Living Random Copolymerization of Propylene and Norbornene with *ansa*-Fluorenylamidodimethyltitanium Complex: Synthesis of Novel Syndiotactic Polypropylene-*b*-poly(propylene-*ran*-norbornene)

Zhengguo Cai, Yuushou Nakayama, and Takeshi Shiono*

Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan, and Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8503, Japan

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Introduction. Cyclic olefin copolymers (COC) such as poly(ethylene-*co*-norbornene) and poly(propylene-*co*-norbornene) have experienced a phenomenal development in academic and industrial research laboratories,[1] since COC are a new interesting class of amorphous and thermoplastic materials with high glass transition temperature (T_g), high transparency, high chemical resistance, low water absorption, and good solubility in organic solvents. These properties of COC can be controlled by comonomer composition, sequence distribution, and microstructure of copolymers. For example, poly(ethylene-*ran*-norbornene) showed a higher T_g value with wider temperature range than poly(ethylene-*alt*-norbornene).[2−6] Although poly(ethylene-*co*-norbornene) can be produced by various transition-metal-based catalysts, there are a few examples of the catalysts that copolymerized ethylene and norbornene in a living manner.[7−12] Several block copolymers consisted of polyethylene as crystalline segment and poly(ethylene-*alt*-norbornene) as amorphous segment were synthesized by the living system.[10−12] The T_g value of the block copolymers was, however, limited because of the alternate structure of ethylene and norbornene.

Poly(propylene-*ran*-norbornene) showed a higher T_g value than poly(ethylene-*ran*-norbornene) with the same norbornene content and molar mass, but the catalysts which copolymerize propylene and norbornene are very limited.[13] We have previously reported that [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (**1**) activated by Me$_3$Al-free dried aluminoxane (dMAO) not only conducted living polymerization of propylene and norbornene[14,15] but also copolymerized propylene and norbornene with high activity to produce random copolymers, of which T_g values showed a good linear relationship with norbornene content in the copolymers.[16] We have recently found that the introduction of the *tert*-butyl substituents on the fluorenyl ligand of **1** at the 3,6-position [*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**2**) improved the activity and syndiospecificity in propylene polymerization to give living polypropylene (PP) with the syndiotactic triad of 0.93 and melting point of 142 °C.[17]

In this Communication, we report the preliminary results of propylene−norbornene copolymerization with **2**-dried modified MAO (dMMAO). The catalytic system promoted living random copolymerzation of propylene and norbornene with high activity and was effective for the synthesis of novel block copolymers consisting of syndiotactic PP (*s*PP) and poly(propylene-*ran*-norbornene) sequences.

Table 1. Copolymerization of Propylene and Norbornene with 2-dMMAO[a]

entry	time (min)	yield (g)	M_n [b] ($\times 10^4$)	M_w/M_n [b]	N in copolymer[c] (mol %)	T_g [d] (°C)
1	1	0.12	2.1	1.21	−[e]	247
2	2	0.25	4.3	1.13	−[e]	245
3	3	0.39	6.4	1.11	−[e]	248
4	4	0.53	8.2	1.12	78	252

[a] Polymerization conditions: toluene = 30 mL, Ti = 10 μmol, Al = 2.0 mmol, propylene = 1.0 atm, N = 0.9 M. [b] Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration. [c] Determined by from ^{13}C NMR. [d] Determined by DSC. [e] Not determined.

Results and Discussion. Copolymerization of propylene and norbornene by **2**-dMMAO was performed in toluene at 25 °C under an atmospheric pressure of propylene. The results are summarized in Table 1. The catalytic system showed high activity and gave high-molecular-weight (M_n) copolymer for 1 min with narrow molecular-weight distribution (MWD) (entry 1, Table 1). We therefore investigated the living nature of the copolymerzation by changing the polymerization time.

Figure 1a illustrates the GPC curves of the copolymers obtained, which shifted to the higher molecular weight region according to the polymerization time. The M_n and MWD values are plotted against the yield in Figure 1b, which shows a good linear relationship with keeping narrow MWDs. The results testified that the copolymerization of propylene and norbornene proceeded in a living manner.

