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Ethylene/Norbornene Copolymerization with *i*Pr(Cp)(Flu)ZrCl$_2$ Catalyst: Effect of MAO Cocatalyst and 3rd Monomer

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Summary: The copolymerization of ethylene and norbornene (N) was carried out with *i*Pr(Cp)(Flu)ZrCl$_2$ catalyst and modified methylaluminoxane (MMAO) cocatalyst. The catalytic activity was dependent on the structure of MMAO, i.e., MMAO-4 exhibited higher catalyst activity than MMAO-3A containing more *i*-butyl groups. The glass transition temperature (T$_g$) and the composition of the produced copolymer were not affected by MMAO type. With styrene derivatives as 3rd monomer, T$_g$ of copolymer increased while the catalytic activity decreased. With the addition of 3rd monomer, not only the content of 3rd monomer but also the content of N increased.

Keywords: *ansa*-metallocene catalyst; copolymerization; ethylene and norbornene; MMAO cocatalyst; 3rd monomer

Introduction

Since Kaminsky discovered that the *ansa*-metallocenes produce copolymer of ethylene (E) and norbornene (N), much effort were devoted to the development of cycloolefin copolymer (COC).[1] Recently the COC had been commercialized under the trade names such as Zeonex, Arton, Apel and Topas from Nippon Zeon, JSR (Japan Synthetic Rubber), Mitsui Sekka and Hoechst, respectively.[2]

The COC is comprised in the new classes of polymers based on cyclic olefin monomers and olefin. Because of the bulky cyclic olefin units randomly or alternately attached to the polymer backbone, the copolymer becomes amorphous and shows the properties of high glass transition temperature (T$_g$), good optical clarity, low shrinkage, low moisture absorption and low birefringence.[3]

The statistical COC resins are transparent due to their amorphous character, colorless and show a high optical anisotropy. Due to their high carbon/hydrogen ratio, these copolymers have the high refractive index and good stability against hydrolysis as well as chemical degradation. In combination with its stiffness and good processability, COC had been considered to the interesting materials for optical applications such as compact discs, DVD, lenses and optical fibers.[2]

Due to the low reactivity ratio of N in copolymerization with E, many copolymerization systems have been examined [4,5] and it is necessary to enhance the incorporation of N in copolymer for the practical production of COC.[6]

For the metallocene catalyst, the MAO cocatalyst is essential for the olefin polymerization and the effects of the structure and amount of MAO on ethylene polymerization had been studied for semi-batch process.[6]

In this article, the copolymerizations of E and N were carried out with *i*Pr(Cp)(Flu)ZrCl$_2$ and two types of modified methylaluminoxane (MMAO) cocatalyst,

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and the effects of MMAO type on the catalytic activity and glass transition temperature of copolymer had been investigated. In addition, various styrene derivatives were examined as a 3rd monomer, and the effects of 3rd monomer on the catalytic activity and the polymer structure were investigated.

Experimental Part

Materials

The *ansa*-metallocene, *i*Pr(Cp)(Flu)$ZrCl_2$ (Boulder Sci., U.S.A.) was purchased and used as received. Two types of modified methylaluminoxanes (MMAO-4: 6.4 wt% Al, and MMAO-3A: 7.1 wt% Al, Tosoh Finechemical Corp., Japan) were used without further purification. Ethylene (Korea Petrochem. Ind. Co., Korea) was used after passing through the columns of $CaSO_4$ and P_2O_5, and norbornene (Tokyo Kasei, Japan) was distilled under vacuum and dissolved in the purified toluene. The styrene derivatives such as styrene (S, Junsei Chem., Japan), *p*-methylstyrene (pMS, Tokyo Kasei, Japan) and α–methylstyrene (αMS, Tokyo Kasei, Japan) were purified by vacuum distillation after drying with CaH_2 (Junsei Chem., Japan). Toluene (Duksan Chemical Co., Korea) was purified after refluxing with sodium-benzophenone complex.

Polymerization Procedure

All operations were carried out under a nitrogen atmosphere. In a 400 ml glass reactor were introduced sequentially the proper amounts of toluene, N and MMAO solutions and then the system was saturated with E. With a continuous flow of E, the polymerization was initiated by injecting the toluene solution of *i*Pr(Cp)(Flu)$ZrCl_2$ and continued for 1h.

Polymer Characterization

The T_g of polymer was measured by means of differential scanning calorimetry (DSC, DuPont TA 2000) at 20 °C/min with 2nd run. The composition of copolymer was analyzed with carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR, Varian, Unity, 500MHz) in 1,1,2,2-tetrachloroethane / dimethyl-d_6-sulfoxide (4/1 vol/vol) at 75 °C.

