Articles

Highly Efficient Ti-Based Catalyst Systems for Vinyl Addition Polymerization of Norbornene

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ABSTRACT: Norbornene polymerization via "vinyl addition" proceeded with (*t*-BuNSiMe$_2$Flu)TiMe$_2$ (**1**) in the presence of various cocatalysts [methylaluminoxane (MAO), modified methylaluminoxane (MMAO), and $Ph_3CB(C_6F_5)_4$/Oct_3Al] at wide range of temperatures (20−80 °C) with high activity. The **1**−$Ph_3CB(C_6F_5)_4$/Oct_3Al system produced 4.8×10^3 kg of polymer per mole of Ti per hour at 20 °C. All the catalyst systems produced high molecular weight (M_n) polymers. In the **1**−MMAO system, the yield and M_n values increased linearly keeping narrow molecular weight distribution against the Al/Ti ratio, suggesting that MMAO should take part not only in the initiation but also in the propagation reaction. The rate enhancement with higher Al/Ti ratio was also observed in the $Ph_3CB(C_6F_5)_4$/Oct_3Al system. The activity of the **1**−dried MAO and **1**−MMAO systems increased with raising reaction temperature up to 60 °C, whereas that of **1**−$Ph_3CB(C_6F_5)_4$/Oct_3Al decreased. The polynorbornenes obtained with **1** were amorphous, soluble in halogenated aromatic solvents, and stable up to 420 °C. The film of polynorbornene prepared by solvent casting was highly transparent in the UV−vis region.

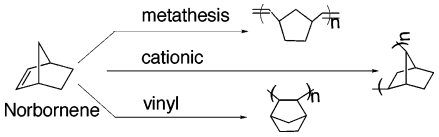
Introduction

Norbornene can be polymerized via three different mechanisms, i.e., cationic,[1] ring-opening metathesis,[2] and vinyl addition.[3] Among these mechanisms, the "vinyl addition" gives the polynorbornene that possesses special properties with high thermal stability, high glass transition temperature (T_g), high transparency, and low birefringence due to its constrained structure of saturated carbon skeleton. Such polymeric materials have placed a greater demand on optical plastics in data storage and microelectronics technology.

The research on norbornene polymerization with early transition metal single-site catalysts has been directed to ring-opening metathesis polymerization (ROMP) rather than vinyl addition polymerization because bis(cyclopentadienyl)titanacyclobutane conducts the ROMP of norbornene in a living manner.[4] A variety of transition metal complexes give polynorbornene with the ROMP mechanism.[1,2] The products obtained by ROMP have been commercialized with further modification through vulcanization or hydrogenation of double bond in polymer chain.[5] On the other hand, cationic polymerization of norbornene gives oligomeric product.[1,3b]

The polynorbornene obtained via vinyl addition has several advantages because of the bicyclic structure retained in the main chain. Vinyl addition polymerization of norbornene was studied with $TiCl_4$/R_3Al in the early 1960s[6] and a number of zirconocenes since 1980s.[7] All of them showed very low catalytic activity, and the products produced were insoluble in common solvents. Recently, the monocyclopentadienyltitanium catalyst system, $CpTi(OBz)_3$/MAO, was reported to show better activity than the other metallocene catalysts.[8] Late transition metal catalysts were reported to be highly active for vinyl addition polymerization of norbornene.[9−11]

Scheme 1. Methods of Norbornene Polymerization



In the practical point of view, the improvement of catalytic activity and the precise control of product structures are the targets of polymerization catalysts. In olefin polymerization by group IV single-site catalysts, the catalytic activity and the structure of polymer produced depend on the nature of active species, which is the ion pair formed from a metal complex precursor and an activator. Cyclopentadienylamido (CpA) group IV complexes show high performance in olefin polymerization due to their open coordination sites.[12] We have previously reported that (*t*-BuNMe$_2$SiFlu)TiMe$_2$ (**1**) activated with Me_3Al-free methylaluminoaxane (dried MAO) produced polynorbornene in a living manner at 20 °C with moderate activity.[13]

In this paper, we conducted norbornene polymerization with **1** using various activators to find the most suitable polymerization conditions and investigated the physical properties of the produced polymers.

