

High Temperature Polymerization of Propylene Catalyzed by MgCl_2 -Supported Ziegler–Natta Catalyst with Various Cocatalysts

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ABSTRACT: Four cocatalysts, referred to as ethylaluminumoxanes, were synthesized by the reaction between triethylaluminum (AlEt_3) and water under various molar ratios of $\text{H}_2\text{O}/\text{Al}$ at -78°C . Aluminumoxanes were used as cocatalysts for a MgCl_2 -supported Ziegler–Natta catalyst for propylene polymerization at temperatures ranging from 70 to 100°C . When the polymerization was activated by AlEt_3 , the activity as well as the molecular weight and isotacticity of the resulting polymer gradually dropped as the temperature varied from 70 to 100°C . When ethylaluminumoxane was employed as the cocatalyst, good activity and high molecular weight and isotacticity were obtained at 100°C . Furthermore, when the cocatalyst varied from AlEt_3 to ethylalumi-

noxane, the atactic fraction and polymer fraction with moderate isotacticity decreased and the high isotactic fraction slightly increased, which indicated that the variation of the cocatalyst significantly affects the isospecificity of active sites. It was suggested that the reactivity of the Al–Et group and the size of the cocatalyst were correlated to the performance of the Ziegler–Natta catalyst at different temperatures. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1978–1982, 2006

Key words: cocatalyst; Ziegler–Natta polymerization; high temperature polymerization

INTRODUCTION

Both the activity and the stereospecificity are known to decrease when the polymerization temperature is over 80°C in olefin polymerization with MgCl_2 -supported Ziegler–Natta catalysts. Hoeg and Liebman (cited by Boor¹) reported that the fractions of isotactic polymer with triethylaluminum (AlEt_3) were higher than with triisobutylaluminum ($\text{Al}(i\text{-Bu})_3$) in propylene polymerization from 75 to 175°C using a $\text{TiCl}_3/\text{AlR}_3$, (R–Et, *i*-Bu) catalyst system. Chadwick et al.² reported that an increase in the polymerization temperature from 20 to 80°C led to an increase in both the proportion of the isotactic polymer fraction and its stereoregularity for propylene polymerization using various MgCl_2 -supported Ziegler–Natta catalysts. They believed that a greater relative increase in polymerization activity with increasing temperature for highly isospecific as opposed to moderately isospecific sites suggests easier propagation after the occasional regioirregular (2,1-) insertion. Kojoh et al.³ reported that the activity and molecular weight were both decreased by increasing the polymerization temperature

using TiCl_4 /dioctylphthalate/ MgCl_2 - AlEt_3 /diphenyldimethoxysilane (DDS), which showed the activity and molecular weight obtained with $\text{Al}(i\text{-Bu})_3$ as a cocatalyst was higher than with AlEt_3 . A small amount of ethylene units decomposed from AlEt_3 was found in the polypropylene prepared by AlEt_3 at high temperature. The authors suggested that the efficiency of formation of active sites in the polymerization with $\text{Al}(i\text{-Bu})_3$ is higher than with AlEt_3 at 100°C . Zhong et al.⁴ also reported a similar decrement of the activity and tacticity in propylene polymerization from 50 to 120°C using a TiCl_4 /9,9-bis(methoxymethyl)fluorine/ MgCl_2 catalyst activated with AlR_3 without an external donor.

Polymerization at high temperature, such as over 90°C , is preferable industrially to reduce the burden of removing the polymerization heat in commercial plants. Recently developed supercritical olefin polymerization technology also requires a higher polymerization temperature ($>94^\circ\text{C}$) for propylene polymerization. Therefore, it is important to improve the high temperature performance of a Ziegler–Natta catalyst to meet the requirements of polymerization technology. Cocatalysts have proved to play an important role in olefin polymerization catalysts, such as Ziegler–Natta,⁵ metallocene,^{6–8} and late transitional metal catalysts.^{9–11} It seems that the strong reactivity

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of AlEt_3 affects the performance of the Ziegler-Natta catalyst, such as the polymerization activity, molecular weight, and isotacticity of the polymer. In this work, we attempt to modify the performance of the Ziegler-Natta catalyst in high temperature polymerization by varying the cocatalyst. Various ethylaluminumoxanes (EAOs) with different oligomeric degrees were prepared by the reaction between AlEt_3 and H_2O with different molar ratios, which is believed to afford relatively lower reactivity than AlEt_3 . The high temperature polymerization of propylene in the presence of a MgCl_2 -supported Ziegler-Natta catalyst activated by various cocatalysts is investigated.

