Random Copolymerization of Propene and Norbornene with *ansa*-Fluorenylamidodimethyltitanium-Based Catalysts

Tariqul Hasan,[†] Tomiki Ikeda,[†] and Takeshi Shiono*,[‡]

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

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ABSTRACT: Copolymerization of propene and norbornene (P−N) was conducted with (t-BuNSiMe$_2$Flu)-TiMe$_2$ (**1**) activated by Me$_3$Al-free methylaluminoxane (dried MAO), modified methylaluminoxane (MMAO), and Ph$_3$CB(C$_6$F$_5$)$_4$/Oct$_3$Al at 20 °C under atmospheric pressure of propene. The **1**−Ph$_3$CB(C$_6$F$_5$)$_4$/Oct$_3$Al system showed the highest activity and gave the copolymer with the lowest molecular weight and broad molecular weight distribution. The **1**−dried MAO system produced the copolymer with the narrowest molecular weight distribution. The detailed investigation of this system clarified that the norbornene content in the copolymer was almost proportional to the N/P feed ratio with a narrow polydispersity of 1.1−1.2 and the glass transition temperatures of the P−N copolymers increased linearly against the norbornene content in the copolymers, that is, 53 °C with 17 mol % of norbornene and 249 °C with 71 mol % of norbornene. The ^{13}C NMR spectra also suggested the random distribution of the comonomers in the copolymers obtained.

Introduction

Cyclic olefin copolymers (COC) are exciting materials in the polyolefin industry due to their high glass transition temperature, high humidity resistance, and excellent transparency. Ethene−norbornene (E−N) copolymers are well-known COC materials, and their properties depend on the composition and comonomer sequence distribution in the copolymer chain. The E−N copolymers with a variety of compositions, microstructures, and high glass transition temperatures (T_g) up to 220 °C were produced by a number of metallocene-based catalysts.[1−8]

The higher T_g could be expected if propene was employed instead of ethene, because of the higher T_g of polypropene than polyethene. The copolymerizations of propene and norbornene (P−N) have, however, been scarcely studied because the metallocene-based catalysts show poor ability for copolymerization of norbornene with propene. Tritto et al. recently reported[9] that the zirconocene, *rac*-Et(Indenyl)$_2$ZrCl$_2$, activated with methylalumenoxane (MAO) produced P−N copolymers containing isolated norbornene unit, of which norbornene contents were relatively richer than those of the E−N copolymers prepared in similar conditions, although the activities and the T_g values of the copolymers were rather low. *rac*-Me$_2$Si(Indenyl)$_2$ZrCl$_2$ activated with MAO also conducted P−N copolymerization with low activity and produced the copolymer with norbornene content up to 98 mol %, where the compositions of copolymer were calculated from the ^{1}H or ^{13}C NMR spectra, although the analytical procedures were not described in detail.[10]

We have previously reported that (t-BuNSiMe$_2$Flu)-TiMe$_2$ (**1**) activated with Me$_3$Al-free MAO (dried MAO) conducted living polymerization of both propene[11] and norbornene[12] with high activity. In this paper, therefore, the copolymerization of propene and norbornene was carried out with **1** activated by several cocatalysts including dried MAO.

Experimental Section

Materials. The preparation and handling of the titanium complex **1** were operated under a nitrogen atmosphere with Schlenk techniques. Complex **1** was synthesized according to the literature[13] and the references therein. Alkylaluminums and the borate (Ph$_3$CB(C$_6$F$_5$)$_4$) were provided by Tosoh Finechem Co. Dried MAO was prepared according to the procedure reported previously.[11] MMAO solution in toluene was used without any treatment. Norbornene (Aldrich) was purified by stirring it over calcium hydride at 60 °C for 24 h, and then distilled. The stock solution of norbornene was prepared in toluene (5.14 M). Research grade propene (purchased from Takachiho Chemicals Co.) was purified by passing it through columns of NaOH, P$_2$O$_5$, and molecular sieves 3 Å. All of the solvents were commercially obtained and dried by standard methods.