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Table 1. Polymerization of Norbornene with (*t*-BuNSiMe$_2$Flu)TiMe$_2$ (1) Using Different Cocatalysts[a]

entry	cocatalyst	time (min)	yield (g)	activity[b]	conv[c] (%)	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	N[e] (μmol)
1	dMAO	5	1.81	1090	56	29.6	1.26	6
2	MAO	5	0.10	56	3	0.55	1.26	18
3	MMAO	3	0.95	953	29	7.9	1.07	12
4	$Ph_3CB(C_6F_5)_4$ + ^{i}Bu$_3$Al[g]	2	2.85	4280	85	20.2	1.41	14
5	$Ph_3CB(C_6F_5)_4$[h]	10						

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, [N] = 1.2 M, solvent = toluene, total volume = 30 mL, temperature = 20 °C. [b] Activity = kg$_{(poly)}$ mol$^{-1}_{(Ti)}$ h^{-1}. [c] Conversion was calculated from yield. [d] Number-average molecular weight and molecular weight distributions were measured by GPC using polystyrene standard. [e] Number of polymer chain (N) calculated from the yield and M_n. [f] B = 20 μmol, Oct$_3$Al = 400 μmol. [g] B = 20 μmol, [i] Bu$_3$Al = 400 μmol. [h] Without alkylaluminum.

Experimental Section

Materials. The preparation and handling of the catalyst were operated in a nitrogen atmosphere with Schlenk techniques. The titanium complex **1** was synthesized according to the literature and the references therein.[14] Alkylaluminums and borate ($Ph_3CB(C_6F_5)_4$) were provided by Tosoh Finechem Co. MAO was used before and after drying. The dried MAO was prepared according to the procedure reported previously.[13] MMAO solution in toluene was used without any treatment. The compositions of MAOs were determined from the ^{1}H NMR spectra.[15] 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). 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. At first, the reactor was charged with MAO and a stock solution of norbornene in toluene was added. After the addition of solvent (toluene) the reactor was kept in an oil or water bath for 30 min to reach at required reaction temperature. A 1 mL solution of complex (20 μmol) in toluene was added to start the polymerization. For the borate system, polymerization was started by the successive additions of alkylaluminum, the borate, and the complex to the monomer solution. Temperature was kept constant during polymerization. Polymerization was terminated with acidic methanol. The polymer obtained was precipitated in acidic methanol, filtered, adequately washed with methanol, and finally dried under vacuum at 60 °C for 6 h.

Analytical Procedure. Molecular weight and molecular weight distribution of polymer were measured by GPC (Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^{1}H and ^{13}C NMR spectra of polynorbornene 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. For ^{13}C NMR, the pulse angle was 45°, and about 10 000 scans were accumulated in a pulse repetition of 4.0 s. For DEPT (distortionless enhancement by polarization transfer) method, the DEPT135 spectrum was measured. The sample solution was prepared in 1,1,2,2-tetrachloroethane-d_2, and the central peak of 1,1,2,2-tetrachloroethane-d_2 (at 74.47 ppm) was used as an internal reference. Thermal gravimetric analysis (TGA) was studied with a Seiko I & E DTA-220 under a nitrogen atmosphere up to 500 °C at a heating rate of 10 °C/min. Differential scanning calorimetric (DSC) analysis was made on a Seiko DSC-220 under a nitrogen atmosphere from 20 to 400 °C at a heating/cooling rate of 10 °C/min. Transparency of polymer film was determined using an UV−vis spectrometer (JASCO, V-550) in the range 350−700 nm. The polymer film was prepared by solvent casting from the solution of polymer in chlorobenzene followed by drying at 60−80 °C under vacuum.

Results and Discussion

The polymerizations of norbornene were performed by **1** activated with various MAOs and the borate under the same monomer concentration at 20 °C. The results obtained are summarized in Table 1.

The catalytic behaviors of the polymerization of norbornene were strongly depended on the activators used. The MAO (untreated) system showed about 20 times lower activity than the dried MAO system (entries 1 and 2). On the other hand, the activity of the MMAO system was similar to that of the dried MAO system (entries 1 and 3). The borate/^{i}Bu$_3$Al system showed the highest activity (>4000 kg$_{(poly)}$ mol$^{-1}_{(Ti)}$ h^{-1}), although no activity was observed in the absence of ^{i}Bu$_3$Al (entries 4 and 5).

