Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 4527–4531 **4527**
DOI: 10.1021/ma1006107

Highly Active Living Random Copolymerization of Norbornene and 1-Alkene with *ansa*-Fluorenylamidodimethyltitanium Derivative: Substituent Effects on Fluorenyl Ligand

Zhengguo Cai, Ryotaro Harada, Yuushou Nakayama, and Takeshi Shiono*

Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1,
Higashi-Hiroshima 739-8527, Japan

Received January 14, 2010

ABSTRACT: Copolymerizations of norbornene with propylene and 1-octene were conducted with a series of *ansa*-fluorenylamidodimethyltitanium complexes, [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (**1**), [*t*-BuNSiMe$_2$(3,6-^{t}Bu$_2$Flu)]-TiMe$_2$ (**2**), [*t*-BuNSiMe$_2$(2,7-^{t}Bu$_2$Flu)]TiMe$_2$ (**3**), and [*t*-BuNSiMe$_2$(C$_{29}$H$_{36}$)]TiMe$_2$ (**4**; C$_{29}$H$_{36}$, octamethyloctahydrodibenzofluorenyl), activated by trialkylaluminum-free modified methylaluminoxane. The catalytic systems promoted random copolymerizations in a living manner regardless of the titanium complex used. The activity increased by the introduction of the ^{t}Bu groups on the Flu ligand, and **4** showed the highest activity for each copolymerization. The comonomer content of the copolymers obtained was controllable in a wide range by changing comonomer feed ratio with these catalytic systems. The linear relationships were observed between the norbornene content and the glass transition temperature of the copolymer, whereas the slopes depended on the titanium complex used. The result suggested that the titanium complexes affected the microstructures of the copolymers produced. The evaluation of the monomer reactivity ratios in the copolymerization of norbornene with 1-octene indicates a preference for the norbornene insertion regardless of the last inserted monomer unit in growing polymer chain in all the catalytic systems.

Introduction

Cyclic olefin copolymer (COC) is an attractive material due to its good heat and chemical resistance as well as high transparency, nonhygroscopicity, and low dielectric constants.[1] The developments of homogeneous Ziegler–Natta catalysts have realized the synthesis of various COCs, of which properties can be easily controlled with comonomer content and comonomer sequence. Among those COCs, norbornene-based copolymer is one of the most promising COC as a new interesting class of commercial thermoplastic materials.[2] Since the first norbornene–ethylene copolymer was synthesized by Kaminsky et al. with *ansa*-zirconocene in 1991,[3] the extensive effort on copolymerization of ethylene and norbornene has been paid to produce poly(norbornene-*alt*-ethylene) as well as poly(norbornene-*ran*-ethylene), and the glass transition temperature (T_g) of random copolymer is controllable in a wide range by the norbornene content in the copolymer.

The properties of COC should also be modified by the comonomer employed. However, the catalysts which copolymerize norbornene or dicyclopentadiene with propylene and/or higher 1-alkene are limited, and their activity and the M_n values of the copolymers obtained were not sufficient.[4−9]

We have previously reported that [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (**1**) combined with Me$_3$Al-free dried MAO, modified MAO (MMAO), or Ph$_3$CB(C$_6$F$_5$)$_4$ showed high activity for homo- and copolymerization of norbornene with ethylene, propylene, and higher 1-alkene to produce high-molecular-weight random copolymers, of which T_g values were proportional to the norbornene content in the copolymers.[10] The introduction of the ^{t}Bu groups on the fluorenyl ligand of **1** at 3,6-position ([*t*-BuNSiMe$_2$(3,6-^{t}Bu$_2$Flu)]TiMe$_2$ (**2**)) and 2,7-position ([*t*-BuNSiMe$_2$(2,7-^{t}Bu$_2$Flu)]TiMe$_2$ (**3**)) enhanced the activity more than 3 times in syndiospecific living polymerization of propylene using trialkylaluminum-free dried MMAO (dMMAO) as a cocatalyst, and the syndiospecificity increased in the following order: **1** < **3** < **2**.[11] We applied the **2**–dMMAO system to synthesize the block copolymers composed of crystalline syndiotactic polypropylene sequence and amorphous poly(propylene-*co*-norbornene) sequence.[12]

