7886 *Macromolecules* **1995,** *28,* 7886−7892

Living Polymerizations and Copolymerizations of Alkyl Acrylates by the Unique Catalysis of Rare Earth Metal Complexes

Eiji Ihara, Masakazu Morimoto, and Hajime Yasuda*

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

Received December 20, 1994; Revised Manuscript Received August 14, 1995®

ABSTRACT: Rare earth metal complexes such as $SmMe(C_5Me_5)_2(THF)$ or $YMe(C_5Me_5)_2(THF)$ (THF = tetrahydrofuran) catalyze the living polymerization of alkyl acrylates (alkyl = methyl (Me), ethyl (Et), *n*-butyl (nBu), *tert*-butyl (tBu)) to give high molecular weight polymers, with extremely narrow molecular weight distributions, in high conversion. Random living copolymerization of methyl acrylate with *n*-butyl acrylate was successful by the effective catalytic action of $SmMe(C_5Me_5)_2(THF)$. By taking advantage of the living polymerization of alkyl acrylates and alkyl methacrylates, a triblock copolymer of methyl methacrylate/*n*-butyl acrylate/methyl methacrylate was prepared, and the resulting polymer exhibited good elastic properties. In particular, an 8:72:20 copolymer had an ultimate elongation of 163% and compression set of 58%. Block copolymerizations of alkyl acrylates with lactones gave lactone rich copolymers with narrow molecular weight distributions.

Introduction

Polymerization of alkyl acrylates has long been examined with radical initiators and affords polymers with rather broad molecular weight distributions. In general, living polymerizations of alkyl acrylates (alkyl = methyl (Me), ethyl (Et), *n*-butyl (nBu), and *tert*-butyl (tBu)) have been hampered due to termination reactions involving nucleophilic attack by the α-carbon.[1] More recently, bulky alkyllithium/inorganic salt (LiCl) initiator systems were found to produce a living polymer of the bulky alkyl acrylate, *tert*-butyl acrylate (tBuA) (M_n = 21 000, M_w/M_n = 1.06).[2] Furthermore, group transfer polymerization of ethyl acrylate provided living polymers when ZnI_2 was used as a catalyst (M_n = 3300, M_w/M_n = 1.03).[3] Aluminum/porphyrin initiator systems also give a living polymer of *tert*-butyl acrylate (M_n = 12 200, M_w/M_n = 1.13).[4] Whereas the preparation of a monodisperse diblock copolymer poly(MMA−tBuA) (MMA = methyl methacrylate) with a high molecular weight poly(tBuA) block (M_n = 100 000) has been reported,[5] the upper limit of the molecular weight of homopoly(alkyl acrylates) with narrow molecular weight distributions is approximately 20 000. More recently, organosamarium complexes such as $(C_5Me_5)_2Sm$ and $[(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH-)]_2$ are reported to serve as good initiators for polymerization of methyl acrylate (M_n = 20 000, M_w/M_n = 1.1).[6] We describe herein the use of $SmMe(C_5Me_5)_2(THF)$[7] and $YMe(C_5Me_5)_2(THF)$[8] as efficient initiators for the living polymerization of alkyl acrylates. By taking advantages of living polymerization ability of alkyl acrylates and alkyl methacrylates, a triblock copolymer of methyl methacrylate−*n*-butyl acrylate−methyl methacrylate (MMA/nBuA/MMA) was prepared with organolanthanide(III) complexes and was found to exhibit elastic properties.

Results and Discussion

Living Polymerizations of Alkyl Acrylates. Methyl acrylate (MeA), ethyl acrylate (EtA), *n*-butyl acrylate (nBuA), and *tert*-butyl acrylate (tBuA) were polymerized with $SmMe(C_5Me_5)_2(THF)$ or $YMe(C_5Me_5)_2(THF)$ (THF = tetrahydrofuran) in toluene at 0 °C, and the results of these polymerizations are summarized in Table 1. The initiator efficiency exceeds 85% in every case except for the tBuA system, presumably due to its increased termination reaction because of the electronic effect of the bulky substituent. One can conclude that polymerizations of MeA, EtA, and nBuA proceed in a living fashion, since, for example, the M_n of poly(*n*-butyl acrylate) initiated by $SmMe(C_5Me_5)_2(THF)$ increases linearly with conversion, while M_w/M_n remains constant and narrow irrespective of the initiator concentration (Figure 1). The M_n of poly(MeA) and poly(EtA) was also linearly related to conversion when the initiator concentration was fixed at 0.2 mol % (Figure 2).