The structure of poly(propylene-*co*-norbornene) (entry 4, Table 1) was investigated by ^{13}C NMR spectroscopy. In the spectrum shown in Figure 2a, the resonances appear at the range of 20.1−21.6, 14.0−19.1, 35.4−37.5, and 33.3−34.2 ppm, which are assignable to the methyl carbon of propylene−propylene sequence (P_{pp}), the methyl carbon of propylene−norbornene sequence (P_β), the bridged methylene carbon of norbornene in the norbornene−norbornene sequences (C7), and the bridged methylene carbon of norbornene in the propylene−norbornene sequence (C7′), respectively.[16] These resonances indicate the production of poly(propylene-*ran*-norbornene), and the norbornene content was determined to be 78 mol %. The thermal properties of the copolymers were then investigated by DSC, and the results are shown in Table 1. All the copolymers were amorphous with high T_g values near 250 °C, which indicates that similar random copolymers were formed irrespective of the polymerization time.

These results encouraged us to synthesize *s*PP-*b*-poly(propylene-*ran*-norbornene) with **2**-dMMAO. To increase the syndioregularity of *s*PP, we conducted propylene polymerization in toluene at −20 °C under atmospheric pressure of propylene. After the 5 min homopolymerization, a prescribed amount of norbornene was added, and copolymerization was conducted for 6 min with raising the polymerization temperature to 25 °C.[18] The results are summarized in Table 2. The PP obtained in the first step had the M_n value of 108 000 with MWD of 1.36 and showed the melting point at 135 °C. After the copolymerization, the yields were increased accompanied by the increase of M_n values (208 000−226 000) and the decrease of MWD values (1.21−1.32) regardless of the amount of norbornene added.

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* Corresponding author: e-mail tshiono@hiroshima-u.ac.jp; Tel +81-82-424-7730; Fax +81-82-424-5494.

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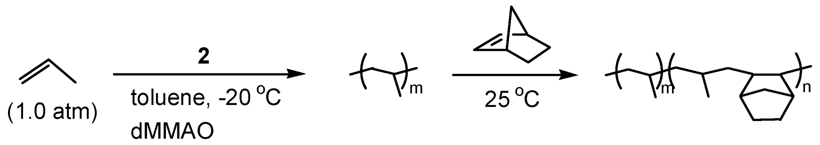
Table 2. Sythesis of Polypropylene-*b*-poly(propylene-*ran*-norbornene) with 2-dMMAO[a]



entry	N (g)	time (min)	yield (g)	M_n [b] ($\times 10^4$)	M_w/M_n [b]	T_m [c] (°C)	T_g [c] (°C)
prepolymer[d]	0	0	0.48	10.8	1.36	135	
5	2.77	6	0.92	20.8	1.21	135	311
6	2.07	6	1.12	22.4	1.30	133	231
7	1.38	6	1.09	22.6	1.32	133	93

[a] Conditions: toluene = 30 mL, Ti = 10 μmol, Al = 2.0 mmol, propylene = 1.0 atm. [b] Determined by GPC using polystyrene standards. [c] Determined by DSC. [d] Temperature = −20 °C, propylene = 1.0 atm, time = 5 min.

