Random Copolymerization of Norbornene with Higher 1-Alkene with *ansa*-Fluorenylamidodimethyltitanium Catalyst

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Cycloolefin polymer (COP) and cyclic olefin copolymer (COC), which consist of rigid alicyclic polymer backbone, are attractive materials because of their good heat and chemical resistance as well as their low dielectric constants, nonhygroscopicity, and high transparency. COP is synthesized via ring-opening metathesis polymerization of norbornene derivatives followed by hydrogenation of C═C bonds in the main chain,[1] whereas COC via copolymerization of ethene and cycloolefin such as norbornene.[2] One of the advantages of COCs is that the polymer properties can be easily controlled with comonomer content and comonomer sequence distribution. Development of metallocene catalysts enables us to synthesize various COCs. The extensive study on copolymerization of ethene and norbornene has realized the synthesis of poly(norbornene-*alt*-ethene) (or norbornene content ≤50 mol %)[3] as well as poly(norbornene-*ran*-ethene) (or norbornene content >50 mol %), of which glass transition temperature (T_g) can be controlled in a wide range.[4]

The other advantage of COCs should be that the polymer properties can also be modified by the comonomer employed. Despite the easy access to propene, the examples of copolymerization of norbornene with propene are much less than those with ethene.[5] Tritto et al. reported that *rac*-Et(indenyl)$_2$ZrCl$_2$ activated with methylaluminoxane (MAO) produced poly(norbornene-*co*-propene) containing isolated norbornene.[6] Random copolymerization of norbornene and propene was reported by Henschke et al. using *rac*-Me$_2$Si(indenyl)$_2$ZrCl$_2$-MAO, where the linear relationship was observed between the norbornene content in the copolymer and the T_g value.[7] The T_g value of the copolymer with 98 mol % of norbornene was however only 255 °C, which was much lower than that expected from the norbornene content. They ascribed the low T_g value to the low molecular weight of the copolymer (M_w = 13 700, M_w/M_n = 1.9). Kaminsky et al. recently investigated copolymerization of norbornene with propene using a series of metallocene catalysts and reported that *rac*-Me$_2$C(indenyl)$_2$ZrCl$_2$-MAO gave poly(norbornene-*ran*-propene) with T_g of 192−206 °C and M_n of 2600−3600 depending on the polymerization temperature.[8] In these systems, the catalyst activity drastically decreased with increasing the norbornene in feed. On the other hand, we reported that *ansa*-fluorenylamidodimethyltitanium, Me$_2$Si(η^1-N^{t}Bu)(fluorenyl)TiMe$_2$ (**1**), activated with dried MAO, modified MAO (MMAO), or Ph$_3$CB(C$_6$F$_5$)$_4$, which showed high activity for homopolymerization and random copolymerization of norbornene with ethene,[9] also gave high molecular weight poly(norbornene-*ran*-propene) with high activity. The copolymer possessing 71 mol % of norbornene and M_n of 156 000 showed the T_g value of 249 °C.[10]

On the other hand, only a few papers reported on the copolymerization of cycloolefin with higher 1-alkene. The LG Chemical Group conducted the copolymerization of propene, 1-hexene, and 1-octene using H$_2$C(Me$_2$C$_5$H$_2$)$_2$ZrCl$_2$-MAO,[11] where the activities and the M_n values of the copolymers increased according to the amount of norbornene in feed accompanied by the increases of the norbornene contents and the T_g values of the copolymers. The activity (kg-polymer mol-Zr^{-1} h^{-1}), M_n, norbornene content (mol %), and T_g (°C) obtained with the highest norbornene feed were as follows: propene, 3600, 13 700, 97.0, 239; 1-hexene, 960, 9500, 90.5, 224; 1-octene, 1090, 10 200, 87.5, 208. Kaminsky at al. conducted copolymerization of norbornene and 1-hexene using several metallocene catalysts, where the activity decreased in a logarithmic scale against the amount of norbornene in feed and the norbornene content in the copolymer leveled off at 50 mol %.[12] On the hand, Hou et al. reported copolymerization of 1-hexene and dicyclopentadiene with a cationic CpSc complex isolated or derived in situ to obtain random copolymers possessing T_g of 9−210 °C and M_n of 1300−2200 with the activities of 3.4−3.9 kg-polymer mol-Sc^{-1} h^{-1}.[13]

Despite the expectation for copolymerization of cyclic olefins with higher 1-alkene giving new COCs, the catalytic systems available for the copolymerization are limited, and their activity and the molecular weights of the products are not sufficient as described above. We have fortunately found that **1** activated with Ph$_3$CB(C$_6$F$_5$)$_4$, which was a excellent catalyst for homo- and random copolymerization of norbornene with ethene or propene,[4f,9,10] was also very effective for the random copolymerization of norbornene with higher 1-alkene. This communication reports the preliminary results of the copolymerization and the properties of the obtained copolymers.

