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Copolymerization of Ethylene with Dicyclopentadiene Using a Constrained Geometry Cyclopentadienyl-phenoxytitanium Catalyst*

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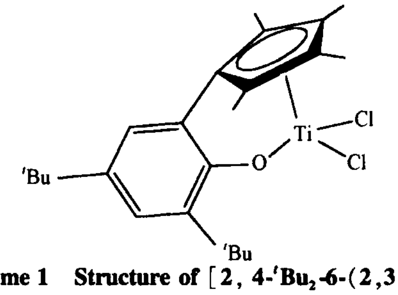
The copolymerization of ethylene with dicyclopentadiene (DCP) in the presence of a constrained geometry tetramethylcyclopentadi-enyl-phenoxytitanium catalyst $[2,4\text{-}^tBu_2\text{-}6\text{-}(2,3,4,5\text{-}Me_4\text{-}Cp)\text{-}PhO]TiCl_2$, combined with $Al(^iBu)_3/Ph_3C^+B(C_6F_5)_4^-$ cocatalyst system was studied. The copolymers that were formed were characterized by ^1H and ^{13}C NMR, differential scanning calorimetry (DSC), SEM, and X-ray diffraction (XRD) analyses. The results of the analysis indicate that the copolymers of ethylene with dicyclopentadiene are amorphous and display two or more melting temperatures in their DSC diagrams. Moreover, the morphologies of the copolymers are quite different from that of polyethylenes.

Keywords Ethylene polymerization; Dicyclopentadiene; Copolymers; Metallocene; Polyethylene

Introduction

The discovery of metallocene catalyst systems has provided a unique opportunity for producing novel tailor-made polyethylenes[1—3]. The introduction of functional groups into polyethylene chains *via* catalyzed copolymerization can produce novel polymers with improved chemical and physical properties[4]. Dicyclopentadiene (DCP) is a suitable comonomer for this purpose and has been used in industry to produce the EPDM terpolymer by its copolymerization with ethylene and propylene[5,6]. However, the copolymerization of ethylene with DCP has not been extensively studied in academia[7]. The unreacted C$=$C bonds in the ethylene-DCP copolymer can be converted into desirable polar groups through chemical reactions[8], which may be a promising method to synthesize functionalized polyethylenes. The copolymerization of ethylene with DCP has been carried out in the presence of typical metallocene catalysts, such as Cp_2ZrCl_2, $Et[Ind]_2ZrCl_2$, and $Ph_2C(CpFluZrCl_2)$[7,9,10]. It is well known that the constrained geometry catalysts (CGC) are suitable catalysts for the copolymerization of ethylene with α-olefins because of the open nature of their active site[11—13]. To the best of our knowledge, the copolymerization of ethylene with DCP over CGC catalysts has not been reported so far.

In this work the copolymerization of ethylene with DCP catalyzed by a CGC catalyst $[2,4\text{-}^tBu_2\text{-}6\text{-}(2,3,4,5\text{-}Me_4\text{-}Cp)\text{-}PhO]TiCl_2$ (see Scheme 1) combined with cocatalyst $Al(^iBu)_3/Ph_3C^+B(C_6F_5)_4^-$ was studied, and the copolymers obtained were characterized with ^1H and ^{13}C NMR, differential scanning calormetry (DSC), SEM, and X-ray diffraction (XRD) analyses.



Scheme 1 **Structure of $[2,4\text{-}^tBu_2\text{-}6\text{-}(2,3,4,5\text{-}Me_4\text{-}Cp)\text{-}PhO]TiCl_2$**

Experimental

1 Materials

$[2,4\text{-}^tBu_2\text{-}6\text{-}(2,3,4,5\text{-}Me_4\text{-}Cp)\text{-}PhO]TiCl_2$ and $Ph_3C^+B(C_6F_5)_4^-$ were synthesized according to the

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** To whom correspondence should be addressed. E-mail: ymu@mail.jlu.edu.cn procedures described in the refcrences [14, 15]. Al(^{i}Bu)$_3$ was purchased from Adrich. Commercial toluene was dried by refluxing over sodium/benzophenone and was distilled under nitrogen atmosphere. Polymerization-grade ethylene was obtained from the Daqing petrochemical Plant and was used after passing through a column of 10A molecular sieves and MnO. Dicyclopentadiene was dried over CaH_2 at room temperature for 2 days and subsequently filtered under nitrogen atmosphere. All manipulations were carried out under nitrogen atmosphere.