Miller et al. reported that sterically expanded zirconium dichloride complex [*t*-BuNSiMe$_2$(C$_{29}$H$_{36}$)]ZrCl$_2$·Et$_2$O (C$_{29}$H$_{36}$: octamethyloctahydrodibenzofluorenyl) showed excellent abilities for highly syndiospecific polymerization of propylene and 1-alkenes as well as copolymerization of ethylene with higher 1-alkenes.[13] We succeeded in the synthesis of the corresponding THF-coordinated titanium complex, which was found to be an excellent catalyst for the copolymerization of ethylene and dicyclopentadiene.[14] We also synthesized THF-noncoordinated [*t*-BuNSiMe$_2$(C$_{29}$H$_{36}$)]TiMe$_2$ (**4**) and found that **4** showed 5 times higher activity than those of **2** and **3** in propylene polymerization.[15]

In this paper, we conducted copolymerization of norbornene and 1-alkenes by the use of **1**, **2**, **3**, and **4** combined with dMMAO to investigate the effects of the titanium complex on the copolymerization.

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 complexes and dMMAO were prepared according to the method reported previously.[11,15] Research grade propylene (Takachiho Chemicals Co.) was purified by passing it through dehydration column of NIKKASEIKO DC-L4 and deoxidization column of

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

Table 1. Copolymerization of Norbornene and Propylene with 1, 2, 3 and 4−dMMAO[a]

entry	cat.	Al/Ti (mol/mol)	time (min)	yield (g)	activity[b]	M_n[c] ($\times 10^4$)	M_w/M_n[c]	norbornene[d] (mol %)	conv[e] (%)	T_g[f] (°C)
1	**1**	400	3.0	1.88	1880	15.1	1.10	79	40	292
2	**2**	200	2.0	2.00	3000	16.7	1.14	81	43	291
3	**3**	200	1.0	1.64	4920	15.9	1.33	76	34	285
4	**4**	200	0.5	2.85	17100	23.2	1.30	71	57	250

[a] Polymerization conditions: Ti = 20 μmol, propylene = 1.0 atm, norbornene = 1.5 M, solvent = toluene, total volume = 30 mL, temperature = 20 °C. [b] Activity in kg-polymer mol-Ti^{-1} h^{-1}. [c] Molecular weight and molecular-weight distribution were measured by GPC using polystyrene standards. [d] Norbornene content in copolymer determined by ^{13}C NMR. [e] Norbornene conversion calculated from yield and comonomer content. [f] Glass transition temperature determined by DSC.

NIKKASEIKO GC-SLX. Norbornene (Aldrich) and 1-octene (Tokyo chemical Ind. Co. Ltd.) were dried over calcium hydride and freshly distilled before use.

Polymerization Procedure. Polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer and carried out as the following methods. At first, the reactor was charged with prescribed amounts of dMMAO and the stock toluene solution of norbornene. For the copolymerization of norbornene with propylene, after the solution of dMMAO and norbornene was saturated with gaseous propylene under atmospheric pressure, 1 mL solution of the titanium complex was added to start copolymerization. Copolymerization of norbornene with 1-octene was started by the successive addition of 1-octene and 1 mL solution of the titanium complex to the solution of dMMAO and norbornene. The polymerization was terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Analytical Procedure. The molecular weights and molecular weight distributions of the copolymers obtained were determined by gel permeation chromatography with a Waters 150 CV at 140 °C using *o*-dichlorobenzene as a solvent and calibrated by polystyrene standards. The ^{13}C NMR spectra of the copolymers were measured at 130 °C on a JEOL GSX 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) analysis was performed on a Seiko DSC-220 instrument under a nitrogen atmosphere with a heating and cooling rate of 10 °C/min from 20 to 400 °C. The T_g values were determined from the middle point of the phase transition of the second heating scan.

Results and Discussion

Copolymerizations of norbornene and propylene with **1**, **2**, **3**, and **4** activated by dMMAO were performed in toluene at 20 °C under an atmospheric pressure of propylene. The results are summarized in Table 1.

As described in the Introduction, **2**, **3**, and **4** showed higher activity than **1** in propylene polymerization. We therefore reduced the Al/Ti ratio in these catalytic systems to evaluate the copolymerization activity precisely. All the catalytic systems showed higher activity than **1** even at the lower Al/Ti ratio. Moreover, the **4**−dMMAO system, which resembles the 2,3,6,7-^{t}Bu$_4$Flu derivative, showed about 8 times higher activity than **1**. These results are in good agreement with that of propylene polymerization with the same catalytic systems,[15] where the introduction of alkyl substituents on the fluorenyl ligand enhanced the propagation rate by the electronic effect of the alkyl groups.

