New Approach to Block Copolymerizations of Ethylene with Alkyl Methacrylates and Lactones by Unique Catalysis with Organolanthanide Complexes

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Block copolymerizations of ethylene or propylene with polar monomers remain an ultimate goal in polyolefin engineering since these processes promise to endow hydrophobic polymeric 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 put to practical use as an amendment process, this traditional technique possesses only a limited utility because it produces elastomers with variable composition only under drastic conditions (high temperature and high pressure). Grafting of polyolefins with polar poly(MMA) or poly(acrylonitrile) also gave structurally rather complex branched polymers.[3] In this context, more intelligent synthetic methodology is required for realizing structurally well-defined linear copolymers comprised of nonpolar and polar polymer units. A block copolymerization of propylene with MMA by a $V(acac)_3/AlEt_2Cl$ system may be the sole example of this type of sequential addition polymerization,[4] while block copolymerizations of norbornene derivatives bearing polar substituents have recently been attained by using ROMP (ring-opening metathesis polymerization) technique.[5]

We describe herein the first example of well-controlled block copolymerizations allowed by the unique dual catalytic function of $LnR(C_5Me_5)_2$ (Ln = Sm, Yb, Lu; R = H, Me) organolanthanide(III) complexes toward both polar and nonpolar olefins (Scheme I). This idea occurred from our previous finding that the alkyl- or hydridolanthanides exhibit a versatile catalytic activity, i.e., for initiating the ideally living polymerization of MMA, a typical polar monomer, leading to remarkably high molecular weight polymers (M_n > 100 000) with an exceptionally narrow polydispersity (M_w/M_n < 1.05).[6] The excellent catalytic activity of $(C_5Me_5)_2LnR$ toward nonpolar monomers has already been reported in the case of the ethylene polymerization.[7]

The desired copolymerization of ethylene with MMA was achieved by a two-step procedure: homopolymerization of ethylene (17–20 mmol) with $SmMe(C_5Me_5)_2$(THF) or $[SmH(C_5Me_5)_2]_2$ (0.05 mmol) at 20 °C in toluene under atmospheric pressure, followed by sequential addition of MMA (10 mmol; Table I). The initial ethylene polymerization proceeds very rapidly and completes in 2 min to give the polymer of M_n = ca. 10 100 with M_w/M_n = 1.42–1.44. The subsequent copolymerization with MMA proceeds rather slowly, and reaction was carried out for 2 h at 20 °C in that case. Resulting polymers are soluble

Scheme I

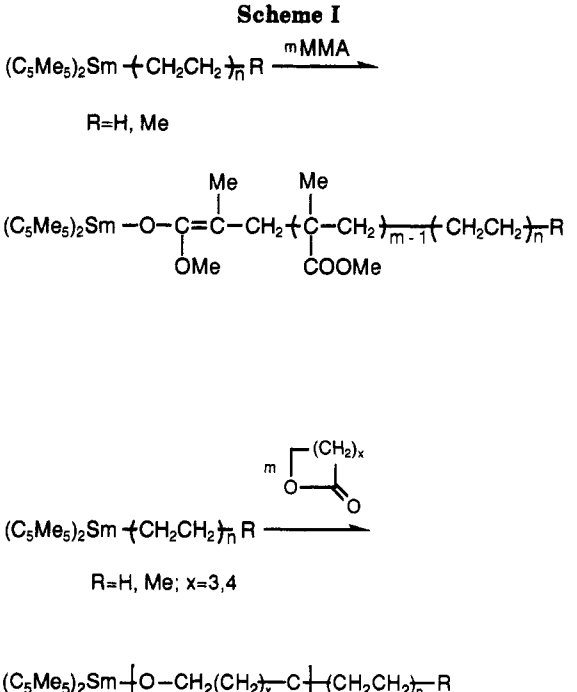

Table I
Block Copolymerization of Ethylene with Polar Monomers Catalyzed by Organolanthanides(III)[a]

polar monomer	polyethylene block $M_n \times 10^3$	polyethylene block M_w/M_n	polar polymer block $M_n \times 10^3$ [c]	polar polymer block M_w/M_n [d]	unit ratio
MMA	10.3	1.42	24.2	1.37	100:103
	26.9	1.39	12.8	1.37	100:13
	40.5[b]	1.40	18.2	1.90	100:12
MA	6.6	1.40	15.0	1.36	100:71
	24.5	2.01	3.0	1.66	100:4
EA	10.1	1.44	30.8	2.74	100:85
	24.8	1.97	18.2	3.84	100:21
VL	10.1	1.44	7.4	1.45	100:20
	24.8	1.97	4.7	1.97	100:5
CL	6.6	1.40	23.9	1.76	100:89
	24.5	2.01	6.9	2.01	100:7

[a] Room temperature in toluene, catalyst $SmMe(C_5Me_5)_2$(THF). [b] Catalyst $[(C_5Me_5)_2SmH]_2$. [c] Determined by ^1H NMR with reference to M_n values of the initial polyethylene. [d] Apparent polydispersity of the AB copolymers.

