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Ethene−Norbornene Copolymer with High Norbornene Content Produced by *ansa*-Fluorenylamidodimethyltitanium Complex Using a Suitable Activator

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ABSTRACT: Ethene−norbornene (E−N) copolymerizations were carried out by (t-BuNSiMe$_2$Flu)TiMe$_2$ (**1**) and (t-BuNSiMe$_2$C$_5$Me$_4$)TiMe$_2$ (**2**) activated with methylaluminoxane (free from Me$_3$Al) under an atmospheric pressure of ethene at 40 °C. **1** showed higher activity than **2.** The activity of **1** increased with increasing the feed ratio of norbornene/ethene, but the opposite trend was observed for **2**. In the same feed ratio (N/E = 8), the incorporation of norbornene was higher with **1** (N = 50 mol %) than with **2** (N = 38 mol %). The ^{13}C NMR spectrum of the E−N copolymer obtained with **1** was completely different from that with **2**. The former showed the resonances of norbornene dyad and triad, whereas the latter showed only those of alternating and isolated norbornene structures. Some new signals were assigned to the *rac,rac*-NNN triad. The effects of activators and polymerization temperature were investigated with **1** in more detail, and the **1**-Ph$_3$CB(C$_6$F$_5$)$_4$/Oct$_3$Al system was found to show the highest activity at 80 °C and gave the E−N copolymer with the highest N content of 82 mol % and the glass transition temperature of 237 °C.

Introduction

Ethene−norbornene (E−N) copolymer is well-known thermoplastic for its superior properties such as high glass transition temperature (T_g), transparency, chemical resistance, low water absorption, and good solubility.[1] These versatile properties of the copolymers therefore enable them for a vast use in packaging, electronic data storage, and optical applications as well as a variety of engineering components. The properties of the E−N copolymers are controlled by monomer composition, sequence distribution, and the stereoregularity of norbornene units in the copolymers, which depend on the structure of the catalyst employed.

The recent development of single-site catalysts has brought several catalytic systems that conduct E−N copolymerization with considerable activities.[1,2] Most of them, however, gave the E−N copolymer containing less than 50 mol % of norbornene with isolated or alternate norbornene unit. A perfectly alternating E−N copolymer was produced with sterically hindered [^{i}Pr(3-RCp)Flu]ZrCl$_2$ (R = Me, ^{t}Bu)[1b,2c] and Me$_2$Si(3-^{t}BuCp)(adamantylamido)MMe$_2$ (M = Zr, Hf) complexes.[3] The Ti complex with pyrrolidimine ligand produced alternating E−N copolymer in a living manner at 30 °C.[4] Usual *ansa*-zirconocenes are less active for homopolymerization of norbornene and produced mainly alternating E−N copolymer.[1,3,5−7]

A few examples reported to produce random E−N copolymer containing more than 50 mol % of norbornene. Kaminsky et al. reported that C_s symmetrical complexes Me$_2$C(Flu)(Cp)ZrCl$_2$ and Ph$_2$C(Flu)(Cp)ZrCl$_2$ showed higher activity than C_2 symmetrical complexes Me$_2$Si(Ind)$_2$ZrCl$_2$ and Ph$_2$Si(Ind)$_2$ZrCl$_2$ in the presence of MAO. These C_s symmetric complexes showed constant activities of 2200 and 2400 kg (poly) mol^{-1} (Zr) h^{-1} at high N/E feed ratios. At the feed ratio of N/E = 16, 56 mol % of norbornene was incorporated with the T_g value of 157 °C, whereas that of 184 °C at N/E = 25 although norbornene content was not determined.[1d]

Fink et al.[2a,c] conducted E−N copolymerization with *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ and *rac*-Me$_2$C(Ind)$_2$ZrCl$_2$ activated with MAO at low pressure of ethene. The polymer produced contained a maximum 63 mol % of norbornene with a significant amount of *meso,meso- and rac,meso*-NNN sequence. They also reported that ^{i}Pr(Cp)(Ind)ZrCl$_2$-MAO produced E−N copolymer containing a maximum 68.5 mol % of norbornene.