All the catalytic systems except using untreated MAO produced high molecular weight (M_n) polymers with narrow molecular weight distributions (M_w/M_n). We have previously reported that **1**−dried MAO conducted living polymerization of norbornene.[13] Since **1**−MMAO showed the narrowest M_w/M_n value, the living nature of this system was investigated by postpolymerization at 20 °C. It was however found that chain transfer slightly occurred before the addition of second monomer. Considering the fact that the postpolymerization successfully proceeded in the dried MAO system,[13] the chain transfer should have been caused by ^{i}Bu$_3$Al in MMAO in the absence of monomer. In the vinyl addition polymerization of norbornene, the chain termination via β-H elimination is prohibited because the β-H of the propagation chain end is at the endo position of the norbornene unit. The chain transfer to monomer should be also prohibited because of the sterically hindered propagation chain end and norbornene monomer.

Usual metallocene activated with MAO needs a large amount of MAO to achieve high activity, of which reason is, however, not clear at present. The effect of Al/Ti ratios, therefore, investigated in the dried MAO and MMAO systems. The results are summarized in Table 2. In all the catalyst systems, the activity and M_n values increased with increasing Al/Ti ratios. **1**−MMAO showed better performance than **1**−dried MAO, especially at the highest Al/Ti ratio (Al/Ti = 800). In the case of the **1**−MMAO system, both the yield and M_n value increased linearly against the Al/Ti ratio with keeping narrow M_w/M_n values (Figure 1). The GPC traces are displayed in Figure 2. These results indicate that the larger amount of MMAO enhanced the propagation rate with a slight increase in the number of active centers (Table 2).

The additive effect of R$_3$Al was then investigated in the MMAO and borate systems. The addition of Oct$_3$Al (Al/Ti = 15) in the MMAO system increased the activity, whereas ^{i}Bu$_3$Al (Al/Ti = 15) did not show a significant effect. On the other hand, the addition of Me$_3$Al or Et$_3$Al drastically decreased the activity, and a trace amount of polymer was obtained in the presence of Et$_3$Al. The increase of Oct$_3$Al in the borate system also increased the activity accompanied by the increase of the M_n value.

Table 2. Effect of Al/Ti Ratio on Norbornene Polymerization with 1 Activated by Different Cocatalysts[a]

catalyst	Al/Ti	time (min)	Y (g)	activity[b]	conv[c] (%)	M_n[d] × 10^{-4}	M_w/M_n[d]	N[e] (μmol)
1−dMAO	dMAO(200)	5	0.28	168	8	3.2	1.43	8
1−dMAO	dMAO(400)	5	1.81	1090	56	29.6	1.26	6
1−dMAO	dMAO(800)	5	1.99	1190	59	13.1	1.50	15
1−MMAO	MMAO(200)	3	0.35	350	12	3.3	1.10	11
1−MMAO	MMAO(400)	3	0.95	953	29	7.9	1.07	12
1−MMAO	MMAO(800)	3	2.06	2060	61	14.7	1.07	14
1−MMAO (400)	Oct_3Al(15)	3	1.24	1240	37	10.8	1.20	11
1−MMAO (400)	$^iBu_3Al$(15)	3	0.85	850	25	10.6	1.15	8
1−MMAO (400)	Me_3Al(15)	3	0.23	230	7	2.4	1.15	10
1−MMAO (400)	Et_3Al(15)	3	trace					
1−borate	$^iBu_3Al$(20)	3	2.85	4280	85	20.2	1.41	14
1−borate	Oct_3Al(10)	3	0.66	665	20	11.5	1.36	6
1−borate	Oct_3Al(20)	2	3.21	4820	95	33.5	1.40	10

[a] Polymerization conditions: Ti = 20 μmol, B = 20 μmol, [N] = 1.2 M, solvent = toluene, total volume = 30 mL, temperature = 20 °C. [b] Activity = $kg_{(poly)}\ mol^{-1}{}_{(Ti)}\ h^{-1}$. [c] Conversion was calculated from yield. [d] Number-average molecular weight and molecular weight distributions were measured by GPC using polystyrene standard. [e] Number of polymer chain (N) calculated from the yield and M_n.

