3 with phenyl mercaptan[6]
Trioctyltrithiophosphite	TOTTP	Prepared by the reaction of PCl_3 with octyl mercaptan[6]
Trilauryltrithiophosphite	TLTTP	From Johoku Kagaku Co.
Tristearyltrithiophosphite	TSTTP	From Johoku Kagaku Co.

perature of the liquid phase reached 60°C, the third component, $AlEt_2Cl$, and $TiCl_3$ were added in that order. The polymerization was subsequently performed at 60°C under atmospheric pressure for 2 h.

The polymerization was stopped by the addition of 20 mL of isopropyl alcohol. The resultant polymer was separated by the addition of 700 mL of isopropyl alcohol, and the mixture was kept overnight at room temperature. The white powdery polymer was filtered and dried under vacuum at 60°C for 20 h. The portion of the resultant polymer which was insoluble in hot *n*-heptane, a measure of crystallinity, was determined by Soxhlet extraction of the polymer with *n*-heptane for 20 h. The kinetic curves were obtained by measuring the amount of gas consumed with gas meters during polymerization.

Reaction of $AlEt_2Cl$ and TLTTP. TLTTP (2.25 mmol) was added to the *n*-heptane solution of $AlEt_2Cl$ (15.0 mmol) under nitrogen atmosphere at room temperature. TLTTP reacted with $AlEt_2Cl$ exothermically, and the resultant solution turned yellow at the beginning of the reaction. After 20 h, a small amount of yellow material precipitated from the solution. The upper solution became clear. The amount of the yellow precipitate was 2–3% based on the $AlEt_2Cl$ used. This precipitate with $TiCl_3$ did not show catalytic activity.

RESULTS AND DISCUSSION

Polymerization of Propylene with $TiCl_3$–$AlEt_2Cl$–TLTTP Catalyst. Table II shows the effect upon addition of TLTTP to the $TiCl_3$–$AlEt_2Cl$ catalyst

TABLE II
Polymerization of Propylene with $TiCl_3$–$AlEt_2Cl$–TLTTP Catalysts

No.	Addition order of Catalysts	TLTTP (mmol)	$TiCl_3$ (mmol)	$AlEt_2Cl$ (mmol)	Polym time (min)	Total polymer (g)	*n*-Heptane insoluble (%)
1	Al[a] → Ti	—	5.0	15.0	120	30.53	95.7
2	(Al + Ti)[b] → TLTTP	2.25	5.0	15.0	120	22.87	97.3
3	(Al + TLTTP) → Ti	2.25	5.0	15.0	120	39.90	97.9
4	(Ti + TLTTP) → Al	2.25	5.0	15.0	120	23.16	97.5

[a] Al = $AlEt_2Cl$; Ti = $TiCl_3$.

[b] ( ): premixed at room temperature for 20 h.

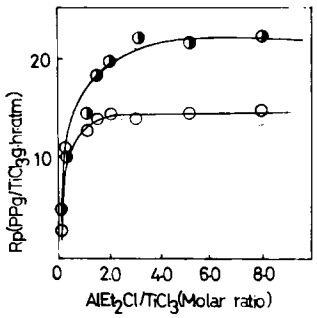

Fig. 1. The effect of addition of TLTTP on the rate of propylene polymerization with the $TiCl_3$–$AlEt_2Cl$ catalyst: (○) without TLTTP; (◑) with TLTTP.

system with different orders of addition of the catalyst components. It is obvious that TLTTP showed its effects on the polymerization rate, and the steroregularity of polymer obtained only in the case where the $AlEt_2Cl$ was treated with TLTTP for 20 h. The effect of the molar ratio ($AlEt_2Cl/TiCl_3$) on the propylene polymerization rate and the stereoregularity of polymer obtained with both the $TiCl_3$–$AlEt_2Cl$ and the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system are shown in Figures 1 and 2. Both catalyst systems showed almost the same polymerization rate at the smaller molar ratio ($AlEt_2Cl/TiCl_3$ = 0.5). However, at the larger molar ratio ($AlEt_2Cl/TiCl_3$ = 3.0), the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system showed a greater polymerization rate than the $TiCl_3$–$AlEt_2Cl$ catalyst system. Also, the stereoregularity of the polymer obtained showed a similar tendency. In the $TiCl_3$–$AlEt_2Cl$ catalyst system, the stereoregularity of the polymer slightly decreased at still larger molar ratio ($AlEt_2Cl/TiCl_3$ = 6.0); however, in the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system, it was almost constant.