Tritto et al. reported that C_2 symmetric zirconocenes, *rac*-Et(Ind)$_2$ZrCl$_2$ and *rac*-Me$_2$Si(2-Me-Benz-[*e*]-Ind)$_2$ZrCl$_2$, produced the E−N copolymers containing predominantly *meso*-ENNE sequence and a trace amount of *meso,meso*-NNN sequence.[8]

Most recently, Nomura et al. reported that the nonbridge (aryloxo) cyclopentadienyltitanium(IV) complexes produced random E−N copolymers where the highest norbornene content was 49 mol %.[9]

The thermal properties of E−N copolymers depend on the microstructure of copolymer as well as the

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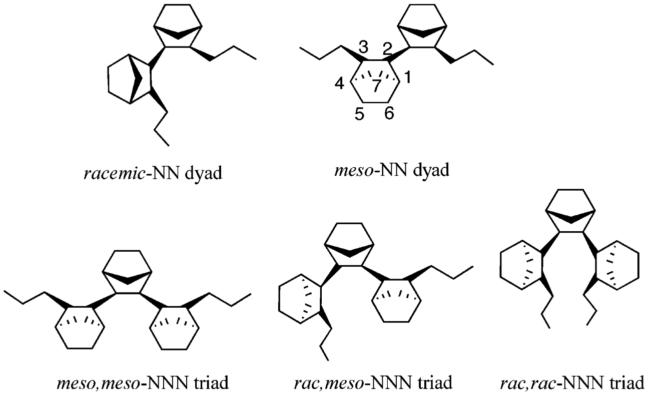
Scheme 1. Different Stereoisomers of NN Dyad and NNN Triad in Ethene−Norbornene Copolymer



norbornene content. The glass transition temperatures of the E−N copolymer increase according to the norbornene content and also varied with the distribution of norbornene units in the copolymer even with the same norbornene content. The presence of norbornene diad and triad in the E−N copolymer significantly increased the glass transition temperature up to 220 °C.[2,8,10] Constrained geometry catalysts (CGCs) are highly active for copolymerization of ethene and higher α-olefins to give random copolymer.[11] Most of the CGC derivatives, however, gave the E−N copolymers with isolated norbornene unit or almost alternating norbornene sequences depending on the norbornene content.[3,12] We have previously reported that the complex (t-BuNMe$_2$-SiFlu)TiMe$_2$ (**1**) combined with dried methylalumenoxane (MAO) which was free from Me$_3$Al conducted vinyl polymerization of norbornene in a living manner at 20 °C whereas (t-BuNSiMe$_2$C$_5$Me$_4$)TiMe$_2$ (**2**)-dried MAO showed no activity.[13] The **1**-dried MAO system was also found to conduct living copolymerization of ethene and norbornene at 0 °C.[14]

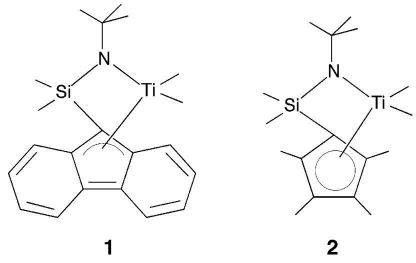
The present work has focused the effect of various activators and reaction conditions in E−N copolymerization with **1** and **2**. Complex **1** was found to show high activity irrespective of the activator up to 80 °C and produced E−N copolymers with high norbornene content of 82 mol %.

Experimental Section

Materials. The preparation and handling of the catalysts were operated under a nitrogen atmosphere with Schlenk techniques. The titanium complexes **1** and **2** were synthesized according to the literature and the references therein.[15a] Alkylaluminums and borate (Ph$_3$CB(C$_6$F$_5$)$_4$) were provided by Tosoh Finechem Co. Dried MAO was prepared with the same procedure reported previously.[15b] MMAO solution in toluene was used without any treatment. A standard solution of the borate (20 mM) was prepared in toluene. 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 ethene (purchased from Takachiho Chemicals Co.) was purified by passing it through columns of NaOH, P$_2$O$_5$, and molecular sieves 3 Å. All solvents were commercially obtained and dried by standard methods.

Polymerization Procedure. Polymerizations were performed in a 100 mL glass reactor equipped with a seal septum and a magnetic stirrer under a nitrogen atmosphere. At first, the reactor was charged with 0.464 g (8.0 mmol of Al) of dried MAO, and the stock solution of norbornene was added with a syringe under nitrogen gas flow. Toluene as a solvent was added to make the total volume to 50 mL, and ethene gas was charged at an atmospheric pressure after the reactor had been evacuated. The reactor was kept in an oil bath to reach at required temperature, and the reaction mixture was saturated with ethene. The amount of ethene dissolved (observed by a flow meter) was used to calculate the concentration of ethene. A 1 mL solution of complex (20 μmol) in toluene was added to start the polymerization.

Scheme 2. Complexes Used



In the case of MMAO or borate/Oct$_3$Al as an activator, after the norbornene solution had been saturated with ethene, the activator and the Ti complex were added successively to start the polymerization. Polymerization temperature and the pressure of ethene gas (1 atm) were kept constant during the polymerization. The polymerization was terminated with methanol and precipitated in acidic methanol. The polymers obtained were filtered, adequately washed with methanol, and dried under vacuum at 60 °C for 6 h.

