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Living Polymerization of Norbornene via Vinyl Addition with *ansa*-Fluorenylamidodimethyltitanium Complex

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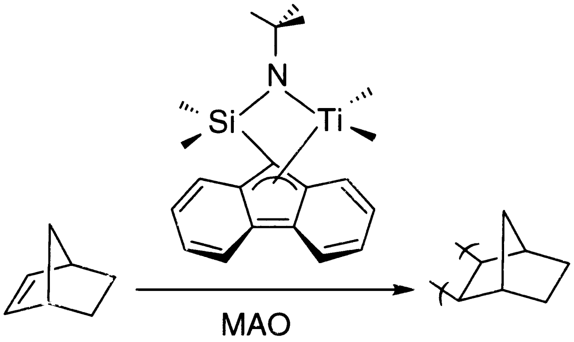
Polycycloalkenes, via vinyl addition, show special properties, i.e., good heat resistivity, mechanical strength, transparency, and excellent dielectric properties, that allow their use as a coating material of optical disks and as interlevel dielectrics in the microelectronics industry, which led to an increasing interest in this area of polyolefin research.[1]



Vinyl addition polymerization of norbornene was first reported with $TiCl_4/AlR_3$ in the early 1960s.[2] Pd(II)-based complexes were found to be a better catalyst for the polymerization very soon thereafter.[3] Recently, Ni and Co compounds have been reported to produce polynorbornene via vinyl addition with a good activity.[4,5] The research on norbornene polymerization with early transition metal single-site catalysts has been directed to ring-opening metathesis polymerization rather than vinyl polymerization because of their low activity for the latter. A number of C_2 and C_s symmetric zirconocenes and (t-$BuNMe_2SiMe_4Cp)TiCl_2$ ($CGCTiCl_2$) showed very low activity for addition polymerization of norbornene, and the polynorbornenes produced were insoluble in common solvents.[6,7] The monocyclopentadienyltitanium catalyst system [$CpTi(OBz)_3$/MAO] showed better activity than the other metallocene catalysts.[8] Recently, Kaminsky et al. found a chelating titanium alkoxide, and $CGCTiCl_2$ combined with MAO conducted vinyl polymerization of norbornene and switched the mechanism from vinyl addition to metathesis by the addition of phenylactylene during the polymerization.[9] The vinyl polymerization of norbornene with zirconocenes using methylaluminoxane or borate has also been described in a number of patents.[10]

Table 1. Polymerization of Norbornene with (t-$BuNMe_2SiFlu)TiMe_2$ (1) and (t-$BuNMe_2SiMe_4Cp)TiMe_2$ (2) Using Dried MAO as Cocatalyst at Different Temperatures[a]

entry	catalyst	temp (°C)	polym time (min)	yield (g)	activity[b]	conv (%)[c]	$M_n \times 10^{-4}$ [d]	M_w/M_n [d]
1	**1**	0	120	1.44	36	43	18.7	1.48
2	**1**	20	5	1.81	1087	56	29.6	1.26
2	**1**	40	5	2.73	1637	81	24.0	1.13
3	**2**	0	120	trace				
4	**2**	40	120	0.18	2.2	6	n.d	n.d

[a] Polymerization conditions: Ti = 20 μmol, Al/Ti = 400, [norbornene] = 1.2 M, solvent = toluene, total volume = 30 mL. [b] Activity = $kg_{(polymer)}\ mol^{-1}{}_{(Ti)}\ h^{-1}$. [c] Conversion was calculated from yield. [d] Number-average molecular weight and molecular weight distributions were measured by GPC analysis using polystyrene standard.

The precise control of molecular weight and molecular weight distribution and synthesis of well-defined block copolymer can be achieved by living polymerization. Development of the single-site catalysts has resulted in a variety of living systems for olefin polymerization. Although there are many living systems for metathesis ring-opening polymerization of norbornene, only the Pd-based catalyst $[Pd(CH_3CH_2CN)_4][BF_4]_2$ has been reported to produce polynorbornene via vinyl addition in a living manner at 0 °C when the mixture of chlorobenzene and nitrobenzene (2:1) was used as solvent.[3f] We have previously reported that (t-$BuNMe_2SiFlu)$-$TiMe_2$ (**1**) activated with $B(C_6F_5)_3$ produced syndiotactic-rich polypropene at −50 °C in a living manner and the use of Me_3Al-free methylaluminoaxane (dried MAO), which was prepared by repeated vacuum-drying and hexane washing, raised the living polymerization temperature up to 0 °C accompanied by the improvement of syndiospecificity.[11] On the other hand, almost atactic polypropylene was produced with $CGCTiMe_2$ (**2**) in a quasi-living manner under the same polymerization conditions.[12]

In this communication, **1** and **2** were applied for the polymerization of norbornene in the presence of dried MAO, and **1** was found to produce vinyl addition polymer in a living fashion at ambient temperature with high activity.