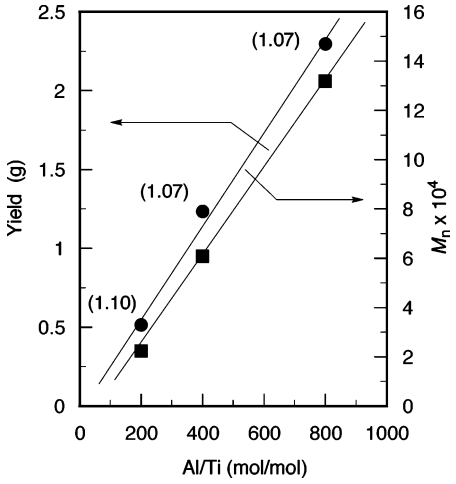

Figure 1. Plots of yield and M_n values against Al/Ti ratio in the **1**−MMAO system. M_w/M_n values are shown in parentheses.

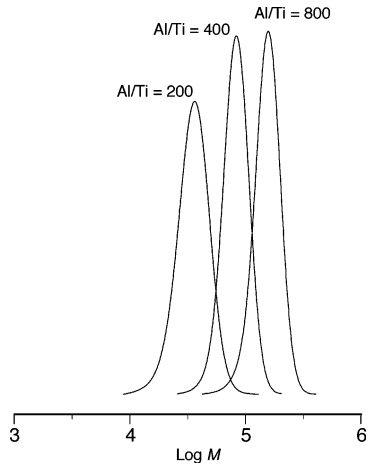

Figure 2. GPC traces of polynorbornenes obtained with **1**−MMAO at different Al/Ti ratios.

The effect of different MAOs on norbornene polymerization with **1** is explained by their composition. The higher activity of **1**−dried MAO (free from Me_3Al) than that of **1**−untreated MAO is ascribed to the higher propagation rate of this system. In the case of **1**−untreated MAO, the low activity is probably due to the coordination of free Me_3Al (14 mol %) to the active species, which might also cause chain transfer reaction.

The addition of Me_3Al in the polymerization of propene with [*rac*-$Me_2Si(Ind)_2Zr(\mu\text{-}Me)_2AlMe_2]^+B(C_6F_5)_4$/$Me_3Al$ system decreased both the activity and M_n value,[16] and the similar inactive bimetallic active species was detected in the $Cp_2Zr(^{13}CH_3)_2$/MAO system.[17]

In the case of MMAO, the drying process is not necessary because $^iBu_3Al$ cannot form the bimetallic species with the active Ti complex.[18,19] Since the M_n value increased with increasing the Al/Ti ratio, $^iBu_3Al$ reacts or interacts with MAO rather than with the active Ti species, which provides better separation of the ion pair. The rate enhancement by $^iBu_3Al$ and Oct_3Al in the borate system supports this assumption. The extremely narrow M_w/M_n should come from the higher solubility of MMAO compared with that of dried MAO, which makes the former more homogeneous. On the other hand, the borate system showed a high activity, which makes it difficult to keep the polymerization system uniform, i.e., temperature and stirring state, and hence the M_w/M_n value became broad.

Table 3 shows the effect of temperatures on norbornene polymerization with the **1**−dried MAO, **1**−MMAO, and **1**−borate/Oct_3Al systems. Each catalyst system showed good activity over a wide range of reaction temperatures. Both the **1**−dried MAO and **1**−MMAO systems showed better activity with increasing reaction temperature, and the highest activity was observed at 60 °C. On the other hand, the activity of the borate/Oct_3Al system at 60 °C was less than half of that at 20 °C. The M_n values were decreased with broadening of M_w/M_n values at higher temperatures, which suggests chain transfer and/or deactivation should occur at high temperature.

The ^1H and ^{13}C NMR spectra of all the polynorbornenes obtained were similar and indicate the vinyl addition of norbornene irrespective of the activator employed.[13] Figure 3 shows the ^{13}C NMR spectrum of polymer obtained by **1**−dried MAO. Several signals were observed from 28 to 55 ppm. The absence of any signal at 20−24 ppm indicates that the polynorbornene is exo enchained.[20] Each signal of the saturated carbon was split into several peaks, which comes from the different stereoisomers of norbornene unit in the polymer chain.

