

# Synthesis of Crystallizable Syndiotactic-Atactic Stereoblock Polypropylene Using a Living Polymerization System<sup>1</sup>

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**Abstract**—Propylene polymerizations were conducted by  $[t\text{-BuNSiMe}_2(3,6\text{-}t\text{-Bu}_2\text{Flu})]\text{TiMe}_2$  using dried modified methylalumininoxane as a cocatalyst in heptane, chlorobenzene (CB), and a mixture of heptane/CB (1 : 1 in volume) at 0°C. Postpolymerizations testified that the propylene polymerization proceeded in a living manner regardless of the solvent used. The heptane system gave highly syndiotactic crystalline polypropylene (PP), whereas the CB and heptane/CB mixture systems gave amorphous PP. After the first polymerization in heptane had been completed, the same amounts of propylene and CB were added for the second polymerization. This procedure gave the syndiotactic-atactic stereoblock PP with a melting point of 119°C.

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## INTRODUCTION

Development of homogeneous catalytic systems based on substituted stereorigid group 4 *ansa*-metallocenes has brought epochal advances for polymerization of olefins, which can precisely control the molecular structures of polymers produced. For example, the clear-cut relationship between the symmetry of the metallocene catalyst and stereospecificity has enabled us to synthesize atactic, isotactic, hemiisotactic and syndiotactic polypropylenes (PPs) [1–5]. PPs composed of atactic and isotactic or syndiotactic stereoblock sequences are industrially useful material as thermoplastic elastomers, which was discovered by Natta during the fractionation studies of PP obtained with  $\text{TiCl}_4\text{-Et}_3\text{Al}$  [6]. Collette et al. found that elastomeric PP was obtained using tetraalkyl group 4 catalysts supported on metal oxides [7].

Chien et al. first reported the synthesis of stereoblock PP using a homogeneous single-site catalyst. They proposed a mechanism where “the migration of polymer chain” between two different coordination sites of a  $C_1$ -symmetric *ansa*-titanocene gave isotactic-atactic stereoblock PP [8–10]. Several papers have reported on the synthesis of stereoblock PPs, which are based on the statistical isomerization between stereospecific and non-stereospecific sites by chain migration or ligand rotation [11–23]. These procedures cannot control the molecular weight, molecular-weight distributions (MWD), or the block length of the stereoblock PPs precisely.

Living polymerization is a useful method for the synthesis of block copolymers with precisely controlled molecular weight and block sequences.

Recently, the stereospecific living polymerization of olefin using transition metal catalysts has been developed in academic and industrial research laboratories [24]. Sita et al. reported that  $(\text{C}_5\text{Me}_5)\text{ZrMe}_2[\text{N}(t\text{-Bu})\text{C}(\text{Me})\text{N}(\text{Et})]$  combined with  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)]$  was effective for isospecific living polymerization of  $\alpha$ -olefins, and the degenerative transfer living polymerization, where the propagation chain exchanges between the enantiomeric active species, gave [atactic] [poly(1-hexene)]-block-[isotactic] [poly(1-octene)] with well-controlled block length and narrow MWD [25].

We have previously reported that Ti complex **1** ( $[t\text{-BuNSiMe}_2\text{Flu}]\text{TiMe}_2$ ) possessing fluorenyldimethylsilylamido ligand conducted syndiospecific living polymerization of propylene at 0°C when activated by dried methylalumininoxane (dMAO) in toluene [26]. We investigated the solvent effects on the living propylene polymerization by **1** combined with dried modified MAO (dMMAO), which is more soluble in hydrocarbon than dMAO, and found that the syndiospecificity was controlled by the polarity of the solvent. PP with a syndiotactic triad (*rr*) of 0.73 and melting point ( $T_m$ ) of 94°C was obtained in heptane, whereas atactic PP was obtained in chlorobenzene (CB) with high activity [27]. This result was applied to the synthesis of syndiotactic-atactic stereoblock PP by sequential addition of monomer and CB as additional solvent [28]. The  $T_m$  of the syndiotactic sequence, however, disappeared in the block copolymer obtained, because of the low stereoregularity of the syndiotactic sequence. We have recently realized highly active and highly syndiospecific (*rr* = 0.93) living polymerization of propylene in heptane using  $[t\text{-BuNSiMe}_2(3,6\text{-}t\text{-Bu}_2\text{Flu})]\text{TiMe}_2$  (**2**) by

<sup>1</sup> The text was submitted by the authors in English.