in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene at 100 °C but insoluble in THF and $CHCl_3$, indicating quantitative conversion into the desired linear block copolymer.[8] Repeated fractionation of the block copolymer in hot THF did not change the molar ratio of the polyethylene to poly(MMA) blocks, whereas the poly(MMA) in the blend of polyethylene is easily extracted with THF. In fact, the elution volume for maximal GPC absorption shifted to a higher molecular weight region, keeping its initial unimodal pattern (Figure 1). No peak assignable to homopolyethylene was detected in the GPC trace of the product. The relative molar ratio of polyethylene to poly(MMA) blocks can be controlled voluntarily in the range of 100:1 to 100:103 when M_n of the initial polyethylene was fixed to ca. 10 300. ^1H and ^{13}C NMR spectra in addition to IR absorption of the resulting copolymers are superimposable upon those of the corresponding samples prepared by mixing respective homopolymers, and no signal assignable to a random copolymer was detected. The acceptable relative ratio of poly(MMA) to polyethylene units, however, decreased with an increase of M_n of the prepolymer, especially when its M_n exceeds ca. 12 000

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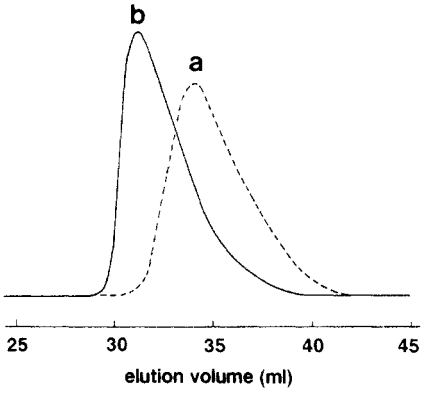

Figure 1. GPC traces of the polymers before and after incorporating MMA: (a) polyethylene with M_n = 5800, (b) poly(ethylene/MMA) with M_n = 29 600.

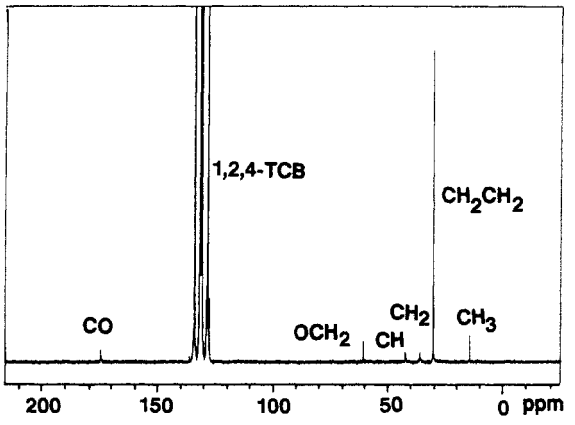

Figure 2. Block copolymer of ethylene with ethyl acrylate (100:14) with M_n = 40 100 after extraction with hot THF. Solvent: 1,2,4-trichlorobenzene.

where the polyethylene precipitates as fine colorless particles (diameter ca. 65–95 nm).[8] Encapsulation of the active sites by the crystalline polyethylene (mp 128 °C for the crude polymer) may inhibit the diffusion of MMA into the active sites and hence causes suppression of further copolymerization.

Noteworthy is the smooth block copolymerization of ethyl acrylate (EA) or methyl acrylate onto the growing polyethylene chain (M_n = 6600–24 800) by the sequential addition of these polar monomers. Living polymerization of these monomers has scarcely been reported because the chain transfer or termination occurs due to the high sensitivity of acidic α-hydrogen to the nucleophilic attack. However, the desired copolymerization occurs smoothly in this case. A typical ^{13}C NMR spectrum of block copoly(ethylene/EA) after extraction with THF is shown in Figure 2.

As an extension of this study, we have also explored the block copolymerizations of ethylene with lactones. Incorporation of δ-valerolactone and ϵ-caprolactone to a growing polyethylene end proceeds smoothly at ambient temperature to produce the expected AB type copolymers (100:1 to 100:89 ratio) in high yield (Table I). Reversed addition of the respective monomers (MMA or lactones and then ethylene), however, did not initiate a block copolymerization at all even in the presence of excess ethylene. Only homopolymerizations of polar monomers occur. This is ascribed to the relatively weak coordination or donating property of ethylene as compared with MMA or lactones.

Dyeing of the resulting block copoly(ethylene/MMA) (100:3, M_n = 35 000) and block copoly(ethylene/ϵ-caprolactone) (100:11, M_n = 12 000) with disperse dyes (Dianix AC-E) resulted in successful deep coloration of these films into three primary colors, while polyethylene itself was inert to these dyes. Thus, the present copolymers display a very desirable chemical reactivity. Measurements of their permeability barrier to moisture and of their dielectric constant are also underway.

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(8) The block copolymers obtained are estimated to exhibit $-OC(OMe)=C(Me)CH_2[CMe(COOMe)CH_2]_{m-1}(CH_2CH_2)_nR$ on the basis of X-ray studies of $(C_5Me_5)_2SmOC(OMe)=C(Me)CH_2C(Me)_2CO(OMe)$.
(9) Further reaction produced the polymer of $M_w/M_n > 4.0$.