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Living Random Copolymerization of Ethene and Norbornene Using *ansa*-Fluorenylamidodimethyltitanium Complex

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Summary: Ethene-norbornene copolymerizations were conducted by (t-BuNMe$_2$SiFlu)TiMe$_2$ (**1**) activated with dried methylaluminoxane (MAO) (free from Me$_3$Al) at 0 °C and 20 °C under atmospheric pressure of ethene at various norbornene concentrations. At 0 °C and high norbornene concentration, the molecular weight of the copolymer increased linearly against polymerization time while keeping narrow molecular-weight distribution. The ^{13}C NMR spectrum revealed that random copolymer with 53 mol-% of norbornene was obtained. The glass transition temperature was above 150 °C.

Keywords: amorphous; copolymerization; living polymerization; norbornene; Ziegler-Natta polymerization

Introduction

Ethene-norbornene (E-N) copolymers are high performance materials due to their high glass transition temperature (T_g) and optical transparency.[1] The recent development of single-site catalysts has brought several catalytic systems which conduct E-N copolymerization with considerable activities.[2] Most of them gave the copolymers with isolated norbornene unit or almost alternate structure. Ni-based catalysts, which are active for norbornene polymerization, also produced almost alternating E-N copolymers.[3] Constrained geometry catalysts (CGCs) are highly active for copolymerization of ethene and higher α-olefins to give random copolymers.[4] Most of the CGC derivatives, however, produce E-N copolymers with isolated or alternating norbornene sequences depending on the norbornene content.[5] A few *ansa*-zirconocenes like *rac*-Et(Ind)$_2$ZrCl$_2$, ^{i}Pr[FluCp]ZrCl$_2$, ^{i}Pr[IndCp]ZrCl$_2$, and MeCH[Cp]$_2$ZrCl$_2$ were reported to produce random copolymers containing more than 50 mol-% of norbornene.[6-8]

The living polymerization is a useful tool for the synthesis of tailor-made polymers. So far a few

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examples of the living E-N copolymerization have been reported. Tritto *et al.* reported the quasi-living polymerization of ethene and norbornene with C_2-symmetric zirconocene catalysts[9, 10] and (t-BuNMe$_2$SiC$_5$Me$_4$)TiCl$_2$[11] using MAO as cocatalyst. Fujita *et al.* recently reported that the Ti complexes containing pyrrolide-imine ligand also produced alternating E-N copolymer in a living manner at 30 °C.[12] In this study, (t-BuNMe$_2$SiFlu)TiMe$_2$ (**1**) activated with dried methylaluminoxane (MAO) (free from Me$_3$Al), which we have previously reported as an excellent catalyst for homopolymerization of norbornene,[13] was applied for the copolymerization of ethene and norbornene, and was found to produce random copolymer in a living manner.

Experimental

Materials. The preparation and handling of the complex **1** was operated under nitrogen atmosphere with Schlenk techniques. The titanium complex **1** was synthesized according to the literature, and the references therein.[14] Dried MAO was prepared with the same procedure reported previously.[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). Research grade ethene (purchased from Takachiho Chemicals Co.) was purified by passing it through columns of NaOH, P_2O_5, and molecular sieves 3*A*. 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 0.464 g (8.0 mmol of Al) of dried MAO and a prescribed volume of the stock solution of norbornene was added under nitrogen gas flow. The solvent toluene was added to make the total volume 30 mL, and ethene gas was charged at atmospheric pressure after the reactor had been evacuated. The reactor was kept in an ice or water bath to obtain desired temperature, and the reaction mixture was saturated with ethene. A solution of catalyst (1 mL) in toluene was added to start the polymerization. The temperature was kept constant during the polymerization. The polymerization was terminated with methanol and precipitated with acidic methanol. The polymer obtained was adequately washed with methanol, and dried under vacuum at 60 °C for 6 h.

Analytical Procedures. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of

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copolymer were measured by gel permeation chromatography (GPC, Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. The ^{13}C NMR spectrum of copolymer was recorded at 120 °C on a JEOL GX 500 spectrometer operated at 125.65 in pulse Fourier-Transform mode in tetrachloroethane-d_2 as solvent with a 4-s delay between the pulses. Differential scanning calorimetry (DSC) was investigated under nitrogen from 20 to 240 °C with heating and cooling rate of 10 °C/min with a Seiko DSC-220 instrument. T_g values were determined from the second heating run.

Results and Discussion

E-N copolymerizations were carried out with complex **1** using dried MAO as a cocatalyst at 0 °C and 20 °C at different norbornene concentration under atmospheric pressure of ethene. The results of the polymerization are shown in Table 1. The catalyst system showed higher activity at higher temperature. The polymerization activity increased with increasing norbornene ratio in feed at 20 °C whereas the opposite trend was observed at 0 °C.