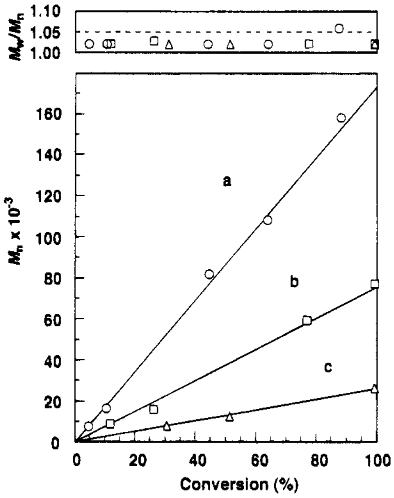


Figure 1. M_n and M_w/M_n vs conversion plots for polymerization of *n*-butyl acrylate: initiator concentration of $SmMe(C_5Me_5)_2(THF)$, (a) 0.1, (b) 0.2, and (c) 0.5 mol %; polymerization temperature, 0 °C.

The apparent rate of polymerization is very fast, and it follows the order nBuA > EtA > MeA, while the order was reversed in the case of methacrylic esters, MMA > EtMA > nBuMA (EtMA, ethyl methacrylate; nBuMA, *n*-butyl methacrylate).[9] In the case of the polymerization of MeA, the polymerization is complete in 300 s at 0 °C and both M_n and conversion increase with polymerization time, whereas the polymerization is complete in 5 s for polymerization of EtA and nBuA. The observed apparent rates of polymerization for MeA, EtA, and nBuA by $SmMe(C_5Me_5)_2(THF)$ or $YMe(C_5Me_5)_2$-

---

® Abstract published in *Advance ACS Abstracts,* October 15, 1995.

0024-9297/95/2228-7886$09.00/0

Table 1. Polymerization of Alkyl Acrylates Catalyzed by Organolanthanide Comlexes at 0 °C[a]

initiator	monomer	obsd $10^{-3}M_n$	obsd M_w/M_n	calcd $10^{-3}M_n$	tacticity rr	tacticity mr	tacticity mm	conversion, %	initiator efficiency, %
$SmMe(C_5Me_5)_2(THF)$	MeA	48	1.04	43	30	50	20	99	89
	EtA	55	1.04	50	51		49	94	86
	EtA[b]	56	1.03	50	50		50	96	86
	nBuA	70	1.05	64	28	53	19	99	91
	nBuA[b]	69	1.02	64	20	60	20	96	89
	tBuA[c]	16	1.03	13	27	47	26	99	79
$YMe(C_5Me_5)_2(THF)$	MeA	50	1.07	43	33	51	16	99	86
	EtA	53	1.05	50	47		53	96	91
	nBuA	72	1.04	64	22	51	27	98	88
	tBuA[c]	17	1.03	13	25	45	30	99	75

[a] Reaction conditions: initiator concentration, 0.2 mol % of monomer; solvent, toluene; reaction time, 10 min. [b] Reaction conditions: initiator concentration, 0.2 mol % of monomer; solvent, toluene; reaction time, 1 h; reaction temperature, −78 °C. [c] Reaction conditions: initiator concentration, 1.0 mol % of monomer; solvent, toluene; reaction time, 24 h.

