Influence of Process Parameters on Ethylene-Norbornene Copolymers Made by Using [2,2'-Methylenebis(1,3-dimethylcyclopentadienyl)]-Zirconium Dichloride and MAO

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Abstract−Ethylene-norbornene copolymerization was investigated by using metallocene catalysts, [2,2'-methylenebis(1,3-dimethylcyclopentadienyl)]zirconium dichloride(2,2'-CH_2 (1,3-Me_2Cp)$_2ZrCl_2$, Catalyst A) and *racemic*-ethylenebis(indenly)zirconium dichloride (*rac*-Et(Ind)$_2$ZrCl$_2$, Catalyst B), in the presence of methylaluminoxane as a cocatalyst. The influences of different process parameters such as polymerization temperature and ethylene pressure were studied by using a 56 wt% norbornene solution in toluene. The results show that Catalyst A has a higher activity in copolymerization than Catalyst B. Catalyst A also has a superior norbornene insertion performance to Catalyst B, resulting in polymers with higher glass transition temperatures, by approximately 70 °C, at similar polymerization conditions, indicative of a great commercial potential of Catalyst A.

Key words: Ethylene-Norbornene Copolymerization, Metallocene Catalysts, Glass Transition Temperature

INTRODUCTION

Cyclic olefin copolymers (COCs) are engineering thermoplastics in which cycloolefins such as norbornene are incorporated into the polymer backbone. COCs are dimensionally stable, stiff, and hard. They are produced by Ticona in Germany and Mitsui Chemical Industries and Nippon Zeon in Japan. Ticona operates a 30,000 tons/year capacity plant and produces TOPAS (Thermoplastic Olefinic Polymer Amorphous Superior) starting with dicyclopentadiene (DCPD) and ethylene feedstocks. Mitsui Chemical Industries produce similar cyclic olefin copolymers, APO (Amorphous Polyolefins) but utilizes different catalysts and comonomers. Nippon Zeon produces, by a ring-opening metathesis polymerization, ZEONEX and ZEONOR, also based on DCPD; they use different olefins as comonomers [McNally, 2001].

Copolymerization of ethylene with norbornene without ring opening, using single site metallocene catalysts, has produced an amorphous polymer with glass-like transparency, low density, high heat-deflection temperature, excellent electrical properties and chemical resistance [Lamonte and McNally, 2000; Lasarov et al., 1998]. For these reasons, the ethylene-norbornene copolymers belong to a new class of technical thermoplastics for high-quality applications such as digital data storage devices, CD-ROM, packaging, medical equipment, optics, capacitors, and toner binders for printers [Brock and Osan, 1998].

The properties of ethylene-norbornene copolymers can be tailor-made by changing the polymerization conditions or metallocene catalysts. Here, metallocene catalysts must show good activity for norbornene and produce copolymer with uniform comonomer distribution. Generally the catalyst activity, comonomer incorporation and distribution, tacticity, and molecular weights of the polymer depend heavily on the ligand structures of the metallocene catalysts.

Recently, a novel *ansa*-zirconocene catalyst [2,2'-methylenebis

(1,3-dimethylcyclopentadienyl)]zirconium dichloride (Catalyst A) bearing methyl substituents only on the carbons adjacent to a bridgehead carbon was produced by the LG Chem Research Park. Catalyst A is reported to show good catalyst reactivity toward ethylene-norbornene copolymerization [Lee et al., 2002]. The high activity for a bulky norbornene is due to the electronic effect by the methyl substituents and the minimum steric hindrance on the reaction site.

In this study, in order to demonstrate the influences of the main process parameters such as polymerization temperature and ethylene pressure on its catalyst activity and the properties of copolymers produced by it, Catalyst A was used for ethylene-norbornene copolymerization and *rac*-Et(Ind)$_2$ZrCl$_2$ (Catalyst B) was also used for the comparison. Catalyst B is a well known *ansa*-zirconocene catalyst which was tested by many others [Bergström and Seppälä, 1997; Kaminsky et al., 1991; McKnight and Waymouth, 1999]. The copolymer properties of interest were the glass transition temperature and the molecular weight of the copolymer. They were determined by differential scanning calorimetry (DSC) and high temperature gel permeation chromatography (GPC), respectively [Cho et al., 2000]. The catalyst activity was calculated with the amount of polymers produced by the catalyst.

