Synthesis of Stereoblock Polypropylene by Change of Temperature in Living Polymerization

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Abstract

[*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**1**) combined with trialkylaluminum-free modified methylaluminoxane (dMMAO) conducted living polymerization of propylene in toluene at -20, 0 and 25 °C with the control of the syndiospecificity. After the first polymerization at -20 °C had been completed, the same amounts of propylene were added at 25 °C for the second polymerization. The produced PP was syndiotactic-rich (rr = 0.75), the value of which is the arithmetical average ((0.89 + 0.60)/2 = 0.745) of those produced at -20 and 25 °C. The results indicate the formation of the expected syndiotactic-atactic di-stereoblock PP.

Introduction

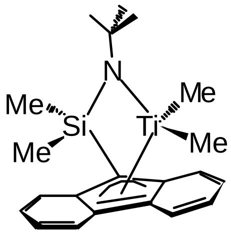
Since the discovery of thermoplastic elastomeric polypropylene (PP) composed of atactic and isotactic stereoblock sequences by Natta during the fractionation studies of PP obtained with TiCl$_4$-Et$_3$Al,[1] the synthesis of stereoblock PPs have attracted much attention and made considerable achievement by subsequent research in academic and industry.

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 enable us to synthesize atactic, isotactic, hemiisotactic and syndiotactic polypropylenes (PPs).2-7)

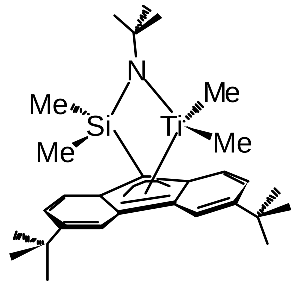
Chien et al. first reported the synthesis of stereoblock PP using a homogeneous single-site catalyst. They proposed a mechanism where “the migration of polymer chain” between two different coordination sites of a C_1-symmetric *ansa*-titanocene gave isotactic-atactic stereoblock PP.[8] Several papers have reported on the synthesis of stereoblock PPs based on the statistical isomerization between stereospecific and non-stereospecific sites by the chain migration or the ligand rotation,[9-16] in which the molecular weight, molecular weight distributions, and the length of stereoblock cannot be controlled precisely.

Living polymerization is a useful method for the synthesis of block copolymers with precisely-controlled molecular weight and block sequences.[17] Sita et al. recently reported a new class of PPs in the form of discrete, multiblock, isotactic-atactic stereoblock microstructures (e.g., di-, tri-, and tetrablocks) with well-controlled molecular weight and block sequences using degenerative living polymerization system.[18]

We have previously investigated the solvent effects on the syndiospecific living polymerization of propylene by [*t*-BuNSiMe$_2$Flu]TiMe$_2$ combined with trialkylaluminum-free modified methylaluminoxane (dMMAO)[19] and found that the syndiospecificity was controlled by the polarity of the solvent. This result was applied for the synthesis of syndiotactic-atactic di-stereoblock PPs by sequential addition of monomer and polar solvent used.[20]



[*t*-BuNSiMe$_2$Flu]TiMe$_2$



[*t*-BuNSiMe$_2$(3,6-^{t}Bu$_2$Flu)]TiMe$_2$ (**1**)

We also realized highly active and highly syndiospecific living polymerization of propylene using [*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**1**)–dMMAO and synthesized crystallizable stereobokck PP using the same method.[21] This method is useful for the synthesis of di-stereoblock PPs but not applied for the synthesis of multiblock PP, because the control of the stereospecificity is irreversible after the addition of polar solvent. We have recently succeeded in facile synthesis of multi-stereoblock PP via successive variation of monomer pressure during the living polymerization with **1**–dMMAO.[22]

The effects of polymerization temperature on the living propylene polymerization with **1**–dMMAO were investigated, and the syndiospecificity was controlled by changing polymerization temperature.[23] In this paper, we investigated the living nature of this catalytic system at -20, 0 and 25 °C in toluene, and the catalytic system was applied for the synthesis of syndiotactic-atactic stereoblock PP by changing polymerization temperature during polymerization.

Experimental

Materials

All operations were performed under nitrogen gas using standard Schlenk techniques and all solvents were dried by usual procedures and freshly distilled before use. The Ti complex and dMMAO were prepared according to the method reported previously.[21a] Research grade propylene (Takachiho Chemicals Co.) was purified by passing it through drycolumn DC-A4 and gasclean GC-RX (Nikka Seiko Co.).

