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First Controlled Block Copolymerizations of Higher 1-Olefins with Polar Monomers Using Metallocene Type Single Component Lanthanide Initiators

Guillaume Desurmont, Tohru Tokimitsu, and Hajime Yasuda*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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Block or random copolymerizations of olefins with polar monomers remain an ultimate goal in the polyolefin chemistry since these processes promise to endow the hydrophilic materials with remarkably high adhesive, dyeing, and moisture absorption properties. Although random copolymerizations of olefins with methyl methacrylate (MMA)[1] or vinyl acetate[2] have been used as an amendment process in industry, this traditional technique possesses only a limited utility because it produces elastomers with complex structures only under drastic conditions. Grafting of polyolefins with polar poly(MMA) or poly(acrylonitrile) also gave structurally rather complex branched polymers.[3] Block copolymerizations of ethylene with polar monomers such as MMA, alkyl acrylate, and ϵ-caprolactone (CL)[4] and the block copolymerization of norbornene derivatives bearing polar substituents using the ROMP (ring-opening metathesis polymerization) technique[5] may be the sole example of this type of sequential addition polymerization. Recently, Brookhart et al. reported the random copolymerization of olefins with alkyl acrylates, but the resulting acrylate unit is located primarily at the terminal end of branches. In this sense, the resulting polymers are not the real random copolymers.[6,7]

Despite the extensive studies on the living polymerization systems, no type of initiator has carried out block or random copolymerizations of 1-olefins with polar monomers. We describe herein the first example of well-controlled block copolymerization of 1-olefins with MMA or CL using unique dual catalytic function of organolanthanide complexes toward both polymerizations of polar[8−10] and nonpolar monomers[11,12] using bridged $Me_2Si(C_5R_4)_2LnR$ type complexes. These initiators are highly active by themselves for the copolymerization without the presence of any cocatalyst such as MAO or borate derivatives.

The block copolymerization of 1-pentene or 1-hexene with MMA or CL was realized by a two-step polymerization procedure using complexes **1** and **2** (Scheme 1), whose structures have been characterized by ^{1}H NMR spectra[13] and X-ray analyses,[14,15] i.e., homopolymerization of 1-pentene (5 mmol) or 1-hexene (5 mmol) at 20 °C in toluene under atmospheric pressure, followed by the reaction of MMA (10 mmol) or CL (10 mmol). In sharp contrast to the rapid polymerization of ethylene, the polymerizations of 1-pentene and 1-hexene proceeded rather slowly and completed in 24−32 h to give poly(1-pentene) of $M_n = 2.8 \times 10^4$ with $M_w/M_n = 1.51$ and poly(1-hexene) of $M_n = 5.3 \times 10^4$ with $M_w/M_n = 2.46$ in ca. 90% yield using complex **1**. The catalysis of complex **2** is very low as compared with that of **1**. Therefore, the addition of MMA or CL was carried out before completing the polymerization of 1-olefins (after 4 h polymerization). Bridged structures of **1** and **2** should be broken upon monomer addition as illustrated in Figure 1. Such dissociation was reported for bridging $[(C_{13}H_8)SiR_2(C_5H_4)Ln(\mu\text{-Cl})]_2$ (Ln = Dy, Y) complexes which converted monomeric $SiR_2(C_{13}H_8)(C_5H_4)LnCH$-

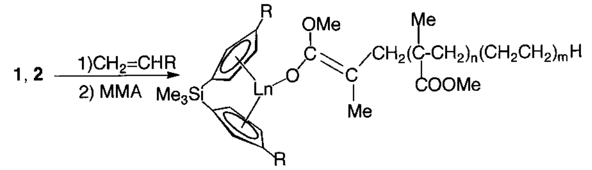

Figure 1. Proposed reaction mechanism for block copolymerization.