Analytical Procedures. Molecular weight and molecular weight distribution of copolymer were measured by GPC (Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^{13}C 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 tetrachloroethane-d_2 as solvent. In the ^{13}C 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, DEPT 135 spectra were measured. The central peak of tetrachloroethane-d_2 (74.47 ppm) was used as internal reference. Differential scanning calorimetry (DSC) was studied with a Seiko DSC-220 instrument under a nitrogen atmosphere at heating and cooling rate of 10 °C/min. T_g values were determined from the middle point of the phase transition of the second heating scan.

Results and Discussion

Catalytic Behaviors. Copolymerization of ethene and norbornene was performed by **1** and **2** activated with dried MAO at 40 °C under an atmospheric pressure of ethene by changing the concentration of norbornene in feed. Polymerization time was varied depending on the catalyst for keeping the norbornene conversion below 20%. The results of the copolymerization are shown in Table 1 together with the molecular weights and molecular weight distributions of the E−N copolymers obtained. The activity of **1** increased with norbornene/ethene (N/E) ratio in feed, while that of **2** decreased as reported previously.[2,5c,12] This opposite trend of complex **1** could be explained by its high ability for homopolymerization of norbornene, which was ascribed to the more open nature of active species due to the η^3 coordination between Ti and Flu ligand.[14] The activity of **1** reached at a plateau value at the ratio of N/E = 13, of which value was about 8 times higher than that of **2** in the same reaction conditions, and then dropped rapidly above N/E = 13. Both complexes were found to produce the E−N copolymers with high molecular weights and narrow molecular weight distributions.

Copolymerization of ethene and norbornene with **1** was then carried out using various activators (dried

Table 1. Copolymerization of Ethene and Norbornene with (t-BuNMe$_2$SiFlu)TiMe$_2$ (1) and (t-BuNMe$_2$SiMe$_4$Cp)TiMe$_2$ (2) Using Dried MAO as Cocatalyst[a]

entry	complex	N/E	time (s)	activity[b]	[c]$M_n \times 10^{-4}$	M_w/M_n[c]	N content in copolym[d] (mol %)	T_g[e] (°C)
1	**1**	2.5	60	520	6.3	1.63	35	88
2	**1**	5	120	1050	5.3	1.20	44	131
3	**1**	8	60	1650	6.1	1.35	50	156
4	**1**	10	45	2590	6.0	1.34	53	173
5	**1**	13	40	3250	6.3	1.32	58	185
6	**1**	18	60	885	4.8	1.63	58	185
7	**2**	8	120	540	4.2	1.34	38	88
8	**2**	13	240	375	5.8	1.27	41	97
9	**2**	15	240	280	7.9	1.21	44	114

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, solvent = toluene, total volume = 50 mL, ethene = 1 atm, temperature = 40 °C. [b] Activity = kg (poly) mol^{-1}(Ti) h^{-1}. [c] Molecular weight and molecular weight distributions were measured by GPC using polystyrene standard. [d] Norbornene content calculated from the ^{13}C NMR spectrum of copolymer. [e] T_g was measured with differential scanning calorimetry.

Table 2. Copolymerization of Ethene and Norbornene with (t-BuNMe$_2$SiFlu)TiMe$_2$ (1) Using Different Activators[a]

entry	cocatalyst	temp (°C)	yield (g)	activity[b]	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	N content in copolym[d] (mol %)	T_g[e] (°C)
10	dried MAO	40	0.87	2600	6.0	1.34	50	156
11	dried MAO	60	0.99	2970	4.3	1.44	56	178
12	dried MAO	80	0.93	2790	3.1	1.81	66	202
13	MMAO	40	0.91	2730	3.2	1.60	nd	168
14	MMAO	60	0.87	2610	1.2	1.70	56	174
15	MMAO	80	0.78	2340	1.3	1.65	61	189
16[f]	borate	40	0.23	690	4.6	1.90	48	143
17	borate	60	1.42	4260	9.2	1.60	68	198
18	borate	80	1.74	5220	11.8	1.40	82	237

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, solvent = toluene, total volume = 50 mL, [N] = 0.62 M, ethene = 1 atm, time = 1 min. [b] Activity = kg (poly) mol^{-1} (Ti) h^{-1}. [c] Molecular weight and molecular weight distributions were measured by GPC using polystyrene standard. [d] Norbornene content was calculated from the ^{13}C NMR spectrum of copolymer. [e] T_g was measured with differential scanning calorimetry. [f] $Ph_3CB(C_6F_5)_4$ = 20 μmol, Oct_3Al = 400 μmol.

