

Preparation of Ethylene/1-Octene Copolymers from Ethylene Stock with Tandem Catalytic system

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Received 21 June 2007; accepted 23 September 2007

DOI 10.1002/app.27513

Published online 26 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Tandem catalysis offers a novel synthetic route to the production of linear low-density polyethylene. This article reports the use of homogeneous tandem catalytic systems for the synthesis of ethylene/1-octene copolymers from ethylene stock as the sole monomer. The reported catalytic systems involving a highly selective, bis(diphenylphosphino)cyclohexylamine/Cr(acac)₃/methylaluminumoxane (MAO) catalytic systems for the synthesis of 1-hexene and 1-octene, and a copolymerization metallocene catalyst, *rac*-Et(Ind)₂ZrCl₂/MAO for the synthesis of ethylene/1-octene copolymer. Analysis by means of DSC, GPC, and ¹³C-NMR suggests that copolymers of 1-hexene and ethylene and copolymers of 1-octene and ethylene are

produced with significant selectivity towards 1-hexene and 1-octene as comonomers incorporated into the polymer backbone respectively. We have demonstrated that, by the simple manipulation of the catalyst molar ratio and polymerization conditions, a series of branched polyethylenes with melting temperatures of 101.1–134.1 °C and density of 0.922–0.950 g cm⁻³ can be efficiently produced. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3071–3075, 2008

Key words: ethylene tetramerization; metallocene catalysts; tandem catalytic system; linear low-density polyethylene (LLDPE)

INTRODUCTION

Linear low-density polyethylene (LLDPE) is conventionally produced by ethylene copolymerization with α -olefin comonomers, such as 1-butene, 1-hexene, and 1-octene, using classical Ziegler-Natta catalysts and single-site-type catalysts. This conventional route is a two-stage operation, that is, ethylene oligomerization to produce an α -olefin followed by ethylene copolymerization with the α -olefin comonomer.¹ Recently there has been a significant amount of interest in producing LLDPE with ethylene as the sole monomer stock via the utilization of tandem catalytic systems.^{2–11} This novel approach employs the tandem action between two different catalysts: one catalyst oligomerizes ethylene into 1-alkene, while the other catalyst simultaneously copolymerizes the *in situ* generated 1-alkene with ethylene to produce LLDPE. Through selecting a suitable oligomerization catalysts and adjusting its concentration, LLDPEs with different branch lengths and densities can be effectively produced. Compared with the con-

ventional copolymerization approach, this tandem catalytic approach shows its advantage in using ethylene as the only monomer, which avoids the use of comonomers in LLDPE production. However, all these reported systems produced mainly short ethyl-branched ethylene-butene copolymers, butyl-branched ethylene-hexene copolymers or polymer mixtures of linear PEs and branching PEs with very complex branch structures due to the generation of 1-alkenes with broad chain-length distributions. Here we report the tandem system involving a highly selective, bis(diphenylphosphino)cyclohexylamine/Cr(acac)₃/MAO catalytic systems for the synthesis of 1-hexene and 1-octene, and a copolymerization metallocene catalyst, *rac*-Et(Ind)₂ZrCl₂/MAO for the synthesis of ethylene/1-octene copolymer, to prepare hexyl-branched ethylene-octene copolymers, which are usually more expensive and have significantly improved physical properties compared with ethylene/1-butene copolymers and ethylene/1-hexene copolymers.⁶

EXPERIMENTAL

Materials

Cr(acac)₃ and cyclohexylamine were purchased from Aldrich and used as received. MAO solution (1.4 mol/L) in toluene was purchased from Albemarle (USA). *rac*-Et(Ind)₂ZrCl₂ was purchased from Aldrich and used as received. Cyclohexane, dichloromethane and ethanol were dehydrated and degassed before

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Contract grant sponsor: New Century Excellent Talents In University (NCET).

Contract grant sponsor: Program for New Century Excellent Talents In Heilongjiang Provincial University; contract grant number: NCET-06-010.