EXPERIMENTAL

1. Materials

Catalyst A was synthesized according to procedures found in the literature [Lee et al., 2002] and Catalyst B was purchased from Aldrich. The cocatalyst was 10 wt% MAO (methylaluminoxane) in toluene from Akzo. The comonomer, norbornene (bicyclo[2,2,1] hept-2-ene), was obtained from Aldrich; its purity was 99%. The ethylene (99.9%) was purified in columns containing molecular sieves, CuO, and Al_2O_3.

2. Polymerization Procedure and Polymer Characterization

Ethylene-norbornene copolymerization experiments were performed with a 0.5 L jacketed stainless steel reactor equipped with a

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mechanical stirrer. All manipulations were done in an inert atmosphere by using a standard Schlenk technique or a VAC dry-box. The appropriate amount of norbornene was dissolved in toluene so that a 150 mL solution was obtained. The solution was passed through the purification column and poured into the reactor. After the reactor temperature had been stabilized at the desired value, the ethylene was introduced to a chosen pressure set point until the toluene solution was saturated. The MAO-toluene solution was then injected into the reactor and the mixing continued for 15 min. Finally, the catalyst-toluene solution was injected into the reactor. After the addition of the catalyst ($1.33 \cdot 10^{-6}$ mol/L), the polymerization was allowed to continue for 20 min, and the ethylene consumed was constantly replaced by pressurizing at a constant pressure. After polymerization, the reactor was vented and the reaction mixture was poured into acetone. The precipitated polymer was filtered, washed and dried in a vacuum oven at 80 °C.

The glass transition temperatures (Tg) were measured with a TA instrument DSC2010. The sample was first heated to 300 °C, then cooled to 30 °C (20 °C/min), and reheated to 250 °C or 300 °C (20 °C/min). The data used in this work was taken from the second heating. The weight average molecular weight (M_w) and the molecular weight distribution were measured by a Waters 150 CV equipped with four Waters columns. 1,2,4-trichlorobenzene was used as a solvent with the flow rate of 1 mL/min at 140 °C. The polystyrene (PS) standards, with narrow molecular weight distribution, were used for the calibration of molecular weights vs. retention time of column set.

RESULTS AND DISCUSSION

1. Activities of Catalysts

Table 1. Experimental conditions and yields of ethylene-norbornene copolymerization[a]

Run	Catalyst[b]	Temp. (°C)	Pressure (bar)	[N]/[E][c]	Yield (g)[d]
1	A	30	4.1	8.4	11.60
2	A	50	4.1	11.0	26.11
3	A	70	4.1	13.8	38.19
4	A	100	4.1	18.7	36.87
5	A	70	2.1	23.1	15.65
6	A	70	3.4	16.0	32.60
7	A	70	6.9	9.0	52.83
8	B	50	4.1	11.0	1.34
9	B	70	4.1	13.8	3.50
10	B	100	4.1	18.7	2.55
11	B	70	2.8	18.9	3.16
12	B	70	3.4	16.0	5.16
13	B	70	6.9	9.0	7.71

[a]Polymerization conditions: batch reaction, [Zr]=$1.33 \cdot 10^{-6}$ mol/L, Al/Zr=2000, 56 wt% norbornene solution=150 mL, and Polymerization time of 20 min.
[b]Catalyst A=2,2'-CH$_2$(1,3-Me$_2$Cp)$_2$ZrCl$_2$, Catalyst B=rac-Et(Ind)$_2$ZrCl$_2$.
[c]Norbornene/ethylene mole ratio in the reaction medium.
[d]Yield is defined as the weight of copolymer obtained.

Activity of catalysts is very important because it deals with the economics of a production plant [Ma and Hackett, 1998]. Much larger production of polymer is possible with the same size polymerization reactor by using a catalyst with a higher activity. Two sets of experiments were performed for Catalyst A and B. The first and second sets of data were obtained by changing polymerization temperature and ethylene pressure. The experimental conditions and copolymer yields are summarized, for both catalysts, in Table 1. Yield, which is defined as the weight of copolymer obtained, was used to calculate catalyst activity in terms of kg-polymer/(mol-Zr·h).