EXPERIMENTAL

Materials

Toluene was purified by refluxing over sodium-benzophenone ketyl under a nitrogen atmosphere and distilled prior to use. AlEt_3 (Aldrich Co.) was used as obtained. Octane was purified by passing over activated 4 Å molecular sieves. DQ catalyst,¹² composed of TiCl_4 /di-iso-butylphthalate/ MgCl_2 , is a commercial catalyst from SINOPEC with a titanium content of 2.8 wt %; it was used as received. DDS was distilled before use.

Synthesis of EAOs

The EAOs as cocatalysts were prepared by hydrolysis of AlEt_3 with various $\text{Al}/\text{H}_2\text{O}$ molar ratios with the following procedure: the required amount of pure water was slowly added to 50 mL of a toluene solution of AlEt_3 (0.05 mol) at -78°C with vigorous stirring. The solution was allowed to warm to room temperature slowly and stirred for a further 2 h. EAOs A, B, C, and D were prepared with $\text{Al}/\text{H}_2\text{O}$ molar ratios of 2/1, 3/2, 5/4, and 10/9, respectively.

Propylene polymerization

Propylene polymerization was performed in a 500-mL autoclave. Octane (200 mL) and the required amount of cocatalyst and DDS were injected into the reactor, and the system was pressured by propylene. Upon balancing the system to the desired temperature, the polymerization was initiated by the addition of the supported catalysts. After 1 h the polymerization was terminated by the addition of the acidified ethanol. The resulting polymer was separated, washed with ethanol, and dried in a vacuum at 70°C to constant weight.

Polymer analysis

Polypropylene was extracted with boiling heptane for 12 h and the isotactic index (II) was the weight

percent of the heptane-insoluble fraction. The molecular weight and molecular weight distribution were measured with a PL-GPC 220 apparatus using 1,2,4-trichlorobenzene as the solvent at 150°C . The weight-average and number-average molecular weights of the polymers were calculated on the basis of polystyrene standards. The melting temperatures of the polymers were measured by a Perkin-Elmer DSC-7, and the second heating run was recorded at $10^\circ\text{C}/\text{min}$. The isotacticity distribution of the polypropylene was determined by temperature rising elution fractionation (TREF, Senshu SSC-7300) with *o*-dichlorobenzene as the solvent. The fraction column packed with Chromosorb (Celite Corp. Japan) was cooled down at $6.7^\circ\text{C}/\text{h}$ from 140 to 20°C . Elution at a flow rate of 150 mL/h was first carried out at 20°C for 0.5 h, followed by heating at $16^\circ\text{C}/\text{h}$ up to 140°C . The eluted solution was analyzed with a refractive index detector.

RESULTS AND DISCUSSION

The reaction between AlEt_3 and water was studied previously. Tetraethylaluminumoxane, existing in a trimer form, can be prepared by the reaction of AlEt_3 and water at an $\text{H}_2\text{O}/\text{Al}$ molar ratio of 1/2.¹³ Oligomeric EAO with a large molecular weight is obtained with a ratio close to 1/1. Four EAOs were prepared with different $\text{H}_2\text{O}/\text{Al}$ molar ratios ranging from 1/2 to 9/10. With the increment of the $\text{H}_2\text{O}/\text{Al}$ molar ratio, the oligomeric degree of aluminumoxane is proposed to gradually increase. Such aluminumoxanes have been proved to be efficient cocatalysts for iron and nickel complexes for ethylene polymerization.¹⁰ Both the EAOs and AlEt_3 were used as cocatalysts for the DQ catalyst with DDS as the external electron donor in the polymerization of propylene. The results of the propylene polymerization are summarized in Table I.