The Relationship between the Polymerization Rate in $TiCl_3$–$AlEt_2Cl$–TLTTP Catalyst System and The Aging Time of $AlEt_2Cl$ with TLTTP. The rate of propylene polymerization with $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system increased with the aging time of $AlEt_2Cl$ with TLTTP at room temperature. When $AlEt_2Cl$ was aged with TLTTP more than 20 h, the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system showed constant polymerization rate. As shown in Figure 3, the active complex between $AlEt_2Cl$ and TLTTP was considered to be stable for the long period of time under the nitrogen atmosphere.

Polymerization of Propylene with $TiCl_3$–$AlEt_2Cl$–Trialkylthiophosphites Catalyst System. The results of the propylene polymerization using

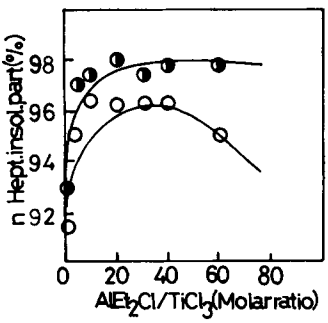

Fig. 2. The effect of TLTTP on the stereoregularities of resultant polymers: (○) without TLTTP; (◑) with TLTTP.

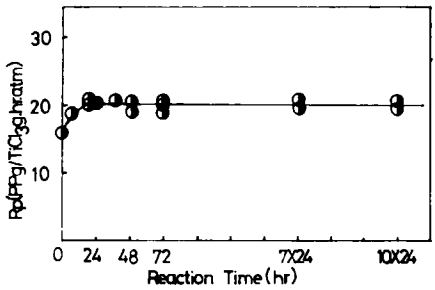

Fig. 3. The effect of the reaction time between TLTTP and $AlEt_2Cl$ on the rate of propylene polymerization with the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst.

various trialkylthiophosphites as modifiers of $AlEt_2Cl$ are shown in Figure 4. The rate of polymerization decreased by the aging of $AlEt_2Cl$ with trialkylthiophosphites which have alkyl groups that contain eight carbon atoms or less, but, in the case of TLTTP or TSTTP, the rate of polymerization was enhanced by their addition. Figures 5 and 6 show the effects of the bulkiness of alkyl groups in trialkylthiophosphites on the rate of polymerization and the stereoregularities of resultant polymer, respectively. The rate of polymerization increased with increase of the number of carbon atoms in the alkyl groups; however, the stereoregularity of the resultant polymer showed a peak at 12 carbon atoms. Since trialkylthiophosphites have differences only in the number of carbon atoms contained in the alkyl groups, it is quite clear that there are definite effects being exerted by the bulkiness of alkyl groups both on the rate of polymerization and the stereoregularity of the resultant polymer.

Time Dependency of the Polymerization Rate. The time dependency of the polymerization rate in both the $TiCl_3$–$AlEt_2Cl$ and the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst systems are shown in Figure 7. The $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst system obviously shows a larger polymerization rate, not only at the nonsteady state period. As shown in Figure 8, when the $AlEt_2Cl$ modified with TLTTP was added after 30 min to the polymerization system which had been initiated with $TiCl_3$–$AlEt_2Cl$ catalysts, the polymerization rate instantly in-