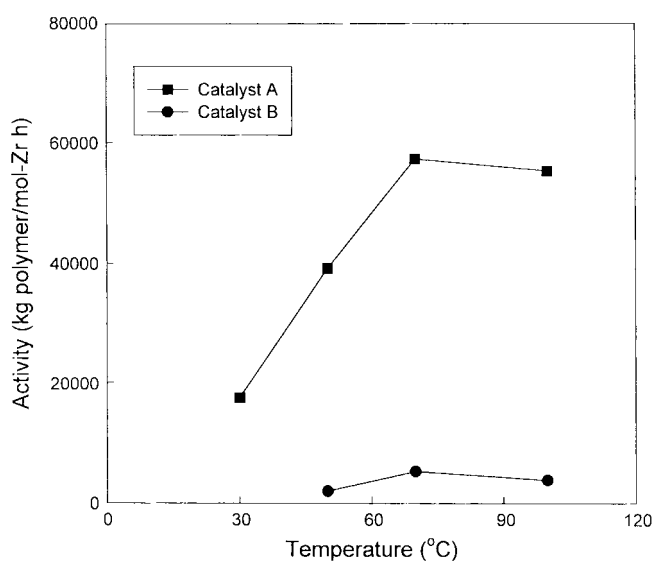Catalyst activities of ethylene-norbornene copolymerization at

Fig. 1. Catalyst activities of ethylene-norbornene copolymers produced at different polymerization temperatures with a constant ethylene pressure (4.1 bar). Catalyst A=2,2'-CH$_2$(1,3-Me$_2$Cp)$_2$ZrCl$_2$, Catalyst B = rac-Et(Ind)$_2$ZrCl$_2$.
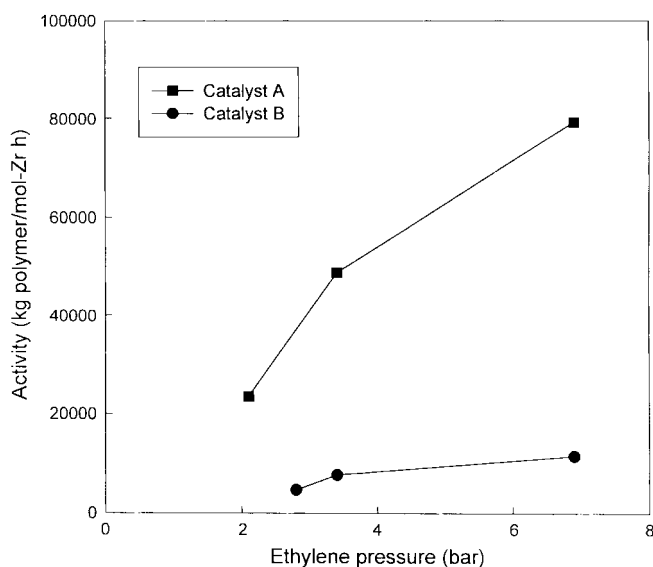

Fig. 2. Catalyst activities of ethylene-norbornene copolymers produced at different ethylene pressures with a constant temperature (70 °C). Catalyst A=2,2'-CH$_2$(1,3-Me$_2$Cp)$_2$ZrCl$_2$, Catalyst B=rac-Et(Ind)$_2$ZrCl$_2$.

different polymerization temperatures are shown in Fig. 1. The activity of Catalyst A increased by increasing the polymerization temperature from 30 °C to 70 °C at a constant ethylene pressure [Run No. 1 to 3], a further increase in temperature to 100 °C resulted in a slight decrease in catalyst activity. The latter result is due to decreased ethylene solubility, which supersedes the positive effect on reactivity [Bergström and Seppälä, 1997]. Similarly, Catalyst B showed the highest activity at 70 °C, revealed by a series of experiments [Run No. 8 to 10].

Fig. 2 shows the activities of both catalysts at different ethylene pressures with a constant polymerization temperature. The catalyst activity increased as the ethylene pressure rose from 2.1 bar to 6.9 bar for Catalyst A [Run No. 5 to 7] and from 2.8 bar to 6.9 bar for Catalyst B [Run No. 11 to 13], respectively. The same trend in the catalyst activity has been observed elsewhere for Catalyst B [Lee et al., 2000].