Journal of Applied Polymer Science, Vol. 107, 3071–3075 (2008)
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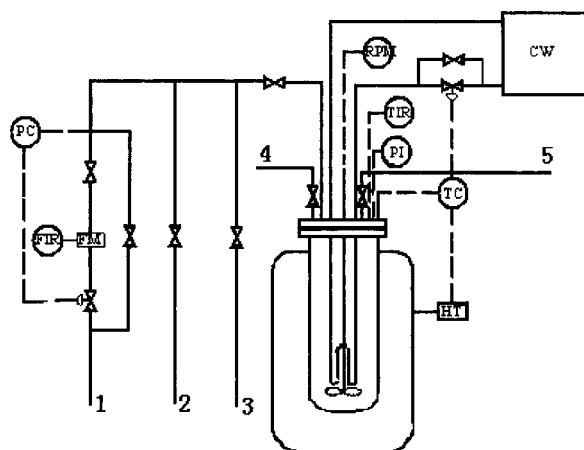


Figure 1 Polymerization reactor system 1, ethylene; 2, nitrogen; 3, vacuum pump; 4, release; 5, solvent and catalyst inlet; CW, cooling water; HT, Heater; FM, mass flow meter; PC, pressure control; TC, temperature control; PI, pressure indicator; TIR, temperature indicator and recorder; FIR, flow indicator and recorder; RPM, rotate speed indicator control.

used. Polymerization grade ethylene was obtained from Daqing Petro-Chemical Ltd. (China). Handling of the air and/or moisture sensitive materials was conducted in a nitrogen-filled dry-box or under nitrogen protection. Bis(diphenylphosphino)cyclohexylamine was synthesized according to the method described in the Ref. 12.

Ethylene tetramerization and polymerization

The polymerization reactor was a 250 mL autoclave fitted with a mechanical stirrer and internal cooling coil with coolant flow automated for temperature control. The flow rate of ethylene fed to the reactor was measured with an on-line mass flow meter. Figure 1 illustrates the polymerization reaction system.

Ethylene tetramerization with PNP/Cr(III)/MAO

Ethylene tetramerization was processed in a 250 mL autoclave. After evacuation and flushing with nitrogen three times, then with ethylene two times, the

autoclave was charged with 100 mL solvent and mechanically stirred under ambient ethylene atmosphere. When the desired reaction temperature was established, quantitative MAO, PNP ligand, and Cr (acac)₃ were injected into the reactor. Typically 30 min later, the reaction solution was quickly cooled down to 20°C and then quenched by adding ethanol/HCl (10 wt %). The distribution of tetramerization product was analyzed by GC-MS and the catalytic activity was calculated from the increase of product weight.

Ethylene polymerization with tandem system

A procedure similar to the tetramerization process was applied. The stock solutions of tetramerization catalytic system and copolymerization catalytic system were simultaneously added into the reactor to start the concurrent ethylene tetramerization and polymerization process. After 30 min reaction time, the reactor was vented and 20 mL of ethanol/HCl (10 wt %) was added. The polymer was collected, washed with a large amount of ethanol, and dried.

Polymer characterization

The molecular weight and its distribution were determined by gel permeation chromatography (GPC) on a Waters Alliance GPCV2000 at 150°C with 1,2,4-trichlorobenzene as eluent. Melting points of polymers were measured on a Perkin-Elmer DSC-7 in the standard DSC run mode. The 100.6 MHz ¹³C-NMR analyses were conducted on a Bruker DMX400 spectrometer at 120°C. At least 2500 scans were applied for each acquisition to obtain a good signal-to-noise ratio.

