Behaviours of Ethylene/Norbornene Copolymerization with Zirconocene Catalysts

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ABSTRACT

In this study, behaviours of ethylene/norbornene copolymerization using zirconocene catalysts; rac-Et[Ind]₂ZrCl₂ (cat. A) and Cp₂ZrCl₂ (cat. B) were investigated. Based on activity profiles at various norbornene concentrations, it can be observed that although cat. A is more active than cat. B, it is less stable, indicating more rapid deactivation rates with time. It was found that deactivation rates was more pronounced with high concentrations of norbornene for both catalytic systems. Asymmetric activity profiles were observed for both catalytic systems indicating higher deactivation rates compared to the activation rates. The copolymer produced by cat. A exhibited lower melting temperature ($T_m$), but higher incorporation of norbornene. However, both catalysts produced copolymers with random distribution.

Key Words:
- zirconocene;
- copolymerization;
- norbornene;
- ethylene;
- copolymer.

INTRODUCTION

Cyclic olefin copolymers (COC) are recognized as engineering thermoplastics in which a cycloolefin such as cyclobutene, cyclopentene, norbornene, dimethanoctahydronaphthalene, and etc. is incorporated into the polymer backbone. The COC produced by metallocene catalysts which are considered as the metalloocene cyclic olefin copolymers (mCOC) have also brought a commercial interest these days.

It has been known that copolymerization of ethylene with nor-
Bornene without ring opening, using single site metallocene catalysts, is able to produce an amorphous polymer with glass-like transparency, high heat deflection temperature, excellent electrical properties, and chemical resistance [1-7]. Therefore, the ethylene-norbornene copolymers can be considered as a new class of technical thermoplastics for high quality applications such as digital data storage devices, CD ROM, packaging, medical equipment, optics, capacitors, toner binder for printers and other applications [8-9].

These norbornene-ethylene copolymers were recently introduced into the plastic market under the tradenames of APEL and APO (Mitsui Chemical Industries, Japan) and TOPAS (Ticona, Germany) as well. They are expected to compete mainly with polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS) and PC/ABS blends in technical, nonoptical applications and with PC and other COCs in optical applications.

In this present study, behaviours of ethylene/norbornene copolymerization using zirconocene catalysts were investigated. Activity profiles based on the ethylene consumption were monitored at different norbornene concentrations. The copolymers produced were also further analyzed using DSC, $^{13}$C NMR and SEM.

**EXPERIMENTAL**

All operations were carried out under an argon atmosphere using a glove box and/or Schlenk techniques.

**Chemicals**

Zirconocene catalysts: (i) rac-ethylenebis(indenyl)zirconium dichloride (Et[Ind]$_2$ZrCl$_2$) and (ii) bis(cyclopentadienyl)zirconium dichloride (Cp$_2$ZrCl$_2$) were obtained from Aldrich and used as received. Ethylene for polymerization grade was obtained from National Petrochemical Co., Thailand and it was used as received. The comonomer, norbornene, was purchased from Aldrich and purified by distilling over sodium under vacuum before used.

Methylaluminoxane (MAO) 2.534 M in toluene was donated by Tosoh Akzo, Japan. Toluene (commercial grade) was donated by Exxon Chemical, Thailand. It was dried over dehydrated CaCl$_2$ and distilled over sodium/benzophenone under argon atmosphere prior to use. Ultrahigh purity argon (99.999%) was purchased from Thai Industrial Gas Co., and was further purified by passing through a molecular sieve 3 Å, BASF catalyst R3-11G, sodium hydroxide (NaOH), and phosphorous pentaoxide (P$_2$O$_5$) to remove oxygen and moisture.