From both sets of experiments, it is noted that the activity of Catalyst A is much higher than that of Catalyst B, due to the electronic effect and the less steric nature of the ligand structure [Lee et al., 2002].

2. Thermal Properties of Copolymer

The glass transition temperature of ethylene-norbornene copolymer depends on the composition of ethylene and norbornene in the copolymer. As the norbornene content in the copolymer increases, the glass transition temperature of the copolymer also increases [Land and Osan, 1997].

The influences of polymerization temperature and ethylene pressure, on the glass transition temperature of the copolymer, are presented in Figs. 3 and 4 for catalysts A and B. The glass transition temperature of the copolymer increased with increasing temperature, but decreased with increasing ethylene pressure for both catalysts. This implies that increasing polymerization temperature or reducing ethylene pressure, the norbornene content in the copoly-

Fig. 4. Glass transition temperatures of ethylene-norbornene copolymers produced at different ethylene pressures with a constant temperature (70 °C). Catalyst A=2,2'-CH₂(1,3-Me₂Cp)₂ZrCl₂, Catalyst B=*rac*-Et(Ind)₂ZrCl₂.

mer increases.

The norbornene/ethylene mole ratio in the reaction medium is a major factor determining the composition of copolymer. As the norbornene/ethylene mole ratio in the reaction medium increases, the norbornene content in the copolymer increases, and, consequently, the glass transition temperature increases. Figs. 3 and 4 also show that an increase in the polymerization temperature raised the norbornene/ethylene mole ratio in the reaction medium; however, an increase of ethylene pressure reduced the norbornene/ethylene mole
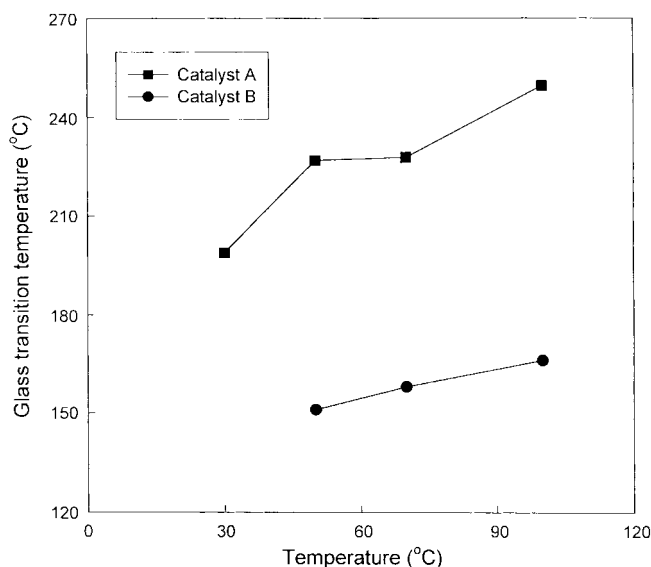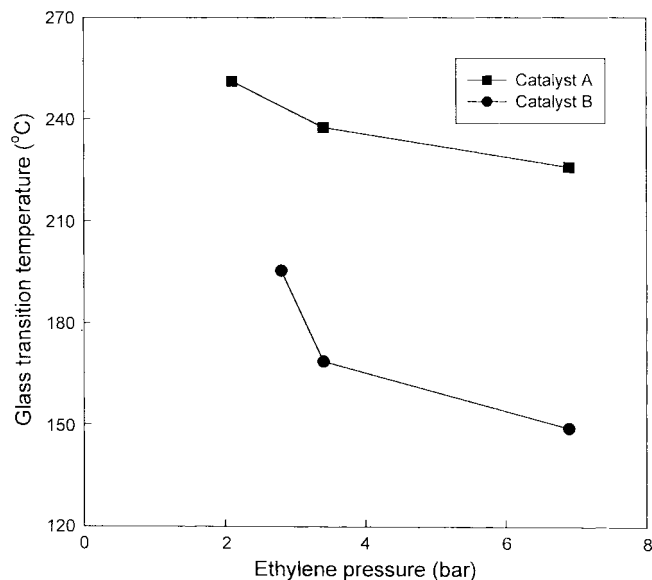