RESULTS AND DISCUSSION

Effects of reaction pressure and reaction temperature on ethylene tetramerization

The PNP/Cr(III)/MAO catalytic system has been shown to be highly active and selective for ethylene tetramerization toward 1-octene.¹²⁻¹⁵ As shown in Tables I and II, tetramerization of ethylene with Bis(diphenylphosphino)cyclohexylamine/Cr(III)/MAO

TABLE I
Effects of Reaction Pressure on Catalytic Activity and Product Selectivity

| Run | Pressure (MPa) | Activity (10 ⁶ g/mol cat.h) | Product selectivity (%) | | | | | | | | | | |
|-----|----------------|--|-------------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|--|
| | | | 1-C ₄ ⁻ | 1-C ₆ ⁻ | 1-C ₈ ⁻ | 1-C ₁₀ ⁻ | 1-C ₁₂ ⁻ | 1-C ₁₄ ⁻ | 1-C ₁₆ ⁻ | 1-C ₁₈ ⁻ | 1-C ₂₀ ⁻ | >1-C ₂₂ ⁻ | |
| 1 | 1.0 | 2.00 | 1.03 | 33.51 | 54.43 | 0.81 | 0.17 | 0.11 | 0.09 | 0.06 | 0.05 | 0.03 | |
| 2 | 2.0 | 3.54 | 0.98 | 22.94 | 60.67 | 1.03 | 0.28 | 0.24 | 0.25 | 0.20 | 0.13 | 0.15 | |
| 3 | 3.0 | 9.14 | 0.66 | 18.95 | 64.25 | 1.17 | 0.35 | 0.34 | 0.40 | 0.33 | 0.24 | 0.37 | |
| 4 | 4.0 | 10.64 | 0.56 | 16.83 | 68.53 | 1.32 | 0.48 | 0.46 | 0.49 | 0.37 | 0.25 | 0.41 | |
| 5 | 5.0 | 12.70 | 0.64 | 15.06 | 72.70 | 1.38 | 0.53 | 0.49 | 0.53 | 0.42 | 0.35 | 0.62 | |
| 6 | 6.0 | 16.08 | 0.59 | 14.76 | 73.10 | 1.45 | 0.56 | 0.54 | 0.69 | 0.59 | 0.48 | 0.88 | |

Reaction conditions: solvent: cyclohexane; reaction temperature: 60°C; Cr(III) : PNP : MAO = 1 : 2 : 300; reaction time: 30 min.

TABLE II
Effects of Reaction Temperature on Catalytic Activity and Product Selectivity

| Run | Temperature (°C) | Activity (10 ⁶ g/mol cat.h) | Product selectivity (%) | | | | | | | | | |
|-----|------------------|--|-------------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|
| | | | 1-C ₄ ⁻ | 1-C ₆ ⁻ | 1-C ₈ ⁻ | 1-C ₁₀ ⁻ | 1-C ₁₂ ⁻ | 1-C ₁₄ ⁻ | 1-C ₁₆ ⁻ | 1-C ₁₈ ⁻ | 1-C ₂₀ ⁻ | >1-C ₂₂ ⁻ |
| 7 | 40 | 11.60 | 0.15 | 9.38 | 72.60 | 1.11 | 0.39 | 0.44 | 0.51 | 0.38 | 0.24 | 0.24 |
| 8 | 50 | 11.90 | 0.47 | 10.76 | 72.70 | 1.13 | 0.41 | 0.46 | 0.56 | 0.41 | 0.22 | 0.16 |
| 9 | 60 | 12.70 | 0.64 | 15.06 | 72.70 | 1.38 | 0.53 | 0.49 | 0.53 | 0.42 | 0.35 | 0.62 |
| 10 | 70 | 8.53 | 0.50 | 14.55 | 69.30 | 1.37 | 0.75 | 0.56 | 0.79 | 0.48 | 0.30 | 0.43 |
| 11 | 80 | 6.23 | 0.56 | 17.32 | 64.48 | 1.88 | 1.00 | 1.09 | 0.96 | 0.78 | 0.58 | 0.82 |

Reaction conditions: solvent : cyclohexane; reaction pressure: 5.0 MPa; Cr(III) : PNP : MAO = 1 : 2 : 300; reaction time, 30 min.

