

Preparation of High Transparent Olefin Copolymer with Metallocene Catalyst

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Abstract

The copolymerization of ethylene and norbornene was carried out with *ansa*-metallocene and modified methylaluminoxane (MMAO) cocatalyst. The copolymerization behavior was changed with the structure of metallocene catalysts. In addition the catalyst activity was dependent on the structure of MMAO, i.e., MMAO-4 which contains less *i*-butyl group compared to MMAO-3A exhibited higher catalyst activity than MMAO-3A. The glass transition temperature and the composition of the produced copolymer were not affected by MMAO type.

1. Objective and Background

Since Kaminsky discovered that the *ansa*-metallocenes produce copolymer of ethylene and norbornene, much effort were devoted to the development of cycloolefin copolymer (COC). 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. In this study, the copolymerizations of E and N were carried out with *ansa*-metallocene and two types of modified methylaluminoxane (MMAO) cocatalyst, and the structure effects of metallocene catalyst as well as MMAO type on the catalyst activity and glass transition temperature of copolymer had been investigated.

2. Results

2.1 Materials

The *ansa*-metallocenes were 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 CaSO₄ and P₂O₅, and norbornene (Tokyo Kasei, Japan) was distilled under vacuum and dissolved in the purified toluene. Toluene (Duksan Chemical Co., Korea) was purified after refluxing with sodium-benzophenone complex.

2.2 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 metallocene and continued for 1h.

2.3 Polymer characterization

The glass transition temperature of the obtained polymer was measured by means of differential scanning calorimetry (DSC, DuPont TA 2000) at 20 °C/min with 2nd run. The composition of the produced polymer was analyzed with carbon-13 nuclear magnetic resonance spectroscopy (¹³C-NMR, Varian, Unity, 500MHz) in 1,1,2,2-tetrachloroethane/dimethyl-d₆-sulfoxide (4/1 vol/vol) at 75 °C.

3. Results and Discussion

At first, the copolymerizations of Ethylene and Norbornene were carried out with different concentration of *i*Pr(Cp)(Flu)ZrCl₂ catalyst and modified methylaluminoxane-type 4 (MMAO-4) cocatalyst in the constant [cocatalyst]/[catalyst] molar ratio ([Al]/[Zr]). The experimental results for various feed ratio of [N]/[E] were given at Table 1.

Table 1. Effect of Catalyst Concentration on E/N Copolymerization Initiated with *i*Pr(Cp)(Flu)ZrCl₂ and MMAO-4 Cocatalyst ([Al]/[Zr]=3000, 40°C, 1atm, 1h)

[N]/[E]]	[Zr](mol/L)	2.5×10 ⁻⁵		3.5×10 ⁻⁵	
		a) Activity	Tg (°C)	a) Activity	Tg (°C)
0		325	n.d. b)	347	n.d.
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

a) Activity ; Kg-polymer/(mol-Zr·hr·atm)

b) n.d. ; not detected

From Table1, it has been confirmed that the catalyst activity and the glass transition temperature (Tg) of produced copolymer are less changed with the different 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 Tg. With increasing the feed ratio of [N]/[E], the catalyst activity and Tg of produced copolymer were improved steadily. This enhancement of catalyst activity of $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst is comparable to that of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ catalyst which exhibits a serious depression of catalyst activity with increasing [N]/[E].