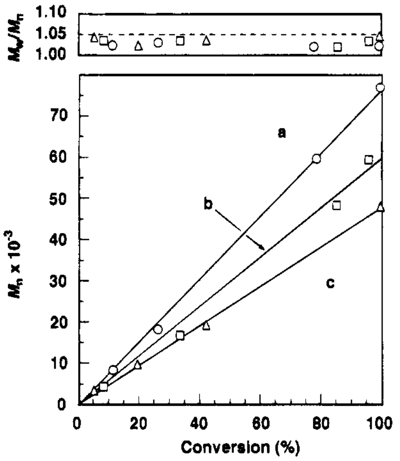


Figure 2. M_n and M_w/M_n vs conversion plots for polymerization of alkyl acrylates by the catalytic action of $SmMe(C_5Me_5)_2(THF)$ (0.2 mol % of monomer): (a) *n*-butyl acrylate, (b) ethyl acrylate, and (c) methyl acrylate; polymerization temperature, 0 °C; solvent, toluene.

Table 2. Apparent Rate of Polymerization of Alkyl Acrylates

initiator	monomer	rate of polymerization, s^{-1} 0 °C	rate of polymerization, s^{-1} −78 °C
$SmMe(C_5Me_5)_2(THF)$	MeA	3.6	0.0001
$YMe(C_5Me_5)_2(THF)$		3.0	0.0001
$SmMe(C_5Me_5)_2(THF)$	EtA	130	0.0543
$YMe(C_5Me_5)_2(THF)$		76	0.0487
$SmMe(C_5Me_5)_2(THF)$	nBuA	134	0.0805
$YMe(C_5Me_5)_2(THF)$		87	0.0701

[a] Reaction conditions: solvent, toluene; toluene/[M_0] = 15 (vol/vol).

(THF) initiator at 0 and −78 °C are listed in Table 2. As mentioned above, bulky acrylates polymerize faster, nBuA > EtA > MeA, possibly due to the electronic effect of the alkyl group. Polymerizations initiated by the samarium derivative are more rapid compared with the yttrium complex, presumably due to the smaller ionic radius of Sm (1.00 Å) compared with Y (1.06 Å). Similar tendencies were observed in polymerizations at lower temperatures, although the exact value decreases significantly. When polymerization temperatures were raised to 60 °C, M_w/M_n values became broader (polymerization time, 10 min) and conversion was lower; i.e., for poly(MeA), M_w/M_n = 1.33 and M_n = 47 × 10^3 (conversion 50%), for poly(EtA), M_w/M_n = 1.26 and M_n = 65 × 10^3 (conversion 69%); for poly(nBuA), M_w/M_n = 1.26 and M_n = 99 × 10^3 (conversion 73%). Thus, the active species is unstable at higher temperature, and polymerizations of alkyl acrylates at lower temperature give polymers with narrow molecular weight distributions. These results indicate that polymerization reaction does not require the participation of f-orbitals because Y ($3s^23p^63d^{10}4s^24p^64d^15s^2$) exhibits no f-orbital configuration.

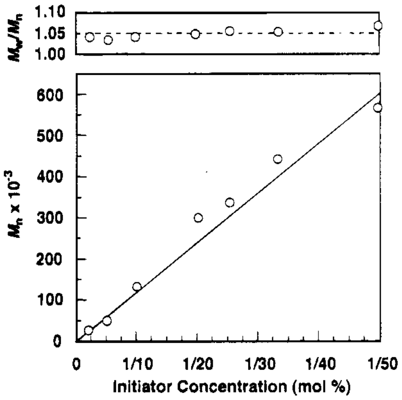


Figure 3. Effect of initiator concentration on the polymerization of ethyl acrylate.

In order to further define the present initiator systems, the effect of catalyst concentration on the polymerization was examined. When the initiator concentration was decreased from 0.1 to 0.02 mol %, one can obtain high molecular weight poly(EtA) of M_n = 500 000 with a very narrow molecular weight distribution (Figure 3). Thus, syntheses of high molecular weight poly(MeA), poly(EtA), and poly(nBuA) with low polydispersity were for the first time achieved using organolanthanide(III) initiators (Table 3).

