Cyclocopolymerization of 1,6-Heptadiene with Styrene Catalyzed by a Half-Sandwich Scandium Dialkyl Complex Bearing a Phosphine Oxide Side Arm

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INTRODUCTION The development of well-defined polymerization catalysts has created new opportunities for the synthesis of olefin copolymers with unique compositions and properties. The cyclocopolymerization of a nonconjugated diene such as 1,5-hexadiene (HD) and 1,6-heptadiene (HPD) with styrene is of much interest, because it may afford a novel family of polymer materials which contain cyclic structures together with aromatic units, and therefore may show unique mechanical and optical properties.1 Previously, group 4 metal-based catalysts were reported to effect the copolymerization of nonconjugated diene with ethylene or propylene,2 but attempts to copolymerize nonconjugated diene with styrene were not successful.2(a) Although a half-metalloocene Ti catalyst was active for the terpolymerization of HD with ethylene and styrene, the styrene content in the copolymer resulted in at most 2.1 mol %.2(a,k) The copolymerization of HPD with styrene has not been reported previously, as far as we are aware.

In our previous studies on the use of half-sandwich scandium complexes for olefin polymerization and copolymerization,3,4 we found that the terpolymerization of HPD with ethylene and styrene could be achieved selectively by using a THF-free aminobenzyl scandium complex 2 (Chart 1), but the copolymerization of HPD with styrene was not successful.2(a) Although a half-metalloocene Ti catalyst was active for the terpolymerization of HD with ethylene and styrene, the styrene content in the copolymer resulted in at most 2.1 mol %.2(a,k) The copolymerization of HPD with styrene has not been reported previously, as far as we are aware.

As we reported previously, complexes 1 and 2 (Chart 1) in the presence of [Ph3C][B(C6F5)4] exhibited very high activity for the syndiotactic polymerization of styrene (Table 1, runs 1 and 4) and moderate activity for the polymerization of HPD (Table 1, runs 2 and 5).3 However, the copolymerization of HPD and styrene by the catalyst system of 1 or 2 gave only a mixture of homopoly(HPD) and syndiotactic homopolystyrene, as confirmed by solvent extraction (Table 1, runs 3 and 6). Complex 3 showed relatively low activity for the syndiotactic polymerization of styrene (Table 1, run 7), and high activity [up to 287 kg of polymer (mol of Sc)−1 h−1] for HPD homopolymerization to afford a cyclopolymer with high molecular weight and relatively narrow molecular weight distribution (Mw = 1.47 × 104, Mw/Mn = 2.47) (Table 1, run 8).6 In contrast to complexes 1 and 2, the 3/[Ph3C][B(C6F5)4] catalytic system is effective for the copolymerization of HPD with styrene and afforded HPD–styrene copolymers containing styrene–styrene sequences (79 mol %) and six-membered ring methylene-1,3-cyclohexane (MCH) units (21 mol %) in the presence of 250 equiv of HPD and styrene (Table 1, run 9). Solvent fractionation experiments confirmed that the resulting polymer products are not a mixture of homopolymers but true HPD–styrene copolymers.7

Additional Supporting Information may be found in the online version of this article.
The monomer content of styrene could be controlled in a wide range (15–93 mol%) by changing the HPD/styrene feeding ratio from 100/400 to 400/100 (Table 1, runs 9–15). When the HPD/styrene feed ratio was changed from 100/400 to 300/200, HPD comonomer produced only MCH units and the resulting HPD–styrene copolymers contained MCH rings (7–35 mol%) and styrene–styrene sequences (65–93 mol%) (Table 1, runs 9–12). When the HPD/styrene feed ratio was raised from 350/200 to 400/100, the HPD content of the resulting copolymers increased from 55 to 85 mol% with both MCH and five-membered ring ethylene-1,2-cyclopentane (ECP) units (Table 1, runs 13–15). The MCH selectivity of copolymerization is higher than that of homopolymerization of HPD, suggesting that the cyclization step of HPD (co)polymerization could be influenced by styrene comonomer. The GPC curves of all the HPD–styrene copolymers are unimodal with moderate molecular weight distributions ($M_w/M_n = 1.85–2.33$), indicating the predominance of a single-site active catalyst species. The melting temperature ($T_m = 224 \degree C$) of the HPD–styrene copolymer with a styrene content of 93 mol% (Table 1, run 9) is lower than that (ca. 260 °C) of the syndiotactic homopolystyrene prepared by 3 (Table 1, run 7). A melting point of the HPD–styrene copolymers with styrene content below 83 mol% was not observed, while the glass transition temperature ($T_g$) varied in the range of 88–94 °C. These results suggest that the syndiotactic selectivity was decreased in the copolymerization of styrene with HPD.

