Synthesis and Functionalization of Poly(ethylene-*co*-dicyclopentadiene)

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ABSTRACT: Copolymerizations of ethylene with *endo*-dicyclopentadiene (DCP) were performed by using Cp_2ZrCl_2 (Cp = Cyclopentadienyl), Et(Ind)₂ZrCl₂ (Ind = Indenyl), and $Ph_2C(Cp)(Flu)ZrCl_2$ (Flu = Fluorenyl) combined with MAO as cocatalyst. Among these three metallocenes, Et(Ind)₂ZrCl₂ showed the highest catalyst performance for the copolymerization. From ¹H-NMR analysis, it was found that DCP was copolymerized through enchainment of norbornene rings. The copolymer was then epoxidated by reacting with *m*-chloroperbenzoic acid. ¹³C-NMR spectrum of the resulting copolymer indicated the quantitative conversion of olefinic to epoxy groups. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 103–108, 1999

Keywords: copolymerization of ethylene and dicyclopentadiene; functionalization of polyolefins; zirconocene catalysts; epoxidation; *endo-* and *exo-*dicyclopentadiene

INTRODUCTION

The metallocene catalysts promote the polymerization of strained cyclic olefins like cyclobutene, cyclopentene, and norbornene without ring-opening reactions.¹ The resulting homopolymers are crystalline and show extremely high melting points. The copolymerization of ethylene with cyclic olefins also proceeds with metallocene catalysts to yield the amorphous copolymers having high glass transition temperatures, which are suitable for optical materials.²

On the other hand, introduction of some polar groups in polyolefins is of importance for improving the polymer properties such as adhesion, dyeability and compatibility with other polymers. Although a direct copolymerization between olefins and polar monomers is highly expected, ordinary Ziegler-Natta and metallocene catalysts hardly permit it, due to the catalyst poisoning caused by polar groups. The use of precursor monomers possessing reactive groups, which are inert in the copolymerization, may be one of the plausible methods to synthesize functionalized polyolefins.³ The reactive groups could be then converted into desirable polar groups by the successive chemical reactions. Chung et al. have conducted the copolymerization of ethylene with 5-hexenyl-9-borabicyclo[3.3.1]nonane using typical metallocenes and introduced some polar groups in the resulting copolymers by chemically modifying the borane groups.⁴ Sivaram et al. have recently synthesized poly(ethylene-co-5-vinyl-2-norbornene) with the Cp_2ZrCl_2 (Cp = Cyclopentadienyl)-methylaluminoxane (MAO) catalyst system and converted the pendant vinyl groups into the hydroxy/epoxy groups.⁵

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Run No.	Catalyst	DCP in cm ³	Polymn. Time	Yield in g	Content of DCP in Copolymer in mol %	$\mathop{T_m}\limits_{\text{in °C}}$	$\mathop{\rm T_g}_{\rm in \ ^{\circ}C}$	$\begin{array}{c} M_n \\ (10^{-4} \text{ g/mol}) \end{array}$	M_w/M_n
1^{b}	Cp_2ZrCl_2	0	5	4.90	_	138.6	n.d.	4.8	3.3
$2^{\rm b}$	opzaronz	1	5	2.82	n.d.	124.2	n.d.		_
3^{b}		3	5	0.43	0.7	116.0	n.d.	_	_
4^{b}		5	5	0.27	1.6	99.1	n.d.	2.3^{f}	2.3^{f}
5	Et(Ind) ₂ ZrCl ₂	0	1	0.96	_	138.3	n.d.	6.5	3.0
6		1	1	0.85	3.7	91.7	n.d.	2.4^{f}	1.7^{f}
7		3	1	0.36	8.9	n.d.	4.5	_	_
8		5	5	0.31	13.2	n.d.	43.6	—	_
$9^{\rm c}$		1	1	0.57	4.6	92.3	n.d.	_	_
$10^{\rm d}$		1	2	1.55	$4.5 \ (endo/exo = 1.17)^{e}$	84.8	n.d.	—	_
11	Ph ₂ C(Cp)(Flu)ZrCl ₂	0	5	0.24	—	139.9	n.d.	6.9	2.0
12		1	5	0.13	4.4	94.3	n.d.	8.6^{f}	1.7^{f}
$13^{\rm b}$		3	5	0.27	6.7	69.1	n.d.	—	_
$14^{\rm b}$		5	5	0.23	10.1	n.d.	9.4	—	—

Table I Results of Ethylene (E)-endo-dicyclopentadiene (DCP) Copolymerization^a

^a Polymerization conditions: $Zr = 1.25 \times 10^{-3}$ mmol, Al/Zr = 1000, toluene + DCP = 300 cm³, C₂' = 1 bar, at 40°C.