**Polymerization**

Ethylene and norbornene copolymerizations were conducted in a 100-mL semi-batch stainless steel autoclave reactor equipped with magnetic stirrer as shown in Figure 1. Toluene (to make a total volume of 30 mL) and desired amounts of norbornene (0.0005 to 0.012 mole) were injected into the reactor in the glove box. The desired amounts of Et[Ind]$_2$ZrCl$_2$ or Cp$_2$ZrCl$_2$ and MAO ([Al]$_{MAO}$/[Zr] = 1000) were mixed and stirred for 5 min at room temperature, then the mixture was added to the reactor. The reactor was immersed in liquid nitrogen for 15 min to freeze the solution and was then evacuated to remove the argon. After the briefly evacuation the reactor was immersed in a hot water bath controlled at the desired reaction temperature. Ethylene was fed into the reactor to start the reaction as soon as the desired polymerization temperature was reached. The pressure in the reactor was kept at 50 psi by a continuous ethylene feed. When the amount of ethylene consumption was 0.018 mole, the reaction was terminated by addition of acidic methanol. Ethylene consumption was fixed to avoid any mass transfer effect and inhomogeneity of the produced copolymer, resulting from changes in comonomer concentration. The copolymer was washed with excess methanol and dried in an oven at 110°C for 6 h.
Polymer Characterization
Characterization of copolymers were performed using scanning electron microscopy, SEM (JSM-5800 LV) in order to study the morphologies of copolymers produced. The thermal properties of copolymers were measured using a Perkin-Elmer DSC 7. The sample was first heated to 150°C, then cooled to 0°C (20°C/min) and reheated to 150°C (10°C/min). The data used in this work were taken from the second heating. The 13C NMR spectra of samples were measured using a JEOL JNM-A500 operating at 125 MHz. The spectra were recorded at 110°C with 1,2,4-trichlorobenzene/benzene-d6 as solvent. All spectra were baseline corrected and calculations were done using integrated intensities (peak areas). The norbornene contents in copolymers were calculated based on Tritto et al. [10].

RESULTS AND DISCUSSION

In this present study, behaviours of ethylene/norbornene copolymerization using zirconocene catalysts along with MAO were investigated. There were two kinds of zirconocene catalysts; rac-Et[Ind]2ZrCl2 (cat. A) and Cp2ZrCl2 (cat. B) used for the copolymerization of ethylene/norbornene. Particularly, the norbornene concentrations were varied throughout polymerization in order to evaluate behaviours of copolymerization. Consequently, activity profiles, morphologies, crystallinity, and copolymer microstructure were monitored.

Comparing the activities during copolymerization by the cat. A and cat. B as is shown in Figure 2, it can be seen that activities of cat. A were much higher than those of cat. B. The activity profiles for both catalysts were similar indicating that a maximum activity for both catalysts occurred at low concentrations of norbornene. It should be mentioned that activities of ethylene/norbornene copolymerization were also higher than homopolymerization of ethylene for both catalysts (not shown). Thus, the addition of such a small amount of norbornene would result in a large increase in the copolymerization activities. Kravchenko et al. [11] reported that the increase in copolymerization activities compared to the homopolymerization were likely due to the activation of dormant catalyst sites by comonomers.

The another type of activation effect was also observed for ethylene polymerization upon the addition of small amounts of 1-olefin comonomers referred to as a comonomer effect. Some explanations have been cited to describe this phenomenon such as the "trigger" mechanism [12]. The improvement of the diffusion rates due to the solubility of active centres by the incor-

![Figure 2. Activity profiles for ethylene/norbornene copolymerization using rac-Et[Ind]2ZrCl2 and Cp2ZrCl2 catalysts: [Zr]= 6.7 × 10^{-5} M, [Al]_{MAO}/[Zr] = 1000, T = 50°C, [ethylene] = 0.018 mole.](image)

![Figure 3. Activity Profiles based on ethylene consumption at different norbornene concentrations for rac-Et[Ind]2ZrCl2 catalyst: [Zr]= 6.7 × 10^{-5} M, [Al]_{MAO}/[Zr] = 1000, T = 50°C, [ethylene] = 0.018 mole](image)
poration of comonomers was also reported by Koivumaki et al. [13].

Activity profiles at various concentrations of norbornene for cat. A and cat. B are shown in Figures 3 and 4, respectively. It can be observed that the activity profiles based on the ethylene consumption for both catalysts were similar indicating deactivation with times. However, it should be mentioned that although activities for cat. A were higher than those for cat. B, the decreased deactivation rates for cat. B were much lower compared to those for cat. A. This is suggested that cat. B is more stable than cat. A. It was also found that higher concentrations of norbornene resulted in lower activities for both catalysts. This was probably because the coordination of norbornene to the catalytic sites caused reduction in capability for ethylene insertion and/or propagation.

Bergstrom et al. [14] also reported that large amounts of norbornene seemed to deactivate the active sites of catalysts in other catalytic systems. In addition, it can be seen that the deactivation rates were more pronounced to norbornene concentrations than the activation rates resulting in an observation of asymmetric activity profiles for both catalytic systems. Besides the effect of norbornene concentrations on both activation and deactivation rates, it was also found that the larger amounts of norbornene resulted in higher deactivation rates as well.