2 Polymerization

A dry 250-mL steel autoclave with a magnetic stirrer was charged with 80 mL of toluene, thermostated at a desired temperature, and saturated with ethylene (1.0×10^5 Pa). The DCP comonomer was added and the polymerization reaction was initiated by simultaneously injecting a mixture of the catalyst and Al(^{i}Bu)$_3$ in toluene (10 mL) and a solution of $Ph_3C^+B(C_6F_5)_4^-$ in toluene (10 mL). The vessel was immediately repressurized to the required pressure with ethylene, and the pressure was maintained by continuous feeding of ethylene. After 30 minutes, the polymerization was quenched by injecting acidified methanol [V(HCl, 3 mol/L): V(methanol) = 1 : 1]. The mixture was stirred overnight and the polymer was collected by filtration, washed with water, methanol, and dried at 60 ℃ *in vacuo* to a constant weight.

3 Characterization

The compositions of the copolymers were determined by ^{1}H and ^{13}C NMR. The ^{13}C NMR measurements were performed in *o*-dichlorobenzene-d_4 at 120 ℃ with an acquisition time of 1 s, a pulse width of 90°, and a pulse delay of 8 s on an AV400 spectrometer operated at 100 MHz. Differential scanning calorimetry(DSC) measurement was performed on a Pyris 1 DSC instrument. Indium was used for temperature and enthalpy calibration of the instrument. The samples were heated from 20 to 180 ℃ at a heating rate of 10 ℃/min. The molecular weights of the copolymers were determined *via* gel permeation chromatography in a PL-GPC220 with 1,2,4-trichlorobenzene as the solvent. The melting temperature (T_m) and the heat of fusion (ΔH_f) were obtained from the heating curve. SEM photographs were obtained on a SSX-550 and X-ray diffraction (XRD) analysis was carried out on a Simens D5005.

Results and Discussion

The ethylene-DCP copolymerizations were performed at 70 ℃ at a pressure of 6.0×10^5 Pa of ethylene by changing the concentration of DCP in the feed. The the results of copolymerizations were summarized in Table 1, where the contents of DCP in the copolymers were calculated based on the ^{13}C NMR spectra. It can be seen from Table 1 that the activity of the catalyst decreases with the increase of the concentration of DCP. The so-called comonomer effect[16—18] observed commonly for the copolymerization of ethylene with α-olefins was not observed in these polymerization experiments. This result may be attributed to the fact that the coordination of the unreacted C=C bonds between the DCP units in the formed polymer chain and the metal center may compete with the coordination of monomer molecules, which would slow down the polymerization reaction. Moreover, the steric hindrance around the metal center of the P-DPC-Ti catalytic active species that was formed after a DCP insertion would also lower the rate of the polymerization.

Table 1 The results of the copolymerization of ethylene with dicyclopentadiene[a]

Run No.	DCP/(mol · L^{-1})	Yield/g	Activity[b]	x(DCP)(%)	T_m/℃	ΔH_f/(J · g^{-1})	X_c(%)	$10^{-4}M_w$	M_w/M_n
1	0.0	5.85	5186	—	127	209.4	77	7.5	3.1
2	0.1	3.68	3262	1.5	92/137	13/26	5/10	4.5	2.7
3	0.2	3.42	3032	5.3	109/124	45/—	17/—	5.2	2.6
4	0.3	3.27	2899	7.3	91/112	22/2	8/—	—	—
5	0.4	2.52	2234	10.8	61/83	4/6	—	—	—

a. Polymerization conditions: solvent 100 mL of toluene, temperature 70 ℃, catalyst 1 mg, n(B)/n(Ti) = 1.5, n(Al)/n(Ti) = 70, reaction time 30 min, ethylene pressure 6.0×10^5 Pa. *b*. kg polymer for (mol^{-1} Ti) · h^{-1}.

The ethylene dicyclopentadiene copolymers (EDCP) that was obtained are slightly soluble in *o*-dichlorobenzene and 1,2,4-trichlorobenzene, and the solubility decreases with the increase of the DCP content. As a result, the molecular weights of the copolymers with a high DCP content could not be obtained because of their low solubility. In addition, the copolymers become insoluble after exposure to air for several days, probably because of cross-linking[19].

Fig. 1 shows the ^{13}C NMR spectrum of an EDCP copolymer obtained in run No. 3. The characteristic resonances of the DCP units are assigned according to references [8,20]. The ^{13}C NMR result indicates that DCP is incorporated into the polymer chains *via* the