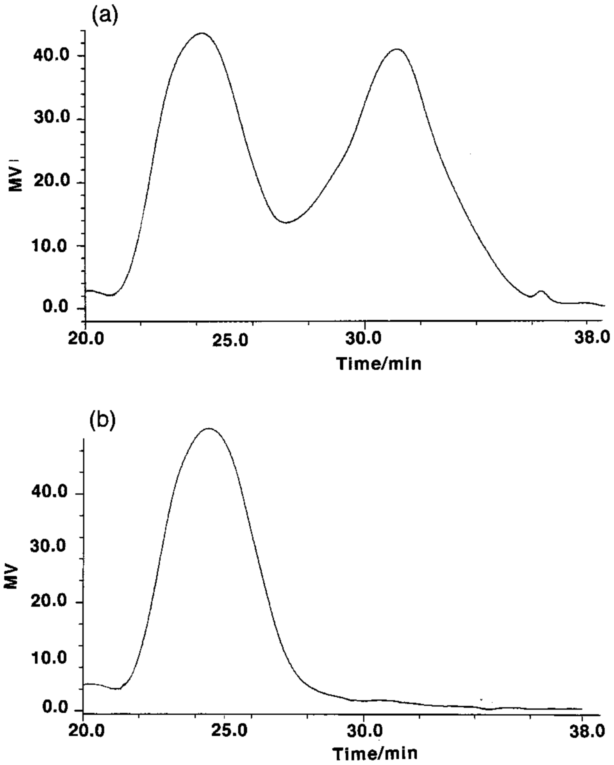

Figure 2. GPC profiles of poly(1-hexene)-*block*-poly(MMA) (a) before and (b) after washing with hexane.

Scheme 1

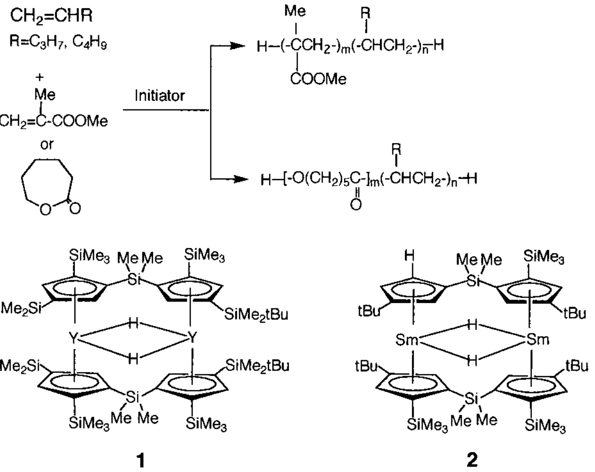

Table 1. Block Copolymerizations of 1-Pentene and 1-Hexene with MMA and CL[a]

initiator	olefin	polar monomers	poly(1-olefin) block $M_n \times 10^{-3\,b}$	poly(1-olefin) block $M_w/M_n{}^b$	polar polymer block $M_n \times 10^{-3\,c}$	polar polymer block $M_w/M_n{}^b$	1-olefin/polar (mol/mol)
1	1-pentene	MMA	13.5	1.41	34.2	1.77	36:64
2	1-pentene	MMA	6.6	1.58	11.5	1.68	45:55
1	1-hexene	MMA	21.0	1.86	35.9	1.99	41:59
2	1-hexene	MMA	5.5	2.00	6.0	2.15	52:48
1	1-pentene	CL	13.5	1.41	124.6	2.15	15:85
2	1-pentene	CL	6.6	1.58	78.7	2.03	12:88
1	1-hexene	CL	21.0	1.86	174.8	2.52	14:86
2	1-hexene	CL	5.5	2.00	60.4	2.09	11:89

[a] Polymerization conditions: (1) Polymerization of 1-olefins: 0.1 mmol of intiator, 5 mmol of 1-olefin, 4 h in 7 mL of toluene, 20 °C. (2) Polymerization of polar monomers: 10 mmol of polar monomer, 1 h, toluene, 20 °C. [b] Determined by GPC using standard poly(styrene) whose M_w values were determined by light scattering method. Solvent, $CHCl_3$. [c] Estimated from the molar ratio of poly(1-olefin) to polar polymer determined by ^1H NMR.