Slurry polymerization of propylene was carried out at 70, 90, and 100°C . The optimal polymerization conditions recommended by Mao et al.'s patent,¹² for example, $\text{Al}/\text{Ti} = 200$ and $\text{Si}/\text{Ti} = 10$, were applied. When propylene polymerization was carried out at 70°C , the activity obtained with AlEt_3 was higher than those with EAOs; and the IIs of the polymers prepared by various cocatalysts were almost the same. However, the polymers obtained with EAOs had higher molecular weight than that with AlEt_3 . When the polymerization temperature was increased to 90°C , the activity with AlEt_3 was close to those with EAOs and the molecular weights of the polymers prepared by EAOs were much higher than by AlEt_3 . The fraction of heptane-insoluble polymer prepared by AlEt_3 was lower than 90%, whereas the same fractions of the polymer prepared by EAOs C and D were as high as 97%. At 100°C , the EAOs gave not only as good activity as at 90°C but also a higher molecular weight and

TABLE I
Propylene Polymerization Catalyzed by DQ Catalyst with Various Cocatalysts

| Run | Cocatalyst | Temp. (°C) | Activity (kgPP/gTi h) | II (wt %) | M_n (10^4) | PDI | T_m (°C) |
|-----|-------------------|------------|-----------------------|-----------|------------------|------|------------|
| 1 | AlEt ₃ | 70 | 20.9 | 96.7 | 2.77 | 8.4 | 159.7 |
| 2 | EAO A | 70 | 15.4 | 97.3 | 4.12 | 6.2 | 163.9 |
| 3 | EAO B | 70 | 14.7 | 97.8 | 5.50 | 5.9 | 163.3 |
| 4 | EAO C | 70 | 4.3 | 96.3 | 6.61 | 5.7 | 161.1 |
| 5 | EAO D | 70 | Trace | ND | ND | ND | ND |
| 6 | AlEt ₃ | 90 | 17.1 | 86.7 | 2.57 | 6.7 | 159.4 |
| 7 | EAO A | 90 | 17.0 | 87.0 | 4.56 | 4.6 | 157.4 |
| 8 | EAO B | 90 | 14.2 | 87.5 | 7.32 | 5.4 | 161.8 |
| 9 | EAO C | 90 | 13.1 | 97.0 | 8.51 | 7.9 | 162.8 |
| 10 | EAO D | 90 | 0.8 | 97.2 | 7.10 | 6.6 | 159.4 |
| 11 | AlEt ₃ | 100 | 7.2 | 84.2 | 1.85 | 7.5 | 159.3 |
| 12 | EAO A | 100 | 11.7 | 85.3 | 4.33 | 4.7 | 158.9 |
| 13 | EAO B | 100 | 12.0 | 85.6 | 6.93 | 5.2 | 159.4 |
| 14 | EAO C | 100 | 12.3 | 94.9 | 7.60 | 6.9 | 161.6 |
| 15 | EAO D | 100 | 0.7 | 97.6 | 5.31 | 10.6 | 161.2 |

The polymerization conditions were 20–30 mg of DQ catalyst, diphenyldimethoxysilane as external donor, 200 mL of octane, Al/Ti = 200, Si/Ti = 10, $P_{\text{propylene}} = 0.4$ MPa, time = 1 h; II, weight percent of heptane-insoluble fraction; M_n , number-average molecular weight; PDI, polydispersity index of isotactic fraction measured by GPC; T_m , melting temperature of isotactic fraction measured by DSC; ND, not detected.

II than AlEt₃. Among the various cocatalysts, EAOs C and D gave the highest II of more than 95%.

When the polymerization temperature was increased from 70 to 100°C, the variation of the polymerization activity, molecular weight, and II of the polymer prepared by various cocatalysts strongly depended on the kind of cocatalyst. When the propylene polymerization was activated by AlEt₃, it was apparent that increasing the polymerization temperature from 70 to 100°C led to not only lower activity and II but also reduced molecular weight, which is in accordance with the results published by Zhong et al.⁴ Moreover, the polymerization activity decreased rapidly when the polymerization temperature was raised from 90 to 100°C. When the polymerization was carried out in the presence of various EAOs, the variation of polymerization activity was not so large. When EAOs A and B were employed as cocatalysts, the polymerization activity slightly increased when the temperature varied from 70 to 90°C, followed by a moderate drop as the temperature further increased to 100°C. The variation of the molecular weight followed the same trend. The II rapidly decreased as the temperature rose from 70 to 90°C and slightly dropped from 90 to 100°C. When the polymerization was promoted by EAO C, the activity was very low at 70°C. High activity and a polypropylene with high molecular weight and II were produced at 90 and 100°C. Although EAO D showed poor activity in propylene polymerization, it produced a polymer with the highest isotacticity with respect to all other cocatalysts used here.