Copolymerizations of 1-hexene, 1-octene, and 1-decene were conducted with **1** activated by Ph$_3$CB(C$_6$F$_5$)$_4$ in the presence of trioctylaluminum at 25 °C in toluene. The copolymerizations were conducted under the fixed concentration of norbornene with various concentrations of 1-alkene for 2 min in order to minimize the change of comonomer feed ratio during the copolymerization. The results are summarized in Table 1.

The copolymerization activity depended on the kind of 1-alkene and higher 1-alkene showed the higher activity. The activity increased with raising the 1-alkene concentration and reached ~2000 kg-polymer mol-Ti^{-1} h^{-1}. The M_n values of the copolymers and the M_w/M_n values were 70 000−90 000 and 1.4−1.7, respectively, and independent of the kind and the concentration of 1-alkene employed.

The structure of the copolymers were investigated by ^{13}C{^{1}H} NMR. As a representative, the spectrum of poly(norbornene-*co*-1-octene) is illustrated in Figure 1, where that of each homopolymer is also shown for comparison. In the spectrum of the copolymer, methyl (H^8) and methylene (H^7) carbons of hexyl branch and C^2 and C^3 carbons of 2,3-inserted norbornene unit are observed at 14, 23, and 47−53 ppm together with those of the other carbons of norbornene and 1-octene units in main chain around 26−46 ppm. In all the spectra of the copolymers, these resonances clearly appeared. The comonomer contents in

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Table 1. Copolymerization of Norbornene and 1-Alkene with 1 by $Ph_3CB(C_6H_5)_4$[a]

entry	comonomer	in feed[b] [M]	yield (g)	activity[c]	M_n[d] ($\times 10^3$)	M_w/M_n[d]	1-alkene[e] (mol %)	conv[f] (%)	T_g[g] (°C)
1	1-hexene	0.03	0.47	698	74.2	1.72	7	23	—[h]
2	1-hexene	0.07	0.54	810	76.7	1.61	9	15	296
3	1-hexene	0.14	0.62	927	74.3	1.63	20	19	251
4	1-octene	0.03	0.85	1280	72.5	1.50	7	42	—[h]
5	1-octene	0.07	0.91	1370	80.0	1.36	11	30	262
6	1-octene	0.14	1.07	1610	76.9	1.37	23	36	192
7	1-octene	0.30	1.35	2030	129	1.38	58	50	110
8	1-decene	0.03	0.98	1480	87.8	1.42	8	54	284
9	1-decene	0.07	1.06	1590	75.8	1.47	23	62	230
10	1-decene	0.14	1.25	1880	69.2	1.54	32	52	152

[a] Polymerization conditions: Ti = B = 20 μmol, trioctylaluminum = 400 μmol, solvent = toluene, total volume = 50 mL, [norbornene] = 0.21 M, temp = 25 °C, time = 2 min. [b] 1-Alkene in feed. [c] Activity in kg-polymer mol-Ti^{-1} h^{-1}. [d] Number-average molecular weight and molecular weight distribution determined by GPC using monodisperse polystyrene standards. [e] 1-Alkene content in copolymer. [f] 1-Alkene conversion calculated from yield and comonomer content. [g] Glass transition temperature determined by DSC. [h] Not detected below 300 °C.

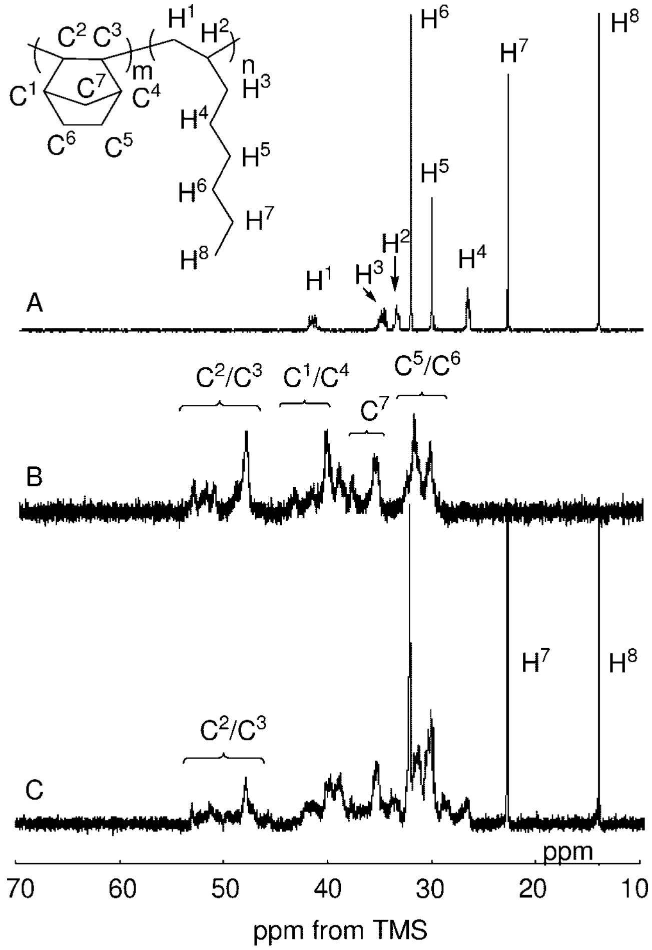

Figure 1. $^{13}C\{^1H\}$ NMR spectra of poly(1-octene) (A), polynorbornene (B), and poly(norbornene-*co*-1-octene) (C).