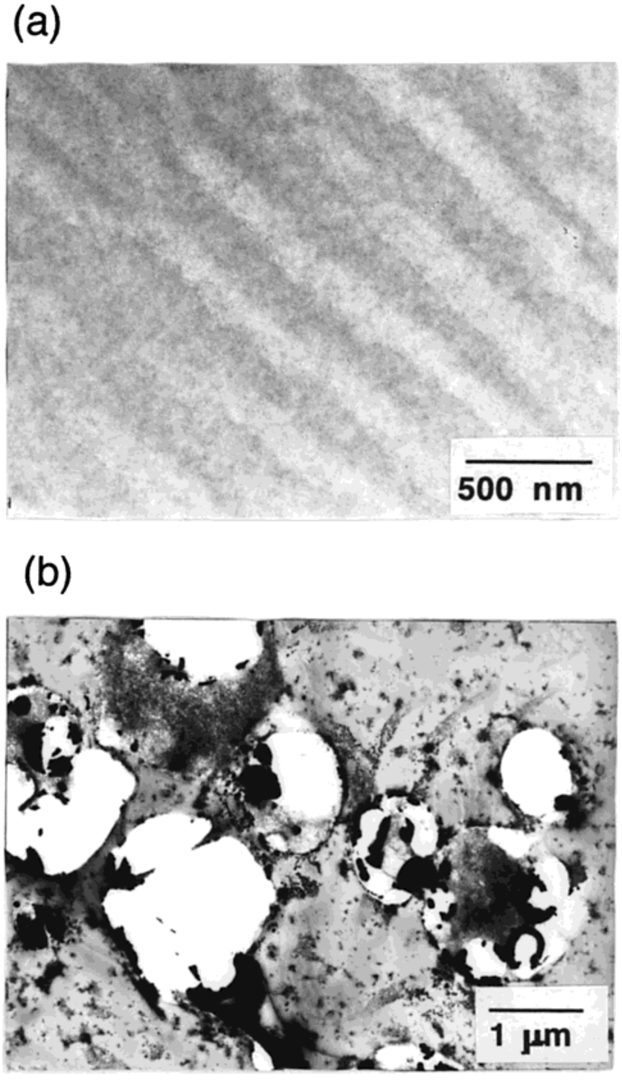

Figure 3. TEM profiles of (a) poly(1-hexene)-*block*-poly(MMA) (40:60) and (b) blended poly(1-hexene)/poly(MMA)(40/60): gray zone poly(1-hexene), black particles RuO_4, poly(MMA) white zone.

$(SiMe_3)_2$ species by introduction of a bulky $CH(SiMe_3)_2$ ligand.[16] Resulting polymers were quenched with excess methanol, and their GPC profiles showed a bimodal pattern (Figure 2a). Washing of the resulting polymer with hot hexane at 45 °C affords the pure block copolymer with unimodal pattern (Figure 2b). Molecular weights of the polymers were calculated from the ratio of poly(1-olefin) unit to poly(MMA) or poly(CL) unit determined by ^1H NMR (Table 1). The fraction extracted with hexane was composed of only homo-polyolefin with the CHR═CH− polymer end (major part, 80 mol %, δ, m, 5.3 ppm by the ^1H NMR) and CH_2═CR− end (minor, 20 mol %, δ, d, 4.9 ppm) resulting from the β-hydride elimination of poly(1-olefin)s. Therefore, the polymerization of a 1-olefin is considered to proceed principally by the 2,1-insertion of 1-olefins. The reaction of MMA with poly(1-olefin) proceeds slowly, while the reaction with CL undergoes very rapidly. Therefore, the relative ratio of poly(1-olefin) to poly(MMA) can be easily controlled voluntarily in the range of 20:80 to 80:20 (mol: mol) by adjusting the reaction time or reaction temperature.

^1H and ^{13}C NMR spectra in addition to the IR adsorption of resulting polymers are superimposable upon those of the corresponding samples prepared by mixing respective homopolymers. Reversed addition of the respective monomers (MMA or CL and then an 1-olefin), however, did not perform the block copolymerization at all even in the presence of excess 1-olefins. Only homo-polymerization of the polar monomer occurred in good yield.

The TEM profiles of the resulting polymers were measured to understand their unique morphologies. The 1-hexene component was heavily stained by RuO_4, but the MMA component was not. The resulting poly(1-hexene)-*block*-poly(MMA)(45:65) revealed no clear microphase separation, and the poly(1-hexene) part (dark zone) is well permeated into the poly(MMA) part (white zone) (Figure 3a). In sharp contrast to the TEM profile of the block copolymer, a blended polymer, poly(1-hexene)/poly(MMA) in a 45:65 ratio, showed the large poly(MMA) (size ∼1 μm) spherulites (white zone) dispersed in poly(1-hexene) component (gray zone, Figure 3b). The remaining RuO_4 is observed also on the poly(MMA) surface. Thus, high diffusivity of the poly(MMA) permeants in the poly(1-hexene) component was observed for the block copolymer.

Dyeing of the resulting poly(1-hexene)-*block*-poly(MMA) film (100:3, M_n = 10 300) with dispersive dyes (Dianix AC-E) resulted in successful deep coloration into three primary colors, while the homo-poly(1-hexene) itself was inert to these dyes. Thus, the present copolymers display a very desirable high chemical reactivity.

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