under different reaction conditions gave 1-octene as the main product. The 1-octene productivity increased with the increase of ethylene pressure and decreased with the increase of reaction temperature. This is in accordance to the results reported by Kuhlmann et al.¹⁶ It is obvious that the distribution of the main products 1-octene and 1-hexene is influenced significantly by increasing ethylene pressure. While only 54.43% 1-octene is formed at 1.0 MPa, a maximum yield of 73.10% could be obtained at 6.0 MPa. This is accompanied by an equivalent shift in 1-hexene selectivity from 33.51% to 14.76%. The catalytic activity increased with ethylene pressure, which is proportional to ethylene concentration in solvent.¹⁷ To further elucidate the most important observation that 1-hexene formation was increased at the expense of 1-octene formation at elevated temperature. Since increased 1-hexene formation was observed at low pressure in the previous series of experiments, it was suspected that the selectivity swing in the temperature variation was in fact due to change in ethylene concentration.

Ethylene polymerization with tandem catalyst

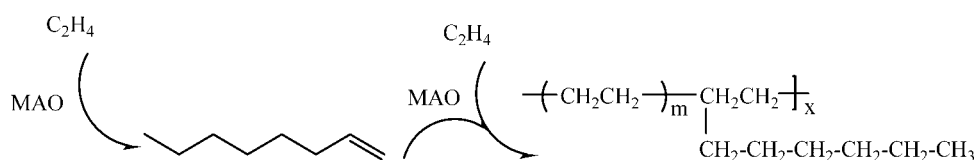
Ethylene polymerizations with the tandem catalyst system were conducted at various reaction conditions.

The overall strategy of the tandem catalytic systems is presented in Scheme 1. The two catalysts were simultaneously added into the reactor to start the concurrent tetramerization and copolymerization processes.

Effects of tetramerization catalyst and copolymerization catalyst ratios

For the reactions conducted under the same reaction conditions, the amount of *rac*-Et(Ind)₂ZrCl₂ was fixed, while the amount of ethylene tetramerization catalyst was varied to see the effect on the polymer properties. Table III summarizes the polymerization conditions and polymer properties.

As shown in Table III, by manipulating the ratio of Cr/Zr, copolymer grades with melting temperatures and densities over a very broad range were efficiently produced with the tandem catalytic system. At a fixed amount of *rac*-Et(Ind)₂ZrCl₂, an increase in tetramerization catalyst led to a significant decrease in the polymer melting temperature and the density because of the higher amount of 1-octene and 1-hexene produced and further incorporated. Figure 2 shows the DSC thermograms for a series of copolymers produced at 3.0 MPa and 55°C with different catalyst ratios. At lower the ratio of Cr/Zr, because of the reduced tetramerization pro-



Scheme 1 The overall strategy of the tandem catalytic systems.

TABLE III
Effects of Tetramerization Catalyst and Copolymerization Catalyst Ratios

| Run | 1/2 | 2 (μmol) | T (°C) | P (MPa) | Al/Cr | Al/Zr | PE (g) | M _w × 10 ⁴ | T _m (°C) | ρ (g cm ⁻³) |
|-----|-----|----------|--------|---------|-------|---------|--------|----------------------------------|---------------------|-------------------------|
| 12 | 0 | 0.29 | 60 | 3.0 | – | 15,000 | 0.98 | 13.26 | 134.1 | 0.950 |
| 13 | 50 | 0.29 | 60 | 3.0 | 300 | 15,000 | 1.94 | 12.13 | 125.1 | 0.942 |
| 14 | 100 | 0.29 | 60 | 3.0 | 300 | 30,000 | 2.43 | 11.06 | 114.2 | 0.934 |
| 15 | 250 | 0.29 | 60 | 3.0 | 300 | 75,000 | 2.40 | 9.28 | 109.9 | 0.923 |
| 16 | 400 | 0.29 | 60 | 3.0 | 300 | 120,000 | 2.37 | 8.44 | 101.1 | 0.922 |

1: Cr(III); 2: *rac*-Et(Ind)₂ZrCl₂; Cr(III) : PNP = 1 : 2.