MAO, MMAO, and borate/Oct$_3$Al) at wide range of temperatures (40−80 °C) under an atmospheric pressure of ethene with the same norbornene feed. The results are summarized in Table 2. The activity strongly depended on the activator used as well as polymerization temperature. Although the activity of dried MAO system showed the maximum at 60 °C and that of the MMAO system decreased with raising temperature, the dependence of the activity on polymerization temperature was not significant in these systems. On the other hand, the activity of the borate system (in the presence of Oct$_3$Al) drastically increased with raising polymerization temperature, and the highest activity was observed at 80 °C.

The molecular weight of the copolymer decreased with raising the polymerization temperature in the dried MAO and MMAO systems, whereas it increased in the borate/Oct$_3$Al system. The molecular weight distributions of all copolymers were below 2. The **1**-borate/Oct$_3$Al system was found to show the highest activity among the activator systems employed, which was also observed for homopolymerization of norbornene.[16]

The enhancement of activity and M_n values in the borate/Oct$_3$Al system could be explained by relatively weaker counterion of $[(t\text{-BuNSiMe}_2\text{Flu})\text{TiMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, which enhances the propagation rate of the copolymeriation. Chen et al. reported the rate enhancement in ethene−1-hexene copolymerization using CGCTiMe$^+$-MePBB$^-$ (PBB = tris(2,2,2-nonafluorobiphenyl)borane) in place of MeB(C$_6$F$_5$)$_3^-$ analogue,[17] which was explained by the weaker coordination ability of MePBB$^-$.

Structure of the E−N Copolymers Obtained. The microstructures of E−N copolymers obtained with **1** and **2** were investigated by ^{13}C NMR. The typical ^{13}C NMR spectra of the E−N copolymers are illustrated in Figure 1. According to the reported assignment[2,5,10] and the DEPT135 spectrum (Figure 2) of the copolymer obtained with **1**, the signals of each chemical shift region were assigned as follows: 44.5−56.0 ppm, C2/C3; 37−44 ppm, C1/C4; 37.5−33.0 ppm, C7; 33−28 ppm, C5/C6,Ca/Cb, although the ^{13}C NMR spectra of the copolymers are strongly dependent on the complexes used.

The ^{13}C NMR spectrum of the E−N copolymer produced with **2** gave only eight major resonances which can be assigned to the alternating (ENEN) and isolated (ENEE) sequences as reported earlier:[12] 30.40, 30.67, 31.08 ppm to C5/C6 and Ca/Cb; 33.34 ppm to C7; 41.84, 42.36 ppm to C1/C4; 47.55, 48.12 ppm to C2/C3.

On the other hand, the copolymer produced with **1** showed a completely different spectrum. The signals at 28.60 and 32.47 ppm and at 29.91 and 31.69 ppm were assigned to carbons C5/C6 of *meso*- and *racemic*-ENNE sequences, respectively, by comparing the chemical shifts of the E−N copolymer obtained with Me$_2$Si(Ind)$_2$ZrCl$_2$−MAO and Me$_2$C(Cp)(Flu)ZrCl$_2$−MAO.[2a−c,8] The signals of C5/C6 in *meso,meso*- and *rac,meso*-NNN triad sequences, which had been observed in the E−N copolymer obtained with *rac*-Me$_2$C(Ind)$_2$ZrCl$_2$−MAO,[2a] were not found in the E−N copolymer obtained with **1**. The signals of C5/C6 in NNN triad sequence might be overlapped with the signals ENNE sequence.

From the relative peak intensities of the carbons C5/C6, the content of *racemic*-ENNE sequences was estimated to be 11 times higher than that of the *meso* sequence. The higher *racemic*-ENNE content of the copolymer obtained with **1** should be due to the C_s symmetric structure of **1**.

The signal of carbon C7 (Figure 1B) was split into several resonances with the resonance at 33.34 ppm