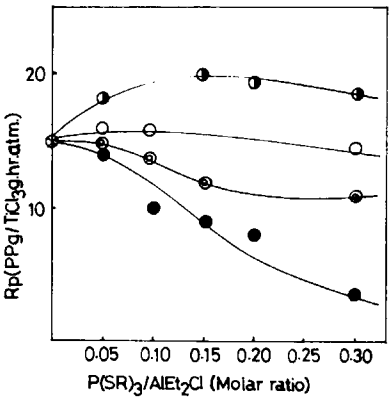

Fig. 4. The effects of molar ratio $P(SR)_3/AlEt_2Cl$ on the rate of propylene polymerization with $TiCl_3$–$AlEt_2Cl$–$P(SR)_3$ catalysts: (◑) TLTTP; (○) TPHTTP; (◎) TPTTP; (●) TETTP. $AlEt_2Cl$ was treated with $P(SR)_3$ for 20 h at room temperature.

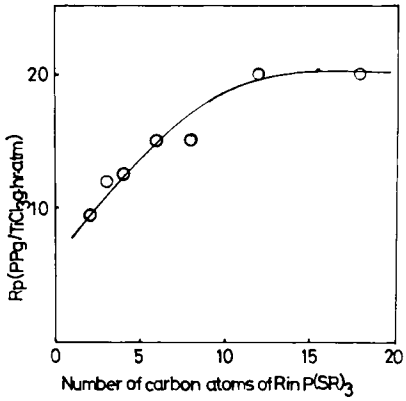

Fig. 5. The relationship between the number of carbon atoms of the alkyl groups in $P(SR)_3$ and the rate of propylene polymerization with $TiCl_3$–$AlEt_2Cl$–$P(SR)_3$ catalysts. $P(SR)_3/AlEt_2Cl$ molar ratio at 0.15. $AlEt_2Cl$ was treated with $P(SR)_3$ for 20 h at room temperature.

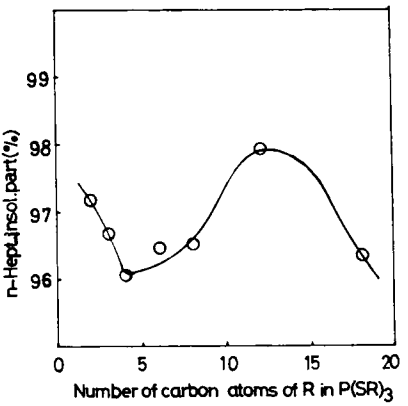

Fig. 6. The relationship between the number of carbon atoms of alkyl groups in $P(SR)_3$ and the stereoregularities of resultant polymers with $TiCl_3$–$AlEt_2Cl$–$P(SR)_3$ catalysts. $P(SR)_3/AlEt_2Cl$ molar ratio at 0.15. $AlEt_2Cl$ was treated with $P(SR)_3$ for 20 h at room temperature.

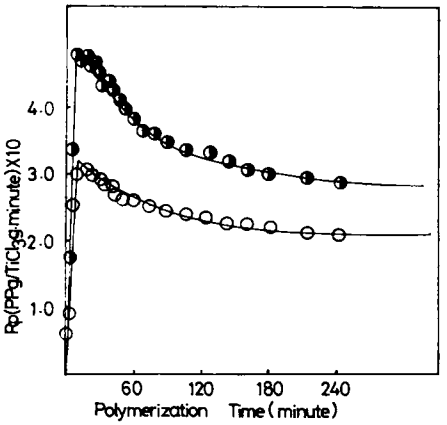

Fig. 7. The time dependency of the rate of propylene polymerization with the $TiCl_3$–$AlEt_2Cl$ catalyst; (○) without TLTTP; (◑) with TLTTP. $AlEt_2Cl$ was treated with TLTTP for 20 h at room temperature. TLTTP/$AlEt_2Cl$ molar ratio at 0.15.