The lifetime of the growing end was measured in toluene and in THF. The polymerization of methyl acrylate (200 mmol) was carried out in toluene with $SmMe(C_5Me_5)_2(THF)$ (0.2 mol % of monomer), and after completion of the polymerization (after 1 min) the same volume of methyl acrylate (200 mmol) was added to the resulting polymer system to reinitiate the polymerization. However, in toluene no further polymerization occurred due to the autodestruction of the growing end. In contrast, the repolymerization occurred after holding the system for 1 min in THF solution and gave polymer with a unimodal molecular weight distribution (MWD). Therefore, the growing end is living for a short time in a polar solvent. This situation could result from the solvation of the growing chain by polar solvent to prevent the autodestruction of the active species and/or displacement of the penultimate ester moiety by THF from the metal center so that backbiting cannot occur as readily. When the resulting polymerization system was held for 5 min in THF, ca. 70% of the growing end survived. After 10 min, all the growing end was destroyed at 0 °C even in THF. In cases of ethyl acrylate

Table 3. Effect of Initiator Concentration[a]

monomer	initiator concn, mol %	$10^{-3}M_n$ obsd	$10^{-3}M_n$ calcd	M_w/M_n	conversion, %	initiator efficiency, %
MeA	0.05	171	145	1.05	84.5	85
	0.03	274	214	1.16	75.0	78
EtA	0.02	558	452	1.07	90.5	81
	0.014	775	535	1.15	75.0	69
nBuA	0.04	350	287	1.24	89.9	82

[a] Polymerization conditions: initiator, $SmMe(C_5Me_5)_2(THF)$; reaction temperature, 0 °C; solvent, toluene; toluene/$[M_0]$ = 15 (vol/vol).

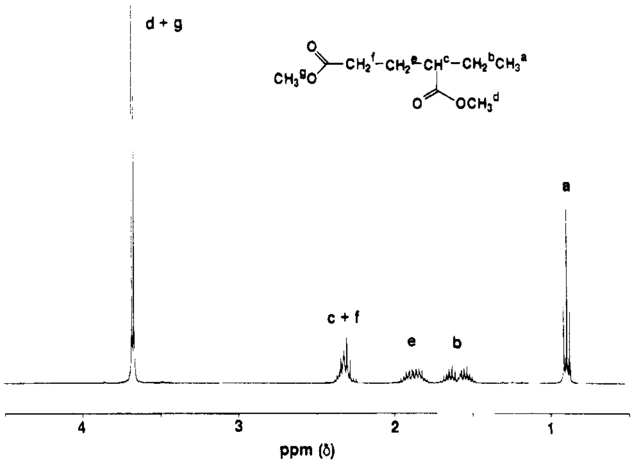


Figure 4. ^{1}H-NMR spectrum of the hydrolysis product of the 1:2 $SmMe(C_5Me_5)_2(THF)$/methyl acrylate reaction.

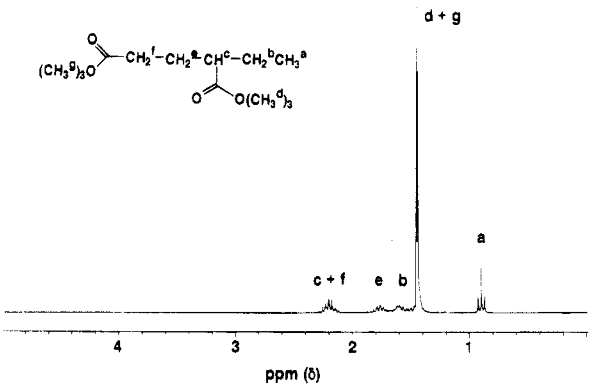


Figure 5. ^{1}H-NMR spectrum of the hydrolysis product of the 1:2 $SmMe(C_5Me_5)_2(THF)$/*tert*-butyl acrylate reaction.