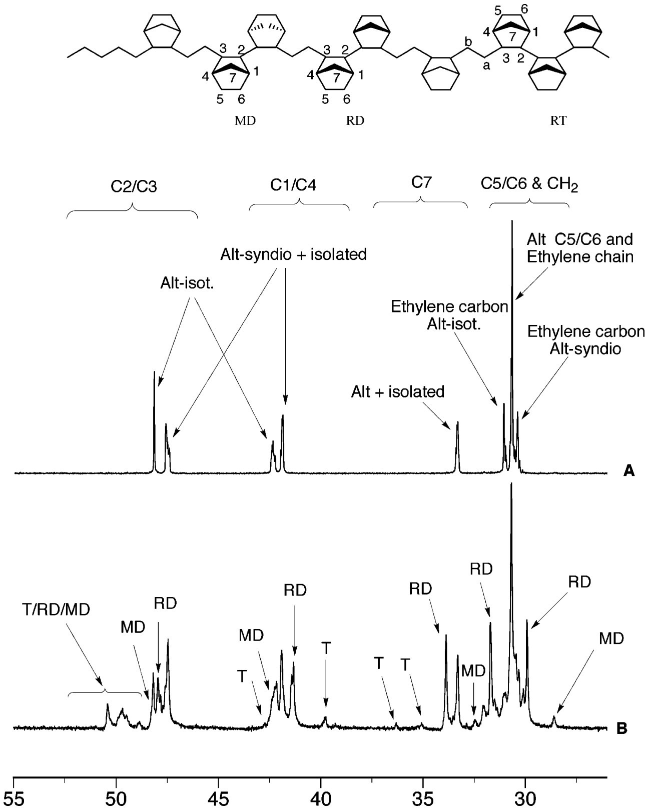


Figure 1. ^{13}C NMR spectra of the E−N copolymers produced with (A) (t-BuNSiMe$_2$CpMe$_4$)TiMe$_2$ (**2**) (norbornene content 44 mol %) and (B) (t-BuNSiMe$_2$Flu)TiMe$_2$ (**1**) in the presence of dried MAO at 40 °C (norbornene content 44 mol %).

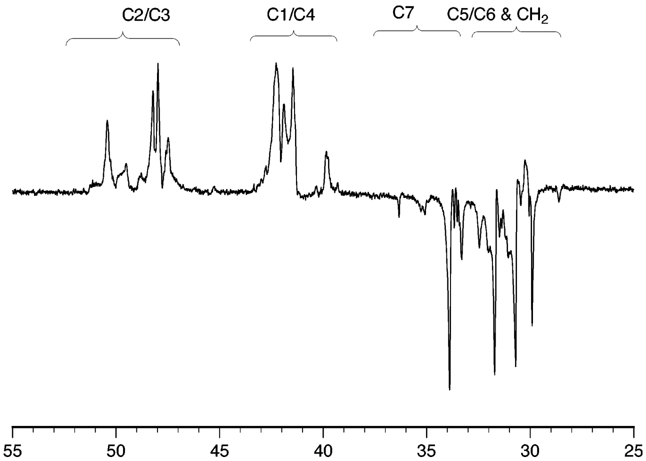


Figure 2. DEPT spectrum of E−N copolymer obtained by **1**.

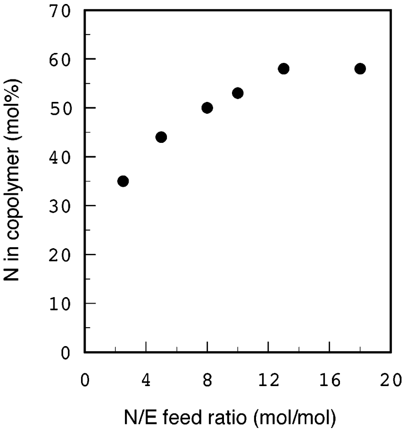


Figure 3. Plot of N/E feed ratio vs norbornene content in copolymers obtained with **1**-dried MAO at 40 °C.

assigned to the alternating ENEN or isolated ENEE sequence. The resonances at 33.8 ppm in ENN and at 35.08 and 36.32 ppm in NNN could be assigned to carbon C7, since the *meso*-ENNE and *meso,meso*- and *rac,meso*-NNN sequences appeared above 33.5 and 35.0 ppm, respectively, in the copolymer obtained with Me$_2$C(Ind)$_2$ZrCl$_2$−MAO.[2a]

The new signals of C1/C4 were observed at 39.0−40.7 ppm, which were predicted as the NNN sequence by Tritto et al.[5c] but have never been observed in the E−N copolymer reported so far. The signals of C1/C4 (39.0−40.7 ppm) and C7 (35.08 and 36.32 ppm) carbons are tentatively assigned for the *rac,rac*-NNN sequence. The signals of C2/C3 of norbornene triad appeared at 49.0 and 51.1 ppm, and no signal was observed around 55 ppm, where the signals of C2/C3 in *meso*,*meso*-NNN and *rac*,*meso*-NNN sequences should appear according to the literature.[2,5c] These results suggest that the norbornene triad in the E−N copolymer obtained with **1** should be *rac,rac*-NNN.