Polymerization of norbornene was performed with **1** and **2** activated with dried MAO at 0, 20, and 40 °C. The results obtained with both catalyst systems are compared in Table 1. The activity strongly depended on the structure of complexes and polymerization temperature. **1** showed high activity at 20 and 40 °C but low activity at 0 °C, and **2** showed very low activity even at 40 °C. Waymouth et al. reported that $CGCTiCl_2$ combined with MAO showed low activity even at high norbornene concentration, and the activity was increased with raising temperature.[7] We assume that **1** provides larger aperture of coordination sphere that favors easy access of norbornene to propagate.[13] The polynorbornenes produced with **1** are highly soluble in chlorinated aromatic solvents, like *o*-dichlorobenzene as GPC solvent, which allows us to characterize the polymers by gel permeation chromatography (GPC). On the other hand, the polynorbornene produced with **2** was insoluble in the GPC solvent and could not be characterized.

Complex **1**, activated with dried MAO, was found to produce high molecular-weight polymers with narrow

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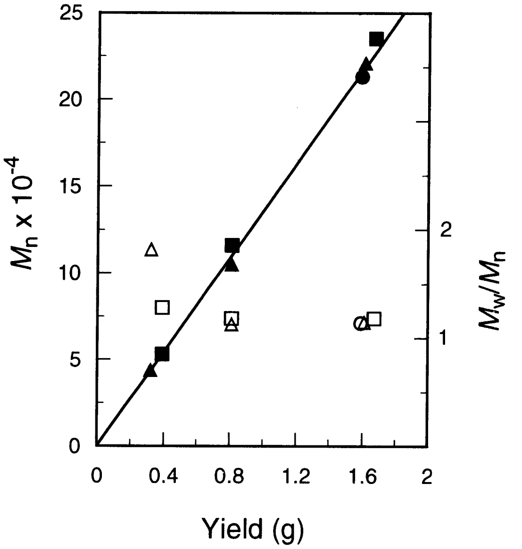

Figure 1. Plots of M_n and M_w/M_n of polynorbornenes obtained with **1** at 20 °C (▲, △) and at 40 °C (■, □) as a function of polymer yield. M_n and M_w/M_n values of postpolymerization at 20 °C (●, ○). Ti = 20 μmol, Al/Ti = 400, total volume = 30 mL.

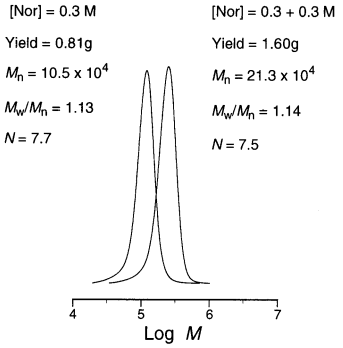

Figure 2. GPC curves of polynorbornenes obtained with **1** at 20 °C. N is the number of polymer chains.

molecular-weight distribution. Since it was of interest to investigate the living nature of this catalyst system, two series of norbornene polymerization were carried out with **1** at 20 and 40 °C by changing monomer concentration in feed. The conversion of norbornene was quantitative, and the number of polymer chains was constant. As shown in Figure 1, the M_n values increased linearly against the polymer yield with keeping narrow molecular weight distributions at 20 and 40 °C. In the postpolymerization experiment at 20 °C, the same amount of norbornene (0.30 M) was added after 30-min polymerization, and the polymerization was conducted for an additional 1 h. The yield became almost double, and the GPC curve shifted to the higher region keeping narrow polydispersity (Figure 2), and the M_n value was also double that of prepolymerization. Although the postpolymerization at 40 °C proceeded quantitatively, the molecular weight was not double of that of prepolymerization, and the number of polymer chains slightly increased. These results indicate the continuous chain growth at 20 °C and some chain transfer at 40 °C probably in the absence of monomer.

Thermal gravimetric analysis (TGA) showed that the polynorbornenes produced (M_n = 240 000) are stable up to 400 °C under a nitrogen atmosphere, and 5% weight loss was recorded at 423 °C. Differential scanning calorimetry (DSC) studies did not show any melting transition heating to 400 °C under a nitrogen atmosphere. Since the glass transition temperatures of polynorbornenes should be very close to decomposition, it is difficult to determine them correctly.[3g]

In the ^{1}H NMR spectrum (in $C_2D_2Cl_4$) of polynorbornenes obtained with **1**, a broad signal containing four main peaks are observed around 0.99−2.30 ppm,[4a] methylene (CH_2) protons at 0.99−1.48, and methine (CH) protons at 1.79−2.30 ppm. No peak assignable to olefinic protons indicates the vinyl addition of norbornene. Wu and Lu recently reported the selective vinyl polymerization of norbornene by monocyclopentadienyltitanium tribenzyloxide combined with MAO, which also gave soluble polymers.[8]

In summary, the titanium complex **1** combined with dried MAO performed vinyl polymerization of norbornene with extremely high activity and produced high-molecular-weight soluble polymers with narrow molecular-weight distributions at 20 and 40 °C. The linear relationship between M_n against polymer yield and the results of postpolymerization indicate the living polymerization with this system at 20 °C. To the best of our knowledge, this is the first example for living polymerization of norbornene via vinyl addition with a Ti-based catalyst. This living system would be applied for synthesizing a variety of norbornene-based block copolymers.

Supporting Information Available: Experimental procedures, results of polymerization with various monomer concentrations and postpolymerization, ^{1}H NMR spectrum of polynorbornene, and DSC and TGA profiles of polynorbornenes. These materials are available free of charge via the Internet at http://pubs.acs.org.

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