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Catalytic Synthesis of Monodisperse Polypropylene Using a Living Polymerization System with *ansa*-Fluorenylamidodimethyltitanium-Based Catalyst

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Since the discovery of the group 4 metallocene catalysts by Kaminsky and co-workers,[1] various homogeneous Ziegler−Natta catalysts, i.e., so-called single-site catalysts, have been investigated for new olefin polymerization catalysis.[2−5] One of the new areas developed by the single-site catalysts is living polymerization of olefins.[6−8] Living polymerization is useful for the synthesis of polymers with precisely controlled structures such as monodisperse polymers, terminally functional polymers, and block copolymers. Living polymerization is however not an efficient method of polymer production because one initiator produces only one polymer chain.

Inoue et al. showed the method to overcome the defect of living polymerization in anionic ring-opening polymerization catalyzed by an aluminum−porphyrin complex, where the addition of a protic compound which usually stops anionic polymerization still gave monodisperse polymers, and the number of polymer chains was proportionally increased with the number of the protic compound and named “immortal” polymerization. In the immortal polymerization, monodisperse polymers and block copolymers are catalytically obtained because the propagation chain and the protic compounds can reversibly exchange, and the exchange rate is much faster than that of propagation.[9−12]

Gibson et al. reported the synthesis of monodisperse polyethylene with the same concept. They conducted ethylene polymerization with a bis(imino)pyridineiron catalyst in the presence of $ZnEt_2$. All the Zn−Et bonds were converted to Zn−polyethylene and a nickel-catalyzed displacement of the polyethylene chain with ethylene gave α-olefins (number-average molecular weight (M_n) ≈ 700) with a Poisson distribution accompanied by the regeneration of $ZnEt_2$.[13] If Zn−alkyl species can transfer propagation polymer chain between two different active species after the insertion of a certain amount of monomers, multiblock copolymers should be obtained when each active species has a different copolymerization ability. Dow Chemical Co. recently reported the catalytic production of multiblock copolymers composed of polyethylene and poly(ethylene-*ran*-1-octene) with this concept and named “chain shuttling” polymerization.[14]

On the contrary, monodisperse polymer should be obtained even in the presence of a chain-transfer reagent if the propagation rate is much faster than that of the chain transfer. In this case, monodisperse polymers can be catalytically obtained by the successive addition of the same amount of monomer at a certain interval. The Mitsui group actually reported the catalytic production of monodisperse Zn-terminated polyethylenes with a bis(phenoxyimine)titanium dichloride activated by methylaluminoxane, where 80 equiv of $ZnEt_2$ was added after the first polymerization and the second polymerization was conducted in the presence of $ZnEt_2$.[15]

Table 1. Postpolymerization of Propylene by 1 Activated with dMMAOs[a]

entry	propylene (g)	cocatalyst	yield (%)	M_n [b] ($\times 10^4$)	M_w/M_n [b]	N[c] (μmol)
1	0.63	dMMAO(0.4)	100	4.9	1.25	12.9
2	0.63 + 0.63	dMMAO(0.4)	99	9.4	1.28	13.4
3	0.63	dMMAO(1.8)	100	5.0	1.49	12.6
4	0.63 + 0.63	dMMAO(1.8)	100	5.2	1.42	24.3
5	0.63 + 0.63 + 0.63	dMMAO(1.8)	100	6.7	1.82	28.2
6	0.63 + 0.63[d] + 0.63	dMMAO(1.8)	100	4.8	1.43	39.0

[a] Polymerization conditions: toluene = 40 mL, Ti = 20 μmol, Al = 4.0 mmol, each polymerization time = 30 min. [b] Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration. [c] Calculated from yield and M_n. [d] After the second polymerization, 20 μmol of TIBA had been added, and the third portion of propylene was added after 20 min.

We have previously reported that [*t*-BuNSiMe$_2$(3,6-*t*-Bu$_2$Flu)]TiMe$_2$ (**1**) activated by trialkylaluminum-free modified methylaluminoxane (dMMAO), which was prepared from a toluene solution of MMAO by vacuum-drying and dissolving in heptane repeatedly, conducted living polymerization of propylene in heptane at 0 and 25 °C.[16] If we select an adequate chain-transfer reagent with a suitable amount, we could obtain monodisperse polypropylene catalytically using this living system. From this viewpoint, we reinvestigated propylene polymerization with **1**−MMAO and found that the presence of a suitable amount of TIBA produced monodisperse polypropylene by the successive addition of the same amount of propylene. This Communication reports the preliminary results of the catalytic synthesis of monodisperse polypropylenes.

We prepared MMAOs containing different amounts of TIBA by controlling the removal of TIBA from MMAO. The amounts of TIBA in each MMAO were determined by ^1H NMR in the mixture of toluene-d_8 and tetrahydrofuran-d_8 (1:4 v/v) to be 6.3, 1.8, and 0.4 mol %. The MMAOs containing 1.8 and 0.4 mol % of TIBA are abbreviated to dMMAO(1.8) and dMMAO(0.4), respectively.

Postpolymerization of propylene was performed with **1** activated by dMMAO(0.4) and dMMAO(1.8) in toluene at 20 °C: the first-step polymerization was conducted with 0.63 g of propylene for 30 min, and the second-step polymerization was continued for another 30 min after the addition of the same amount of propylene. The results are summarized in Table 1.

