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NOTE

High-Temperature Living Copolymerization of Ethylene with Norbornene by Titanium Complexes Bearing Bidentate [O, P] Ligands

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Introduction

In the past decades, transition-metal-catalyzed living polymerization which permits the consecutive enchainment of monomer units without termination has made a significant contribution to produce the polymers with perfectly controlled molecular weight (MW), molecular weight distribution (MWD), composition, and architecture.[1] In general, the living polymerization requires low temperature, normally below room temperature, to suppress chain termination and transfer steps, and thus it generally displayed low catalytic activity.[2−6] Moreover, the precipitation of polymers from solution at low temperature can hinder the controlled nature of living polymerization. These deficiencies have restricted the utility of the living polymerization catalyzed by transition-metal catalysts. Raising reaction temperature favors enhancing catalytic activity and suppressing the precipitation of polymer. However, high reaction temperature also cause chain termination or transfer and/or catalyst deactivation, resulting in the loss of the characters of living polymerization.

Therefore, the discovery and development of the catalytic systems with living polymerization characters at high temperature remain a challenge.[7−10]

Recently, the copolymerizations of ethylene (E) with norbornene (NB) have attracted much attention because of the remarkable properties of E/NB copolymers, such as excellent optical transparency and high refractive index. Up to date, although a great deal of academic research about E/NB copolymerization has been reported,[11−19] the examples for the living copolymerization are limited, and most of the catalytic systems displayed the living copolymerization characters only at low/room temperature.[20−24] For example, Fujita and co-workers reported one type of bis(pyrrolide-imine)titanium catalysts which can mediate room-temperature living E/NB copolymerization with a high propensity to form alternating copolymers, whereas copolymerization at 90 °C for a short time (1 min) resulted in the copolymer with a broad MWD ($M_w/M_n = 1.86$).[23b] Previously, we reported a series of bis(β-enaminoketonato)titanium catalysts which can mediated E/NB copolymerization in a living fashion under the mild conditions. We also found the MWD of the resultant copolymers significantly broadened with reaction temperature.[24a] Therefore, the development of the catalysts for high-temperature living E/NB copolymerization is a comparatively uncharted field. Recently, Gibson and colleagues reported a series of phenoxy-phosphine group 4 metal complexes. The impressive activities of these complexes, especially the zirconium complexes for ethylene and propylene polymerization, indicated that there was a surprising advantage using ligands that contain softer second-row donors in early-transition-metal-based catalysts.[25] The rigid phenylene bridge could help to enforce the phosphine coordination, and the active species could parallel the highly active group 4 metal phenoxy-imine systems.[25,26] Previous reports indicated that fluorine-substituted phenoxy-imine titanium complexes can catalyze the living olefin polymerization.[6,8] Moreover, the living ethylene and propylene polymerization characters can be retained even at high temperature.[8] We are interested in the olefin behavior of the phenoxy-phosphine titanium complexes. In this contribution, we describe the unique performances of the bis(phenoxy-phosphine)titanium complexes which effectively promote high-temperature living E/NB copolymerization.

Results and Discussion

Synthesis and Characterization of Titanium Complexes. The synthetic route for the titanium complexes used in this study is depicted in Scheme 1. Tetrahydropyranyl (THP) ether **1a−c** were lithiated with *n*-BuLi/TMEDA and quenched with PPh_2Cl ($SiMe_3Cl$). The protective group of compounds **2a−c** could be easily removed to give **3a−c** by addition of hydrochloric acid.[27] Compared with the methods reported by Gibson et al. using methoxymethyl (MOM) protection,[25] the synthetic route was more facile for THP protection and deprotection. These ligands were deprotonated by 1.0 equiv of *n*-BuLi at −78 °C, followed by reacting with 0.5 equiv of $TiCl_4$. Desired complexes **4a−c** were isolated in good yields (**4a**, 68%; **4b**, 73%; **4c**, 75%) by recrystallization from a mixture of THF and hexane at room temperature. All the complexes were identified by elemental analysis and NMR.