The norbornene content in the copolymer was calculated from the ^{13}C NMR spectrum by the following equation

$$\text{mol \% of N} = \frac{1/3(I_{\mathrm{C2/3}} + I_{\mathrm{C1/4}} + 2I_{\mathrm{C7}}) \times 100}{I_{\mathrm{CH2}}} \qquad (1)$$

where $I_{\mathrm{C2/3}}$, $I_{\mathrm{C1/4}}$, and I_{C7} are the peak intensities of C2/3, C1/4, and C7 carbons in norbornene unit, and I_{CH2} is the summation of those of Ca/Cb and C5/C6 carbons as shown in Figure 2.

The incorporation of norbornene in the E−N copolymer strongly depends on the Cp ligand of the Ti complexes. A higher amount of norbornene was incorporated with **1**-dried MAO (50 mol %) than with **2**-dried MAO (38 mol %) in the same (N/E = 8) feed ratio at 40 °C. Figure 3 shows the incorporation of norbornene in E−N copolymer obtained with **1**-dried MAO, which was increased according to the N/E feed ratio. The copolymer with 35 mol % norbornene was obtained at very low feed ratio (N/E = 2.5), and the highest 58 mol % norbornene was incorporated at the N/E = 13 feed ratio.

Figure 4 compares the spectra of E−N copolymer with different norbornene contents. The intensity of the signals assigned for ethene sequences of NEEE or EEEE at 30.9−30.05 ppm were rapidly decreased and almost disappeared in the spectrum of the copolymers with high norbornene contents. One can see that the intensity of the signals of *meso*- and *rac*-ENNE sequences increased whereas that of alternating ENEN sequences decreased with increasing of norbornene content in the E−N copolymer.

The comonomer reactivity ratios of the E−N copolymers obtained with **1**-dried MAO at 40 °C were determined according to the Fineman−Ross method. Since the content of norbornene was saturated above 13 in N/E feed ratio, the data obtained below 10 in N/E feed ratio were plotted in Figure 3. The good linear relationship obtained in Figure 5 indicates that the first-order Markovian process can be applied in the copolymerization at least in the region of N/E ≤ 10, and the monomer reactivity ratios of r_{E} and r_{N} thus calculated were found to be 5.6 and 0.08, respectively. The product of reactivity ratio $r_{\mathrm{E}}r_{\mathrm{N}} = 0.45$ indicates the random nature of the

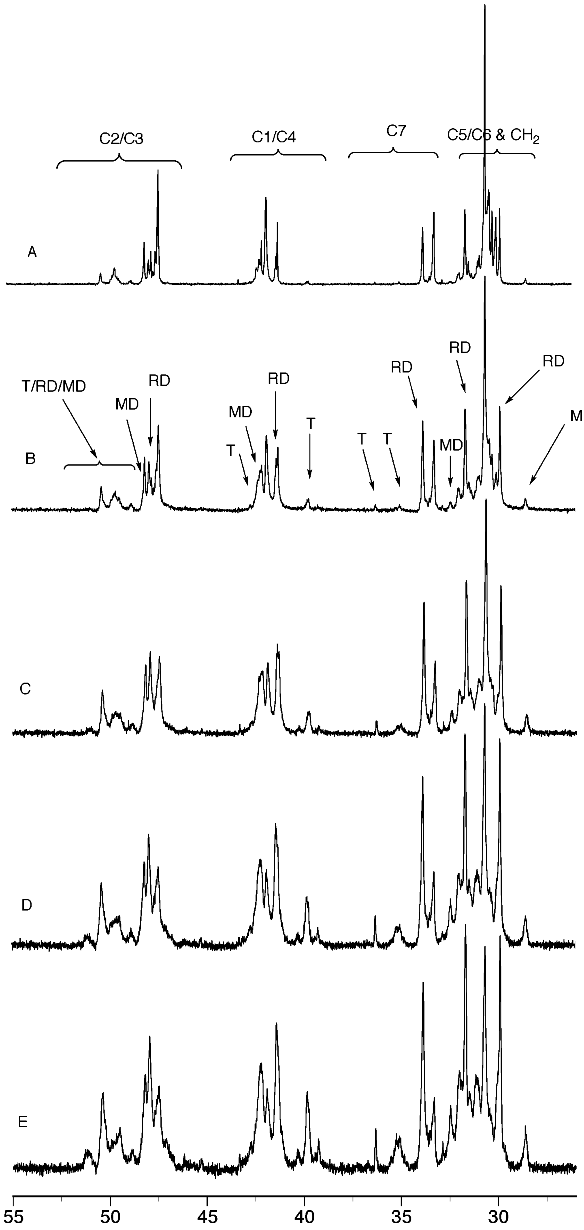


Figure 4. ^{13}C NMR spectra of the E−N copolymers with different norbornene content (A) 35 , (B) 44 , (C) 50 , (D) 53 , and (E) 58 mol % produced by **1**-dried MAO.