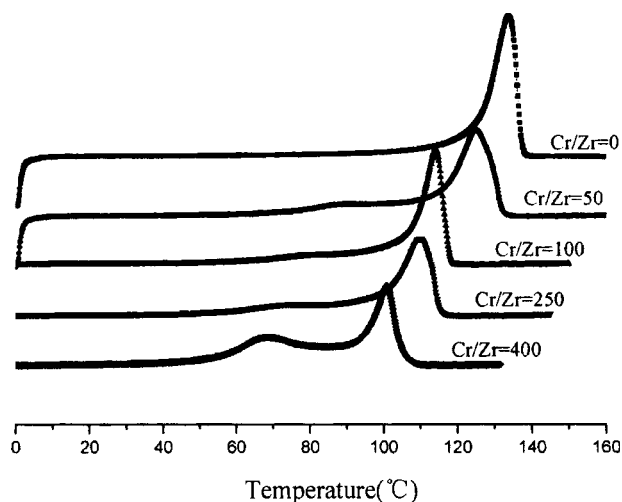


Figure 2 DSC thermograms for the copolymers produced with different Cr/Zr catalyst ratios.

ductivity, the copolymers had higher melting temperatures and crystallinities. A unique feature of the polymers produced with this tandem catalytic system was that the samples exhibited broad melting endotherms especially at a high 1-octene and 1-hexene incorporation. This suggests that the copolymers had a broad 1-octene and 1-hexene composition distribution, which was caused by the unstable concentration of 1-octene and 1-hexene in the semibatch reaction system because of the different kinetic behaviors of 1/MMAO and 2/MMAO.⁸

Effects of catalyst and cocatalyst ratios

MAO is used as cocatalyst to activate both the tetramerization catalyst and copolymerization catalyst. For the reactions conducted under the same reaction conditions, the amount of tetramerization catalyst and copolymerization catalyst was fixed, while the amount of MAO was varied to see the effect on polymerization catalyst activity and the polymer properties. The results are listed in Table IV.

In Table IV, the MAO concentration was increased relative to the chromium concentration. The reaction

with 100 : 1 ratio yielded a relatively high density polymer as evident from the melting temperature of 131.8°C when compared with the polymer produced at higher ratios. Additional increase in the MAO : Cr ratio had only a minor effect on the polymer melting temperatures, but the polymer yield consistently increased with an increase in cocatalyst concentration.

Polymer structure evaluation by ¹³C-NMR

¹³C-NMR spectroscopy was used to determine the composition and chain structure of the copolymers. A typical ¹³C-NMR spectrum, corresponding to products coming from Table III, run 15 is shown in Figure 3. The nomenclature suggested by Kimura was employed.¹⁸ The signals due to branching (ethyl, butyl, and hexyl) are well-defined. The presence of ethyl branches is confirmed by the peak at 11.19, 27.31, and 39.80 ppm, corresponding to carbon atoms 1B₂, 2B₂, and brB₂. The presence of butyl branches is confirmed by the peak at 23.37 ppm, corresponding to carbon atoms 2B₄. The presence of hexyl branches can be detected by the signals at 14.02, 32.17, and 38.21 ppm, corresponding to carbon atoms 1B₆, 3B₆, and brB₆. From Figure 3 the percentage of ethyl branches in run 15 sample is 0.12%, hexyl branches is 0.43% and hexyl is 1.02%.