In order to identify the properties of copolymers obtained from both catalytic systems, differential scanning calorimeter (DSC), $^{13}$carbon nuclear magnetic resonance ($^{13}$C NMR), and scanning electron microscopy (SEM) were performed. The thermal properties such as melting temperatures ($T_m$) and glass transition temperatures ($T_g$) were measured by DSC. Microstructures and incorporations of norbornene in the polymer backbone were determined using $^{13}$C NMR and scanning electron microscopy (SEM) was conducted in order to study the morphologies of copolymers.

Some properties of ethylene/norbornene copolymers are shown in Table 1. As mentioned earlier, at the same polymerization condition, activity of cat. A was much higher than that of cat. B. However, the $T_m$ and also the crystallinity of copolymer obtained from cat. B were higher than that from cat. A. It is known that $T_g$ of copolymer produced depends on the compositions of ethylene and norbornene in the copolymer.

In general, $T_g$ of the copolymer increases with increasing the incorporation of norbornene in the polymer backbone [8]. However, based on our investigation, $T_g$ cannot be observed. This is probably due to a very low content of norbornene in the copolymer. The

![Figure 4. Activity profiles based on ethylene consumption at different norbornene concentrations for Cp$_2$ZrCl$_2$ catalyst: [Zr] = 6.7 × 10$^{-5}$ M, [Al]$_{MAO}$/[Zr] = 1000, T = 50°C, [ethylene] = 0.018 mole.](image)

Table 1. Properties of ethylene (E)/norbornene (N) copolymers obtained.

<table>
<thead>
<tr>
<th>Catalyst used</th>
<th>Activity$^a$ (kg Cop./mol. Zr./h)</th>
<th>$T_m$$^b$ (°C)</th>
<th>Crystallinity$^b$ (%)</th>
<th>NB Incorporation$^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et [Ind$_2$ZrCl$_2$</td>
<td>3278</td>
<td>66.4</td>
<td>8.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Cp$_2$ZrCl$_2$</td>
<td>1476</td>
<td>103.5</td>
<td>20.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

$^a$Polymerization condition: [Zr] = 6.7 × 10$^{-5}$ M, [Al]$_{MAO}$/[Zr] = 1000, T = 50°C, [ethylene] = 0.018 mole.

$^b$[NB] = 0.003 mole; $^b$obtained from DSC; $^c$obtained from $^{13}$C NMR.
NMR spectra of copolymers for both catalysts were similar (not shown). They were identified based on the reference [10]. It was found that both catalysts produced the random copolymers. The incorporation of norbornene in the copolymer was also determined from the NMR spectrum. The results are also shown in Table 1 indicating that higher incorporation of norbornene can be achieved by cat. A. This is due to the wider coordination space of zirconium, resulting from the electronic effect and the less steric nature of ligand structure.

Morphologies of copolymers obtained from cat. A and cat. B are shown in Figures 5 and 6, respectively.

**Figure 5.** SEM Micrographs of the ethylene/norbornene copolymer produced by rac-Et[Ind]$_2$ZrCl$_2$ catalyst: [Zr] = 6.7 x 10$^{-5}$ M, [Al]MAO/[Zr] = 1000, T = 50°C, [ethylene] = 0.018 mole, [NB] = 0.003 mole: Top with x 500 and bottom with x 5,000.

**Figure 6.** SEM Micrographs of the ethylene/norbornene copolymer produced by Cp$_2$ZrCl$_2$ catalyst: [Zr] = 6.7 x 10$^{-5}$ M, [Al]MAO/[Zr] = 1000, T = 50°C, [ethylene] = 0.018 mole, [NB] = 0.003 mole: Top with x 500 and bottom with x 5,000.

Essentially, with a difference in norbornene incorporation in the copolymer, the morphologies would be different. With higher amounts of norbornene incorporation, the morphologies of copolymer seemed to be more uniform compared to the lower one.

**CONCLUSION**

The present study was performed to investigate behaviors of ethylene/norbornene copolymerization. It was found that rac-Et[Ind]$_2$ZrCl$_2$ (cat. A) was more active than Cp$_2$ZrCl$_2$ (cat. B) regardless of norbornene concentrations. However, considering the activity profiles,
it was noted that cat. B was more stable than cat. A resulting in slower decreases in deactivation rates. It should be noted that although norbornene incorporation of cat. A was higher, $T_m$ of the copolymer produced from cat. A was much lower than that produced by cat. B. The copolymers produced by both catalytic systems were random copolymers.

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REFERENCES