Fig. 3. Glass transition temperatures of ethylene-norbornene copolymers produced at different polymerization temperatures with a constant ethylene pressure (4.1 bar). Catalyst A=2,2'-CH₂(1,3-Me₂Cp)₂ZrCl₂, Catalyst B=*rac*-Et(Ind)₂ ZrCl₂.
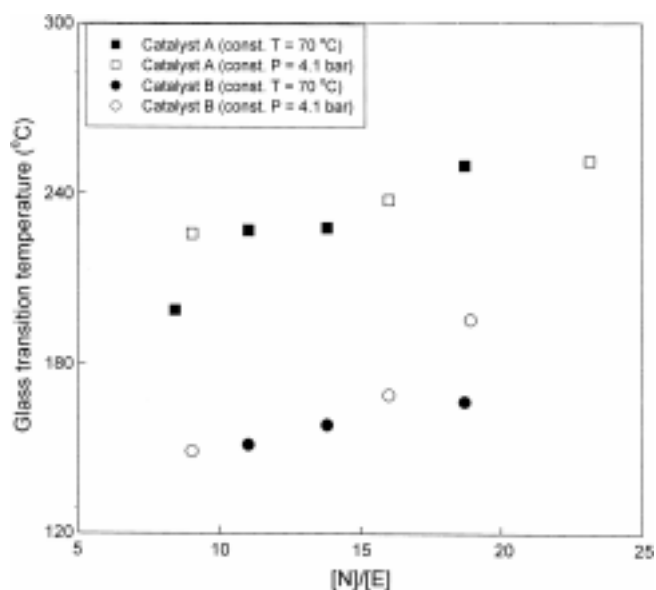

Fig. 5. Glass transition temperature of ethylene-norbornene copolymers produced as a function of norbornene/ethylene mole ratio in the reaction medium. Catalyst A=2,2'-CH₂(1,3-Me₂Cp)₂ZrCl₂, Catalyst B=*rac*-Et(Ind)₂ZrCl₂.

ratio in the reaction medium.

In Fig. 5, the glass transition temperatures of copolymers are plotted as a function of the norbornene/ethylene mole ratio. The ethylene concentration was calculated by using the Henry-Gesetz equation:

$$[C_E] = P_E H_0 \exp\left(\frac{\Delta H_L}{RT}\right) \qquad (1)$$

where C_E is the ethylene concentration (mol/L), P_E is the ethylene pressure (bar), H_0 is the Henry constant (mol/L bar), ΔH_L is the enthalpy of solvation for ethylene (J/mol), R is the universal gas constant (J/mol K) and T is the solution temperature (K). The constant values for ethylene solubility in toluene are given in the literature [McKnight and Waymouth, 1999].

The fact that the glass transition temperature of copolymer strongly depends on the norbornene/ethylene mole ratio is clear from Fig. 5. For Catalyst A, an increase in norbornene/ethylene mole ratio from 8.4 to 23.1 resulted in an increase in the glass transition temperature from 199 °C to 251 °C. On the other hand, for Catalyst B, the glass transition temperature increased from 149 °C to 196 °C as the norbornene/ethylene mole ratio changed from 9 to 18.9. The glass transition temperatures of copolymers obtained at the similar reaction conditions were higher for Catalyst A than for Catalyst B, by approximately 70 °C, which indicates the superior ability of norbornene incorporation of Catalyst A. This can be ascribed to the absence of any substituent on the β-carbons of the cyclopentadienyl ring in the metallocene complex. Thus, the nature of no steric hindrance on the reaction site of Catalyst A results in an easy approach of a bulky norbornene [Lee et al., 2002].

3. Molecular Weights

Considering the weight average molecular weights of copolymers in Figs. 6 and 7, Catalyst A produced relatively lower molecular weight polymers than catalyst B, indicating that Catalyst A is more
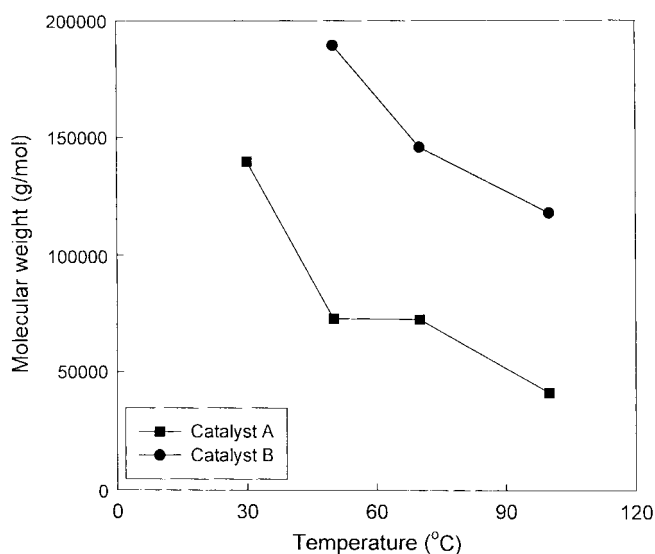