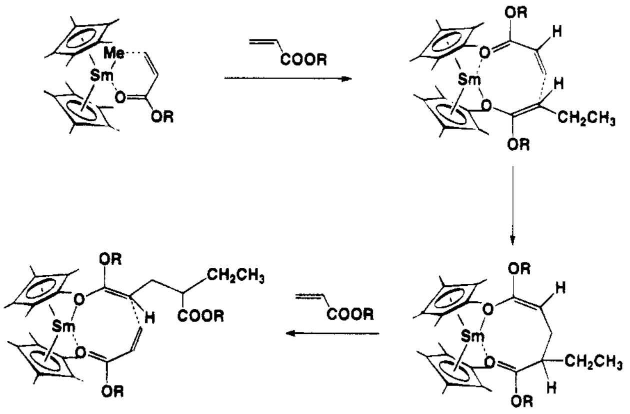
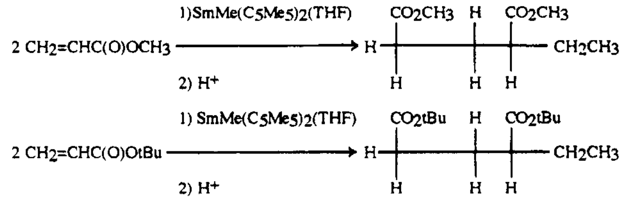


Figure 6. Proposed initiation mechanism for the polymerization of alkyl acrylates.

and *n*-butyl acrylate, repolymerization occurred in ca. 50% conversion even after holding the polymerization system for 1–10 min in THF. The polymers thus formed by the second addition of monomer exhibit rather broad molecular weight distributions because some of the initiator may have been destroyed. To penetrate into the initiation mechanism, the 1:1 or 1:2 reactions of $SmMe(C_5Me_5)_2(THF)$ with methyl acrylate and *tert*-butyl acrylate were examined. Quenching of the 2:1 reaction mixture of methyl acrylate and $SmMe(C_5Me_5)_2(THF)$ gives $CH_3CH_2CH(COOMe)CH_2CH(COOMe)H$ in 65–78% yield (Figure 4); i.e., the CH_2(b) signal absorbs at 1.57 ppm and CH_2(e) signals at 1.88 ppm as revealed by decoupling experiment. More efficient initiation was observed for the 2:1 reaction of *tert*-butyl acrylate with $SmMe(C_5Me_5)_2(THF)$, which gives upon hydrolysis $CH_3CH_2CH(COOtBu)CH_2CH(COOtBu)H$ in 96% yield at 0 °C (Figure 5).



$$2\ CH_2{=}CHC(O)OCH_3 \xrightarrow[2)\ H^+]{1)\ SmMe(C_5Me_5)_2(THF)} H-\underset{H}{\overset{CO_2CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CO_2CH_3}{C}}-CH_2CH_3$$

$$2\ CH_2{=}CHC(O)OtBu \xrightarrow[2)\ H^+]{1)\ SmMe(C_5Me_5)_2(THF)} H-\underset{H}{\overset{CO_2tBu}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CO_2tBu}{C}}-CH_2CH_3$$

These results agree well with the result of hydrolysis of the 2:1 molar reaction of MMA with $[Sm(C_5Me_5)_2H]_2$, which affords $Sm(C_5Me_5)_2(MMA)_2H$ as evidenced by X-ray analysis.[9,10] Although the isolation of the 2:1 reaction product was unsuccessful in this case, we can readily estimate that the polymerization is initiated by the addition of acrylates to an enolate (Figure 6). In fact, methyl acrylate can be polymerized using $[Y(OCH{=}CH_2)(C_5H_4SiMe_3)_2]_2$ or $Y(OCH{=}CH_2)(C_5Me_5)_2(THF)$ as an initiator to give poly(MeA) with M_n = 40 000 and M_w/M_n = 1.15 and poly(MeA) with M_n = 42 000 and M_w/M_n = 1.08, respectively, in the case of the catalytic concentration of 0.2 mol %. The apparent rate of polymerization for MeA at 0 °C (3.4 s^{-1}) is nearly the same as that by $SmMe(C_5Me_5)_2(THF)$. However, $[YOMe(C_5H_5)_2]_2$ and $Sm(OEt)(C_5Me_5)_2(Et_2O)$ are completely inert toward the polymerization of alkyl acrylates.

The temperature dependence of tacticity was measured from −78 to +60 °C. However, little effect was observed in this temperature range.[11] Only a slight increase of syndiotacticity to 60% was observed in the polymerization of methyl acrylate using $SmMe(C_5Me_5)_2(THF)$ as initiator.