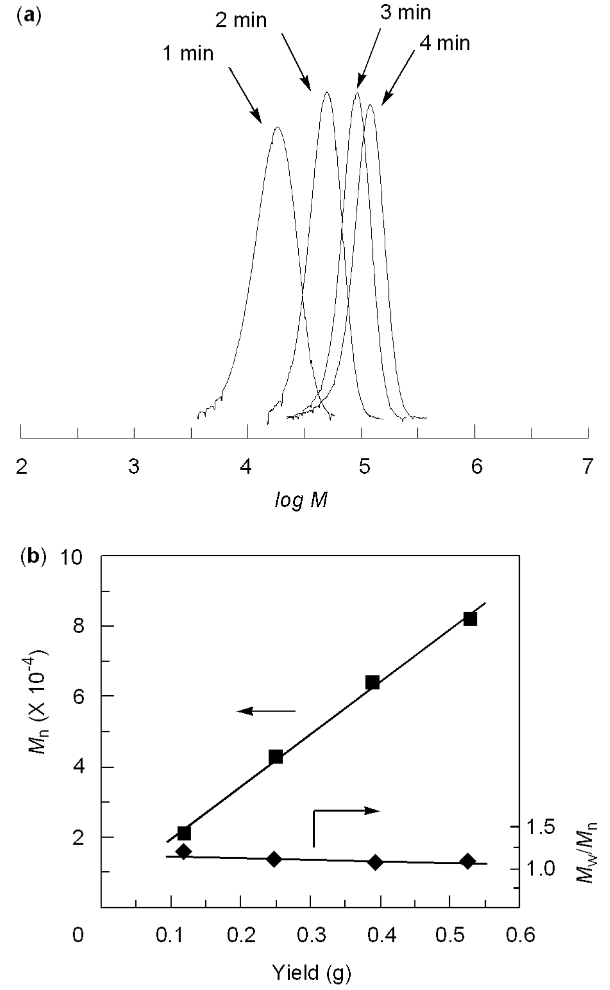


Figure 1. GPC curves of propylene−norbornene copolymers (a) and plots of M_n and M_w/M_n values against yield (b) obtained with **2**-dMMAO.

The ^{13}C NMR spectrum of the block copolymer (entry 5, Table 2) is shown in Figure 2b, where the resonances of the random sequences of propylene and norbornene were observed together with those of *s*PP sequences.

The block copolymers showed both the melting point (133−135 °C) and T_g that correspond to the crystalline *s*PP sequence and amorphous poly(propylene-*ran*-norbornene) sequence, respectively. The T_g values were controlled by the amount of norbornene added (93−311 °C), which is in good agreement with that obtained with the nonsubstituted original complex **1**, where the T_g values of copolymers can be controlled widely (53−249 °C) by changing the propylene/norbornene feed ratio.[16]

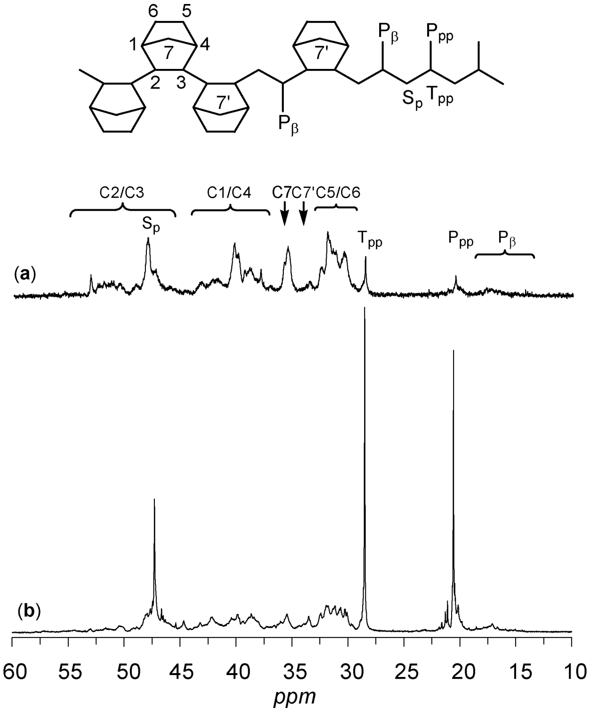


Figure 2. ^{13}C NMR spectra of propylene−norbornene copolymer (a, entry 4) and PP-*b*-poly(propylene-*ran*-norbornene) (b, entry 5) obtained with **2**-dMMAO.

These results also testified the formation of the expected block copolymers, i.e., *s*PP-*b*-poly(propylene-*ran*-norbornene)s.

In summary, the [*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**2**)-dMMAO catalytic system was found to be effective for the living random copolymerization of propylene and norbornene as well as for the syndiospecific living polymerization of propylene. The *s*PP-*b*-poly(propylene-*ran*-norbornene) synthesized with **2**-dMMAO showed the melting point of *s*PP and the glass-transition temperature of the random copolymer sequence, which were controllable according to the polymerization temperature and comonomer composition, respectively.

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Supporting Information Available: Experimental procedures, GPC curves of block copolymers, ^{13}C NMR spectrum of methyl region of prepolymer and the corresponding region of block copolymer, and DSC profiles of block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Copolymerization of propylene and norbornene did not proceed at −20 °C.

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