Polymerization Procedure

Polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer and carried out by the following batch method. After the reactor was charged with prescribed amounts of dMMAO, solvent (toluene) and propylene, polymerization was started by the addition of 1 mL solution of catalyst (20 μmol) in toluene and conducted for 30 min and terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Analytical Procedure

Molecular weight and molecular weight distribution of the polymer obtained were determined by gel permeation chromatography with a Waters 150 CV equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 135 °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 ^{13}C NMR spectra of PPs were measured at 130 °C on a JEOL GSX 500 spectrometer operated at 125.65 MHz in the pulse Fouriertransform 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_2, 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 were recorded upon reheating the polymer samples to 200 °C with a heating rate of 10 °C/min.

Results and Discussion

We have previously investigated the effects of polymerization temperature on the living propylene polymerization with **1**–dMMAO and found that the raise of polymerization temperature enhanced the activity. The steric triad distributions and the melting temperatures of PPs obtained at each temperature are shown in Table 1.

<Table 1>

The system gave highly syndiotactic crystalline PP at -20 °C, which shows T_m of 129 °C. The syndiotacticity of PP was decreased with increasing the polymerization temperature to give amorphous PP at 25 °C.

To investigate the living nature, we conducted postpolymerization in toluene at -20, 0 and 25 °C by a batch method: the first-step polymerization was conducted with a certain amount of propylene for 30 minutes, and the second-step polymerization was continued for another 30 minutes after the addition of the same amount of propylene delete. The results are summarized in Table 2.

<Table 2>

In both steps, the conversions were almost quantitative regardless of the polymerization temperature. In the first-step polymerization, the number of polymer chains (*N*) calculated from the polymer yield and the number average molecular weight (M_n) was almost constant with comparatively narrow molecular weight distributions (MWDs), which was about 60 ~ 65% of the Ti used regardless of the polymerization temperature.

After second-step polymerization, the yield and M_n value became almost double of those of the first-step polymers with keeping the constant *N* value and narrow MWD. The results reply that the growing polymer chain was not deactivated even in the absence of propylene and initiated the successive polymerization quantitatively, indicating the living polymerization of propylene in toluene regardless of the polymerization temperature.

The M_n values of the polymers were determined by GPC using universal calibration. Therefore the turnover frequency (TOF) of propagation in the living system can be directly evaluated by the number-average polymerization degree ($P_n = M_n/42$) and the polymerization time (t_p), and the values thus obtained and N values are plotted against the polymerization temperature are illustrated in Figure 1.

<Figure 1>

The TOF (P_n/t_p) value was increased against the polymerization temperature, and the N value slightly increased from 11.7 μmol at -20 ºC to 13.3μmol at 25 ºC. These results indicate that the increase of polymerization temperatures enhanced the propagation rate but did not affect the living nature of this catalytic system, and the initiation efficiency was slightly dependent on the polymerization temperature.

The steric pentad distributions in main chain and the T_m values of the polymers obtained by a bath method are summarized in Table 3. The PP obtained at -20 °C showed the highest syndiotactic pentad value (rrrr) of 0.82, which decreased according to the raise of polymerization temperature to 0.70 at 0 °C and 0.39 at 25 °C. Consequently the PP obtained at -20 °C was crystalline polymer with melting point of 123 °C, whereas that obtained at 25 °C was amorphous one.

<Table 3>

In the enantiomorphic-site controlled syndiospecific polymerization with a C_s symmetric catalyst, two types of stereodefects should be formed: one is “rmrr” arising from the “chain migration” without monomer insertion and the other is “rmmr” arising from the “monomer miss-insertion” (Scheme 1).[24] Table 3 indicates that rmrr content was increased by the raising polymerization temperature, -20 °C (0.02) < 0 °C (0.10) < 25 °C (0.23), whereas the rmmr content was almost constant and slightly increased only at 25 °C, -20 °C (0.02) = 0 °C (0.02) < 25 °C (0.04). These results imply that the decrease of the syndiospecificity caused by raising the temperature is mainly attributed to the frequent “chain migration”. The similar phenomena were observed in the syndiospecific propylene polymerization with C_s-symmetric zirconocene catalysts.[25-27]

<Scheme 1>

These results encouraged us to synthesize syndiotactic-atactic stereoblock PP with the living polymerization system by **1**–dMMAO. We therefore conducted a postpolymerization, where the second polymerization was conducted at 25 °C by sequential addition of monomer after the first polymerization had been completed at -20 °C (Scheme 2), and the polymerization results are also shown in Table 2 (entry 10). The yield and M_n value became almost double of that of the first-step polymers with keeping the constant N value and narrow MWD. The GPC curves of the polymer obtained by the postpolymerization are illustrated in Figure 2. The curve of second step shifted to higher molecular weight region, and no peak or shoulders were observed. The results testified that the postpolymerization proceeded quantitatively.