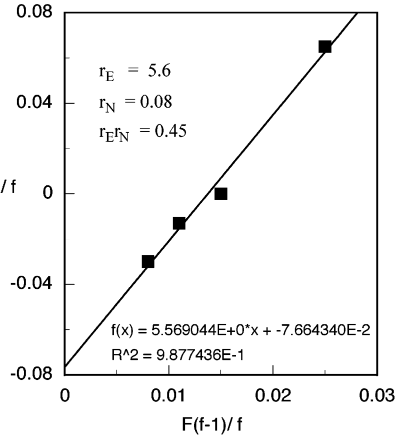


Figure 5. Finemann−Ross plot of E−N copolymers obtained with **1**-dried MAO.

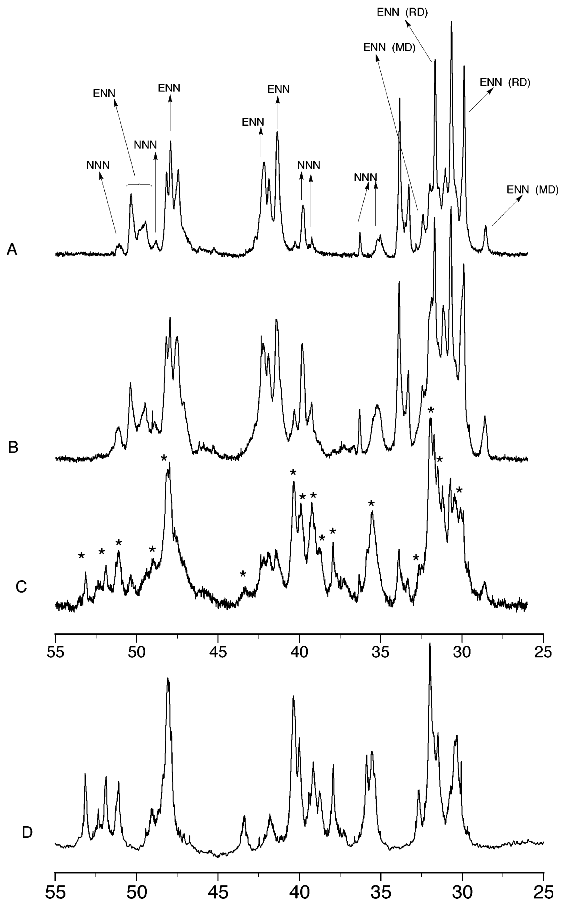


Figure 6. ^{13}C NMR spectra of E−N copolymers produced with **1**-borate/Oct$_3$Al at different temperatures with the norbornene contents of (A) 49 mol % (at 40 °C), (B) 68 mol % (at 60 °C), (C) 82 mol % (at 80 °C), and (D) polynorbornene: the signals marked by the sign (*) are assigned for norbornene homosequences.

E−N copolymerization with **1.** The deviation from the first-order Markovian process in ethene−norbornene copolymerization was reported by Tritto et al. and Fink et al. in the Me$_2$C(Cp)(Flu)ZrCl$_2$−MAO systems.[2b,5c]

The activators and reaction temperatures highly affected the incorporation of norbornene. Norbornene incorporation in the copolymers increased with raising polymerization temperature. In the case of dried MAO and MMAO systems 66 and 61 mol % of norbornene incorporation was observed at 80 °C, whereas 82 mol % in the borate/Oct$_3$Al system at the same conditions.

Figure 6 compares the ^{13}C NMR spectra of E−N copolymers obtained with **1**-borate/Oct$_3$Al at different temperatures. It is clearly observed that the intensity of the signals of ENNE and NNN sequence increased and those of ENEN and ENEE sequences decreased with raising the polymerization temperature to 60 °C. A similar tendency was observed in the dried MAO system, but the signals of NNN sequences drastically increased at 80 °C in the borate/Oct$_3$Al system, and some new signals were observed at low field compared with the signals of NNN sequence. The comparison of the spectrum of the polynorbornene[16] obtained by **1** clarifies that the new signals appeared at almost the same chemical shift of polynorbornene (Table 3).