Homopolymerization of Ethylene and Norbornene. Although olefin polymerization by group 4 metal complexes bearing bidentate phenoxy-phosphine ligands have been previously reported by Gibson and colleagues,[25] the study about titanium complexes is limited. In this report, bis(phenoxy-phosphine)titanium complexes **4a−c** have been investigated in detail as the catalysts for ethylene polymerization in the presence of modified methylaluminoxane (MMAO) as a cocatalyst. The representative results are collected in Table 1. Under the mild conditions (25 °C, Al/Ti = 1000/1, atmospheric pressure), these complexes revealed marked catalytic activities. The steric bulk of substituents R_1 and R_2 exhibited little influence on both the catalytic activity and the MW of the polymers produced (entries 1−3). The resultant polyethylenes displayed narrow

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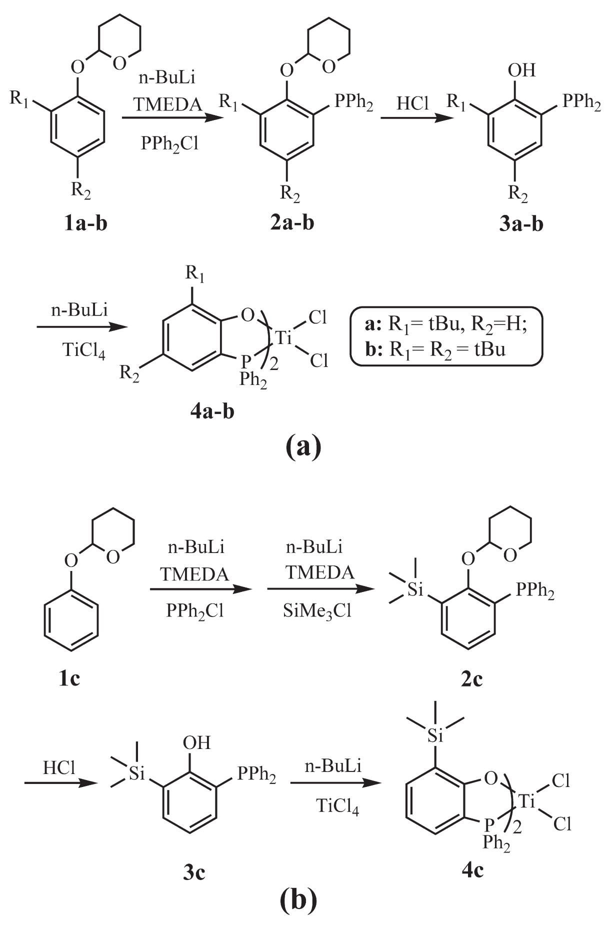
Table 1. E or NB Homopolymerization Results[a]

entry	catalyst (μmol)	Al/Ti	temp (°C)	time (min)	yield (mg)	activity[b]	M_n[c] (10^4)	M_w/M_n[c]
1	**4a** (2)	1000	25	5	168	1008	5.9	1.31
2	**4b** (2)	1000	25	5	181	1086	6.3	1.30
3	**4c** (2)	1000	25	5	146	876	5.6	1.33
4	**4b** (1.5)	1000	25	20	411	822	10.9	1.79
5	**4b** (2)	500	25	5	175	1050	6.5	1.29
6	**4b** (2)	2000	25	5	188	1128	5.9	1.34
7	**4b** (2)	3000	25	5	192	1152	6.1	1.37
8	**4b** (2)	4000	25	5	195	1170	6.0	1.39
9	**4b** (2)	1000	0	5	61	366	2.8	1.20
10	**4b** (2)	1000	50	5	286	1716	7.9	1.71
11	**4b** (2)	1000	75	5	243	1458	4.3	1.93
12[d]	**4b** (5)	1000	25	30				

[a] Conditions: V_{total} = 50 mL, atmospheric pressure. [b] Activity in kg PE/(mol$_{Ti}$ bar h). [c] GPC data in trichlorobenzene vs polystyrene standards. [d] Norbornene homopolymerization: NB in feed: 3.0 g.

Scheme 1. Synthesis of Titanium Catalysts 4a−c



MWD (M_w/M_n = 1.30−1.33), indicating that these titanium catalysts possess some characters of living ethylene polymerization. The controlled nature of the polymerization was confirmed by monitoring MW and MWD as a function of reaction time by complex **4b**. As shown in Figure 1, number-average molecular weight (M_n) increased quite linearly within the first 10 min of reaction, while a relatively narrow MWD (M_w/M_n = 1.26−1.41) was observed. Further extending polymerization time conduced a lost of the controlled nature (entry 4), which was presumably due to mass transport problems. With the increase of polymerization time, excess polymer precipitated from solution. Some molecules of the catalysts were enwrapped by the precipitated polyethylenes, and thus the diffusion of ethylene will control polymerization rate to some extent, which results in the gradual broadening the MWD of the polyethylene and the gradual decreasing catalytic activity.[8a]