the copolymers were therefore calculated from the relative intensities of these carbons using the following equation.

$$\text{1-alkene content (mol \%)} = [(I_{CH_3} + I_{CH_2})/\{I_{C2/C3} + (I_{CH_3} + I_{CH_2})\}] \times 100 \quad (1)$$

where $I_{C2/C3}$, I_{CH_3}, and I_{CH_2} are the intensity of C^2 and C^3 carbons and those of methyl and methylene in the branched chain end of 1-alkene, respectively.

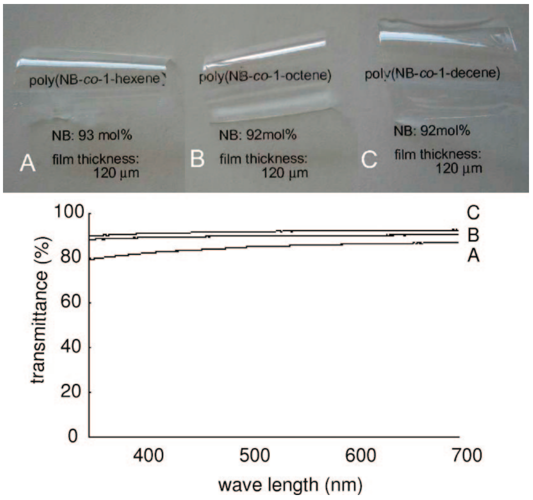

Figure 2. Transparency of poly(norbornene-*ran*-1-alkene) films: A, 1-hexene; B, 1-octene; C, 1-decene.

The 1-alkene contents thus obtained are shown in Table 1, which indicates that 1-alkene content can be controlled with 1-alkene concentration in feed. The conversions of 1-alkene calculated from the comonomer content and the polymer yield are also shown in Table 1. The conversion was almost independent of the concentration of 1-alkene, indicating the first-order dependence of propagation rate on the 1-alkene concentration. On the other hand, the conversion depended on the kind of 1-alkene and decreased as follows: 1-decene > 1-octene > 1-hexene. The higher reactivity of higher 1-alkene with this catalyst is not clear at present. Miller et al. reported that a sterically expanded *ansa*-fluorenylamidozirconium complex, $Me_2Si(\eta^1\text{-N}^t\text{Bu})(\eta^1\text{-C}_{29}H_{36})ZrCl_2\cdot OEt_2$, activated by MAO polymerized 1-octene faster than ethene, and the activity for copolymerization of ethene with 1-octene or 4-methyl-1-pentene increased in proportion to the comonomer concentration.[14] They ascribed the higher activity to the electronic effect of the monomers because the η^1-coordination of $C_{29}H_{36}$ gives a large coordination site where the steric effect of the comonomers should be negligible. The higher activity of **1** for higher 1-alkene should be partially ascribed to the η^3-coordination mode of the fluorenyl ligand in **1**.[15]

The T_g values of the copolymers were then measured by DSC scanned from room temperature to 300 °C, and the results are summarized in Table 1. The copolymers of 1-hexene and 1-octene with the highest norbornene contents (93 mol %) did not show any T_g values up to 300 °C. All the other copolymers showed the T_g value which decreased in inverse proportion to the 1-alkene content in the copolymer. The results indicate the production of random copolymers from norbornene and 1-alkene. These T_g values were 50−80 °C higher than those of the copolymers obtained by the LG Chemical group with similar comonomer contents,[11] which should be ascribed to the higher molecular weight of the present copolymers.

Since the M_n values of the copolymers seemed to be high enough to form self-standing films, we tried to prepare the copolymer films by casting the tetrachloroethane solutions of the copolymers with similar comonomer contents (entries 1, 4, and 8). The self-standing transparent films with a thickness of ~120 μm were successfully obtained irrespective of the 1-alkene comonomer as shown in Figure 2. The UV−vis measurement of these films indicates that the transparency improved with increasing the length of 1-alkene, i.e., 1-decene > 1-octene > 1-hexene, and the transmittance of the poly(norbornene−*co*−1-decene) reached ~90% (Figure 2).

In conclusion, random copolymers of norbornene and higher 1-alkene with high T_g values and high molecular weight were successfully obtained with reasonable activities using $Me_2Si(N^tBu)(fluorenyl)TiMe_2$ (**1**) as a catalyst precursor. Since **1** can conduct homo- and copolymerization of propene and higher 1-alkene[16] as well as norbornene[9] in a living fashion when combined with a suitable activator, the catalytic system is expected to be applied for the synthesis of various tailor-made COCs.

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Supporting Information Available: Experimental procedures, $^{13}C\{^1H\}$ NMR spectra, and DSC curves of the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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