A significant difference of the incorporation of norbornene with various activators suggests that the active species formed have a great effect on copolymerization. The higher incorporation of norbornene with **1**-borate than with **1**-MAOs should reflect the better separa-

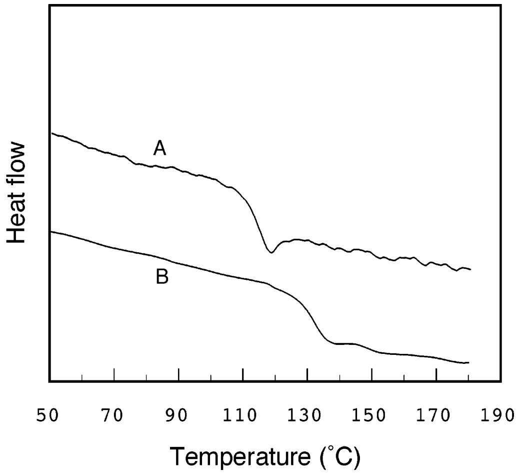


Figure 7. DSC curves of the E−N copolymers with 44 mol % norbornene obtained by (A) **2** and (B) **1**.

Table 3. ^{13}C NMR Signals of Norbornene Unit in E−N Copolymer and Polynorbornene

carbon atom	E−N copolymer (N = 82 mol %)	polynorbornene
C5/C6	30.45	30.44
	31.48	31.50
	31.92	31.97
C7	35.47	35.53
	37.91	37.94
C1/C4	39.23	39.18
	39.89	39.90
	40.33	40.35
C2/C3	47.98	48.00
	51.10	51.12
	51.87	51.87
	53.12	53.17

tion of ion pair in the **1**-borate system, which have been already discussed in the rate enhancement effect in the previous section. At higher temperature, the dissociation of the ion pair is enhanced more in the borate system, which favors the incorporation of norbornene. Chen et al. reported the higher incorporation of 1-hexene in the ethene−1-hexene copolymerization with CGCTiMe$^+$MePBB$^-$ (PBB = tris(2,2,2-nonafluorobiphenyl)borane) than with MeB$(C_6F_5)_3{}^-$.[17]

Thermal Properties of Copolymers. The glass transition temperatures (T_g) of amorphous E−N copolymers depend not only on the amount of norbornene content but also on the comonomer distribution in the E−N copolymers produced. The T_g values of E−N copolymers with the same norbornene content (44 mol %) produced with **1** and **2** are displayed in Figure 7. The former showed higher glass transition temperature (T_g = 131 °C) than the latter (T_g = 114 °C). The higher T_g values of the copolymers obtained with **1** are ascribed to the presence of NN and NNN sequences as described above.

The T_g values of the E−N copolymers obtained with **1** depend on the content of norbornene, which was controlled by the change of N/E feed ratio or the polymerization temperature (Tables 1 and 2). The T_g values were plotted against content of norbornene in Figure 8. The T_g value increased with increasing the content of norbornene, and the highest T_g value of 237 °C was observed for the copolymer with 82 mol % of norbornene.

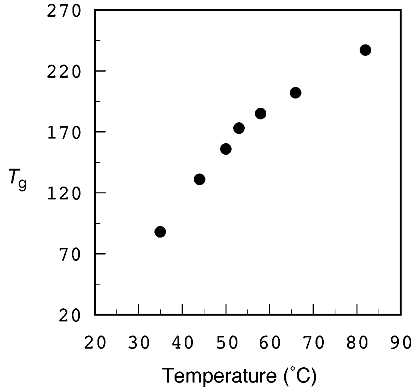


Figure 8. Plot of T_g vs norbornene content of the E−N copolymer with **1**.

Summary

E−N copolymerizations were carried out with (t-BuNSiMe$_2$Flu)TiMe$_2$ (**1**) activated with various activators at a wide range of temperature under an atmospheric pressure of ethene, and (t-BuNSiMe$_2$C$_5$Me$_4$)TiMe$_2$ (**2**) was used for reference. The **1**-dried MAO system showed about 10 times higher activity than the **2**-dried MAO system. The incorporation of norbornene in the copolymer obtained with **1**-dried MAO was higher (N = 50 mol %) than that with **2** (N = 38 mol %) in the same (N/E = 8) feed ratio at 40 °C. Activators as well as polymerization temperatures significantly affected polymerization activity and incorporation of norbornene. The **1**-borate/Oct$_3$Al system showed the highest activity and the highest norbornene incorporation (82 mol %) at 80 °C among all the activators and polymerization conditions. The complex **1** produced the E−N copolymers with norbornene dyad and triad, and some new signals in the ^{13}C NMR spectrum were assigned to the *rac,rac*-NNN triad. The T_g values of the E−N copolymers obtained with **1** were controlled up to 237 °C.

Supporting Information Available: ^{13}C NMR spectra of E−N copolymers obtained with **1**-dried MAO at different temperatures; DSC curves of E−N copolymers obtained with **1** under different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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