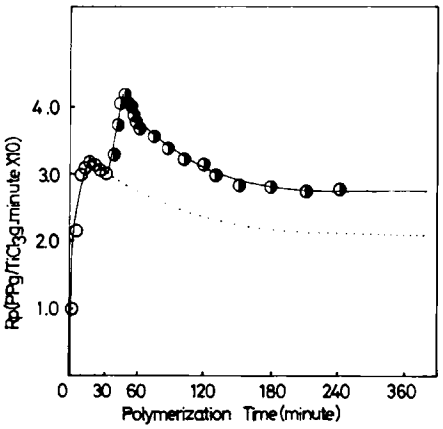

Fig. 8. The effect of addition of $AlEt_2Cl$ modified with TLTTP on the rate of propylene polymerization initiated with the $AlEt_2Cl$–$TiCl_3$ catalyst. $AlEt_2Cl$ modified with TLTTP was added after 30 min. $AlEt_2Cl$ was treated with TLTTP for 20 h at room temperature. TLTTP/$AlEt_2Cl$ molar ratio at 0.15. (○) $TiCl_3$–$AlEt_2Cl$; (◑) $TiCl_3$–$AlEt_2Cl$ + $AlEt_2Cl$ modified with TLTTP.

creased, and the initial kinetic curve shifted to that of the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst. The same experiment with $AlEt_2Cl$ did not show any shift of the initial kinetic curve. This fact supports the assumption that $AlEt_2Cl$ which is already reacted with $TiCl_3$ can be replaced by the $AlEt_2Cl$ modified with TLTTP. This may be due to the difference in their basicity.

Temperature Dependency of the Polymerization Rate. The temperature dependency of the polymerization rate for crystalline polymer (hot *n*-heptane insoluble portion) and the amorphous polymer (hot *n*-heptane soluble portion) for both $TiCl_3$–$AlEt_2Cl$ and $TiCl_3$–$AlEt_2Cl$–TLTTP catalysts are shown in Figures 9 and 10, respectively. The rate of polymerization for the crystalline polymer increased with a rise in the polymerization temperature for both $TiCl_3$–$AlEt_2Cl$ and $TiCl_3$–$AlEt_2Cl$–TLTTP catalysts. However, the rate of polymerization for the crystalline polymer became constant above 70°C with

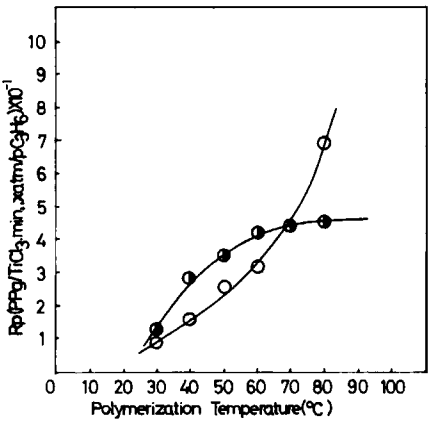

Fig. 9. The temperature dependency of the rate of isotactic polymer formation with $AlEt_2Cl$–$TiCl_3$ catalysts: (○) without TLTTP; (◑) with TLTTP. $AlEt_2Cl$ was treated with TLTTP for 20 h at room temperature. TLTTP/$AlEt_2Cl$ molar ratio at 0.15.

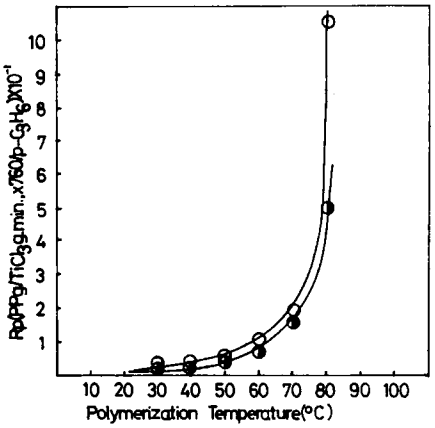

Fig. 10. The temperature dependency of the atactic polymer formation with the $TiCl_3$–$AlEt_2Cl$ catalyst: (○) without TLTTP; (◑) with TLTTP. $AlEt_2Cl$ was treated with TLTTP for 20 h at room temperature. TLTTP/$AlEt_2Cl$ molar ratio at 0.15.

