Copolymerization of ethylene and 5-vinyl-2-norbornene by stereospecific metallocones and epoxidation of the resulting copolymer

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Abstract

Copolymerizations of ethylene with 5-vinyl-2-norbornene (VNB) were carried out with isospecifc rac-1,2-ethylenebis(1-indenyl)Zr(NMe$_2$)$_2$ [rac-(EBI)Zr(NMe$_2$)$_2$] and syndiospecific isopropylidene(cyclo-pentadienyl)(9-fluorenyl)ZrMe$_2$ [iPr(Cp)-(Flu)ZrMe$_2$] compounds combined with Al(i-Bu)$_3$/[Ph][B(C$_6$F$_5$)$_4$] as a cocatalyst. VNB was inserted into copolymer backbone through the endocyclic double bond regioslectively, leaving vinyl double bond. The rac-(EBI)Zr-(NMe$_2$)$_2$ catalyst showed a higher activity and a VNB reactivity than iPr(Cp)(Flu)ZrMe$_2$ catalyst. The vinyl groups contained in the copolymer were converted to the epoxy group quantitatively with m-chloroperbenzoic acid, producing functionalized polyolefin.

Keywords: Copolymerization; Poly(ethylene-co-5-vinyl-2-norbornene); Metallocones; Epoxidation

1. Introduction

Recently, much attention is addressed to the polyolefins with polar groups. The functionalized polyolefins can serve as interfacial modifiers to improve their adhesion to and compatibility with other polar materials. In general, there are two methods to introduce functional group to polymer. One is direct copolymerization with polar monomer and the other chemical modification of synthesized polymer. However, direct copolymerization with metallocone compound is not useful because cationic species generated from metallocone compound coordinates to polar monomer [1], and resulted in low productivity and less amount of incorporated comonomer. Thus, much work has recently been done for the methods of chemical modification of polymer containing reactive site, like vinyl or vinylidene group, etc. [2–4]. In the latter methods the olefin is copolymerized with dienes, such as 1,4-hexadiene [2], 4-vinyl-1-cyclohexene [3], and 5-vinyl-2-norbornene [4–6]. These non-conjugated dienes are copolymerized with ethylene and/or propylene regioslectively in presence of metallocone compound, possibly leaving unsaturated double bonds in pendant group. As a result several
method of functionalization can be utilized in order to introduce a new reactive group into the polymer backbone, leading to various applications, like polymer blending [7–9].

A 5-vinyl-2-norbornene (VNB) is copolymerized through the endocyclic double bond leaving vinyl group unreacted, because of the more ring-strain of endocyclic double bond [4,10]. In this paper we compare the copolymerization behavior of ethylene and 5-vinyl-2-norbornene by two representative stereospecific metallocene catalysts, rac-1,2-ethylenebis(1-indeny)Zr(NMe₂)₂ [rac-(EBI)Zr(NMe₂)₂, CAT-1] and isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe₂, [iPr(Cp)(Flu)ZrMe₂, CAT-2], combined with Al(i-Bu)₃/[PhC][B(CF₃)₄] as a cocatalyst system. In addition, the epoxidation of resulting poly(ethylene-co-5-vinyl-2-norbornene) was investigated.

2. Experimental

2.1. Materials

All reactions were carried out under a purified nitrogen atmosphere using standard dry box and Schlenk techniques. Ethylene (SK Corp., South Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. VNB was distilled from CaH₂. Solvents were distilled from Na/benzophenone and stored over molecular sieves (4A). Al(i-Bu)₃, and m-chloroperbenzoic acid from Aldrich were used without purification. CAT-1 [11] and CAT-2 [12], and anionic [Ph₃C][B(C₆F₅)₄] compound [13] were synthesized according to literature procedures.

2.2. Polymerization

Copolymerizations were carried out in a 250-ml glass reactor equipped with a magnetic stirrer and a thermometer. In a dry box, the reactor was filled with the metallocene catalyst (4.00 μmol for CAT-1 and 4.08 μmol for CAT-2, respectively), 80 ml of toluene, Al(i-Bu)₃, ([Al]/[Zr] = 80.0), and various amount of VNB. The reactor was immersed in a constant-temperature bath previously set to the desired temperature (typically 70°C). When the reactor temperature had been equilibrated to the bath temperature, ethylene (1.34 atm) was introduced into the reactor after removing the argon gas under a vacuum. When no more absorption of ethylene into toluene was observed, a prescribed amount of [Ph₃C][B(C₆F₅)₄] ([B(C₆F₅)₄]/[Zr] = 1.0) dissolved in toluene was injected into the reactor and then the polymerization was started. Polymerization was quenched by the addition of methanol. The polymer obtained was filtered, washed with an excess amount of methanol and dried in vacuum at 50°C for 24 h.

