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Notes

Facile Synthesis of Tailor-Made Stereoblock Polypropylenes via Successive Variation of Monomer Pressure

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Introduction

Developments of homogeneous Ziegler−Natta catalysts, i.e., so-called single-site catalysts, have brought epochal advances for the stereospecific polymerization of propylene through modifications of catalyst ligand or controlling polymerization conditions.[1−5] Since the discovery of thermoplastic elastomeric polypropylene (PP) composed of atactic and isotactic stereoblock sequences by Natta during the fractionation studies of PP,[6] the synthesis of stereoblock PPs has attracted much attention and made considerable achievement by subsequent research in academia and industry.[7−16] These procedures are based on the statistical isomerization between stereospecific and nonstereospecific sites by chain migration or the ligand rotation in which the molecular weight, molecular weight distributions (MWD), 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 using living Ziegler−Natta polymerization.[18]

We have previously investigated the solvent effects on the living propylene polymerization by Ti complex **FluTi** ([*t*-BuNSiMe$_2$Flu]TiMe$_2$) combined with trialkylaluminum-free modified methylaluminoxane (dMMAO)[19a] and found that the syndiospecificity was controlled by the polarity of the solvent.[19b] This result was applied for the synthesis of syndiotactic−atactic stereoblock PP by sequential addition of monomer and polar solvent.[19c] We have recently realized highly active and highly syndiospecific living polymerization of propylene using [*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**1**) and synthesized crystallizable stereoblock PP using the same method.[20] This method is useful for the synthesis of distereoblock PPs but not applied for the synthesis of multiblock PP because the control of the stereospecificity is irreversible after the addition of polar solvent.

In this paper, we introduce novel synthetic procedure for the synthesis of precisely controlled multiblock syndiotactic−atactic stereoblock PPs with a living stereocontrollable polymerization of propylene using the **1**−dMMAO system, where propylene pressure was just changed during the living polymerization.

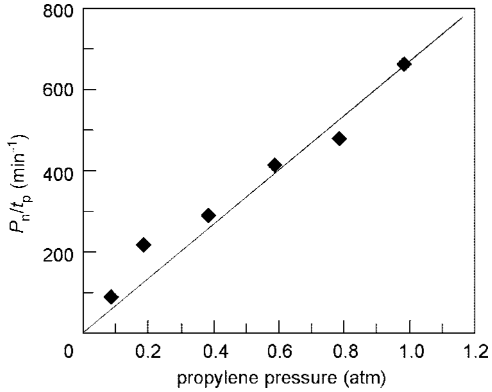

Figure 1. Plots of P_n/t against propylene pressure.

Experimental Section

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.[20a] Research grade propylene (Takachiho Chemicals Co.) was purified by passing it through columns of NaOH, P$_2$O$_5$, and molecular sieves 3 Å, followed by bubbling it through a NaAlH$_2$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 by the following method. After the reactor was charged with prescribed amounts of dMMAO, solvent (heptane), and 1 mL solution of **1** (20 μmol) in heptane, and the nitrogen gas was evacuated by a vacuum pump, the polymerization was started by introducing propylene up to the required pressure, which was monitored by a manometer. The pressure was kept constant during the polymerization by controlling the propylene supply. Polymerization was conducted for a certain time under various pressures of propylene and terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Synthesis of stereoblock PPs was carried out by the following

Table 1. Propylene Polymerization with 1−dMMAO Under Various Pressures of Propylene[a]

entry	pressure[b] (atm)	time (min)	yield (g)	activity[c]	M_n[d] ($\times 10^4$)	M_w/M_n[d]	N[e] (μmol)	P_n[f]/t_p (min^{-1})
1	1.0	4	1.96	1470	11.1	1.35	18	661
2	0.8	6	2.16	1080	12.1	1.33	17	480
3	0.6	8	2.56	960	13.9	1.28	18	413
4	0.4	10	2.09	627	‘12.1	1.27	17	288
5	0.2	10	1.23	369	9.1	1.22	14	217
6	0.1	10	0.47	141	3.7	1.31	13	88

[a] Polymerization conditions: heptane = 30 mL, Ti = 20 μmol, 0 °C. [b] Propylene pressure + vapor pressure of heptane (0.015 atm) at 0 °C. [c] Activity in kg PP/(mol Ti h). [d] Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration. [e] Calculated from yield and M_n. [f] Number-average polymerization degree.