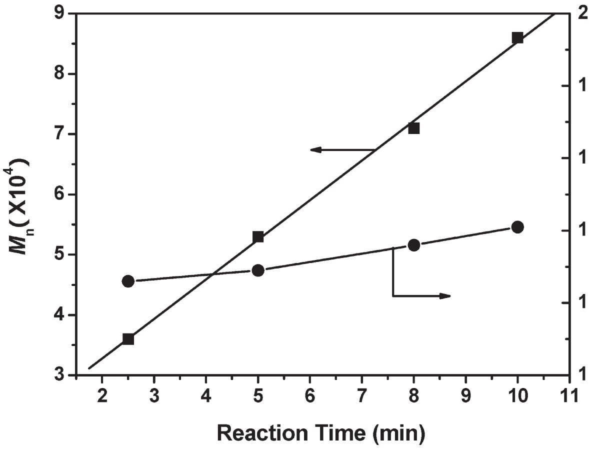


Figure 1. Plots of the number-average molecular weights and the polydispersity indexes of the polyethylenes versus reaction time (catalyst **4b**, 1.5 μmol, Al/Ti molar ratio = 1000:1, 25 °C, atmospheric pressure, V_{total} = 50 mL).

The effect of the reaction parameters, such as Al/Ti molar ratio and reaction temperature, on the polymerization has also been investigated using **4b**. The catalytic activity and MW were independent of the Al/Ti molar ratio (entries 2, 5−8), which indicated that the chain transfer to aluminum is not dominating chain transfer during the polymerization. With the reaction temperature increased from 0 to 75 °C, the catalytic activity first increased, reached a maximum value at ca. 50 °C, and then decreased. The MWD of the resultant polymers broadened with temperature as a result of a common increase of chain transfer reactions (entries 2, 9−11). A much narrower MWD (M_w/M_n = 1.20) was obtained by polymerization at low temperature 0 °C (entry 9), suggesting that no significant chain transfer or termination occurred at low reaction temperature. The resulting polyethylenes have been further characterized by high-temperature ^{13}C NMR spectra. A singlet was observed at the peak at 30.2 ppm, indicating that the polyethylenes possess linear structure with virtually no branching. In addition, complex **4b** was also investigated as a catalyst for norbornene polymerization; neither polymeric nor oligomeric materials were isolated (entry 12).

Copolymerization of Ethylene with Norbornene. Previously, research has suggested that the presence of NB in the reaction medium and/or in the polymer chain seems beneficial for suppressing the chain termination or transfer.[23a,23b] This prompted us to investigate E/NB copolymerization behaviors with these complexes. We hope the

Table 2. E/NB Copolymerization Results[a]

entry	catalyst (μmol)	NB (g)	temp (°C)	time (min)	yield (mg)	activity[b]	M_n[c] (10^4)	M_w/M_n[c]	NB incorp[d] (mol %)
1	**4b** (5)	0.25	25	10	256	307	3.8	1.26	6
2	**4b** (5)	0.50	25	10	177	213	2.7	1.19	10
3	**4b** (5)	1.00	25	10	108	130	2.2	1.17	18
4	**4b** (5)	1.50	25	10	78	94	1.7	1.16	26
5	**4b** (3)	0.50	25	10	106	212	2.6	1.17	10
6	**4b** (3)	0.50	50	10	138	276	3.0	1.19	17
7	**4b** (3)	0.50	75	10	209	418	4.5	1.18	26
8	**4b** (5)	0.50	50	10	221	265	2.9	1.19	18
9	**4b** (5)	0.50	75	5	180	432	3.7	1.17	27
10	**4b** (5)	5.00	75	3	82	328	1.1	1.11	44
11	**4b** (5)	10.0	75	5	86	206	1.0	1.13	47
12	**4b** (5)	0.50	85	3	95	380	2.0	1.10	22
13	**4a** (3)	0.50	75	10	189	378	4.3	1.20	25
14	**4c** (3)	0.50	75	10	176	352	4.1	1.21	23
15	**4b** (5)	0.50	75	3	118	472	2.5	1.13	25
16[e]	**4b** (5)	0.50 + 5.00	75	3 + 3	186		3.2	1.17	35

[a] Conditions: Al/Ti molar ratio = 1000:1, V_{total} = 50 mL, atmospheric pressure. [b] Activity in kg/(mol$_{\mathrm{Ti}}$ bar h). [c] GPC data in trichlorobenzene vs polystyrene standards. [d] Norbornene incorporation determined by ^{13}C NMR. [e] After the treatment of **4b**/MMAO with 0.50 g of NB for 3 min, another 5.0 g of NB was introduced into the resulting mixture.