Results and Discussion

Effect of MMAO Types on Catalytic Activity and T_g of Copolymer

The copolymerizations of E and N were carried out with different concentration of *i*Pr(Cp)(Flu)$ZrCl_2$ catalyst and MMAO-4 cocatalyst in the constant [cocatalyst]/[catalyst] molar ratio ([Al]/[Zr]). The experimental results for various feed ratio of [N]/[E] were given in Table 1.

From Table 1, it has been confirmed that the catalytic activity and T_g of produced copolymer were less changed with the concentration of catalyst. The composition of copolymer was estimated to be independent on the catalyst amount because the N content of E/N copolymer has linear relationship with T_g.[4] With increasing the feed ratio of [N]/[E], the catalytic activity and T_g of produced copolymer were improved steadily. This enhancement of catalytic activity of *i*Pr(Cp)(Flu)$ZrCl_2$ catalyst is comparable to that of *rac*-Et(Ind)$_2$$ZrCl_2$ catalyst which exhibits a serious depression of catalytic activity with increasing [N]/[E].[5]

Table 1.
Effect of Catalyst Concentration on E/N Copolymerization Initiated with *i*Pr(Cp)(Flu)$ZrCl_2$ and MMAO-4 Cocatalyst.

[N]/[E]	[Zr] = 2.5 × 10^{-5} M		[Zr] = 3.5 × 10^{-5} M	
	Activity[a)]	T_g (°C)	Activity[a)]	T_g (°C)
0	325	n.d.[b)]	347	n.d.[b)]
2.5	899	41.5	872	42.0
5.0	1378	80.7	1392	83.0
7.5	1759	101.0	1775	102.2
10	2056	106.4	2110	109.2
20	2607	133.7	2585	135.8
30	3457	153.2	3470	154.1
40	3530	163.6	3572	165.4
50	3592	166.2	3614	167.5

Polymerization condition: [Al]/[Zr]=3000, 40 °C, 1atm, 1h;

[a)] Catalytic activity; Kg-polymer/(mol-Zr · h · atm);

[b)] n.d.; not detected.

The composition of produced copolymer was analyzed measured with ^{13}C-NMR and the typical spectrum of E/N copolymer was given at Figure 1.

The N content of copolymer was calculated from the peak area of -CH_2- and C4 of Figure 1,[7] and it was found that the copolymer produced for [N]/[E] feed ratio = 10/1 contained 25.2 mole% of N.

The MAO cocatalyst for metallocene catalyst is known to act as an alkylating agent of transition metal and to stabilize the positive ion of polymerization active center by anion species. All of the synthetic techniques inevitably produce MAO having various chemical structures, different degrees of oligomerization, and amounts of unreacted trimethylaluminum(TMA). Both cyclic and liner oligomers have been proposed to be produced in the formation of MAO with a degree of oligomerization between 10 and 20.[8] The above factors influence very sensitively the polymerization behaviors of metallocene catalysts.

To examine the effect of MMAO type on polymerization behaviors of *i*Pr(Cp)(Flu)$ZrCl_2$ catalyst for E/N copolymerization, two types of commercial MMAO were used. The exact structure of MMAO was not clear yet, but the molecular structural formula of MMAO-3A and MMAO-4 were noted as -$[CH_3]_{0.7}(i\text{-}C_4H_9)_{0.3}AlO]$x- and -$[CH_3]_{0.9}(i\text{-}C_4H_9)_{0.1}AlO]$x-, respectively.[9]

The catalytic activity of *i*Pr(Cp)(Flu)$ZrCl_2$ catalyst for E/N copolymerization with MMAO-3A or MMAO-4 was obtained for various [N]/[E] feed ratio and the experimental results are shown in Figure 2.

From Figure 2, it was confirmed that the catalytic activity increased with [N]/[E] feed ratio as mentioned before. In addition, the catalytic activity for MMAO-4 was much higher than that for MMAO-3A, which anticipated that MMAO-4 having less *i*-butyl group content exhibited higher catalytic activity. This tendency has been also found in the case of ethylene polymerization.[8]

The T_g of copolymer obtained with *i*Pr(Cp)(Flu)$ZrCl_2$ catalyst and MMAO-3A or MMAO-4 cocatalyst was measured for various [N]/[E] feed ratio and the results were given in Figure 3.

As shown in Figure 3, T_g of copolymer obtained for MMAO-4 or MMAO-3A cocatalyst was almost same, which meant that T_g of copolymer was not influenced by the types of MMAO cocatalyst although it increased with [N]/[E] feed ratio due to the more incorporation of N.