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Table 2. Stereosequence Distributions and Melting Temperatures of PPs Obtained with 1−dMMAO[a]

	stereosequence distribution[a]									
entry	mmmm	mmmr	rmmr	mmrr	mmrm + rmrr	rmrm	rrrr	mrrr	mrrm	T_m[b] (°C)
1	0.00	0.00	0.02	0.03	0.03	0.00	0.83	0.09	0.00	125
2	0.00	0.01	0.02	0.05	0.09	0.02	0.68	0.12	0.01	106
3	0.00	0.02	0.03	0.05	0.13	0.03	0.56	0.16	0.02	88
4	0.01	0.03	0.03	0.05	0.16	0.04	0.45	0.18	0.03	73
5	0.01	0.03	0.04	0.08	0.16	0.05	0.42	0.18	0.03	–[c]
6	0.01	0.04	0.04	0.09	0.17	0.06	0.39	0.16	0.04	–[c]
diblock	0.01	0.02	0.03	0.06	0.10	0.03	0.60	0.13	0.02	118
	(0.00	0.02	0.03	0.06	0.10	0.03	0.60	0.14	0.02)[d]	
triblock	0.00	0.01	0.02	0.04	0.10	0.02	0.69	0.12	0.00	115
	(0.00	0.01	0.03	0.05	0.08	0.02	0.68	0.12	0.01)[d]	

[a] Determined by ^{13}C NMR spectroscopy. [b] Meing temperature determined by DSC. [c] Not detected. [d] Calculated pentad distributions from the weight fraction of each block sequence assuming that the pentad distributions of each block sequence are the same with those of the PPs obtained under 0.2 and 1.0 atm.

methods: the first-step polymerization was conducted under 1.0 atm of propylene pressure for 2 min, the second-step polymerization was continued for another 5 min with decreasing the propylene pressure to 0.2 atm by a vacuum pump, and the third-step polymerization was conducted for another 2 min with increasing the propylene pressure to 1.0 atm.

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 and calibrated with polystyrene standards. The ^{13}C NMR spectra of PPs were measured at 130 °C on a JEOL GX 500 spectrometer operated at 125.65 MHz in the pulse Fourier transform mode. The pulse angle was 45°, and about 10 000 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, and the DSC curves were recorded upon reheating the polymer samples to 200 °C with a heating rate of 10 °C/min.

Results and Discussion

Propylene polymerizations were performed by **1** activated with dMMAO in heptane at 0 °C under various pressures of propylene. The results are summarized in Table 1.

The catalytic system showed high activity and gave PP with high number-average molecular weight (M_n = 111 000) for 4 min under 1.0 atm. The activity was decreased according to the decrease of the propylene pressure. The numbers of polymer chains (N) were smaller than that of the Ti used and slightly decreased from about 18 μmol under 1.0−0.4 atm to 14 and 13 μmol under 0.2 and 0.1 atm with keeping the narrow molecular weight distribution (MWD) regardless of the propylene pressure. The results suggest that the propylene polymerization proceeded in a living manner regardless of the propylene pressure, and the initiation efficiency was slightly dependent on the propylene concentration.

The propagation rates were evaluated from the number-average polymerization degree and the polymerization times and are plotted against the propylene pressure in Figure 1. The propagation rate was increased linearly against the propylene pressure, which indicates the first-order dependence of propylene pressure on the propagation rate. This result is in disaccord with that of propylene polymerization with **FluTi**−B(C_6F_5)$_3$ at −50 °C, where the propagation rate depended on the second-order of propylene concentration.[21] The first-order kinetic in the present catalytic system is probably due to the higher polymerization temperature and/or the lower monomer concentration.