<Scheme 2>

<Figure 2>

The produced PP was syndiotactic-rich (rr = 0.75), the value of which is the arithmetical average ((0.89 + 0.60)/2 = 0.745) of those produced at -20 and 25 °C. The results indicate the formation of the expected syndiotactic-atactic stereoblock living PP by changing polymerization temperature. The T_m and melt enthalpy (ΔH) of PPs were determined by DSC. The second-step PPs showed T_m of 121 °C with ΔH of 30 mJ/mg. These values of T_m and ΔH are lower than that of first-step polymer (123 °C and 69 mJ/mg). The results also testified the formation of the stereoblock PPs.

Conclusions

In summary, the [*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**1**)–dMMAO system conducted living polymerization of propylene in toluene at -20, 0 and 25 °C with the control of the syndiospecificity. This catalytic system was applied for the synthesis of stereoblock PP by changing the polymerization temperature and was found to give crystallizable syndiotactic-atactic di-stereoblock PP.

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Table, Scheme and Figures Captions

Table 1. Results of Propylene Polymerization with **1**–dMMAO at Various Temperature[a]

Table 2. Propylene Polymerization with **1**–dMMAO by a Batch Method[a]

Table 3. Stereosequence Distributions and Melting Temperatures[a]

Scheme 1. Enantiomorphic-site controlled syndiospecific polymerization by C_s-symmetric catalysts.

Scheme 2. Synthesis of stereoblock polypropylene by changing polymerization temperature.

Figure 1. Plots of TOF and *N* values against polymerization temperature.

Figure 2. GPC curves of polypropylenes obtained by changing polymerization temperature in postpolymerization: (a) entry 4 and (b) entry (10).

Table 1. Results of Propylene Polymerization with 1–dMMAO at Various Temperature[a]

entry	temp. (°C)	time (min)	yield (g)	activity[b]	M_n[c] ($\times 10^4$)	$M_\mathrm{w}/M_\mathrm{n}$[c]	N[d] (μmol)	rr[e]	T_m[f] (°C)	TOF[g] (s^{-1})
1	-20	8	0.76	285	6.5	1.35	11.7	0.90	129	3
2	0	4	2.36	1768	18.8	1.36	12.3	0.83	100	18
3	25	3	2.42	2420	17.9	1.32	13.3	0.60	-[h]	24

[a] Polymerization conditions: toluene = 30 mL, Ti = 20 μmol, Al = 4.0 mmol, propylene = 1.0 atm. [b] Activity in kg-PP/(mol-Ti·h). [c] Number average molecular weight and molecular weight distribution determined by GPC using universal calibration. [d] Calculated from yield and M_n. [e] Determined by ^{13}C NMR spectroscopy. [f] Determined by DSC. [g] TOF calculated from number-average polymerization degree (P_n) and polymerization time (t_p). [h] Not detected.

Table 2. Propylene Polymerization with 1–dMMAO by a Batch Method[a]