With the above observations, it could be considered that the MMAO cocatalyst type

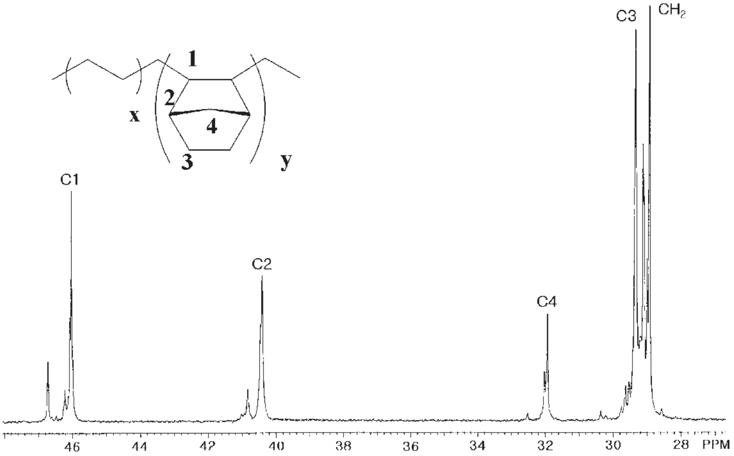

Figure 1.
^{13}C-NMR spectrum of E/N copolymer obtained with *i*Pr(Cp)(Flu)$ZrCl_2$ and MMAO-4 cocatalyst ([N]/[E] feed ratio = 10/1)

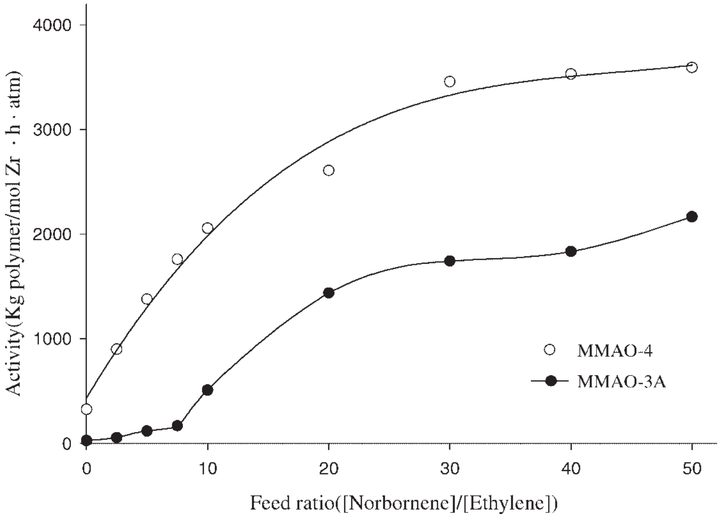

Figure 2.
Effect of MMAO cocatalyst types on catalytic activity for E/N copolymerization initiated with *i*Pr(Cp)(Flu)$ZrCl_2$ ([Zr]=2.5×10^{-5}mol/L, [Al]/[Zr]=3000, 40 °C, 1atm, 1h)

might affect the amount of polymerization active site and the MMAO having less *i*-butyl content produced more active site to result higher catalytic activity. On the other hand, the structure of active site might be independent to the type of MMAO cocatalyst because T_g of copolymer or copolymer composition was not dependent on MMAO cocatalyst type but [N]/[E] feed ratio.

Effect of 3rd Monomer on Catalyst Activity and T_g of Copolymer

In a preliminary study,[6] the catalytic activity and T_g of copolymer as well as the incorporation of norbornene in copoly-

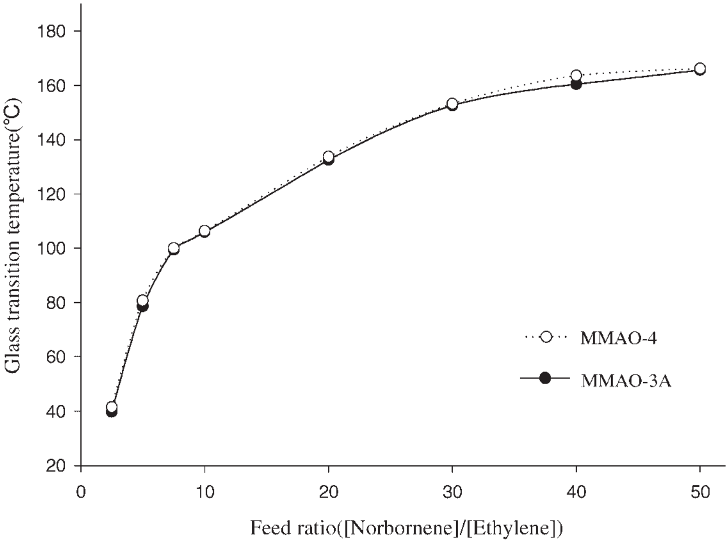

Figure 3.
Effect of MMAO cocatalyst types on T_g of E/N copolymer obtained with *iPr*(Cp)(Flu)$ZrCl_2$ ([Zr]=2.5×10^{-5}mol/L, [Al]/[Zr]=3000, 40 °C, 1atm, 1h).