the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst. This fact shows the thermal instability of $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst. Also, the rate of polymerization for the amorphous polymer sharply increased with a rise in the polymerization temperature in both $TiCl_3$–$AlEt_2Cl$ and $TiCl_3$–$AlEt_2Cl$–TLTTP catalysts. Arrhenius plots of these rates of polymerization are shown in Figures 11 and 12. The apparent activation energy was calculated and is summarized in Table III. Arrhenius plots for the crystalline polymer with $TiCl_3$–$AlEt_2Cl$–TLTPP catalyst did not give a linear relationship. This may be due to the thermal modification of the active centers. Arrhenius plots for the amorphous polymer gave good linear plots for both catalysts. The apparent activation energy for the crystalline polymer was not so different for both catalysts. On the other hand, the apparent activation energy for the amorphous polymer in $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst was larger than in $TiCl_3$–$AlEt_2Cl$ catalyst.

Propylene Polymerization with $TiCl_3$ and Complex between $AlEt_2Cl$ and TLTTP. In order to isolate the complex between $AlEt_2Cl$ and TLTTP from the reaction mixture (TLTTP/$AlEt_2Cl$ = 0.15), excess free $AlEt_2Cl$ was distilled off at below 40°C under a high vacuum, and 60% of the added $AlEt_2Cl$ was recovered. In order to clarify the catalytic behavior of $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst without having excess free $AlEt_2Cl$, this distillation residue (DR) was used with $TiCl_3$ for propylene polymerization, and the results are shown in Table IV. The rate of polymerization with $TiCl_3$–DR catalyst was small, but stereoregularity of resultant polymer was the same as that with $TiCl_3$–$AlEt_2Cl$–TLTTP

TABLE III
Activation Energy in the Propylene Polymerization

Catalyst	Polymer		Activation energy (kcal/mol)	Frequency factor
$TiCl_3$–$AlEt_2Cl$	Atactic polymer		10.81	1.45×10^5
$TiCl_3$–$AlEt_2Cl$	Isotactic polymer		7.32	1.90×10^4
$TiCl_3$–$AlEt_2Cl$–TLTTP	Atactic polymer		15.64	8.32×10^3
$TiCl_3$–$AlEt_2Cl$–TLTTP	Isotactic polymer	70°C	0.61	1.12
		70°C	7.21	2.88×10^4

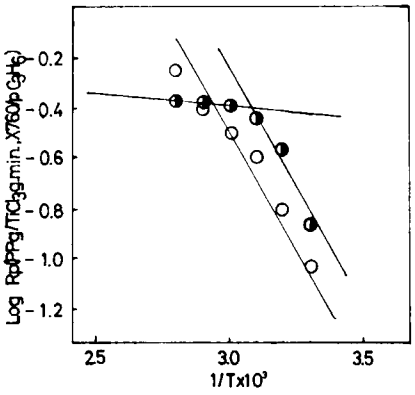

Fig. 11. Arrhenius plots for the rate of isotactic polymer formation with the $TiCl_3$–$AlEt_2Cl$ catalyst: (○) without TLTTP; (◑) with TLTTP. $AlEt_2Cl$ was treated with TLTTP for 20 h at room temperature. TLTTP/$AlEt_2Cl$ molar ratio at 0.15.

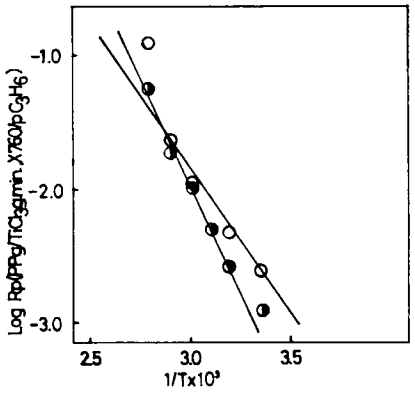

Fig. 12. Arrhenius plots for the rate of atactic polymer formation with the $TiCl_3$–$AlEt_2Cl$ catalyst: (○) without TLTTP; (◑) with TLTTP. $AlEt_2Cl$ was treated with TLTTP for 20 h at room temperature. TLTTP/$AlEt_2Cl$ molar ratio at 0.15.