Table 1. Copolymerization of ethene and norbornene with **1** using dried MAO as cocatalyst.$^{a)}$

Temp. (°C)	N/E (mol/mol)	Activity$^{b)}$	Nor. in copoly. (mol-%)	M_nx10$^{-4\ c)}$	M_w/M_n^c	$T_g^{d)}$
0	6	111	44	10.3	1.26	132
”	9	101	49	9.8	1.21	153
”	13	76	53	7.8	1.16	166
20	1.4	176	25	4.5	1.74	47
”	5	480	44	7.1	1.34	126
”	10	675	54	7.9	1.31	167

$^{a)}$Polymerization conditions: Ti = 20 μmol, Al/Ti =400, solvent = toluene, total vol. = 30 mL, ethene = 1 atm, time = 30 min at 0 °C and 2 min at 20 °C, ethene concentration 0.2M at 0 °C and 0.12 at 20 °C.

$^{b)}$Activity = kg$_{(poly)}$. mol^{-1}$_{(Ti)}$. h^{-1}.

$^{c)}$Molecular weight and molecular weight distributions were measured by GPC analysis using polystyrene standards.

$^{d)}$Glass transition temperature was measured with differential scanning calorimeter and the midpoint of the transition was used as the T_g value.

The ^{13}C NMR spectrum of an E-N copolymer produced with **1** is shown in Figure 1, which differs from that of the alternating structure, which should show only five signals[2, 6]. The

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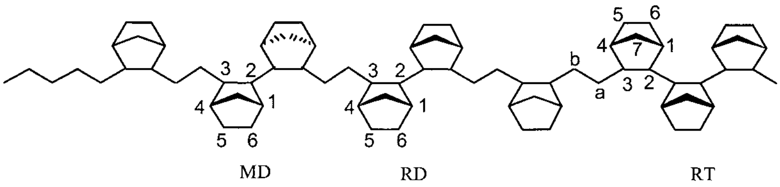
signals of NN dyad and NNN triad reported by Tritto *et al.*[7] were observed as follows: 28.60 and 32.47 ppm, C5/C6 of *meso* ENNE; 29.91 and 31.69 ppm, racemic-ENNE; 33.8 ppm, C7 of ENNE; 35.08 and 36.32 ppm, NNN. No signal was observed above 52 ppm, where the signals of C2/C3 carbons of meso-NNN sequences should appear as reported earlier.[8] New signals appeared from 39.0 to 40.7 ppm and at 35.08 and 36.32 ppm which had never been observed in the E-N copolymers reported so far. They can be tentatively assigned to C1/C4 (39.0-40.7 ppm) and to C7 (35.08 and 36.32 ppm) carbons of racemic-NNN sequence.



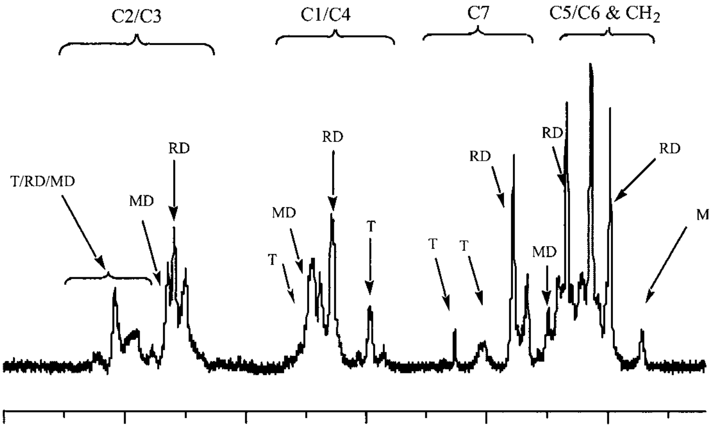


Figure 1. ^{13}C NMR spectrum of the E-N copolymer (norbornene content 53 mol-%) produced with **1** at 0°C

The incorporation of norbornene in the copolymer was calculated by eq. 1.

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

where $I_{C2/3}$ and $I_{C1/4}$ and I_{C7} are the peak intensities of C2/C3, C1/C4 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 1.

The norbornene content was dependent on the comonomer feed ratio and the copolymers containing ca. 53 mol-% of norbornene were obtained at the highest feed ratio employed at both temperatures. The T_g values were determined by a differential scanning calorimeter (DSC). The temperature at the midpoint of phase transition was used to determine the T_g value. The T_g values of the copolymers with 53 mol-% norbornene were around 166 °C (Figure 2).