Polymerization Procedure. Polymerization was performed in a 100 mL glass reactor equipped with a seal septum and a magnetic stirrer. Under a nitrogen gas flow, the reactor was charged with 0.464 g (8.0 mmol of Al) of dried MAO, and a prescribed volume of the stock solution of norbornene. Toluene as solvent was added to increase the total volume to 30 mL, and propene gas was charged at an atmospheric pressure after the reactor had been evacuated. The reactor was kept in a water bath to obtain a desired temperature, and then the solvent was saturated with propene. The amount of propene dissolved (observed by a flow meter) was used to calculate the concentration of propene. A 1 mL solution of the Ti complex (20 μmol) in toluene was added to start the polymerization.

In the case of MMAO or borate/Oct$_3$Al as an activator, after the norbornene solution had been saturated with propene, the toluene solution of the activator and the Ti complex were added successively to start the polymerization. The polymerization temperature and the pressure of propene (1 atm) were kept constant during the polymerization. The consumption of the propene was observed by the flow meter. The polymerization

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* Corresponding author. Fax: +81-82-424-5494. E-mail: tshiono@hiroshima-u.ac.jp.

[†] Tokyo Institute of Technology.

[‡] Hiroshima University.

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Table 1. Copolymerization of Propene and Norbornene with 1−Dried MAO[a]

entry	activator	yield (g)	activity[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]	N in copolymer[d] (mol %)	T_g[e] (°C)
1	dried MAO	0.60	900	6.1	1.18	17	53
2	MMAO	0.74	1110	6.0	1.37	15	51
3[f]	borate/Oct_3Al	2.00	3000	1.8	3.04	9	31

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, solvent = toluene, [N] = 0.17 M, total volume = 30 mL, temperature = 20 °C, propene = 1 atm, time = 2 min. [b] Activity = $kg_{(poly)}$ mol $_{(Ti)}^{-1}$ h^{-1}. [c] Molecular weight and molecular-weight distributions were measured by GPC using polystyrene standards. [d] Norbornene in copolymer calculated from the ^{13}CNMR spectrum of copolymer. [e] T_g values were determined by DSC analysis. [f] Al/Ti = 20, borate = $Ph_3CB(C_6F_5)_4$ = 20 μmol.

Table 2. Copolymerization of Propene and Norbornene with 1−Dried MAO[a]

entry	N/P (mol/mol)	time (min)	yield (g)	$M_n \times 10^{-4}$ [b]	M_w/M_n[b]	N in copolymer[c] (mol %)	N conv.[d] (%)
4	0.3	3	0.60	6.1	1.18	17	38
5	0.6	2	1.05	9.5	1.11	36	59
6	1.13	7	2.02	13.8	1.14	58	77
7	2.00	12	3.58	15.6	1.16	71	90

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, solvent = toluene, total volume = 30 mL, temperature = 20 °C, propene = 1 atm. [b] Molecular weight and molecular-weight distributions were measured by GPC using polystyrene standards. [c] Norbornene in copolymer calculated from the ^{13}C NMR spectrum of copolymer. [d] Norbornene conversion was calculated from the content of norbornene in copolymer.

was terminated with methanol and precipitated with acidic methanol. The polymer obtained was filtered, adequately washed with methanol, and dried under vacuum at 60 °C for 6 h.

Analytical Procedures. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of copolymer were measured by gel permeation chromatography (GPC, Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent, and were calibrated with polystyrene standards. The $^{13}C\{^1H\}$ NMR spectra and DEPT (distortionless enhancement by polarization transfer) of copolymers were recorded at 120 °C on a JEOL GX 500 spectrometer operated at 125.65 in pulse Fourier transform mode with tetrachloroethene-d_2 as solvent. In the $^{13}C\{^1H\}$ NMR measurement, the pulse angle was 45° and about 10 000 scans were accumulated in a pulse repetition of 4.0 s. In the DEPT method, DEPT135° spectrum was measured. The central peak of tetrachloroethene-d_2 (74.47 ppm) was used as internal reference. Differential scanning calorimetry (DSC) was studied with a Seiko DSC-220 instrument under nitrogen atmosphere at a heating and cooling rate of 10 °C/min. The T_g values were determined from the middle point of the phase transition of the second heating scan.