All the catalytic systems gave high molecular weight (M_n) polymers with narrow molecular weight distribution (MWD), which suggests that the copolymerization proceeded in a living manner regardless of the titanium complex used.

The polymers obtained were analyzed by ^{13}C NMR spectroscopy. The spectrum of poly(norbornene-*co*-propylene) obtained with **4**−dMMAO is shown in Figure 1 as a representative of the spectra obtained. The resonances of the methyl carbon in the propylene−propylene sequence (P_{pp}: 20.1−21.6 ppm), those in the propylene−norbornene sequence (P_β: 14.0−19.1 ppm), the bridged methylene carbon of norbornene in the norbornene−norbornene sequences (C7: 35.4−37.5 ppm), and that in the propylene−norbornene sequence (C7′: 33.3−34.2 ppm) indicate the production of poly(propylene-*co*-norbornene) as reported in the previous work by the use of **1**.[10c]

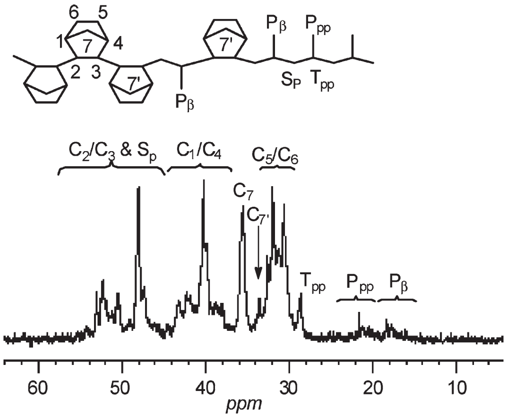

Figure 1. ^{13}C NMR spectrum of poly(norbornene-*co*-propylene) obtained with **4**−dMMAO.

The comonomer contents in the copolymers calculated from the relative intensities of the carbons using the following equation

$$\text{norbornene content (mol \%)} = [\{(I_{\text{tot}} - 3I_{\text{P}})/7\} / \{(I_{\text{tot}} - 3I_{\text{P}})/7 + I_{\text{P}}] \times 100$$

where I_P and I_{tot} are the intensities of the methyl carbon and the total carbons, respectively.

The norbornene contents thus obtained are shown in Table 1. Although the content is slightly dependent on the complex used, all the catalytic systems gave the copolymers with high norbornene contents (> 70 mol %). The thermal properties of the copolymers were then determined by DSC, and the results are also shown in Table 1. All the copolymers were amorphous with high T_g values, which indicates the formation of random copolymers irrespective of the titanium complex.

The copolymerization activity of norbornene and propylene was too high to keep the norbornene conversion low, especially in the **4**−dMMAO system, which prevents the precise evaluation of the monomer reactivity ratios in the copolymerization. In addition, only a few papers reported copolymerization of norbornene or dicyclopentadiene with higher 1-alkene. We therefore conducted copolymerizations of norbornene and 1-octene with **1**, **2**, **3**, and **4**−dMMAO with various comonomer feed ratios in the same conditions with those of copolymerization with propylene. The results are summarized in Table 2.

Although the catalytic systems showed lower activity in 1-octene copolymerization than in propylene copolymerization, the order of the activity of the titanium complexes was the

Table 2. Copolymerization of Norbornene and 1-Octene with 1, 2, 3, and 4−dMMAO[a]

entry	cat.	1-octene (M)	time (min)	yield (g)	activity[b]	M_n[c] ($\times 10^4$)	M_w/M_n[c]	cont N[d] (mol %)	conv N[e] (%)	conv O[e] (%)	T_g[f] (°C)
6	**1**	1.05	5.0	0.57	340	5.3	1.19	80	22	4	213
7[g]	**1**	1.40	5.0	0.26	160	3.2	1.17	73	9	2	162
8[g]	**1**	1.75	5.0	0.34	200	3.1	1.17	66	11	2	140
9	**1**	2.10	5.0	0.53	320	4.3	1.23	63	16	3	128
10	**2**	1.05	1.5	0.40	800	4.9	1.15	82	17	2	233
11[g]	**2**	1.40	1.5	0.26	520	3.4	1.15	74	9	2	176
12[g]	**2**	1.75	1.5	0.33	660	3.8	1.19	69	11	2	147
13	**2**	2.10	1.5	0.36	720	3.6	1.18	67	11	2	138
14[g]	**3**	1.05	1.5	0.31	620	3.2	1.40	74	11	3	169
15[g]	**3**	1.40	1.5	0.35	700	4.0	1.35	68	11	3	153
16[g]	**3**	1.75	1.5	0.40	800	3.6	1.35	63	12	3	130
17[g]	**3**	2.10	1.5	0.34	680	3.1	1.34	59	9	2	113
18	**4**	1.05	1.5	0.83	1660	9.9	1.37	75	30	7	184
19	**4**	1.40	1.5	0.83	1660	6.5	1.46	67	27	7	143
20	**4**	1.75	1.5	1.02	2040	7.5	1.47	60	29	8	112
21	**4**	2.10	1.5	1.15	2300	10.9	1.28	56	30	8	98
22[h]	**4**	2.10	1.0	0.72	8800	36.5	1.3				