^b Zr = 2.5×10^{-3} mmol.

^c *exo*-Dicyclopentadiene was used as comonomer.

^d The mixture of *endo-* and *exo-*isomers (*endo/exo* = 0.96) was used.

 $^{\rm e}$ The molar ratio of *endo-* and *exo*-units in the copolymer was estimated by $^{13}\text{C-NMR.}$

^f For the hydrogenated copolymers.

In comparison to 5-vinyl-2-norbornene, dicyclopentadiene (DCP) is economical, and it is interesting to verify which C=C double bond will take part in the copolymerization.

In this article we have carried out the copolymerization of ethylene and DCP using typical metallocene catalysts with different symmetries, i.e., Cp_2ZrCl_2 , $Et(Ind)_2ZrCl_2$ (Ind = Indenyl), and $Ph_2C(Cp)(Flu)ZrCl_2$ (Flu = Fluorenyl). The olefinic groups left in the resulting copolymer were quantitatively functionalized into the epoxy groups.

EXPERIMENTAL

Materials

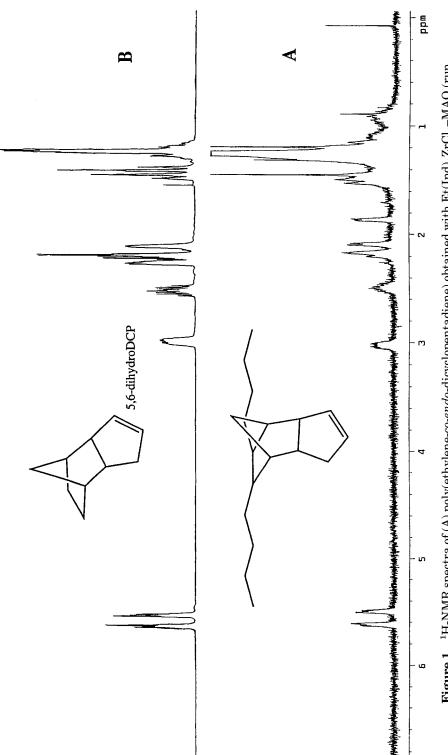
m-Chloroperbenzoic acid, tris(triphenylphosphine)rhodium chloride ((PPh₃)₃RhCl), and triphenylphosphine (PPh₃) (all from Kanto Chemicals Co., Ltd., Japan), Ph₂C(Cp)(Flu)ZrCl₂ (donated by Mitsui Toatsu Chemical, Inc., Japan), and MAO (donated by Tosoh Akzo Co., Japan) were used as received. Et(Ind)₂ZrCl₂⁶ and *exo*-DCP^{7,8} were prepared according to a literature procedure. *endo*-Dicyclopentadiene (DCP) (donated by Sanyo Petrochemical Co., Ltd., Japan), *endo*-5,6-dihydro-dicyclopentadiene (from Tokyo Chemical Industry Co., Ltd., Japan), and toluene (from Kanto Chemicals Co., Ltd., Japan) were dried over CaH_2 and freshly distilled before use. Ethylene (research grade from Takachiho Chem. Co., Ltd., Japan) was further purified by passing through NaOH and P_2O_5 columns. Carbon tetrachloride (from Kanto Chemicals Co., Ltd., Japan) was dried with MgSO₄ and distilled. Cp₂ZrCl₂ (from Tokyo Chemical Industry Co., Ltd., Japan) was used after recrystallization.

Copolymerization of Ethylene with Dicyclopentadiene

To a 1.0-dm³ glass reactor equipped with a mechanical stirrer, solvent, DCP, and catalyst were added. Copolymerization was started by adding MAO to the medium saturated with ethylene. The reaction mixture was quenched with acidic methanol. The obtained polymer was adequately washed with methanol several times and dried *in vacuo* at 60°C.