The steric pentad distributions and the melting temperatures of the PPs obtained under various propylene pressures are shown in Table 2. The catalyst system gave highly syndiotactic crystalline PP under 1.0 atm with the rrrr value of 0.83 and the T_m of 125 °C. The rrrr values of the PPs obtained were decreased with lowering the propylene pressure accompanied by decrease in the T_m of the PPs. As a consequence, amorphous polymers were obtained under 0.2 and 0.1 atm.

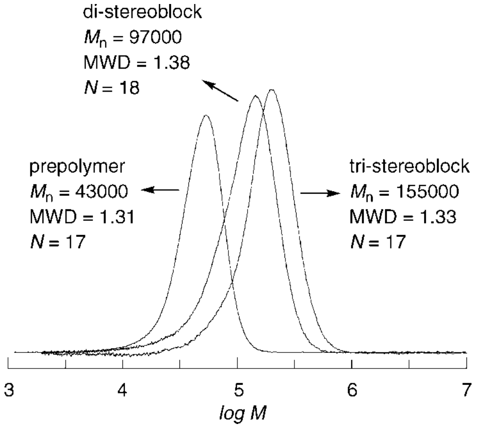

Figure 2. GPC curves of the PPs obtained by changing propylene pressure during polymerization.

In the enantiomorphic-site-controlled syndiospecific polymerization with a C_s-symmetric catalyst, two types of stereodefects should be formed: one is “rmmr” arising from the “monomer miss insertion”, and the other is “rmrr” arising from the “chain migration” without monomer insertion.[22] Table 2 indicates that the rmmr content was almost independent of the propylene concentration, whereas the rmrr content was drastically increased from 0.02 to 0.20 by decrease of propylene pressure. We can therefore conclude that the low syndiospecificity under lower propylene concentration is ascribed to the promotion of the “chain migration” but not to the low selectivity of the prochiral face at the enantiomorphic site. The same phenomenon was already observed in the syndiospecific propylene polymerization with C_s-symmetric zirconocene catalysts.[23]

We therefore tried to synthesize syndiotactic−atactic stereoblock PP by changing the propylene pressure. The polymerization results and the GPC curves of the polymers are shown in Figure 2.

After the second- and third-step polymerization, the yields and M_n values were increased compared with those of the first- and second-step polymers, respectively, with keeping the constant N value and narrow MWD, and any other peaks or shoulders were not observed in the GPC curves of the second and third step. The stereosequence distributions of the block PPs determined by ^{13}C NMR are shown in Table 2. The pentad distributions of the PPs were also calculated from the weight fraction of each block sequence assuming that the pentad distributions of each block sequence are the same with those of the PPs obtained under 0.2 and 1.0 atm, respectively. The calculated values are also shown in parentheses of Table 2. The observed values are in good accordance with the calculated values in both the second- and third-step PPs. The results indicate the formation of the expected syndiotactic−atactic and syndiotactic−atactic−syndiotactic stereoblock living PPs by changing propylene pressure.

The T_m and melt enthalpy (ΔH) of PPs were determined by DSC. The second- and third-step PPs showed T_m of 118 and 115 °C with ΔH of 31 and 39 mJ/mg, respectively. These values of T_m and ΔH are lower than that of first-step polymer (125 °C and 57 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 heptane at 0 °C under various propylene pressure, where the syndiospecificity was controlled by the propylene pressure. This catalytic system was applied to the synthesis of syndiotactic−atactic stereoblock PP for the first time by changing propylene pressure and was found to give crystallizable di- and tristereoblock PPs, of which structure can be precisely controlled by propylene concentration and polymerization time.

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Supporting Information Available: ^{13}C NMR spectra of methyl region of PPs and DSC profiles of prepolymer and stereoblock PPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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