TABLE IV
The Polymerization of Propylene with $TiCl_3$-Distillation Residue Catalyst

Catalyst[a]	TLTTP	$TiCl_3$ (mmol)	$AlEt_2Cl$ (mmol)	Polym time (min)	Total Polymer (g)	*n*-Heptane insoluble (%)	Note
$TiCl_3$–DR	as DR, 2.24 g	5.0	2.0	120	24.62	97.5	Distillation residue contained $AlEt_2Cl$, 2 mmol
$TiCl_3$–DR 13 mmol added	as DR, 2.24 g	5.0	15.0	120	39.12	97.3	$AlEt_2Cl$
$TiCl_3$–$AlEt_2Cl$	—	5.0	15.0	120	30.53	95.7	
$TiCl_3$–$AlEt_2Cl$–TLTTP	2.25 mmol	5.0	15.0	120	39.90	97.9	

[a] DR = distillation residue.

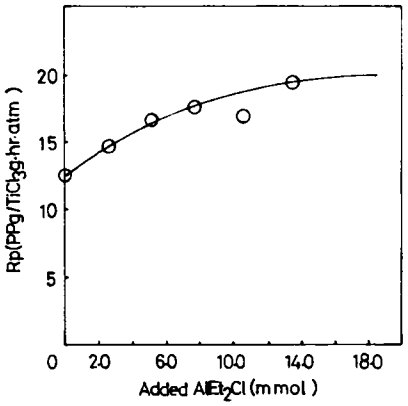

Fig. 13. The addition effect of $AlEt_2Cl$ on the rate of propylene polymerization with $TiCl_3$–DR catalyst. DR was used 2.24 g/g $TiCl_3$ and contained 2.0 mmol $AlEt_2Cl$.

catalyst. The addition of $AlEt_2Cl$ to $TiCl_3$– DR catalysts enhanced the rate of polymerization without a change in the stereoregularity of the resultant polymer. These results are shown in Figures 13 and 14. These results suggest that the additional free $AlEt_2Cl$ did not directly play a role in the active center. Characterization of the DR was unsuccessful.

CONCLUSION

The catalytic behavior of $TiCl_3$–$AlEt_2Cl$–TLTTP catalysts in the polymerization of propylene was studied in comparison with that of unmodified $TiCl_3$–$AlEt_2Cl$ catalysts. Also the effect of TLTTP on the polymerization of propylene was studied in comparison with the effect of alkyl homologues of TLTTP. The catalytic behavior on the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst was different from that of the $TiCl_3$–$AlEt_2Cl$ catalyst. In the $TiCl_3$–$AlEt_2Cl$–TLTTP catalyst, it is suggested that the catalytic active center consists of $TiCl_3$ and the complex between $AlEt_2Cl$ and TLTTP. This is then subsequently activated with excess free $AlEt_2Cl$. It is found that the effect of trialkylthiophosphites as modifiers

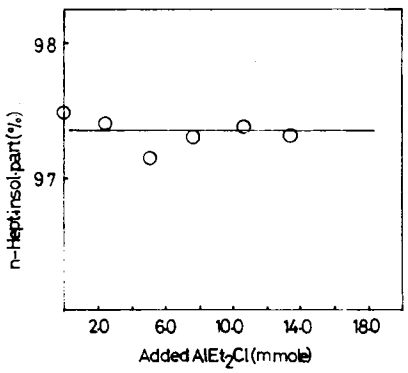

Fig. 14. The effect of addition of $AlEt_2Cl$ on the stereoregularities of resultant polymers with $TiCl_3$–DR catalyst. DR was used 2.24 g/g $TiCl_3$ and contained 2.0 mmol $AlEt_2Cl$.

of $AlEt_2Cl$ on the polymerization of propylene is dependent on the bulkiness of the alkyl groups bound to the phosphorus atom.

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