Results and Discussion

Copolymerization Features. Copolymerization of propene and norbornene (P−N) was conducted by **1** activated with various activators (dried MAO, MMAO, and borate/Oct_3Al) at 20 °C under an atmospheric pressure of propene. The results obtained are compared in Table 1.

In the presence of either dried MAO or MMAO, **1** showed similar catalytic activity and produced almost the same molecular weight copolymers. Although both systems produced the P−N copolymers with narrow molecular weight distribution, the M_w/M_n value was slightly larger in the **1**−MMAO system.

In the case of $Ph_3CB(C_6F_5)_4$, Oct_3Al was also added, because Oct_3Al was found not only to act as a scavenger but also to enhance the propagation rate in the norbornene polymerization with **1**− $Ph_3CB(C_6F_5)_4$.[14] The borate/Oct_3Al system showed about 3 times higher activity than the MAO systems, whereas the M_n value decreased about 3.5 times with broadening of the polydispersity. These results suggest that the higher activity raised the temperature during the copolymerization, which might have caused chain-transfer reactions and/or inhomogeneity of the system. The activity of **1**-based catalysts was about 2 orders higher than that of the zirconocene reported previously.[9] This could be explained by the high catalytic ability of **1** for the homopolymerization of both monomers.[11,12]

Although the borate system showed the highest activity, it was too high to control the copolymerization. The P−N copolymerization was therefore conducted with **1**−dried MAO under atmospheric pressure of propene by changing the norbornene concentration in feed at 20 °C. The results are summarized in Table 2. The P−N copolymers produced by **1**−dried MAO had a high molecular weight and narrow molecular weight distribution (M_w/M_n = 1.11−1.18), which suggests that the uniform copolymers were produced with **1**−dried MAO irrespective of the norbornene concentration.

Copolymer Structure. The structure of the P−N copolymer produced with **1** was investigated by ^{13}C NMR spectroscopy. The spectrum of the P−N copolymer showed several signals at a wide range of chemical shifts from 14 to 57 ppm. The spectrum was completely different from that obtained with *rac*-Et-$(Indenyl)_2ZrCl_2$−MAO,[9] in which only the resonances of the isolated norbornene unit were observed.

The preliminary assignment of the signals of the ^{13}C NMR spectrum of the P−N copolymer obtained with **1**−dried MAO was investigated by comparing it with the DEPT135° spectrum of the corresponding copolymer and the ^{13}C NMR spectra of the polynorbornene[14] and polypropene[11] obtained by the same catalytic system. The spectra are shown in Figure 1.

In the DEPT135° spectrum, the signals of methyl and methine carbons appear as positive and those of methylene appear as negative intensity. The signals of methyl carbon were observed in two different chemical shift regions at 20.1−21.6 and 14.0−19.1 ppm. The former that appears very close to the methyl region of polypropene (Figure 2a) could be assigned to methyl carbon in propene block in the P−N copolymer, and the latter that disappears in the spectrum of polypropene could be assigned to methyl carbon connected to the norbornene unit in the P−N copolymer, which is denoted by P_β. The signal of tertiary carbon at 28.5 ppm and those of secondary carbons around 46−48.3 ppm

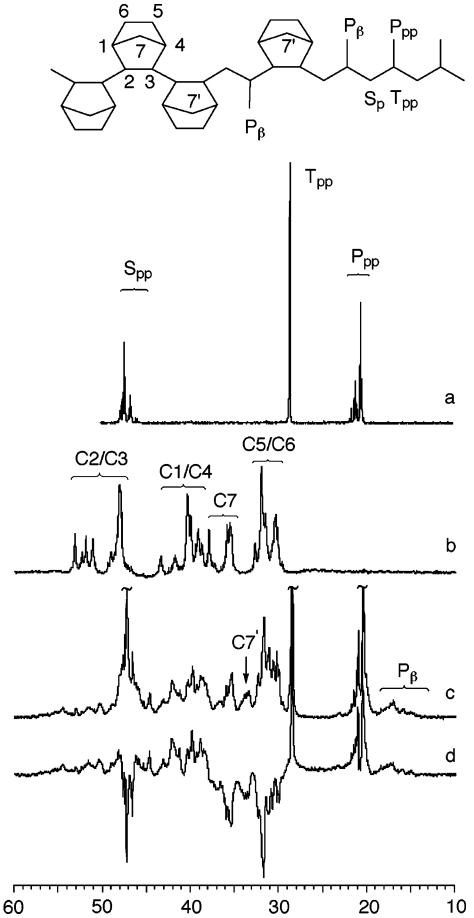

Figure 1. ^{13}C NMR spectra of (a) polypropene, (b) polynorbornene, (c) P−N copolymer, and (d) DEPT of P−N copolymer obtained with **1**−dried MAO.