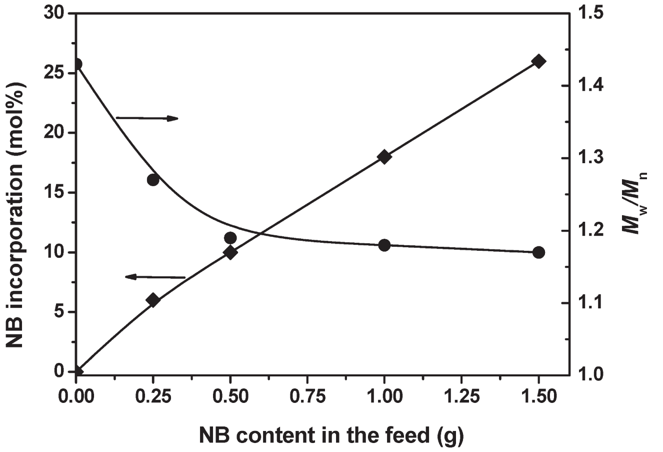
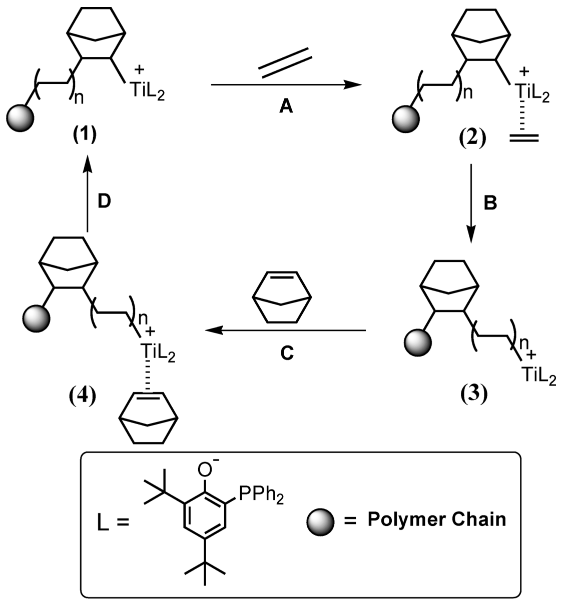


Figure 2. Plots of the NB incorporation and the polydispersity indexes of the polymers versus comonomer content in the feed (catalyst **4b**, 5 μmol, Al/Ti molar ratio = 1000:1, atmospheric pressure, V_{total} = 50 mL, polymerization at 25 °C for 10 min).

Scheme 2. A Plausible Mechanism for Living E/NB Coploymerization



addition of the NB into the reaction medium will also benefit for MW control. Table 2 summarizes the typical results of E/NB copolymerization using these catalysts. Copolymerizations were first carried out with complex **4b** as a function of the amount of NB charged at 25 °C under the atmospheric pressure. In the presence of MMAO, **4b** was found to work as an efficient catalyst for E/NB copolymerization. The catalytic activity and the MW as well as the NB content of the copolymers were significantly influenced by the concentration of NB charged (entries 1–4). As expected, all the copolymers obtained displayed narrower MWD compared with the polyethylene produced under the similar conditions. NB incorporation and M_w/M_n values of the resultant polymers versus NB content in the feed are shown in Figure 2. It seems that NB incorporation of larger than about 10 mol % is a critical value for producing the copolymers with narrow MWD (M_w/M_n < 1.2).[23b] A plausible copolymerization mechanism is presented in Scheme 2; refer to the literature reported by Fujita et al.[23b] After the formation of species **1**, propagation predominantly occurs by the insertion of one or successive ethylene followed by NB one after the other according to the sequence A–B–C–D. The highly controlled nature of the copolymerization may probably attribute to two sides: (i) NB-last-inserted species **1** is fairly stable toward chain transfers because of the difficulty in β-H transfer step,[12d] (ii) the characteristics of a quasi-living ethylene polymerization would allow the successive ethylene enchainment without chain transfer or termination for a short time polymerization. The E/NB copolymers obtained displayed narrower MWD compared with the polyethylene is the consequence of the stabilization of an E-last-inserted species toward chain transfers and its smooth transformation to a chain-transfer-wise stable norbornene-last-inserted species during the reaction. At low norbornene content (less than 10 mol %), the copolymers predominantly consist of isolated NB units in polyethylene sequences. The peaks observed at 47.7, 42.1, 33.4, and 30.1–30.7 ppm are assigned to isolated NB units and polyethylene sequences. With increasing NB incorporation, we can track the appearance of the peaks at 48.4, 47.8, and 42.6 ppm which are characteristics of alternating NB sequences.[15a]