2.3. Epoxidation

An amount of 0.5 g of poly(ethylene-co-VNB) containing 16.65 mol% of VNB was placed in 250-ml, three-necked round-bottomed flasks with 70 ml dry toluene, and then the flask was heated at 65°C until the copolymer was dissolved completely. A total of 0.91 g of m-chloroperbenzoic acid dissolved in 10 ml of toluene was added, and stirred for 4 h. Then the reaction was stopped by the addition of methanol. The epoxy-containing polymer obtained was filtered, washed with an excess amount of methanol and dried in vacuum at 50°C for 24 h.

2.4. Characterization

¹H NMR and ¹³C NMR spectra of the polymers were recorded at 120°C on a Varian Unity Plus 300 spectrometer. Samples were prepared by dissolving the polymer in CDCl₃-tetrachloroethane (1/5, v/v). Melting curves were recorded with a DuPont differential scanning calorimeter (DSC, Model 910) at a 10°C/min. The intrinsic viscosities of polymers were determined in decalin at 135°C using an Ubbelohde viscometer. FTIR spectra were obtained with an ATI Mattson Genesis Series FTIR.
Raman spectra were recorded on a Bruker IFS55 FTIR spectrometer with the Raman modulus (FRA 106), CaF$_2$ beamsplitter, and Ge detector. The excitation source was a diode pumped Nd:YAG laser operated at 1064 nm. The laser power was 350 mW.

3. Results and discussion

3.1. Copolymerization kinetics

Figs. 1 and 2 show the polymerization rate curves obtained at 70°C for 20 min by using CAT-1 and CAT-2, respectively. CAT-1 shows much higher activity than CAT-2. All polymerizations by both catalysts are marked by very high initial rates which reach maximum rate ($R_{p,max}$) within 1–2 min after the introduction of [Ph$_2$C][B(C$_6$F$_5$)$_2$]. Within this period a pronounced change in the viscosity of the solvent was observed and the formation of fibrous polymer entangled on the stirrer was also noted. Evidently during this period the growing active sites are encapsulated in precipitated polymer which may prevent monomers from diffusing into the active sites, resulting in decaying to almost zero rates. In case that the initial rate is not so high and the crystallinity of polymer is low due to the large incorporation of VNB in polymer, the polymerization rates remain steady (Fig. 1f–h), since the viscosity change of polymerization medium is not so pronounced. The $R_{p,max}$ value decreases monotonously as the VNB amount in feed increases.

The comonomer content incorporated was determined by $^1$H NMR spectroscopy [8] and the results are summarized in Fig. 3, which is the plot of VNB molar percentage in feed versus VNB molar percentage in copolymer. Surprisingly isospecific catalyst CAT-1 shows a higher reactivity of VNB than syndiospecific catalyst CAT-2. These results are not common in that the syndiospecific catalyst is generally
more reactive toward comonomer in the copolymerization of ethylene and/or propylene with high \( \alpha \)-olefins than the isospecific catalyst [14–16]. In that the highly bulky VNB is incorporated in the polymer chain by using the cis-CH=CH– bond in the norbornene cycle (vide infra), this result is seemed to be deeply related with the bulkiness of the comonomer.

Copolymerizations were also carried out at various temperatures in the presence of CAT-1, by maintaining the [VNB]/[E] ratio in feed constant. The polymerization activity as an average rate of polymerization \( R_p \) decreases dramatically as the temperature decreases (Table 1), even if the comonomer reactivity increases slightly as the temperature decreases. The decrease of activity is mainly caused by the precipitated polymer pronounced at lower temperature due to the lower solubility of the resulting copolymer.