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 200, norbornene = 0.7 M, solvent = toluene, total volume = 33 mL, temperature = 20 °C. [b] Activity in kg-polymer mol-Ti^{-1} h^{-1}. [c] Molecular weight and molecular-weight distribution were measured by GPC using polystyrene standards. [d] Norbornene content in copolymer determined by ^{13}C NMR. [e] Norbornene and 1-octene conversions calculated from yield and comonomer content. [f] Determined by DSC. [g] A different lot of dMMAO with that used in other entries. [h] Ti = 5 μmol, Al/Ti = 800.

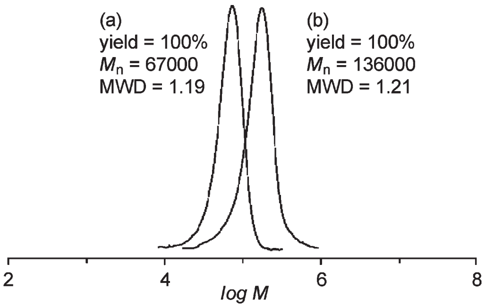

Figure 2. GPC curves of poly(norbornene-*co*-1-octene)s obtained before (a) and after (b) postcopolymerization with **4**−dMMAO.

same: **4**−dMMAO exhibited the highest activity of 2300 kg-polymer mol-Ti^{-1} h^{-1}, which is about 6 times higher than that of **1**−dMMAO. All the catalytic systems gave high molecular weight polymers with comparatively narrow MWD, and the M_n value was almost independent of the concentration of 1-octene.

The activity of **4**−dMMAO further increased to 8800 kg-polymer mol-Ti^{-1} h^{-1} by increasing Al/Ti ratio from 200 to 800 to give higher-molecular-weight copolymer with the M_n value of 365 000 for 1 min copolymerization. We have previously reported that the activity increased linearly against the Al/Ti ratio in the living homopolymerization of norbornene with **1**−MMAO and that of propylene with **2**−dMMAO, respectively, where the larger amount of MMAO enhanced the propagation rate because of the separation of active ion pair.[11,16]

In order to investigate the living nature of the copolymerization with **4**−dMMAO, we conducted postcopolymerization, where the same amounts of norbornene (0.2 M) and 1-octene (0.1 M) were sequentially added after the first-step copolymerization had been completed. The polymerization results and the GPC curves of the copolymers are shown in Figure 2. The conversions were quantitative in both steps. The GPC curve of second step shifted to higher-molecular-weight region compared with that of first step without any other peak or shoulders, and the M_n value of the polymer obtained in the second step was almost double of that in the first step with keeping the narrow MWD. These results imply that the copolymerization of norbornene and 1-octene proceeded in a living manner with **4**−dMMAO.

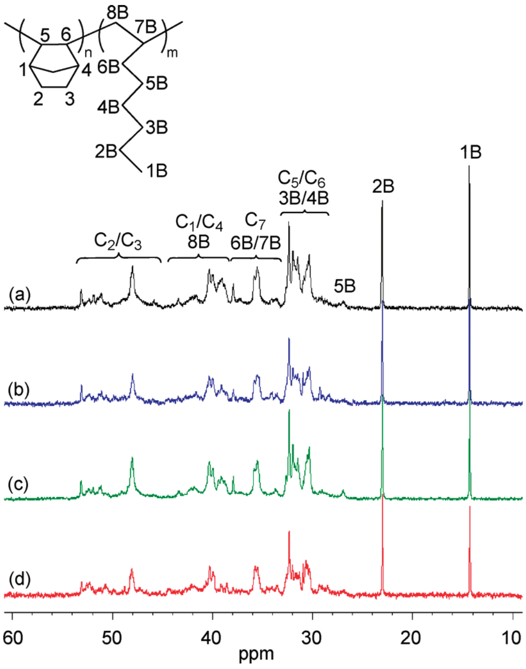

Figure 3. ^{13}C NMR spectra of poly(norbornene-*co*-1-octene) obtained with **1** (a, 75 mol %), **3** (b, 73 mol %), **2** (c, 74 mol %), and **4** (d, 75 mol %) with approximately the same norbornene content.