To further study the influence of cocatalysts on the microstructure of polymers, the isotacticity distributions of polypropylenes prepared by various cocatalysts were measured by the TREF method. The TREF profiles of isotactic fractions of the polymers prepared

at various temperatures are shown in Figures 1 and 2. One sharp peak at 114°C and a small shoulder peak at 107°C were detected in the TREF profile. Two peaks found in the TREF profile indicate the existence of two kinds of active sites with different isospecificities besides the aspecific active site. One is the highly isospecific active site (site A) generating the fraction eluted around 114°C, and the other is the moderately isospecific site (site B) producing the fraction eluted around 107°C. It is evident that there was no apparent difference in the isotacticity distribution among samples obtained by various cocatalysts at 70°C, which is consistent with the similar IIs of all samples. Regarding various TREF curves of polymers obtained at 100°C,

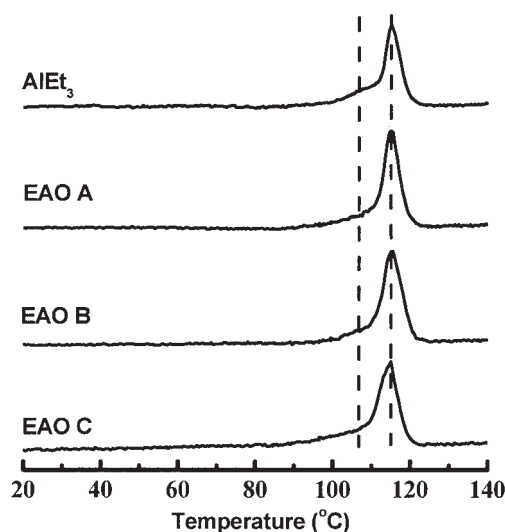


Figure 1 TREF profiles of the isotactic fraction of polypropylene prepared by various cocatalysts at 70°C.

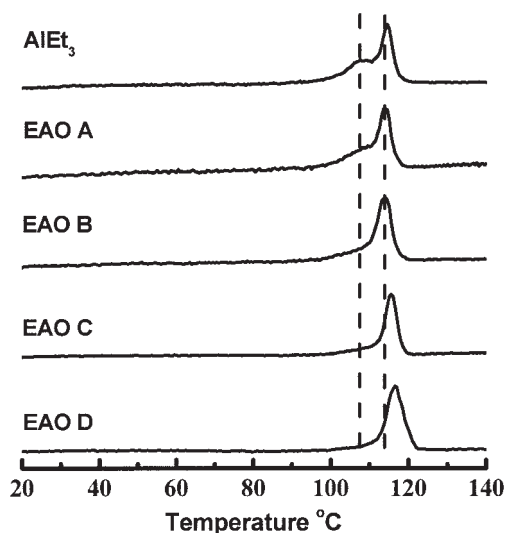


Figure 2 TREF profiles of the isotactic fraction of polypropylene prepared by various cocatalysts at 100°C.

some differences among samples were found. One sharp peak and a small shoulder peak were also detected for the polypropylene obtained with AlEt_3 . As the cocatalyst changed from EAO A to D, the main peak shifted slowly to a high temperature and the shoulder peak gradually decreased and almost disappeared for EAOs C and D. As illustrated by the curves of EAOs A–D in Figure 2, not only the amount of site B decreased, but also the stereospecificity of site A was improved as the oligomeric degree of EAO increased when polymerization was carried out at 100°C. Such variations were in good agreement with the variation of the IIs and melting temperatures of corresponding polymers.