Fig. 6. Weight average molecular weights of ethylene-norbornene copolymers produced at different polymerization temperatures with a constant ethylene pressure (4.1 bar). Catalyst A=2,2'-CH$_2$(1,3-Me$_2$Cp)$_2$ZrCl$_2$, Catalyst B=rac-Et(Ind)$_2$ ZrCl$_2$.
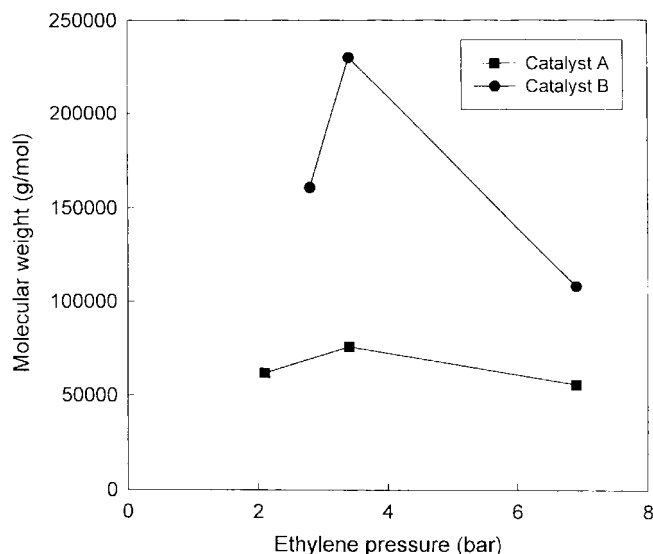

Fig. 7. Weight average molecular weights of ethylene-norbornene copolymers produced at different ethylene pressures with a constant temperature (70 °C). Catalyst A=2,2'-CH$_2$(1,3-Me$_2$Cp)$_2$ZrCl$_2$, Catalyst B=rac-Et(Ind)$_2$ZrCl$_2$.

favorable than Catalyst B for chain transfer reaction owing to the difference in steric hindrance and electronic effects originating from the ansa-ligands.

Fig. 6 shows that lower molecular weights were obtained for both catalysts at higher polymerization temperatures, with a constant ethylene pressure of 4.1 bar. This is due to more chain transfer reactions in relation to the propagation reaction, as is the case for catalysts in an olefin polymerization [Bergström and Seppälä, 1997].

It is interesting to note that for both catalysts, the copolymers have the highest weight average molecular weight at 3.4 bar. This means that when ethylene pressure was increased to 3.4 bar, the propagation reaction was more active, compared to the termination and chain transfer reactions. However as the ethylene pressure further increased to 6.9 bar, the norbornene composition of reaction medium became lower, resulting in an increase in the extent of the chain transfer reaction [Ruchatz and Fink, 1998].

CONCLUSIONS

The influence of process parameters such as polymerization temperature and ethylene pressure on the copolymerization of norbornene and ethylene were studied by using Catalyst A and Catalyst B. Catalyst A showed much higher activity and norbornene incorporation ability compared to Catalyst B. Relatively lower molecular weight copolymers were produced by Catalyst A than Catalyst B. The glass transition temperature of the copolymer increased with increasing temperature or decreasing ethylene pressure and mainly depended on the norbornene/ethylene ratio in the reaction medium for both catalysts. The glass transition temperatures of the copolymer obtained by using Catalyst A are as high as 250 °C and can be changed to a different temperature by adjusting the polymerization conditions. Consequently, Catalyst A enables us to produce the ethylene-norbornene copolymer with a wide range of norbornene content, at a reduced cost.

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