The effect of the reaction temperature on E/NB copolymerization behaviors was investigated in detail. As shown in entries 5–7 of Table 2, the catalytic activity increased from 212 to 418 kg/(mol$_{\mathrm{Ti}}$ bar h) with the reaction temperature increased from 25 to 75 °C, indicating that the catalyst system displays excellent temperature tolerance toward the

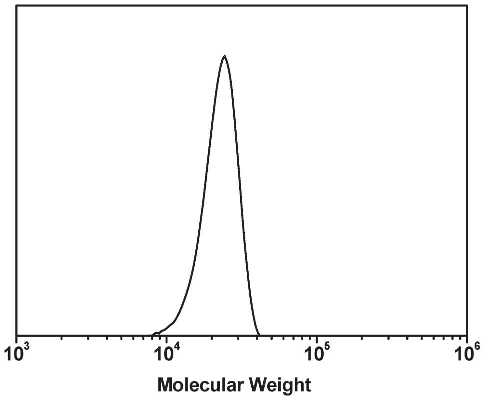


Figure 3. GPC profiles of E/NB copolymer obtained at 85 °C for 3 min by catalyst **4b** (M_n 2.0 × 10^4, M_w/M_n 1.10, entry 12 of Table 2).

E/NB copolymerization. Moreover, high temperature also favors enhancing the MW and NB incorporation of the resultant copolymer. It is noteworthy that all the copolymers obtained at different temperatures exhibited narrow MWD, suggesting the MW control is retained even at high temperature. Considering that MW is determined by the relative rate of chain propagation and chain transfer, the increase in MW of the resultant copolymer with reaction temperature predominantly due to an advance of the chain propagation rate without chain transfer and termination. Since the ethylene concentration in the polymerization medium will be lower at higher temperature, the increase in NB incorporation was probably a consequence of the smaller E/NB molar ratios at higher temperature. The copolymerization was investigated at a higher catalyst concentration, and the controlled nature was retained at different temperature (entries 8−12). High catalytic activities were achieved by polymerizing from 50 to 85 °C, and the best result was obtained at 75 °C. NB incorporation up to 47 mol % was obtained by increasing the NB content in the feed at 75 °C. Copolymerization at 85 °C in a short time (3 min) produced the copolymer with a much narrower MWD (M_w/M_n = 1.10) as shown in Figure 3, and the catalytic activity was still higher than those observed at 25 or 50 °C. In addition, complexes **4a** and **4c** gave similar results at 75 °C (entries 13 and 14). To further confirm the high-temperature living nature of the copolymerization, the evolutions of M_n and M_w/M_n over the polymer yield by catalyst **4b** were conducted at 75 °C. As shown in Figure 4, the M_n increased proportionally with the polymer yield, and narrow MWDs were retained for each case, thus corroborating the highly controlled nature of the copolymerization.

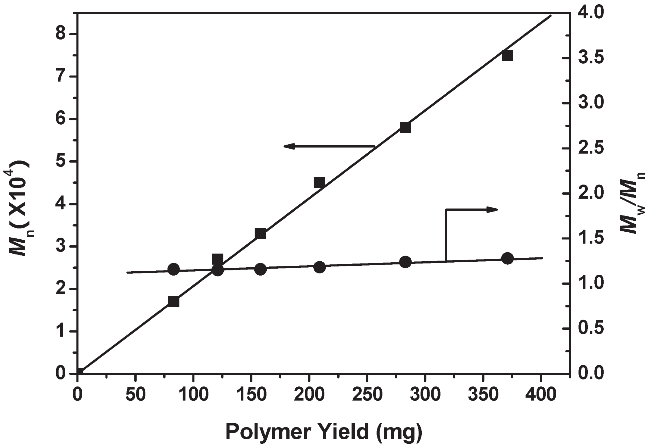


Figure 4. Plots of the number-average molecular weights and polydispersity indexes of the copolymers versus polymer yield (catalyst **4b**, 3 μmol, NB in feed: 0.5 g, Al/Ti molar ratio = 1000:1, 75 °C, atmospheric pressure, V_{total} = 50 mL).