**Table 1.** Results of propylene polymerization with **2**-dMMAO<sup>a</sup>

Entry	Propylene, g	Solvent <sup>b</sup>	Yield, %	$M_n^c, \times 10^4$	$M_w/M_n^c$	$N^d, \mu\text{mol}$
1	0.63	H	100	6.1	1.37	10.3
2	0.63	CB	100	5.8	1.33	10.9
3	0.63	H/CB	99	5.6	1.30	11.3
4	0.63 + 0.63	CB	100	11.4	1.31	11.1
5	0.63 + 0.63	H/CB	100	11.6	1.30	10.9
6	0.63 + 0.63	H + CB <sup>e</sup>	100	11.9	1.29	10.6

Note: <sup>a</sup> Polymerization conditions: solvent = 30 ml, Ti = 20  $\mu\text{mol}$ , Al = 4.0 mmol, 0°C, 1 h.

<sup>b</sup> Solvent: H = heptane, CB = chlorobenzene, H/CB = 1 : 1 in volume.

<sup>c</sup> Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration.

<sup>d</sup> Calculated from yield and  $M_n$ .

<sup>e</sup> After the propylene polymerization with 0.63 g propylene in heptane for 1 h, 0.63 g of propylene and 30 ml of CB were added, and the polymerization was conducted for a further 1 h.

the introduction of *t*-butyl groups on fluorenyl ligand of **1** at the 3,6-position [29].

In this paper, we describe the application of **2** for the synthesis of syndiotactic-atactic stereoblock PP with crystallizable syndiotactic sequence.

## EXPERIMENTAL

**Materials.** All operations were performed under argon gas using standard Schlenk techniques and all solvents were dried by usual procedures and freshly distilled before use. The complex and dMMAO were prepared according to the procedure reported previously [29, 30]. Research-grade propylene (Takachiho Chemicals Co.) was purified by passing it through columns of NaOH,  $\text{P}_2\text{O}_5$ , and molecular sieves 3A, followed by bubbling it through a  $\text{NaAlH}_2\text{Et}_2$ /1,2,3,4-tetrahydronaphthalene solution.

**Polymerization procedure.** Polymerization was performed in a 100-ml glass reactor equipped with a magnetic stirrer and carried out as follows. After certain amounts of dMMAO and gaseous propylene were dissolved in the selected solvent, polymerization was started by the addition of a 1-ml solution of the catalyst (20  $\mu\text{mol}$ ) in the same solvent and conducted for 1 h. For the synthesis of block polymer, after the propylene polymerization was conducted with 0.63 g of propylene in heptane for 1 h, 0.63 g of propylene and 30 ml of CB were added, and the polymerization was conducted for a further 1 h. Polymerization was terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60°C for 6 h.

**Analytical procedure.** The molecular weight and molecular weight distribution of polymer obtained were determined by gel permeation chromatography with a Waters 150 CV at 140°C using *o*-dichlorobenzene as a solvent. The parameters for universal calibration were  $K = 7.36 \times 10^{-5}$ ,  $\alpha = 0.75$  for polystyrene standard and  $K = 1.03 \times 10^{-4}$ ,  $\alpha = 0.78$  for PP samples. The

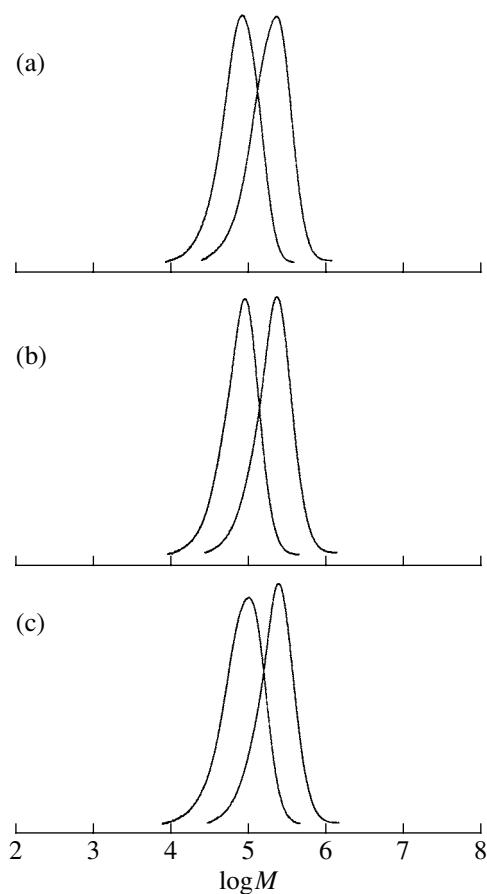
<sup>13</sup>C NMR spectra of PPs were measured at 130°C on a JEOL JNM-400 spectrometer operated at 400 MHz in the pulse Fourier transform mode. The pulse angle was 45° and about 10000 scans were accumulated in pulse repetition of 5.0 s. Sample solutions were prepared in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> and the central peak of the solvent (74.47 ppm) was used as an internal reference. Differential scanning calorimetry (DSC) analyses were performed on a Seiko DSC-220. The samples were encapsulated in aluminum pans and annealed at 80°C for 4 h to ensure sufficient time for crystallization. After annealing, the DSC curves of the samples were recorded under a nitrogen atmosphere at a heating rate of 10 K/min from 20 to 200°C.