Table 2.
Copolymerizations of E and N Initiated with *i*Pr(Cp)(Flu)$ZrCl_2$ and MMAO-4 in Addition of 3^{rd} Monomer.

[3rd monomer]/[E]		Activity[a)]	T_g (°C)	E/N/3rd monomer (mol%)[b)]
[S]/[E]	0	899	41.5	84.7/15.3/0.0
	0.2	674	46.0	80.7/18.4/0.9
	0.4	546	46.8	78.4/20.3/1.3
	1.0	225	47.7	75.0/22.5/2.5
[pMS]/[E]	0.2	552	46.3	81.8/17.2/1.0
	0.4	374	48.6	79.9/18.7/1.4
	1.0	186	50.0	75.8/21.4/2.8
[αMS]/E]	0.2	688	44.5	82.7/16.5/0.8
	0.4	597	46.8	81.4/17.0/1.6
	1.0	405	49.3	76.9/20.6/2.5

Polymerization conditions: [Zr] = $2.5 \times o^{-5}$ mol/L, [Al]/[Zr]=3000, [N]/[E]=2.5, 40 °C, 1 atm, 1h;

a) Catalytic activity: kg-polymer/mol-Zr · h · atm;

b) Composition of polymer characterized by ^{13}C-NMR.

mer could be changed by the addition of α-olefins as a 3^{rd} monomer depending on the structure of the metallocene catalyst.

To investigate the effect of added 3^{rd} monomer on the copolymerization of E and N in details, the copolymerizations were catalyzed with *i*Pr(Cp)(Flu)$ZrCl_2$ and modified MMAO-4 with or without the addition of 3^{rd} monomer. As a 3^{rd} monomer, S and its derivatives such as pMS and αMS were applied and the experimental results are shown in Table 2.

With the addition of a 3^{rd} monomer, the catalytic activity decreased and T_g of copolymer became higher than that of E/N copolymer irrespective of the structure of 3^{rd} monomer.

Even with the addition of a small amount of 3^{rd} monomer, it was found that the content of N estimated by ^{13}C-NMR analysis was improved up to 5~7 mol-%. For a constant feed ratio of 3^{rd} monomer, the N content of copolymer produced in the presence of S was larger than that with other derivatives as 3^{rd} monomer. The N content enlargement with the addition of 3^{rd} monomer might be due to the enhancement of monomer diffusion,[10,11] or it could

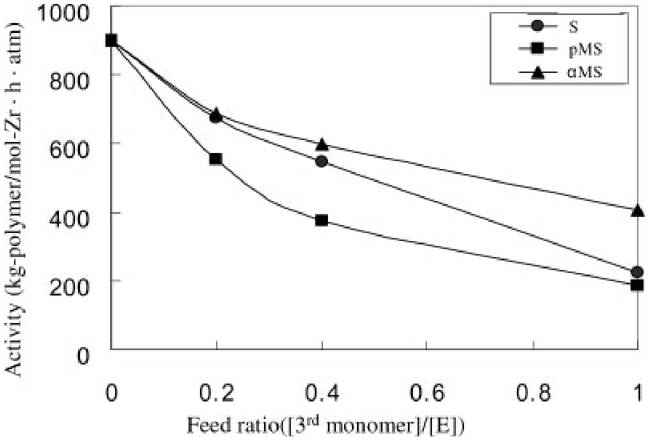

Figure 4.
Effect of 3^{rd} monomer addition on catalytic activity initiated with *i*Pr(Cp)(Flu)$ZrCl_2$ and MMAO-4 catalyst system. (Polymerization conditions: [Zr]=2.5×10^{-5} mol/L, [Al]/[Zr]=3000, [N]/[E]=2.5, 40 °C, 1 atm, 1h)

be speculated that the presence of 3rd monomer produced an environmental change of the active site.[12]

For various 3rd monomers, the change of catalytic activity with amount of 3rd monomer in the copolymerization of E and N at constant feed ratio of [N]/[E] was plotted in Figure 4.