Hydrogenation of Poly(ethylene-*co*-dicyclopentadiene)

The hydrogenation of copolymer was performed according to the literature.⁹ In a 0.1-dm³ stainless autoclave equipped with a magnetic stirrer, 100





mg of the copolymer was dissolved in 40 cm³ toluene. An amount of 0.02 mmol of $(PPh_3)_3RhC_1$ and 0.38 mmol of PPh₃ were introduced under nitrogen (450 mol of carbon–carbon double bonds per mol of Rh). The reactor was purged with H₂ of 50 bar and kept at 55°C for 48 h.

Epoxidation of Poly(ethylene-co-dicyclopentadiene)

The epoxidation was performed according to the literature.⁵ An amount of 200 mg of the copolymer and 40 cm³ of toluene were added in a 100-cm³ flask equipped with a magnetic stirrer. Under N₂ atmosphere, the reaction mixture was heated at 55°C until the copolymer was completely dissolved. An amount of 10 cm³ of a 0.06 *M m*-chloroperbenzoic acid solution in toluene was added, and the reaction was continued for 3 h. The reaction mixture was poured into methanol. The precipitated polymer was filtered and dried *in vacuo* at 60°C.

Characterization of Polymers

¹H- and ¹³C-NMR analysis of the polymers were recorded at 60°C on a Varian Gemini 300 spectrometer operating at 300 and 75 MHz, respectively. The solution was made up in carbon tetrachloride/CDCl₃ (volume ratio = 5/1) up to 10 wt %. Thermal transitions were measured on a Seiko DSC220C differential scanning calorimeter with the rate of 10°C/min. Infrared (IR) spectra of the polymer films were recorded using a JASCO VALOR-III FTIR spectrometer. Molecular weight and molar mass distribution (MMD) of the polymer were measured at 145°C by gel-permeation chromatography (GPC; Senshu Scientific, SSC7100) using ODCB as the solvent.

RESULTS AND DISCUSSION

Copolymerization of Ethylene with Dicyclopentadiene

As described above, three kinds of metallocene catalysts, Cp_2ZrCl_2 , $Et(Ind)_2ZrCl_2$ and $Ph_2C(Cp)-(Flu)ZrCl_2$, were employed for the copolymerization of ethylene with DCP. The copolymerization was performed at 40°C under atmospheric pressure of ethylene by changing the concentration of

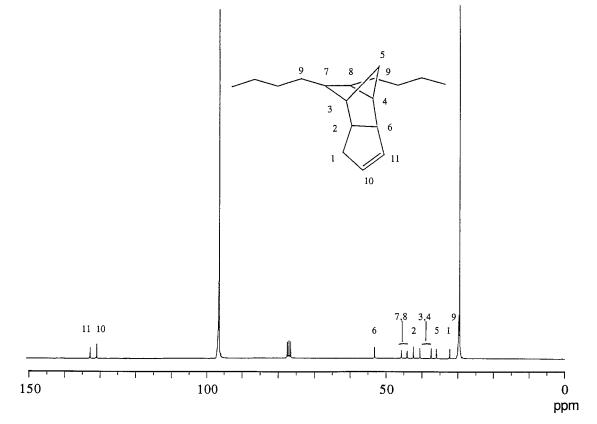


Figure 2 13 C-NMR spectrum of poly(ethylene-*co-endo*-dicyclopentadiene) obtained with $Et(Ind)_2ZrCl_2$ -MAO (run No. 6).

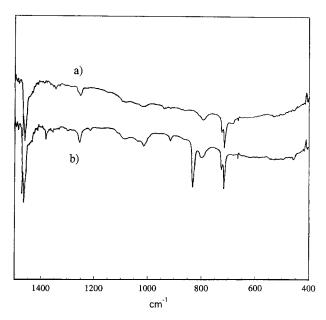


Figure 3 IR spectra of (a) poly(ethylene-*co-endo*-dicyclopentadiene) (run No. 6), and (b) after epoxidation.

DCP in the feed. Table I summarizes the results of copolymerizations, where the contents of DCP in the copolymers were estimated from the ¹³C-NMR spectra.