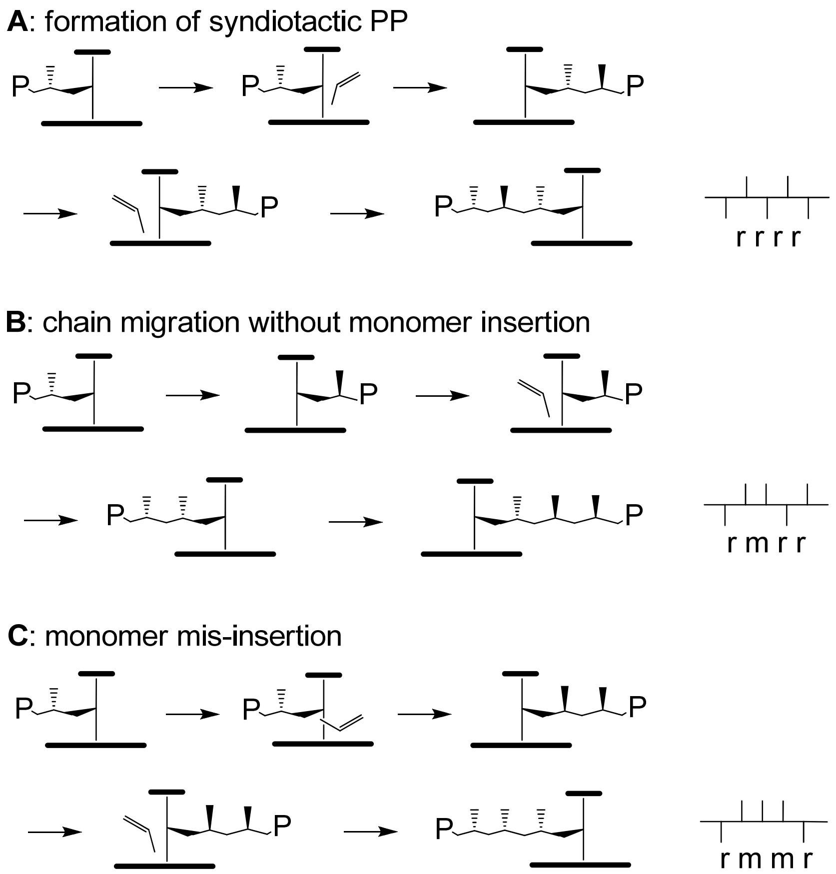
entry	propylene (g)	temperature (°C)	yield (%)	M_n[b] ($\times 10^4$)	M_w/M_n[b]	N[c] (μmol)
4	0.63	-20	100	5.5	1.31	12
5	0.63	0	99	5.2	1.30	12
6	0.63	25	100	4.9	1.25	13
7	0.63 + 0.63	-20	99	11.1	1.30	11
8	0.63 + 0.63	0	100	10.2	1.32	12
9	0.63 + 0.63	25	99	9.4	1.28	13
10[d]	0.63 + 0.63	-20→25	100	10.1	1.32	12

[a] Polymerization conditions: toluene = 30 mL, Ti = 20 μmol, Al = 4.0 mmol, 30 min. [b] Number average molecular weight and molecular weight distribution determined by GPC using universal calibration. [c] Calculated from yield and M_n. [d] After the propylene polymerization with 0.63 g of propylene at -20 °C for 30 min, 0.63 g of propylene was added at 25 °C, and the polymerization was conducted for further 30 min.

Table 3. Stereosequence Distributions and Melting Temperatures [a]

entry	stereosequence distribution [a]									T_m [b]	ΔH
	mmmm	mmmr	rmmr	mmrr	mmrm+rmrr	rmrm	rrrr	mrrr	mrrm	(°C)	(J/g)
4	0.00	0.00	0.02	0.05	0.03	0.01	0.82	0.07	0.00	123	69
5	0.00	0.00	0.02	0.04	0.10	0.01	0.70	0.13	0.00	100	26
6	0.00	0.01	0.04	0.09	0.20	0.06	0.39	0.20	0.01	-	-

[a] Determined by ^{13}C NMR spectroscopy.

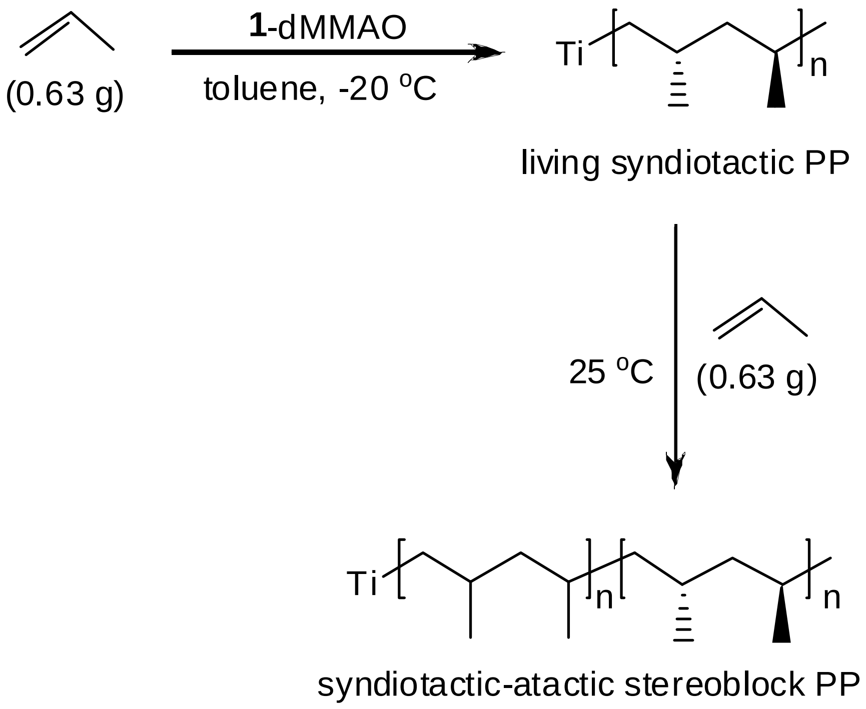


A: formation of syndiotactic PP

B: chain migration without monomer insertion

C: monomer mis-insertion

Scheme 1. Enantiomorphic-site controlled syndiospecific polymerization by C_s-symmetric catalysts.