The ^{13}C NMR spectra of the copolymers containing ~75 mol % of norbornene obtained with each catalytic system are shown in Figure 3. The resonances of the methyl (1B) and methylene (2B) carbons of hexyl branch and C_2 and C_3 carbons of 2,3-inserted norbornene unit are observed at 14.1, 23.0, and 47.0−53.0 ppm together with those of the other carbons around 26.0−46.0 ppm, indicating the production of poly(norbornene-*co*-1-octene) with all the catalytic systems.[10d] Although the detailed assignments of the resonances are not clear at present, the shapes of the spectra are slightly different from each other. This implies that the microstructure of the copolymers is dependent on the titanium complex used. We previously reported that the structure of the fluorenyl ligand affects the syndiospecificity of propylene polymerization in heptane, where the syndiotactic pentad (rrrr) of the PPs decreased in the following order: **2** (0.86) > **3** (0.69) > **1** (0.60) > **4** (0.45).[15] The difference in the ^{13}C NMR spectra of the copolymers is probably ascribed to the difference in the stereoregularity of the copolymers.

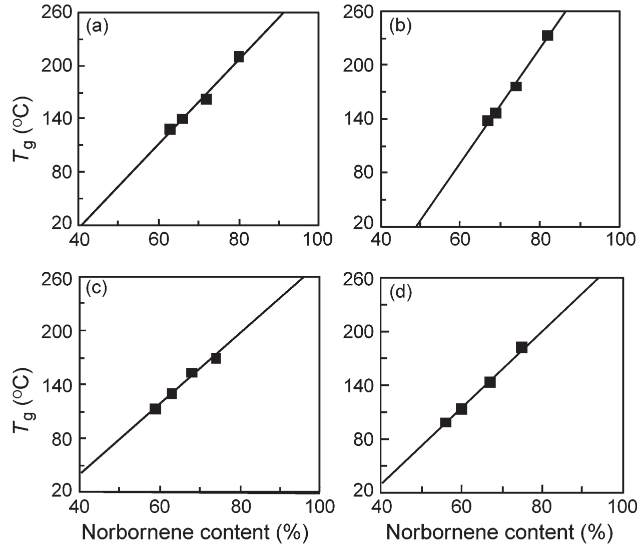

Figure 4. Plots of T_g value against norbornene content in poly(norbornene-*co*-1-octene) obtained with **1** (a), **2** (b), **3** (c), and **4** (d).

The comonomer contents in the copolymers calculated from the relative intensities of C_2 and C_3 carbons of norbornene and 1B and 2B of hexyl branch using the following equation:

$$\text{norbornene content (mol \%)} = [I_{C2/C3}/\{I_{C2/C3} + (I_{1B} + I_{2B})\}] \times 100$$

The norbornene contents thus obtained are shown in Table 2. The content decreased with the increase of the 1-octene concentration in each catalytic system.

The T_g values of the copolymers were then determined by DSC and are plotted against the norbornene content in Figure 4. The T_g value showed a linear relationship with the norbornene content in all the catalytic systems, indicating the formation of the uniform random copolymers regardless of the complex used. The slope of the straight line is however dependent on the titanium complex used. The results also testified the microstructures of the copolymers were depended on the complex. Tritto et al. reported that the stereoregularity of the norbornene sequence affected the T_g value of poly(norbornene-*co*-ethylene) with high norbornene contents.[17]

The conversions of norbornene and 1-octene calculated from the comonomer content and the polymer yield are also shown in Table 2. The low conversions of 1-octene were kept below 8% in all the catalytic systems, whereas the norbornene conversions were not kept low, especially in the **4**−dMMAO system due to its high activity for norbornene. However, for comparison, we evaluated reactivity ratios for each catalytic system by using the Fineman−Ross method.[18]

Fineman−Ross plots and the monomer reactivity ratios ($r_N = k_{NN}/k_{NO}$ and $r_O = k_{OO}/k_{ON}$) determined from the plots are shown in Figure 5. These values indicate a preference for the insertion of norbornene regardless of the last inserted monomer unit. The product of the reactivity ratios ($r_N r_O = 0.97$) obtained with **3** indicates a tendency of the formation of random copolymer, whereas the products of the reactivity ratios ($r_N r_O$: 2.5−3.5) obtained with **1**, **2**, and **4** testify a preference for the formation of homonorbornene sequence in the copolymer.