The catalyst performance was very different among the three zirconocenes. The C_{2v} symmetric Cp_2ZrCl_2 complex showed the highest activity for ethylene homopolymerization, as reported previously.¹⁰ For the copolymerization, however, the catalyst displayed a fairly low activity to yield the copolymers with low contents of DCP. On the other hand, the C_2 symmetric $Et(Ind)_2ZrCl_2$ complex gave the copolymers with high contents of DCP. In the case of C_s , where the symmetric $Ph_2C(Cp)(Flu)ZrCl_2$ complex seemed to be apparent, polymerization activity was not as dependent on the concentration of DCP.

The melting temperature (T_m) of the copolymer decreased and eventually disappeared with increasing DCP content. The copolymers with higher amounts of DCP composition were amorphous, and displayed glass transition temperature (T_g) at 4.5–43.6°C, depending upon the DCP content.

The copolymer was soluble in toluene, carbon tetrachloride, etc., but it became insoluble after exposing to the air for several days probably due to the crosslinking.

¹H-NMR spectra of a typical poly(ethylene-*co*-DCP) (obtained in run No. 6) and *endo*-5,6-dihy-drocyclopentadiene are shown in Figure 1. Spec-

trum A displays two peaks of olefinic protons of the cyclopentene ring in DCP at 5.51 and 5.62 ppm assignable to it, suggesting that polymerization of DCP through enchainment of the cyclopentene ring did not take place. For detailed investigation, the copolymerization of ethylene with *endo*-5,6-dihydrocyclopentadiene was conducted with the $Et(Ind)_2ZrCl_2$ -MAO catalyst system. The ¹³C-NMR spectrum of resulting polymer did not display any peaks arising from *endo*-5,6-dihydrocyclopentadiene unit, which proves that the obtained polymer is homopolyethylene. It may be concluded that DCP is selectively polymerized through enchainment of the norbornene ring.

In ethylene-propylene-DCP terpolymerization with ordinary Ziegler-Natta catalysts, it was reported that *endo*-DCP was copolymerized with olefins accompanied by the *endo-exo* rearrangement reaction.⁷ From the comparison between spectra A and B in Figure 1, however, the DCP unit in the copolymer seems to retain the *endo*form. *exo*-DCP was also found to keep the *exo*form when copolymerized.

Figure 2 illustrates the ¹³C-NMR spectrum of poly(ethylene-*co*-DCP) obtained in run No. 6. Besides the resonances derived from the ethylene sequence, weak resonances assignable to the DCP unit are also observed.

The molecular weights of poly(ethylene-*co*-DCP)s could not be measured by GPC due to the opposite polarity of the two monomers. Therefore, GPC measurements were performed on the hydrogenated copolymers.

Epoxidation of Poly(ethylene-co-dicyclopentadiene)

Because poly(ethylene-*co*-DCP)s prepared above possess C=C double bonds, functionalization of

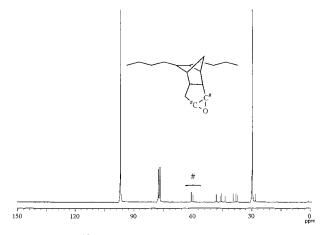


Figure 4 ¹³C-NMR spectrum of poly(ethylene-*co-endo*-dicyclopentadiene) (run No. 6) after epoxidation.

the copolymer might be possible. As an example, epoxidation of the olefinic groups was investigated in this study. The epoxidation of copolymers was performed by reacting with *m*-chloroperbenzoic acid at 50°C in toluene. Figure 3 shows the IR spectrum of a typical epoxidated copolymer, which displays a new absorption at 835 cm^{-1} attributed to the epoxy group, whereas the ¹³C-NMR spectrum of the same copolymer is illustrated in Figure 4, where the peaks assignable to the epoxy group newly appear at 60.1 and 61.1 ppm, accompanied by a complete disappearance of the peaks attributed to the C=C double bonds (Fig. 2). Thus, the C=C double bonds left in the copolymer could be quantitatively converted into the epoxy groups under such mild conditions. The epoxidated copolymer was found to be very stable, even in air atmosphere.

In conclusion, poly(ethylene-*co*-DCP) was synthesized using typical zirconocenes combined with MAO as cocatalyst. It was found that DCP is polymerized through enchainment of norbornene rings without rearrangement. Functionalization with *m*-chloroperbenzoic acid quantitatively convert olefinic groups in the resulting copolymer into the epoxy groups.

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