Scheme 2. Synthesis of stereoblock polypropylene by changing polymerization temperature.

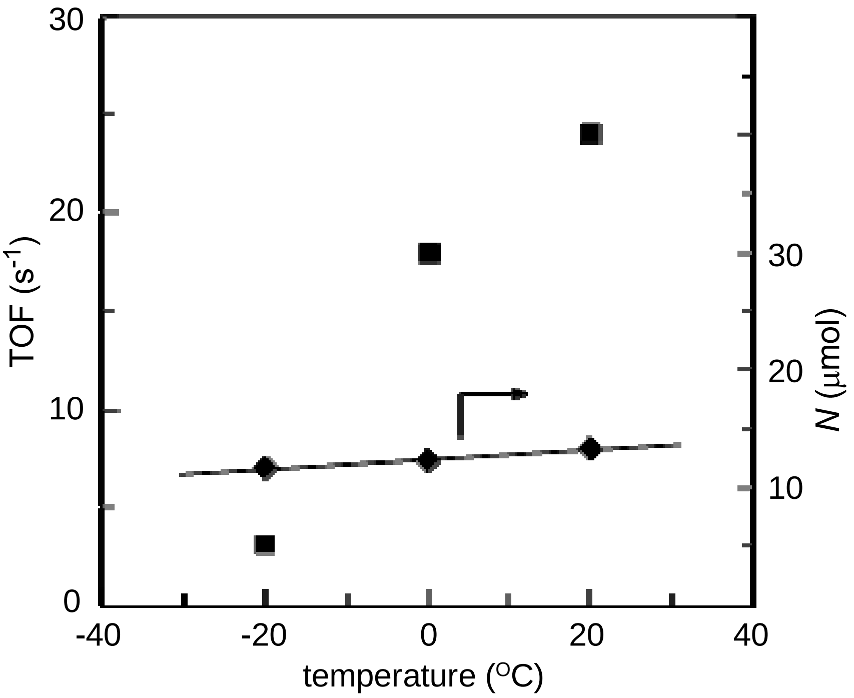


Figure 1. Plots of TOF and *N* values against polymerization temperature.

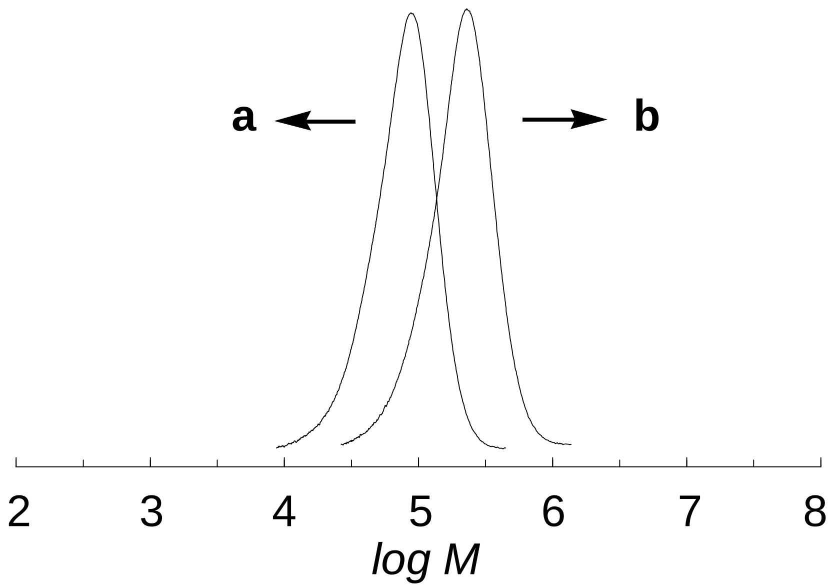


Figure 2. GPC curves of polypropylene obtained by changing polymerization temperature in postpolymerization: (a) entry 4 and (b) entry (10).

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