also appear very close to those of polypropene (Figure 2a). These signals were assigned to the methine and methylene carbons of the propene unit in the P−N copolymer, respectively.

The carbons of the norbornene unit in the P−N copolymer showed several signals, which could be assigned by comparing the spectra of polynorbornene and E−N copolymer. In the ^{13}C NMR spectra of polynorbornene[14] and E−N copolymer,[15] the carbons of norbornene unit were assigned to four chemical shift regions as follows: C5/C6 (29.5−33.5 ppm), C7 (35−38.5 ppm), C1/4 (38.5−44 ppm), and C2/3 (47.5−55 ppm). Because C7 and C5/C6 carbons are located at the δ-position from the methyl group of propene unit, the chemical shifts of these carbons should be close to those of the norbornene unit in the E−N copolymer. The signals around 32.32−37.50 and 28−32.5 ppm were therefore tentatively assigned to C7 and C5/C6 carbons, respectively, of the norbornene unit of the P−N copolymer. The signal of C5/C6 carbon splits into several resonances due to the different comonomer sequence and stereoisomer of the norbornene unit.

The signal of the C7 carbon also splits into several resonances. The broad signal with five resonances at 33.3−34.2 ppm which disappeared in the spectrum of polynorbornene could be assigned to the C7′ carbon of the norbornene unit that connected to the propene unit, that is, isolated, alternating and/or norbornene dyad sequences. The signals at 35.4−37.5 ppm, which were also observed in the spectrum of polynorbornene,[14] could be assigned to the C7 carbon of norbornene triad sequences.

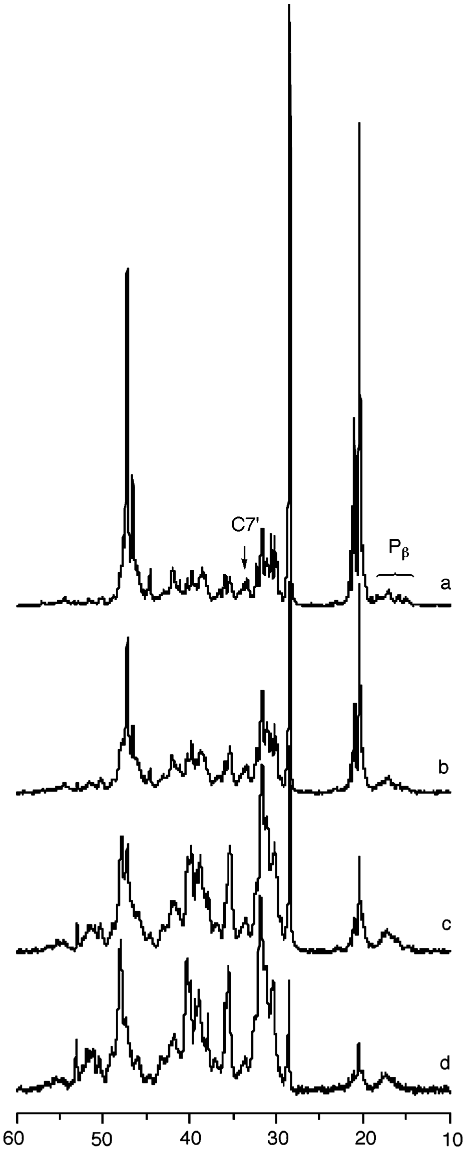

Figure 2. ^{13}C NMR spectra of propene−norbornene copolymers obtained with **1** at N/P feed ratios of (a) 0.3, (b) 0.6, (c) 1.16, and (d) 2.00.