Glass transition temperatures of poly(alkyl acrylate) were measured here again by using differential scanning calorimetry (DSC) to evaluate the exact values since we could obtain pure samples of monodisperse high molecular weight polymers. Transition temperatures of poly(EtA) (−23 °C) and poly(nBuA) (−56 °C) fit those reported in the literature,[12] but the values for poly(MeA) (−1 °C) and poly(tBuA) (+21 °C) are lower than the reported values (+8 and +39 °C), presumably due to the different tacticity of these polymers. The values obtained here are ascribed to the T_g values of atactic poly(alkyl acrylates).

Random Copolymerizations of Alkyl Acrylates. The present system was found to conduct the living

Table 4. Random Copolymerization of Alkyl Acrylates at 0 °C[a]

monomers	$10^{-3}M_n$	M_w/M_n	conversion, %	A/B ratio in polymers
MeA/EtA	53	1.04	99	51/49
MeA/nBuA	60	1.05	99	50/50
EtA/nBuA	65	1.05	99	50/50

[a] Reaction conditions: charged monomer ratio, 1/1 (mol/mol); initiator, $SmMe(C_5Me_5)_2(THF)$; initiator concentration, 0.2 mol %; reaction time, 10 min; solvent, toluene.

Table 5. Monomer Reactivity Ratio of Alkyl Acrylates Monomers[a]

monomers	r_1	r_2	r_1r_2
MeA/EtA	0.959	0.597	0.573
MeA/nBuA	0.426	0.578	0.246
EtA/nBuA	0.535	0.834	0.446
MMA/MeA	0.015	19.9	0.284
MMA/EtA	0.008	15.9	0.133
MMA/nBuA	0.024	21.3	0.511

[a] Reaction conditions: initiator, $SmMe(C_5Me_5)_2(THF)$; initiator concentration, 0.2 mol %; solvent, toluene.

copolymerization of methyl acrylate with ethyl or *n*-butyl acrylate and also the copolymerization of ethyl acrylate with *n*-butyl acrylate. All systems gave high molecular weight polymers with narrow molecular weight distributions by polymerization at 0 °C for 10 min (Table 4). The resulting copolymers are composed of equal amounts of each monomer when conversion reaches 99%. To understand relative monomer reactivity, monomer reactivity ratios were determined using the Fineman–Ross equation. The results are shown in Table 5.

The monomer reactivity ratio of methyl acrylate is higher than that of ethyl acrylate but is nearly the same as that of *n*-butyl acrylate. In contrast to the acrylate systems, MMA exhibits much lower reactivity as shown in Table 5. Similarly, it has been reported that methyl acrylate is much more reactive than MMA in anionic polymerization [r_1(MMA) = 0.1, r_2(MeA) = 4.5, initiator = $NaNH_2$],[13] while their reactivities are comparable in the radical initiating system using AIBN [r_1(MMA) = 1.0, r_2(MeA) = 0.5].[14] Because of the different reactivities of MMA and alkyl acrylates in this initiating system, block copolymerization occurs preferentially even when a mixture of methyl methacrylate with methyl, ethyl, or *n*-butyl acrylate was used. In fact, in the random copolymerization of the MMA with nBuA (charged ratio 1:1), the content of MMA component in the resulting polymer is lower than 12% when conversion reaches 50%.