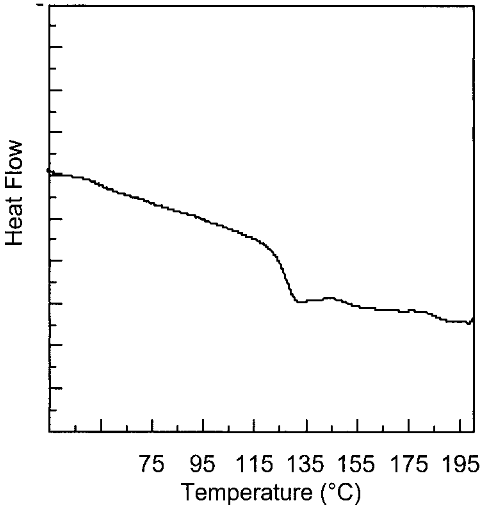

Figure 2. DSC curve of E-N copolymer with 53 mol-% norbornene

The copolymers had high M_n values and narrow M_w/M_n, which became narrower with increasing norbornene ratio in feed. Tritto *et al.* reported that high norbornene concentration and low polymerization temperature below 50 °C were the key factors to achieve "quasi-living" nature of E-N copolymerization with metallocene-MAO systems.[10,11] The extremely narrow polydispersity (M_w/M_n = 1.16) was observed at N/E = 13 feed ratio at 0 °C, which suggests that

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the living copolymerization of ethene and norbornene should proceed with these conditions.

To confirm the living nature at 0 °C, the dependence of M_n on polymerization time was investigated by sampling method: 2 mL of reaction mixture was sampled with a syringe at every 10 minutes. The GPC curves of polynorbornene obtained by sampling were shifted to the higher molecular weight region with increasing polymerization time keeping narrow M_w/M_n (Figure 3). The M_n and M_w/M_n values vs time are plotted in Figure 4. The M_n values linearly increased against polymerization time. The yield of the sampled copolymer also increased linearly with polymerization time (Figure 5). These results indicate that the living E-N copolymerization proceed at 0 °C. The slightly broader M_w/M_n value at 20 °C suggests the presence of some chain transfer reaction.

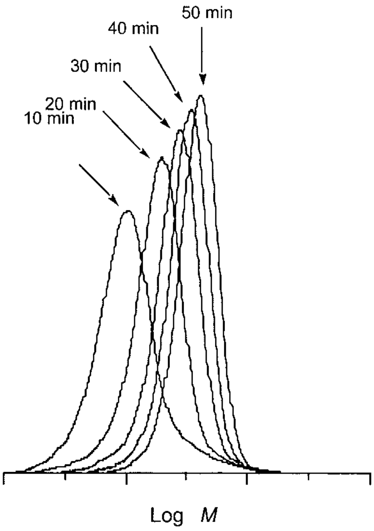

Figure 3. GPC curves of polynorbornene obtained by sampling method at 0 °C

In conclusion, complex **1** activated by dried MAO conducted living copolymerization of ethene and norbornene at 0 °C, and gave random copolymer with high T_g value.

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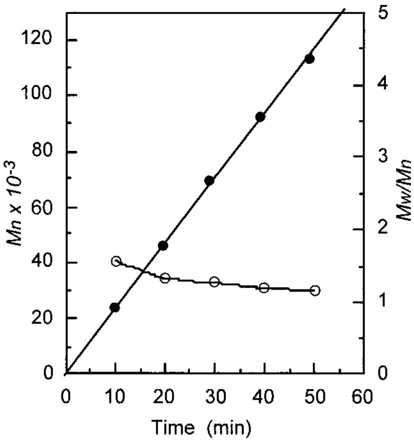

Figure 4. Plots of *M*n (●) and M_w/M_n (○) vs time in E-N copolymerization with **1** at 0°C

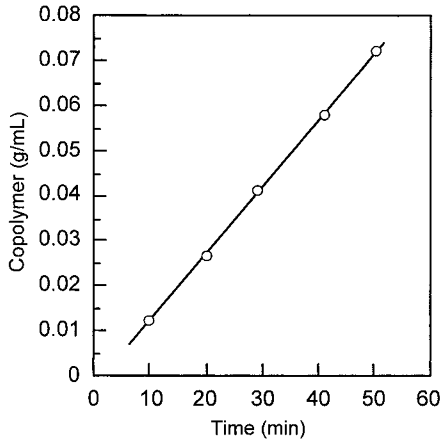

Figure 5. Copolymer concentration in reaction mixture as a function of time

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