The several signals around 38.5−43.5 ppm could be assigned to the C1/C4 carbons of norbornene unit. The signals of C2/C3 of the norbornene unit are overlapped with those of the methylene carbon of the propene unit around 45−48 ppm. The signals around 50−55 ppm, however, indicate the presence of a long norbornene sequence in the P−N copolymer, because the signals of the C2/C3 carbons of the polynorbornene and norbornene triad in the E−N copolymer were observed above 52 ppm.[15]

The ^{13}C NMR spectra of the P−N copolymers obtained with **1**−dried MAO at different N/P feed ratios are displayed in Figure 2. With an increase in the N/P ratio, the intensities of the signals of the propene unit were decreased and those of the norbornene unit were inversely increased. It is apparent that the spectra of copolymers are not the summation of the spectrum of each homopolymer and are gradually close to the spectrum of polynorbornene according to the increase in the N/P ratio in feed. Considering the fact that the M_w/M_n values of these copolymers are close to 1, we

Table 3. Comparison of the Properties of P−N and E−N Copolymer Obtained by 1−Dried MAO at 20 °C

propene−norbornene copolymerization			ethene−norbornene copolymerization		
N/P	N in copolymer[a] (mol %)	T_g[b]	N/E	N in copolymer[a] (mol %)	T_g[b]
0.3	17	53	1.40	25	47
0.6	36	112	2.00	33	79
1.13	58	198	5.00	44	126
2.00	71	249	10.00	53	167

[a] Norbornene in copolymer calculated from the ^{13}C NMR spectrum of copolymer. [b] T_g values were determined by DSC analysis.

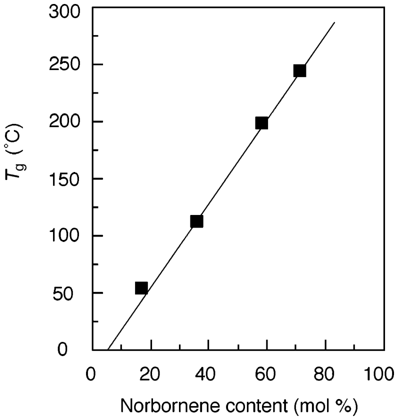

Figure 3. Plot of T_g versus norbornene content in the P−N copolymers.

could conclude the production of random copolymers with this catalytic system.

Norbornene Contents. The molar fraction of propene (F_P) and norbornene (F_N) in the copolymer was calculated from the peak area of the signals via the following equation:

$$\frac{F_P}{F_N} = \frac{I_{CH_3}}{(I_{tot} - 3I_{CH_3})/7}$$

where I_{CH_3} is the observed peak area of the methyl signals and I_{total} is the sum of the areas of all peaks.

The norbornene content in the P−N copolymer thus obtained was almost proportional to the N/P feed ratio. The high incorporation of norbornene was observed even at a low N/P feed ratio, and 71 mol % of norbornene was incorporated at N/P = 2. Because the conversions of norbornene were high (38−90%) while propene pressure was constant during the copolymerizations, the norbornene contents obtained here should be the minimum values. Hence, the comonomer reactivity ratios were not determined under the present polymerization conditions.

If we compare the P−N and E−N copolymerization in the same feed ratio (N/(P or E) = 2), norbornene was incorporated in the P−N copolymer (71 mol %) more than 2 times than in the E−N copolymer (33 mol %) (Table 3).

Thermal Properties of Copolymers. The glass transition temperature (T_g) of the P−N copolymer was determined by DSC at a heating rate of 10 °C/min under nitrogen atmosphere. The T_g values thus obtained are plotted against the norbornene contents in Figure 3. The good linear relationship between T_g and norbornene content also supports the production of random copolymers. The P−N copolymer with 71 mol % of norbornene was found to show the T_g value at 249 °C. The P−N copolymer showed a higher T_g value than E−N copolymer even with a lower content of norbornene (Table 3).

In conclusion, the Ti complex, (t-BuNSiMe$_2$Flu)TiMe$_2$, combined with a suitable activator was found to be an effective catalyst for random copolymerization of propene with norbornene and gave the copolymers with high T_g values.

Supporting Information Available: DSC thermograms of P−N copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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