The peaks are assigned as four groups by comparing with the DEPT135 spectrum (where the signal intensity of methylene (−CH_2−) carbons appears in negative intensity) 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). Although the clear assignment of each peak was not accomplished, the presence of three peaks of C7 carbon indicates that the structure of poylnorbornene

Table 3. Effect of Temperatures on norbornene Polymerization with 1 Activated by Different Cocatalysts[a]

catalyst	temp (°C)	time (min)	Y (g)	activity[b]	conv[c] (%)	M_n[d] × 10^{-4}	M_w/M_n[d]
1−dMAO	20	5	1.81	1090	56	29.6	1.26
1−dMAO	40	5	2.73	1640	81	24.0	1.13
1−dMAO	60	5	2.82	1690	84	19.0	1.41
1−dMAO	80	5	1.60	960	47	8.4	1.69
1−MMAO	20	3	0.95	953	29	7.9	1.07
1−MMAO	40	3	2.46	2460	73	21.8	1.18
1−MMAO	60	3	2.71	2710	80	14.1	1.48
1−MMAO	80	3	2.40	2400	71	16.5	1.75
1−borate[e]	20	2	3.21	4820	95	33.5	1.40
1−borate[e]	60	2	1.50	2250	44	18.1	1.65

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, solvent = toluene, total volume = 30 mL. [b] Activity = $kg_{(poly)}\ mol^{-1}_{(Ti)}\ h^{-1}$. [c] Conversion was calculated from yield. [d] Number-average molecular weight and molecular weight distributions were measured by GPC using polystyrene standard. [e] B = 20 μmol, Oct_3Al = 400 μmol.

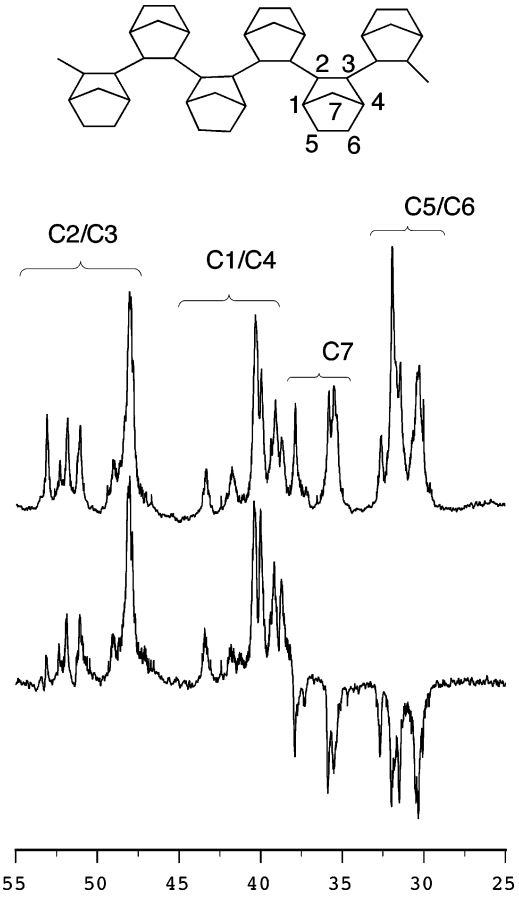

Figure 3. ^{13}C and DEPT NMR spectra of polynorbornene obtained with **1**.

obtained is completely different from that of soluble polynorbornene obtained by Ni complexes. The polynorbornenes produced with [(η^3-crotyl)Ni(1,4-COD)]PF_6 showed two peaks of C7 assigned as mm and mr triad sequences, and the polynorbornene produced with Ni-(2,2,6,6-tetramethyl-3,5-heptanedionate)$_2$ showed one peak of C7 assigned as overlapping peaks of rr and mr triad sequences.[20]

The thermal property of polynorbornenes with M_n values of 8 × 10^4 and 15 × 10^4 obtained by **1**−MMAO were studied by thermogravimetric analysis (TGA). Both samples were stable up to 400 °C. A weight loss of 5% was recorded at a temperature of 423 °C (Figure 4).