![Fig. 3. Copolymerization diagrams of ethylene and 5-vinyl-2-norbornene by (a) CAT-1 and (b) CAT-2 catalysts.](image)

Table 1

Results of copolymerization of ethylene/5-vinyl-2-norbornene

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Catalyst</th>
<th>[VNB] in feed (%)</th>
<th>[Zr] (μmol)</th>
<th>[VNB] in polymer (%)</th>
<th>T_p (°C)</th>
<th>R_p ((× 10^{-5}))</th>
<th>T_m (°C)</th>
<th>ΔH_i (kJ/mol)</th>
<th>[η] (dl/g)</th>
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<td>1.26</td>
<td>70</td>
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<td>6.34</td>
<td>70</td>
<td>2.26</td>
<td>97.84, 121.51</td>
<td>32.18</td>
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<td>4.00</td>
<td>8.00</td>
<td>2.68</td>
<td>121.67</td>
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<td>13.92</td>
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<td>0.97</td>
<td>119.58</td>
<td>21.39</td>
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<tr>
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<td>15.10</td>
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<td>17.24</td>
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<td>3.05</td>
<td>0.61</td>
<td>112.89</td>
<td>80.96</td>
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<td>4.65</td>
<td>70</td>
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<tr>
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<tr>
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<td>119.82</td>
<td>17.72</td>
<td>0.284</td>
<td></td>
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</tr>
</tbody>
</table>

\(^a\) Polymerization conditions: \( P_{\text{ethylene}} = 5 \text{ psig, } [\text{Al}]/[\text{Zr}] = 80, [\text{Ph}_3\text{C}]\text{[BF}_2\text{F}_4\text{]}_3/[\text{Zr}] = 1, \text{toluene} = 80 \text{ ml.} \)

\(^b\) Determined by \(^1\)H NMR.

\(^c\) Unit is g-PE/mol-Zr h.

\(^d\) Measured in decalin at 135°C.
3.2. Copolymerization mechanism and characterization of copolymer

VNB is nonconjugated and contains two different double bonds, one vinyl and the other cis–CH=CH– bond in the norbornene cycle. Because the latter double bond is practically nonreactive in the presence of most heterogeneous Ziegler-Natta catalysts, VNB polymerizes as an α-olefin with a bulky alkyl group branched in the α-position to the double bond [17]. This is not the case with homogeneous metallocene catalysts. The VNB comonomer is copolymerized through the endocyclic double bond leaving vinyl group unreacted, because of the more ring strain of endocyclic double bond (Scheme 1) [4,10]. This reaction is confirmed from the appearance of peaks of vinyl groups at 144.5 (=CH, exo form), 141.6 (=CH, endo form), 113.8 (=CH₂, endo form) and 111.5 ppm (=CH₂, exo form), and the absence of peaks of endocyclic double bonds at 136.9 ppm in 13C NMR. As mentioned above, the copolymerizations were carried out for 20 min to minimize the variation of VNB concentration during polymerization. However, when the copolymerization was done using 350 ml of toluene for 1 h instead of 20 min in a 1-l glass reactor at the same conditions with Run No. 7 in Table 1, the copolymer synthesized was quite different morphology compared to that of all other copolymers, in that it is rubber-like insoluble material. As shown in Scheme 1, it could be assumed that the cross-linking has occurred by the vinyl double bond remained during prolonged polymerization. In summary, the endocyclic double bond in VNB preferentially reacts with active sites to form a backbone, and then vinyl groups contained in the branch may be utilized to form a crosslinked structure.

The microstructures of polyethylene and poly(ethylene-co-VNB) were investigated by FT Raman spectroscopy. Figs. 4 and 5 show Raman spectra of polyethylene and poly(ethylene-co-VNB) synthesized by catalysts CAT-1 and CAT-2, respectively. The amorphous parts of copolymers increase as the content of VNB incorporated in copolymer increases. This is

![Scheme 1](image)

Fig. 4. Raman spectra of polymers produced by CAT-1: (a) Run No. 1 in Table 1, (b) Run No. 2, (c) Run No. 3, (d) Run No. 4, (e) Run No. 5, (f) Run No. 6, (g) Run No. 7, and (h) Run No. 11.
confirmed from the decrease of crystalline peaks of polyethylene at 1170 and 1417 cm\(^{-1}\) and the increase of amorphous peak at 1080 cm\(^{-1}\) [17]. The peak at 1635 cm\(^{-1}\) is assigned to \(\text{C} = \text{C}\) stretching vibration of vinyl double bonds, remained unreacted. The peak at 925 cm\(^{-1}\) is assigned to \(-\text{C} = \text{C}\)– vibration of bicyclic units.