## RESULTS AND DISCUSSION

Propylene polymerizations were performed by **2** activated with dMMAO in heptane, CB, and a mixture of heptane/CB (1 : 1 in volume) at 0°C (entries 1, 2, 3, Table 1).

The conversions were almost quantitative regardless of the solvent used, and the number of polymer chains ( $N$ ) calculated from the polymer yield and the  $M_n$  were about 60–65% of the Ti used and the molecular weight distributions (MWDs) were comparatively narrow. To investigate the living nature in CB and the mixture of heptane/CB, we conducted postpolymerization: the first-step polymerization was conducted with a certain amount of propylene for one hour (entries 2, 3, Table 1), and the second-step polymerization was continued for another hour after the addition of the same amount of propylene in the first step (entries 4, 5, Table 1). The yield and  $M_n$  value became almost double that of the first-step polymers while keeping constant  $N$  values and narrow MWD.

The GPC curves of the polymers obtained are illustrated in Fig. 1. The curves of the second step shifted to a higher molecular weight region than that of the first step in each solvent, and no peak or shoulders were



**Fig. 1.** GPC curves of polypropylenes obtained in postpolymerization: (a) in CB; (b) in a mixture of heptane and CB; (c) in heptane (first step) + CB (second step).

observed. The results indicate that the Ti-polymer bonds were not deactivated even in the absence of propylene and the propylene polymerization proceeded in a living manner regardless of the solvent used.

The steric triad distributions and the melting temperatures of PPs obtained in each solvent are shown in Table 2. The heptane system gave highly syndiotactic

**Table 2.** Steric triad distribution and melting temperature of polypropylenes obtained with **2**

Entry	Steric triad distribution <sup>a</sup>			$T_m^b$ , °C
	<i>mm</i>	<i>mr</i>	<i>rr</i>	
1	0.03	0.08	0.89	123
2	0.17	0.41	0.42	— <sup>c</sup>
3	0.07	0.43	0.50	— <sup>c</sup>
6	0.05	0.26	0.69	119

<sup>a</sup> Determined by  $^{13}\text{C}$  NMR spectroscopy.

<sup>b</sup> Melting temperature determined by DSC.

<sup>c</sup> Not detected.

PP with an *rr* value of 0.89 (entry 1) and the PP shows a  $T_m$  of 123°C. On the other hand, the *rr* values of the PPs obtained in the CB and heptane/CB mixed systems were decreased to 0.42 and 0.50 respectively, and amorphous polymers were obtained (entries 2 and 3). These solvent effects are in good agreement with those reported in propylene polymerization with **1**-dMMAO [28].

These results encouraged us to synthesize more stereoregular syndiotactic-atactic stereoblock PP with the living polymerization system by **2**-dMMAO. We therefore conducted a postpolymerization (entry 6, Table 1), where the same amount of propylene and CB were added after the initial polymerization in heptane (entry 1, Table 1). The yield and  $M_n$  value became almost double that of the first-step polymers while keeping a constant *N* value and narrow MWD. The GPC curve of the polymer obtained by the postpolymerization shifted to a higher molecular weight region, and no peak or shoulders were observed accompanied by narrowing MWD. The results testified that the postpolymerization proceeded quantitatively.

The triad analysis showed that the produced PP (entry 6) was syndiotactic-rich (*rr* = 0.69), the value of which is the arithmetic average ((0.89 + 0.50)/2 = 0.695) of those produced in heptane and heptane/CB. Although the stereoblock PP obtained by the **1**-dMMAO system reported previously did not show any  $T_m$  [28], the PP obtained by the **2**-dMMAO system showed  $T_m$  of 119°C. The results indicate the formation of the expected syndiotactic-atactic stereoblock PP that has a crystallizable syndiotactic sequence.

## CONCLUSIONS

The syndiotactic-atactic stereoblock PP was synthesized with **2**-dMMAO by the method reported previously with **1**-dMMAO, where a polar solvent was just added during the living polymerization. **2**-dMMAO was found to produce crystallizable syndiotactic-atactic stereoblock PP with improved syndiotacticity compared to **1**-dMMAO.

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