The wide-angle X-ray diffraction (WAXD) analysis of the polynorbornene obtained with **1** showed two broad peaks: a relatively high-intensity diffraction signal was observed at 2θ value between 9° and 11°, and a low-

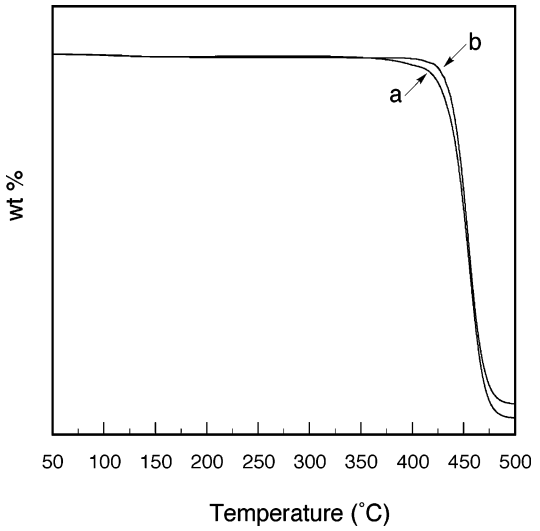

Figure 4. TGA thermograms of polynorbornene obtained with **1**−MMAO: (a) M_n = 7.9 × 10^4; (b) M_n = 14.7 × 10^4.

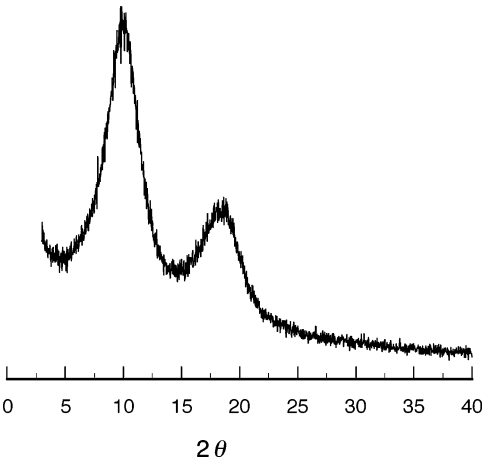

Figure 5. WAXD pattern of polynorbornene obtained with **1**.

intensity diffraction was between 17° and 20° (Figure 5). The result indicates that the polynorbornene produced was predominantly amorphous. The two halos are regarded as a reflection of the interchain/intersegment and intrachain distance of polynorbornene.[9g,10e] No traces of Bragg refraction were observed at crystalline region. The polynorbornene obtained with **1** should, therefore, be amorphous.

The polynorbornene film was prepared by solvent casting from the polymer solution in chlorobenzene, and the transmittance of the film (thickness = 54 μm) was above 93% in the range from 350 to 700 nm (Figure 6).

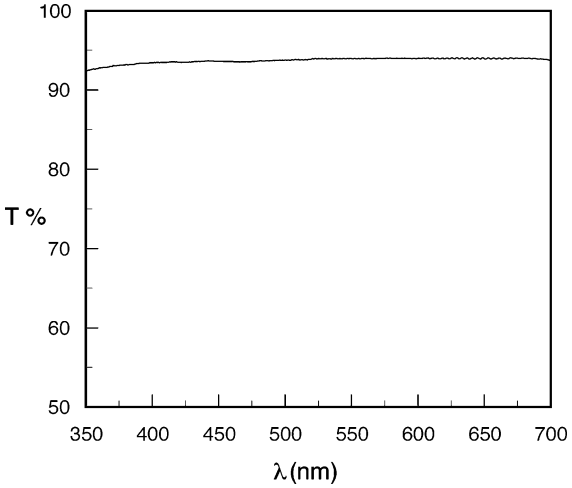

Figure 6. Transmittance (*T*) of polynorbornene film in the UV−vis region (350−700 nm).

In summary, the Ti complex, (*t*-BuNSiMe$_2$Flu)TiMe$_2$ (**1**), showed extremely high activity in vinyl-type polymerization of norbornene in the presence of various cocatalysts at wide range of temperatures. The **1**−borate/Oct$_3$Al system showed the highest activity of 4.8 $\times$ 10^3 kg$_{(poly)}$ mol$^{-1}_{(Ti)}$ h^{-1}. The polynorbornene with extremely narrow molecular distribution ($M_w/M_n = 1.07$) was obtained in high activity using MMAO where the propagation rate was controlled by the Al/Ti ratio. The polynorbornenes obtained were amorphous, soluble in halogenated aromatic solvents, and stable up to 420 °C. The film of polynorbornene obtained was highly transparent in the UV−vis region. The above results indicate that the vinyl-type polynorbornene was synthesized efficiently with **1** by choosing a suitable cocatalyst.

Supporting Information Available: ^{1}H NMR spectra of MAO and MMAO, experimental data, and GPC curves of postpolymerization with **1**−MMAO. This material is available free of charge via the Internet at http://pubs.acs.org.

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