As shown in Figure 4, the catalytic activity was changed depending on the structure and amount of 3rd monomer. With the addition of styrene derivatives as a 3rd monomer, the catalytic activity decreased gradually with the added amount of 3rd monomer. The catalytic activity with addition of αMS was higher than that with S or pMS, which indicated that the catalytic activity was dependent on the structure of 3rd monomer.

In Figure 5, the T_g of polymer obtained with addition of various 3rd monomer was plotted against N content including the case of E/N copolymer. The measured T_g of copolymer exhibited a linear relationship with N content as reported.[4] With simple addition of 3rd monomer, it was sure that the T_g of polymer increased and N content was improved. Although the N content increased with addition of 3rd monomer, the improvement in T_g of E/N/3rd monomer copolymer was not significant as E/N copolymer because the incorporation of 3rd monomer made T_g of produced polymer lower.

Conclusion

The copolymerization of ethylene and norbornene was carried out with *ansa*-metallocene, *i*Pr(Cp)(Flu)ZrCl$_2$ and two different types of MMAO cocatalyst. The catalytic activity for MMAO-4 having less i-butyl group compared to MMAO-3A was higher than that for MMAO-3A. On the other hand, T_g and the composition of produced copolymer were not affected by MMAO type. With the above results, it could be considered that the structure of MMAO cocatalyst affected the concentration of active site while the structure of active site might be independent to the type of MMAO cocatalyst.

With addition of styrene derivatives as 3rd monomer, T_g of copolymer increased while the catalytic activity decreased. In the presence of 3rd monomer, not only the content of 3rd monomer but also the content of N increased, which was called the '3rd monomer effect'.[6] The 3rd monomer addition method can be valuable to prepare a new polyolefin material of

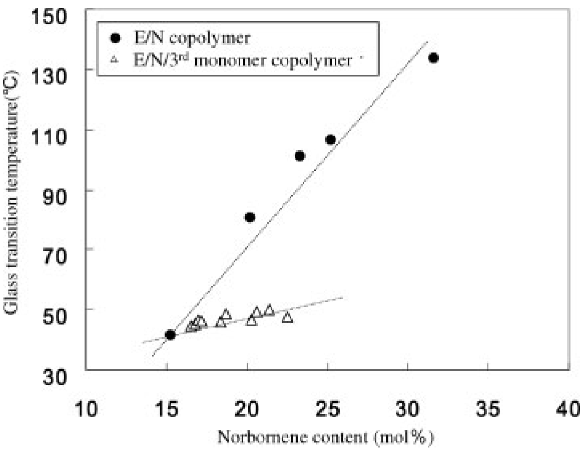

Figure 5.
Dependence of T_g on norbornene content of E/N and E/N/3rd monomer copolymers initiated with *i*Pr(Cp)(Flu)ZrCl$_2$ and MMAO-4 catalyst system.

physical properties different from the polymer obtained by usual copolymerization.

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[1] W. Kaminsky, M. Arndt-Rosenau, in: ''*Metallocene-based Polyolefins*'', J. Scheirs, W. Kaminsky, Eds., Vol. 2, John Wiley & Sons, Chichester **2000**, p. 91.
[2] H. Toreland, ''*Proceedings of Metallocene*'', Schotland Business Research., Brussels, Belgium **1995**, p. 217.
[3] G. Khanarian, *Opt. Engin.* **2001**, *40*, 1024.
[4] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* **1997**, *127*, 143.
[5] D. H. Lee, et al., *Polymer(Korea)* **2000**, *24*, 445, 751; **2001**, *25*, 468.
[6] D. H. Lee, Y. Y. Choi, J. H. Lee, Y. S. Park, S. S. Woo, *e-Polymers* **2001**, no. 19.
[7] A. L. Mcknight, R. M. Waymouth, *Macromolecules* **1999**, *32*, 2816.
[8] P. A. Charpentier, S. Zhu, A. E. Hamielec, M. A. Brook, *Polymer* **1998**, *39*, 6501.
[9] Tosoh Finechemical Corp., *Metal Alkyls Catalog, Japan*, **May 2001**, p. 9.
[10] K. Soga, H. Yanagihara, D. H. Lee, *Makromol. Chem.* **1989**, *190*, 995.
[11] K. Soga, M. Ohgizawa, T. Shiono, D. H. Lee, *Macromolecules* **1991**, *24*, 699.
[12] A. Grassi, S. Saccheo, A. Zambelli, *Macromolecules* **1997**, *31*, 5588.