CONCLUSIONS

Under the reaction conditions in which this study was carried out with Cr(III)/PNP/MAO catalytic system, the main products are 1-octene and 1-hexene. We have shown that it is possible to incorporate the 1-octene and 1-hexene produced by the Cr(III)/PNP/MAO/C₂H₄ system into a growing polyethylene chain at *rac*-Et(Ind)₂ZrCl₂ catalyst. The Cr : Zr ratio and Al : Zr ratio are both factors that influence the amount of α -olefins formed, and therefore the type of copolymer produced. The ethylene/ α -olefin copolymers with 0.12% ethyl branches, 0.43% butyl branches, and 1.02% and hexyl branches can be efficiently produced from ethylene stock as the sole monomer with tandem catalytic systems.

TABLE IV
Effects of Catalyst and Cocatalyst Ratios

| Run | 1/2 | 2 (μ mol) | T ($^{\circ}$ C) | P (MPa) | Al/Cr | Al/Zr | PE (g) | $M_w \times 10^4$ | T_m ($^{\circ}$ C) | ρ (g cm ⁻³) |
|-----|-----|----------------|-------------------|---------|-------|--------|--------|-------------------|-----------------------|------------------------------|
| 17 | 100 | 0.29 | 60 | 3.0 | 100 | 10,000 | 0.37 | 15.31 | 131.8 | 0.945 |
| 18 | 100 | 0.29 | 60 | 3.0 | 200 | 20,000 | 0.90 | 13.86 | 120.1 | 0.944 |
| 19 | 100 | 0.29 | 60 | 3.0 | 300 | 30,000 | 2.43 | 11.06 | 114.2 | 0.934 |
| 20 | 100 | 0.29 | 60 | 3.0 | 400 | 40,000 | 5.08 | 8.15 | 116.8 | 0.933 |
| 21 | 100 | 0.29 | 60 | 3.0 | 500 | 50,000 | 4.78 | 7.93 | 115.9 | 0.924 |

1: Cr(III); 2: *rac*-Et(Ind)₂ZrCl₂; Cr(III) : PNP = 1 : 2.

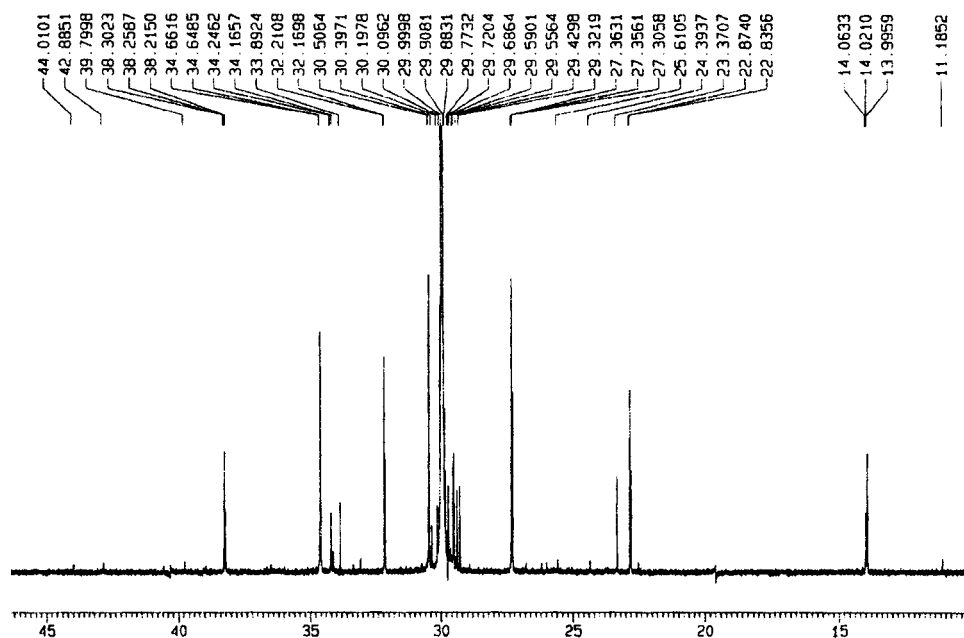


Figure 3 ^{13}C -NMR spectra of the polymer produced in run 15.

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