Figure 3 presents a direct comparison between the TREF profiles of samples prepared by AlEt_3 and EAO C at various temperatures. In the profiles of polypropylene prepared by AlEt_3 , as the polymerization temperature increases from 70 to 100°C, the intensity of the shoulder peak centered at 107°C increases and the main peak at 114°C slightly shifts to a low temperature. On the contrary, the main peak in the TREF profile of polypropylene prepared by EAO C shifted to a high temperature as the polymerization temperature varied from 70 to 100°C together with the reduced shoulder peak. We concluded that more active site B was generated as the polymerization temperature rose from 70 to 100°C when AlEt_3 was used as the cocatalyst.

Variation of the cocatalyst from AlEt_3 to EAO results in a low amount and weak reactivity of the Al-Et group and probably a high oligomeric degree of the cocatalyst. The activation process of Ziegler–Natta polymerization involves alkylation by the cocatalyst and the formation of a bimetallic active site through coordination between the aluminum compound and the

titanium site. Because the reactivity of the Al-Et group of EAO is weaker than that of AlEt_3 , the concentration of active sites generated by EAOs is probably low compared with AlEt_3 , which accounts for the extremely low activities with EAOs C and D at 70°C. When the polymerization temperature rose to higher than 70°C, the alkylation power of EAOs, especially EAOs C and D, was modified. The activities of EAOs C and D were improved, which were almost the same as those of EAOs A and B. The decrement of the polymerization activity obtained by AlEt_3 was also attributed to its strong reactivity. Ti^{3+} species could be further reduced to Ti^{2+} species by AlEt_3 at high temperature, which is inactive for propylene polymerization.¹⁴ The size of the cocatalyst is also believed to affect the properties of the active site. On the one hand, the bulky cocatalyst is proposed to generate additional hindrance for active sites, resulting in high isospecificity of the active site.¹⁵ Not only the isotacticity of the polymer increases as the cocatalyst varies from EAOs A to D, but also the amount of active site B decreases as the size of the cocatalyst increases. On the other hand, protection of the active site by a large cocatalyst leads to good stability of the active site. The active site is formed by the interaction between TiCl_4 and the cocatalyst, but further interactions between them will lead to the deactivation of active species. The bulkiness of the cocatalyst could guard the active site by preventing further attack by other components in the polymerization system.¹⁶ Moreover, it is suggested that the active site generated by the reaction between the titanium site and EAO is more stable than AlEt_3 because of the special interaction between EAO and supporter MgCl_2 . Such a special interaction be-

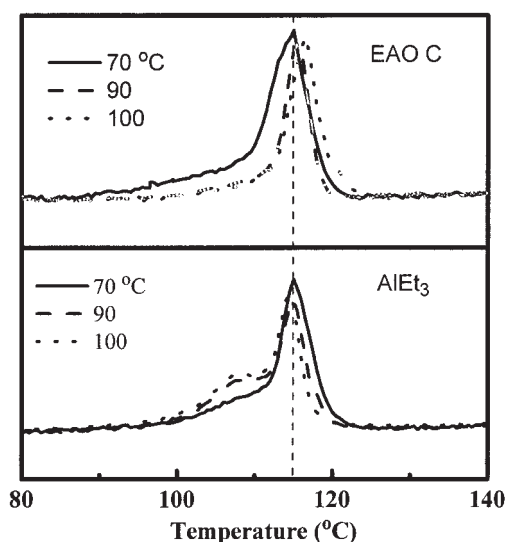


Figure 3 TREF profiles of the isotactic fraction of polypropylene prepared by AlEt_3 and EAO C at various temperatures.

tween EAO and the supporter might make an important contribution to its good performance at high temperature. The higher the temperature is, the stronger the effect. The significant improvement of the molecular weights of polypropylenes obtained with EAOs can also be explained by the guard effect and low reactivity of EAO, which retards the chain transfer to the monomer and aluminum compound.

CONCLUSIONS

Good activities and high isotacticity of polypropylenes obtained with EAOs demonstrated that the low reactivity of a cocatalyst favors high temperature polymerization. The variation of the isotacticity distribution of the polymer produced by different cocatalysts at different temperatures revealed the precise influence of the cocatalyst on the properties of the active site of the Ziegler–Natta catalyst. It was possible to modify and improve the performance of the Ziegler–Natta catalyst at high temperature by modification of the cocatalyst.

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