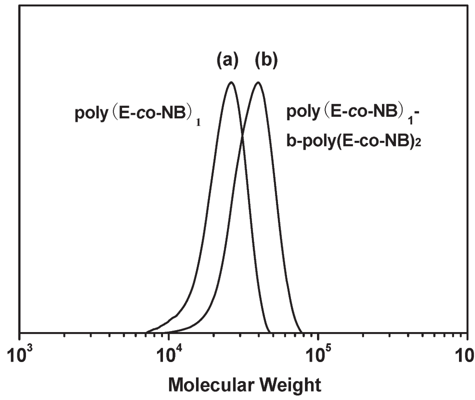


Figure 5. GPC profiles of the poly(E-*co*-NB)$_1$-*b*-poly(E-*co*-NB)$_2$: (a) M_n 2.5 × 10^4, M_w/M_n 1.13 (entry 15 of Table 2); (b) M_n 3.2 × 10^4, M_w/M_n 1.17 (entry 16 of Table 2).

Block copolymer which contains a different NB content was prepared at 75 °C under atmospheric pressure. The reactor was charged with the prescribed amount of toluene and norbornene (0.5 g), and the ethylene gas feed was started followed by equilibration at 75 °C. The polymerization was initiated by the addition of a heptane solution of MMAO and a toluene solution of the titanium complex into the reactor with vigorous stirring. After 3 min, norbornene (5 g) was added to the mixture for another 3 min, affording poly(E-*co*-NB)$_1$-*b*-poly(E-*co*-NB)$_2$. The monomodal GPC curves for the first poly(E-*co*-NB)$_1$ (M_n 2.5 × 10^4, M_w/M_n 1.13) (entry 15) and the final poly(E-*co*-NB)$_1$-*b*-poly(E-*co*-NB)$_2$ (M_n 3.2 × 10^4, M_w/M_n 1.17) (entry 16) indicate a shift toward the higher MW region, while a low M_w/M_n is retained, demonstrating the creation of the target block copolymer (Figure 5). The copolymer incorporates 35 mol % NB, which was between 25 mol % (entry 15) and 44 mol % (entry 10). The viscoelasticity test displays two transformations at 12 and 99 °C, corroborating the copolymer contains two segments with different NB content (see Supporting Information).

Conclusions

Ethylene polymerization and ethylene/norbornene copolymerization were investigated using bis(phenoxy-phosphine)-titanium complexes (2-R$_1$-4-R$_2$-6-PPh$_2$-C$_6$H$_2$ O)$_2$TiCl$_2$ (**4a**: R$_1$ = *t*-Bu, R$_2$ = H; **4b**: R$_1$ = R$_2$ = *t*-Bu; **4c**: R$_1$ = SiMe$_3$, R$_2$ = H) as the catalysts in the presence of MMAO. These titanium complexes are capable of catalyzing living ethylene polymerization at low temperature, while the molecular weight distribution of the polymer gradually broaden with reaction temperature. By adding norbornene into the reaction medium, the possible chain transfer and chain termination can be effectively suppressed, and ethylene/norbornene copolymerization will reposefully proceed in a living fashion, which produces the copolymers with narrow MWD (M_w/M_n < 1.20). Furthermore, these unique titanium catalysts display excellent temperature tolerance toward the living copolymerization of ethylene with norbornene. The living fashion of the copolymerization can be retained up to 85 °C, and the polydispersity indices of the resultant copolymer were still lower than 1.20. To our best knowledge, this is the first example of transition-metal catalysts which can promote high-temperature living ethylene/norbornene copolymerization.

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Supporting Information Available: Detailed experimental procedures for synthesis of complexes **4a**−**c**; ^{13}C NMR spectra of the typical E/NB copolymer samples obtained by catalyst **4b**; charts for viscoelasticity test of poly(E-*co*-NB)$_1$-*b*-poly(E-*co*-NB)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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