In summary, [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (**1**), [*t*-BuNSiMe$_2$(3,6-^{t}Bu$_2$Flu)]TiMe$_2$ (**2**), [*t*-BuNSiMe$_2$(2,7-^{t}Bu$_2$Flu)]TiMe$_2$ (**3**), and [*t*-BuNSiMe$_2$($C_{29}H_{36}$)]TiMe$_2$ (**4**; $C_{29}H_{36}$, octamethyloctahydrodibenzo fluorenyl) activated by dMMAO were applied for the copolymerization of norbornene with propylene or 1-octene. The introduction of the ^{t}Bu groups on the Flu ligand improved activity, and the 2,3,6,7-^{t}Bu$_4$Flu analogue **4** was found to show the highest activity of 17 100 and 8800 kg-polymer mol-Ti^{-1} h^{-1} for the copolymerizations of norbornene with propylene and 1-octene despite the rather low Al/Ti ratios of 200 and 800, respectively. The results of postcopolymerization with **4**−dMMAO imply that the copolymerization proceeded in a living manner.

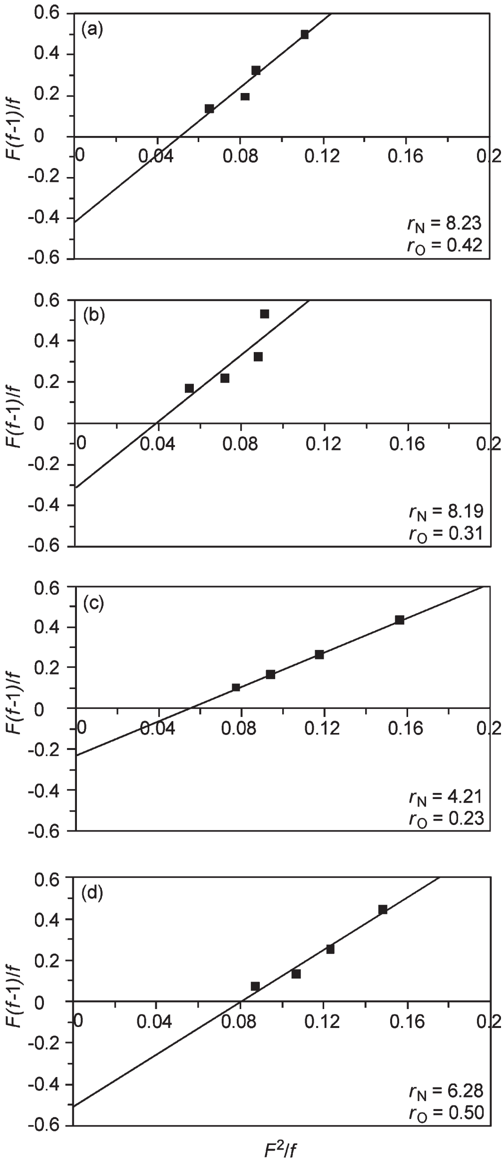

Figure 5. Fineman−Ross plots for copolymerization of norbornene and 1-octene with **1** (a), **2** (b), **3** (c), and **4** (d) (F = [norbornene]/[1-octene] in feed and f = [norbornene]/[1-octene] in copolymer).

The comonomer content of the copolymer obtained was controllable by changing comonomer feed ratio, and the linear relationship was observed between the T_g value and the norbornene content regardless of the titanium complex used. The slope of the norbornene content−T_g plot was however dependent on the titanium complex. The monomer reactivity ratios in the copolymerization of norbornene and 1-octene, which was slightly dependent on the titanium complex, indicate a preference for the insertion of norbornene regardless of the last inserted monomer unit at the growing polymer chain.

Acknowledgment. We thank Tosoh-Finechem Co. for donating MMAO. The measurement of ^{13}C NMR was made using a JEOL GSX 500 at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University.

Supporting Information Available: DSC profiles of copolymers obtained with **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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