The quantitative analysis was also attempted by comparing the intensity ratio of peaks of Raman spectra with the amount of VNB determined by \(^1\)H NMR. The peaks at 1635 and 925 cm\(^{-1}\), assigned to \(-\text{C} = \text{C}\)– and \(-\text{C} = \text{C}\) stretching vibrations, respectively, recorded for representative VNB peaks in copolymer, and 1439 and 1294 cm\(^{-1}\), assigned to \(-\text{CH}_2–\) deformation and twisting vibrations [18], respectively, recorded for representative polyethylene peaks. Baselines were drawn among 889, 962, 1211, 1390, 1527, 1585 and 1727 cm\(^{-1}\) for the determination of Raman intensities. The peaks at 1294 and 1439 cm\(^{-1}\) were used as references. Each plot of \(I_{1635}/I_{1294}\), \(I_{1635}/I_{1439}\), \(I_{925}/I_{1294}\) and \(I_{925}/I_{1439}\) ratio versus the amount of VNB in copolymer determined by \(^1\)H NMR showed good linear relationships (Fig. 6), which can expressed as:

\[
I_{1635}/I_{1294} = 0.068 \text{[mol% of VNB in copolymer]} - 0.027
\]

(1)

\[
I_{1635}/I_{1439} = 0.056 \text{[mol% of VNB in copolymer]} - 0.001
\]

(2)

\[
I_{925}/I_{1294} = 0.033 \text{[mol% of VNB in copolymer]} - 0.006
\]

(3)

\[
I_{925}/I_{1439} = 0.028 \text{[mol% of VNB in copolymer]} + 0.006
\]

(4)
3.3. Epoxidation of poly(ethylene-co-5-vinyl-2-norbornene)

The epoxidation of poly(ethylene-co-VNB) containing 16.65 mol% of VNB (Run No. 11 in Table 1) was conducted at 65°C in toluene for 4 h using m-chloroperbenzoic acid as shown in Scheme 1. The reaction showed a stoichiometric yield. Figs. 7 and 8 show the $^1$H NMR and the IR spectra of epoxidized and pure poly(ethylene-co-VNB), respectively. Complete epoxidation is rationalized in Fig. 5 from the disappearance of the peaks of $=\text{CH}$ in vinyl group at 4.81–5.00 ppm and the appearance of peaks at 2.77 and 2.57–2.62 ppm which are assigned to $\text{CH}$ and $\text{CH}_2$ attached to epoxy group, respectively [4]. In addition, IR spectra (Fig. 6) show the disappearance of the absorption of $=\text{C}=$C– stretching vibration (1634 cm$^{-1}$) and $=\text{CH}$ out-of-plane bending (991 and 903 cm$^{-1}$).
cm$^{-1}$), which are recorded from vinyl double bonds of VNB, and the appearance of the absorption of epoxy ring stretching vibration (1259 cm$^{-1}$, symmetric, and 875 cm$^{-1}$, asymmetric) [19]. The properties of epoxidized copolymer ($T_m = 117.02^\circ$C, $\Delta H_f = 19.30$ and $[\eta] = 0.253$) are similar with those of pure copolymer (see Run No. 11 in Table 1). The detailed investigations of physical properties and applications of the epoxidized polymer are ongoing and will be reported later.

4. Conclusions

The isospecific CAT-1 showed a higher polymerization activity and an incorporation of VNB ([VNB]$_{\text{in polymer}} = 13.92\%$ when [VNB]$_{\text{in feed}} = 75.07$ mol%) than CAT-2 ([VNB]$_{\text{in polymer}} = 9.58\%$ when [VNB]$_{\text{in feed}} = 75.07$ mol%). VNB was inserted through the endocyclic double bond regioselectively, leaving vinyl double bond to pendant group. The prolonged polymerization resulted in cross-linked polymer due to the reaction of the vinylic double bonds. The vinyl group remained in copolymer was converted into the epoxy group quantitatively with $m$-chloroperbenzoic acid. The properties of functionalized copolymer were similar with those of parent copolymer.

Acknowledgements

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References