Because no NMR information on HPD–styrene copolymers could be found in the literature, we then carried out a detailed characterization of our copolymer products by the $^1$H, $^{13}$C, DEPT-$^{13}$C, HSQC, H2BC, HMBC, and HETCOR NMR analyses (see Supporting Information) to establish the microstructures and comonomer distribution in the copolymers.

**TABLE 1**: Copolymerization of 1,6-Heptadiene (HPD) with Styrene (St) by Using Half-Sandwich Scandium Complexes

<table>
<thead>
<tr>
<th>Run</th>
<th>[Sc]</th>
<th>HPDb</th>
<th>Stb</th>
<th>Time (min)</th>
<th>Yield (g)</th>
<th>Activityc</th>
<th>Composition (mol %)</th>
<th>M_n (×10^4)</th>
<th>M_w/M_n</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
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<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>500</td>
<td>1</td>
<td>0.989</td>
<td>3125</td>
<td>St 100, MCH 0, ECP 0</td>
<td>8.6</td>
<td>1.38</td>
<td>271</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>500</td>
<td>0</td>
<td>15</td>
<td>0.813</td>
<td>171</td>
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<td>0.3</td>
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<tr>
<td>3</td>
<td>1</td>
<td>250</td>
<td>250</td>
<td>15</td>
<td>0.645</td>
<td>n.d.</td>
<td>MCH 100, ECP 0, St 0</td>
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</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
<td>500</td>
<td>1</td>
<td>0.898</td>
<td>3125</td>
<td>St 100, MCH 0, ECP 0</td>
<td>25.2</td>
<td>1.53</td>
<td>271</td>
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</tr>
<tr>
<td>5</td>
<td>2</td>
<td>500</td>
<td>0</td>
<td>90</td>
<td>0.758</td>
<td>27</td>
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<tr>
<td>8</td>
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<tr>
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<td>0.387</td>
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<td>0.724</td>
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<td>2.18</td>
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* Conditions: [Sc] (19 μmol), [Ph3C][B(C6F5)4] (19 μmol), T = 25 °C, Toluene (6 mL).

b Molar ratio to [Sc].
c kg of polymer (mol of Sc)^{-1} h^{-1}.
d Determined by $^1$H NMR and $^{13}$C NMR.
e Determined by GPC in THF at 40 °C against polystyrene standard.
f Determined by DSC.
g A mixture of homopoly(HPD) and syndiotactic polystyrene.
h n.d. = not determined.
i Syndiotactic selectivity (rrrr = 89%).
a styrene content of 79 mol % is shown in Figure 1(a). This polymer is a random HPD-styrene copolymer containing syndiotactic-rich styrene-styrene sequences with a significant amount of atactic styrene-styrene sequences and MCH units. The multiplets at 145.8 (ipso-Ph), 43.8, and 40.9 ppm suggest that this polymer contains atactic polystyrene blocks. The resonances at 26.4 and 21.1 ppm are assigned to one methylene carbon of the cis-MCH unit and trans-MCH unit, respectively. The lack of the signal at 46.5 ppm for the joint carbon of two MCH ring units suggests that HPD is mainly incorporated in an isolated form. The $^{13}$C NMR spectrum of the HPD-styrene copolymer with a styrene content of 45 mol % is shown in Figure 1(b). It was revealed that this polymer is a random HPD-styrene copolymer containing atactic styrene-styrene sequences, MCH-MCH blocks and ECP units. It is also noteworthy that the MCH contents in all the copolymers are significantly increased compared with homopoly(HPD).

The reaction mechanisms of the homopolymerization of HPD and styrene catalyzed by complexes 1 and 2 have been described in our previous reports. On the basis of the previous studies and the results described above, a possible scenario of the HPD-styrene copolymerization by 3 is shown in Scheme 1. The addition of the Sc$^+$-alkyl bond to the coordinated vinyl double bond of styrene in a 2,1-fashion gives a cationic scandium benzyl complex such as a. The 1,2-insertion of a C=C double bond of HPD into the Sc$^+$-alkyl bond could yield b. The intramolecular 1,2-insertion of the remaining C=C double bond of the HPD unit into the Sc=C bond in b would afford c. The insertion of HPD to the Sc=C-alkyl bond in successive 2,1- and 1,2-insertion mode would give f. Further insertion of HPD or styrene to a, c, f would give styrene-MCH-ECP units. As to the cyclization of HPD monomer, cis-ring closure in intermediate b affording a cis-MCH unit would be sterically more favorable than trans-ring closure to give a trans-MCH unit. Furthermore, the MCH formation process could be more favored than the ECP formation process, because 1,2-inserted intermediate b (for MCH) is less hindered than 2,1-inserted intermediate e (for ECP). Such tendency would be increased by the coordination of styrene monomers, in consistent with the fact that the MCH selectivity of copolymerization is higher than that of homopolymerization of HPD.