In both steps, the conversions were quantitative regardless of the cocatalyst used. In the **1**−dMMAO(0.4) system, the number-average molecular weight (M_n) of the second-step polymer became almost double of that of the first-step polymer with keeping the narrow molecular weight distribution (MWD) and the number of polymer chains (N) (entries 1 and 2, Table 1). The GPC curves of the polymers obtained are illustrated in Figure 1. The curve of the second step perfectly shifted to the higher molecular weight region. The results testified that propylene polymerization proceeded in a living manner with **1**−dMMAO(0.4) in toluene at 20 °C.

In the **1**−dMMAO(1.8) system, the M_n and N values of the polymer produced in the first step were almost the same with

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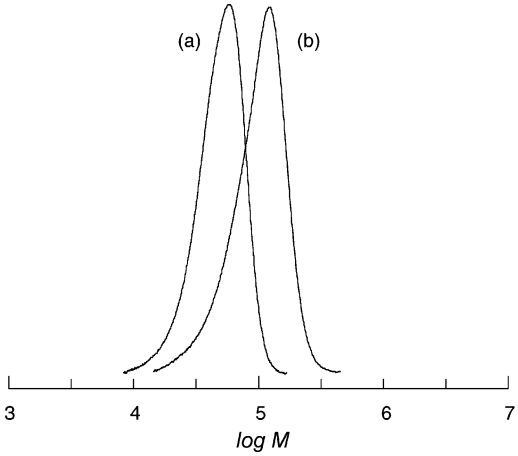


Figure 1. GPC curves of polypropylenes obtained before (a) and after (b) postpolymerization with **1**−dMMAO(0.4).

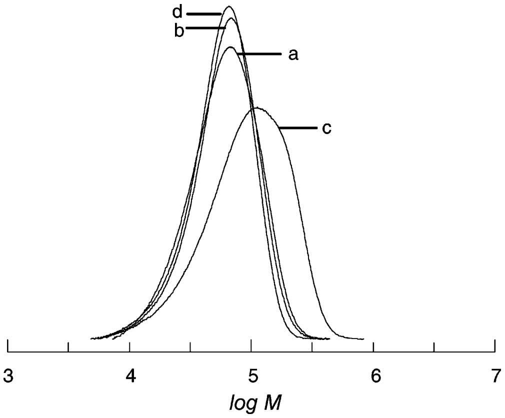


Figure 2. GPC curves of polypropylenes obtained in postpolymerization with **1**−dMMAO(1.8): (a) entry 3, (b) entry 4, (c) entry 5, and (d) entry 6.

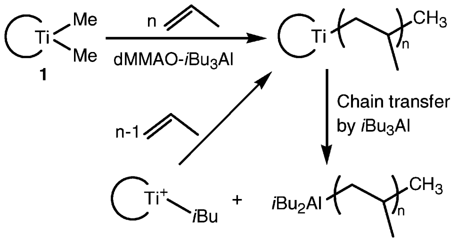
those obtained by **1**−dMMAO(0.4) although the MWD was slightly broader than that of the dMMAO(0.4) system. The result indicates that the chain transfer with TIBA in dMMAO(1.8) was also negligible. After the postpolymerization, however, the M_n value did not change, and consequently the N value became double. The GPC curve of the second-step polymer was almost the same with that of the first-step one (Figure 2b), although the MWD became slightly narrower.

The broader MWD of dMMAO(1.8) should be ascribed to slow initiation because we previously reported that the addition of a small amount of TIBA or trimethylaluminum retarded the initiation in the living polymerization of propylene with $[ArN(CH_2)_3NAr]TiMe_2$−dMMAO.[17] The narrower MWD in the second step (Figure 2b) than in the first step (Figure 2a) supports this assumption.

These results indicate that TIBA in dMMAO(1.8) worked efficiently as a chain-transfer reagent only after all the propylene monomers had been consumed, and the new living polymer chains were generated by the addition of successive propylene monomers (Scheme 1).

To check the repeatability of this method, we continued third-step polymerization after the second step (entry 5, Table 1). The conversion was quantitative, and the M_n value was increased accompanied by broadening of MWD and a slight increase of N value. The GPC curve of the third-step polymer appeared in the higher molecular weight region remaining the low molecular weight fraction that corresponds to the GPC curves of the previous steps (Figure 2c). These results can be interpreted by the incomplete chain transfer with TIBA after the second polymerization because TIBA had been consumed in the chain transfer after the first polymerization.

Scheme 1



We therefore added TIBA with the same amount of the Ti complex after the second polymerization, and the third-step polymerization was started after 20 min by the addition of the same amount of propylene (entry 6, Table 1). The conversion was quantitative, and the M_n value obtained was the same with that of the first-step polymer, and consequently the N value became 3 times of that of first step. The GPC curve of the polymer obtained in the third step was almost the same with that in the second step (Figure 2d). These results indicate that the catalytic formation of monodisperse polypropylenes was achieved with the present catalytic system in the presence of a suitable amount of TIBA.

In summary, the $[t\text{-BuNSiMe}_2(3,6\text{-}t\text{-Bu}_2\text{Flu})]\text{TiMe}_2$ (**1**)−dMMAO(0.4) catalytic system conducted living polymerization of propylene in toluene at 20 °C. The catalytic system also gave monodisperse polypropylene in the presence of a suitable amount of TIBA, and the repeated addition of the same amount of propylene produced the polypropylene with the same molecular weight and molecular weight distribution because of the selective chain transfer after the monomer consumption.

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Supporting Information Available: Experimental procedures and the ^1H NMR spectra of MMAOs. This material is available free of charge via the Internet at http://pubs.acs.org.

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