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

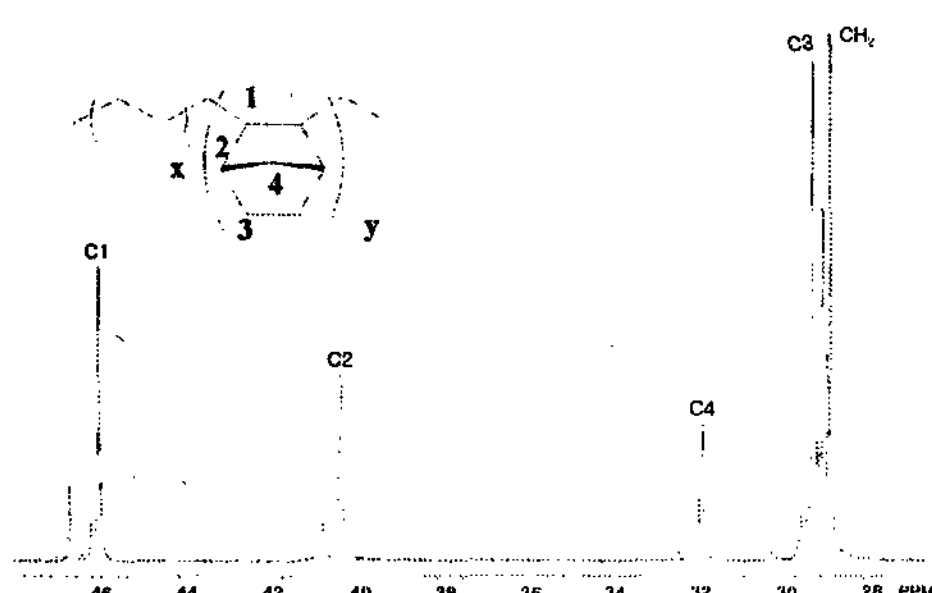


Fig. 1. ^{13}C -NMR spectrum of E/N(1/10) copolymer obtained with $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and MMAO-4 cocatalyst ([N]/[E] feed ratio = 10/1)

The N content of copolymer was calculated from the peak area of $-\text{CH}_2-$ and C4 of Fig. 1,^[7] and it was found that the copolymer produced for [N]/[E] feed ratio = 10/1 contained 25.2 mole% of N.

MAO cocatalyst for metallocene catalyst is known to act as a alkylating agent of transition metal and to stabilize the positive ion that is polymerization active center by anion species.

To examine the effect of MMAO type on polymerization behaviors of $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst for E/N copolymerization, two types of commercial MMAO were used. The exact structure of MMAO was not clear yet, but the molecule structural formula of MMAO-3A and MMAO-4 were noted as $-\text{[CH}_3\text{]}_{0.7}(\text{i-C}_4\text{H}_9)_{0.3}\text{AlO[}x\text{]}-$ and $-\text{[CH}_3\text{]}_{0.9}(\text{i-C}_4\text{H}_9)_{0.1}\text{AlO[}x\text{]}-$, respectively. The Tg of copolymer obtained with $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst and cocatalyst of MMAO-3A or MMAO-4 was measured for various [N]/[E] feed ratio and the results were given in Fig. 2.

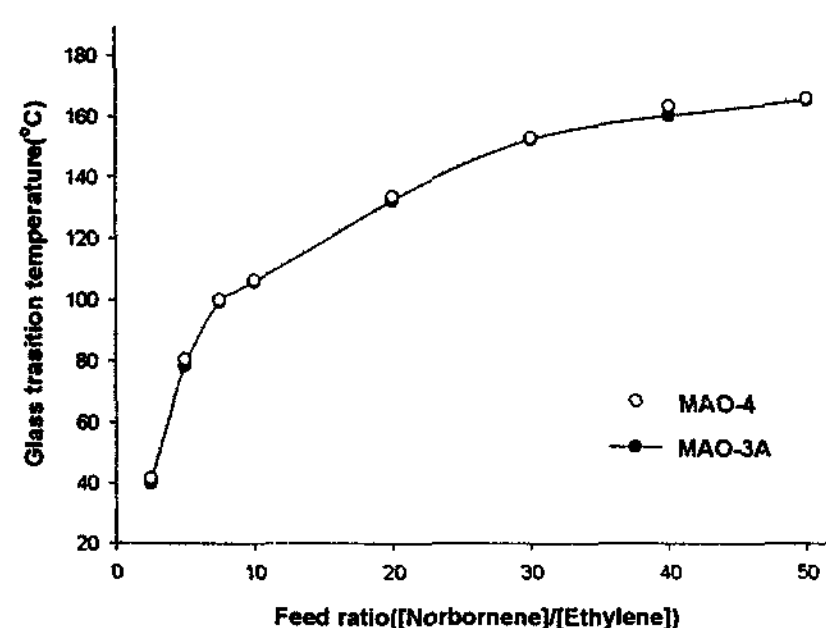


Fig. 2. Effect of MMAO cocatalyst types on Tg of E/N copolymer obtained $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ ([Zr]= 2.5×10^{-5} mol/L, [Al]/[Zr]=3000, 40°C, 1atm, 1h)

As shown in Fig. 3, Tg of copolymer obtained for MMAO-4 or MMAO-3A cocatalyst was almost same, which meant that Tg 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 may affect the amount of polymerization active site and the MMAO having less *i*-butyl content produces more active site to result higher catalyst activity. On the other hand, the structure of active site might be independent to the type of MMAO cocatalyst because Tg of copolymer or copolymer composition is not dependent on MMAO cocatalyst but [N]/[E] feed ratio.

The more detailed experiments are now on progress and the results will be appeared in near future.

4. Conclusion

The copolymerization of ethylene and norbornene was carried out with *ansa*-metallocene $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and two different types of MMAO cocatalyst. The catalyst activity for MMAO-4 having less *i*-butyl group compared to MMAO-3A was higher than that for MMAO-3A. On the other hand, Tg and the composition of the 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.

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