The coordination of a phosphine oxide side arm in 3 to the scandium may suppress successive insertion of styrene, thus
facilitating the insertion of HPD to the Sc—styrene bond to form styrene—HPD copolymers. The lower syndiotactic selectivity for styrene in the copolymerization, compared to that of homopolymerization of styrene, might be caused by the coordination of HPD monomer to the scandium atom, which could possibly hamper coordination of incoming styrene monomer in an appropriate manner required for syndiotacticity.

In summary, we have demonstrated that the half-sandwich scandium bis(trimethylsilylmethyl) complex bearing the cyclopentadienyl ligand with a phosphine oxide side arm (3) in combination with [Ph3C][B(C6F5)4] can serve as a unique catalyst for the cyclocopolymerization of HPD with styrene, affording a new series of polymer materials having unique microstructures (five and six member ring cyclic units and polystyrene blocks) which are difficult to prepare by other means. The different performance observed between 1, 2, and 3 suggests that the copolymerization activity and selectivity of the half-sandwich rare-earth catalysts can be fine-tuned by changing the substituents on the Cp ligands.

EXPERIMENTAL

All manipulations of air and moisture-sensitive compounds were performed under a nitrogen atmosphere by use of standard Schlenk techniques or in an Mbraun glovebox. Anhydrous toluene was purified by use of a SPS-800 solvent purification system (Mbraun), and dried over fresh 4 Å molecular sieves in the glovebox. Styrene was purchased from Kanto Chemical, dried by stirring with CaH2 for 24 h, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. HPD was purchased from TCI, dried over sodium and tripropyl aluminum, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. [Ph3C][B(C6F5)4]3 was purchased from Tosoh Finechem Corporation and used without purification. The scandium complexes 1, 2, and 3 were prepared according to literature methods.

The NMR data of homopolymers and copolymers were obtained on JEOL JNM-EX 300 and JNM-ECS 400 spectrometers in 1,1,2,2-tetrachloroethane-d2 at room temperature. All two-dimensional NMR experiments were performed on a JEOL ECS 400 NMR spectrometer, operating at 399.78 MHz for 1H and 100.53 MHz for 13C NMR. Methine and methylene carbons were distinguished by the DEPT spectrum. Direct 1H-13C correlations were established by HSQC and HETCOR spectral data. The H2BC and HMBC cross-peaks from aromatic protons were used to assign styrene and styrene-MCH units. The molecular weights and the molecular weight distributions of HPD homopolymers and HPD-styrene copolymers were determined at 40 °C by gel permeation chromatography (GPC) on a HLC-8220 GPC apparatus (Tosoh Corporation). THF was employed as an eluent at a flow rate of 0.35 mL/min. The calibration was made by polystyrene standard. The DSC measurements were performed on a DSC6220 (SII) at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 20 °C/min to −50 °C, and then recording the second DSC scan.

A Typical Procedure for the Copolymerization of HPD with Styrene

In a glovebox, a mixture of HPD (548 mg, 5.7 mmol) and styrene (396 mg, 3.8 mmol) was added under vigorous stirring to a reaction mixture of complex 3 (11.6 mg, 19 μmol) and [Ph3C][B(C6F5)4]3 (18 mg, 19 μmol) in toluene (6 mL). The polymerization was terminated by addition of methanol after 60 min (Table 1, run 12). The resulting mixture was poured
into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol and dried under vacuum at 60 °C to a constant weight. The styrene, MCH, and ECP contents of the HPD–styrene copolymer were calculated according to the formula: styrene mol % = \(\frac{0.2I_5}{2I_5 + 1 - 12(I_6 - 0.6I_6)}\), HPD mol % = 100 – St mol %, MCH/ECP/ = \(\frac{I_2}{I_3 + I_4}\), in which \(I_1\) is the integration of the resonance at 26.42 ppm (one methylene carbon of the cis-MCH unit), \(I_2\) is the integration of the resonance at 21.16 ppm (one methylene carbon of the trans-MCH unit), \(I_3\) is the integration of the resonance at 22.56 ppm (one methylene carbon of the cis-ECP unit), and \(I_4\) is the integration of the resonance at 23.85 ppm (one methylene carbon of the trans-ECP unit) in the \(^{13}\)C NMR spectrum, and \(I_5\) is the integration of the resonances from 6.6 to 7.0 ppm (five phenyl protons of the styrene unit) and \(I_6\) is the integration of the resonances from 0 to 2.5 ppm (three aliphatic protons of the styrene unit and 12 aliphatic protons of the HPD unit) in the \(^1\)H NMR spectrum of the HPD–styrene copolymer.

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REFERENCES AND NOTES


7 Homopoly(HPD) is soluble in hexane at room temperature. Atactic polystyrene is soluble in ethyl acetate at room temperature. The copolymers are insoluble in hexane and ethyl acetate at room temperature.