Block Copolymerization of Alkyl Acrylates with Methyl Methacrylate. ABA type triblock copolymers of MMA/nBuA/MMA should provide thermoplastic elastomers since MMA is a hard segment while nBuA is a soft segment, where the hard segment will act as a node and soft segments act as elastomers in the resulting network system. For examination of this possibility, we have demonstrated first AB type block copolymerizations. MMA (290 equiv of initiator) was polymerized by $SmMe(C_5Me_5)_2(THF)$ initiator, and nBuA (290 equiv of initiator) was subsequently polymerized to give a 52:48 block copolymer of MMA with nBuA (M_n = 47 000, M_w/M_n = 1.04) in toluene. On the other hand, when nBuA was first polymerized and then MMA was next polymerized after holding 5 min, the resulting polymer exhibits anomalously large molecular weight (M_n = 217 000, M_w/M_n = 1.19) because of the partial decomposition of the growing end. Therefore, the addition of MMA should be completed in a short time after completion of the polymerization of nBuA. Thus, triblock copolymerization was conducted under the most suitable conditions; i.e., MMA was polymerized for 30 min, and nBuA was added at once. After completion of the polymerization of nBuA (2 min), MMA was again added. In the first step, the poly(MMA) exhibits M_n = 15 000 and M_w/M_n = 1.04 in a unimodal pattern, in the second step, poly(MMA–*block*-nBuA) exhibits M_n = 36 000 and M_w/M_n = 1.05 (unimodal, MMA/nBuA in the polymer = 43:57), and finally, a mixture poly(MMA–*block*-nBuA–*block*-MMA) bearing M_n = 144 000 and M_w/M_n = 1.09 (MMA/nBuA/MMA ratio in the polymer = 11:14:75) and poly(MMA–*block*-nBuA) (M_w/M_n = 38 000, M_w/M_n = 1.05) were obtained. Thus, an ABA type triblock copolymer was formed together with AB type diblock copolymer in ca. 1:1 ratio in toluene. The ratio was changed to 1.0:0.2 when THF was used as the solvent. However, we could fortunately fractionate the resulting copolymer with a mixture of $CHCl_3$ and hexane as the ABA copolymer was insoluble and the AB copolymer dissolved. The resulting ABA type triblock copolymer is largely free from contamination by the AB copolymer (Figure 7). Thus fractionation is necessary to obtain pure ABA triblock copolymer by the sequential addition of A, B, and A monomers.

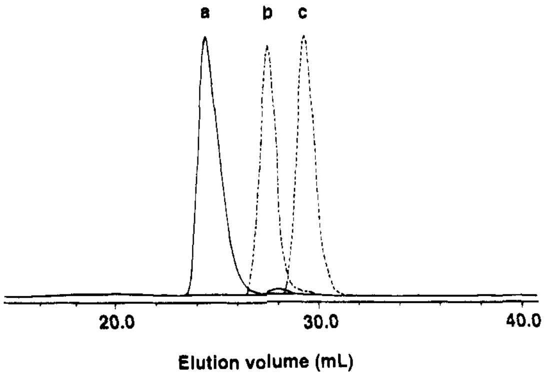


Figure 7. Gel permeation chromatograph of (a) poly(MMA–*blo*–nBuA–*blo*–MMA) (M_n = 144 000, M_w/M_n = 1.09), (b) poly(MMA–*blo*–nBuA) (M_n = 36 000, M_w/M_n = 1.05), and (c) poly(MMA) (M_n = 15 000, M_w/M_n = 1.04).

For improvement on this, a mixture of MMA and nBuA was added at once to the growing end of poly(MMA). In this case living triblock copolymerization proceeds ideally and we have obtained triblock copolymers composed of MMA/nBuA/MMA in 6:91:3, 8:72:20, and 25:51:24 ratios. All of these polymers possess unimodal molecular weight distributions.

The mechanical properties of the resulting triblock copolymers were evaluated by several methods as shown in Table 6. Poly(MMA) has a large tensile modulus and large tensile strength but has very low elongation and Izod impact strength. Furthermore, poly(MMA) does not show any decrease in compression set (typical rubber shows 10–20%). In sharp contrast to the properties of poly(MMA), the triblock copolymer (8:72:20) shows 58% compression set. In this case the Izod impact strength is >400 J/m, while hardness was lowered to 20 JISA. The most interesting property lies in the relatively large elongation (163%). However, the observed mechanical properties are very far away from those reported for the S–B–S thermoplastic elastomers of the Kraton type (tensile strength, 30 MPa; elongation at break, 1000%).[15] In contrast to the this triblock copolymer, the triblock copolymers composed of MMA/nBuA/MMA in 6:91:3 or 25:51:24 ratios show the increased compression set of 97 or 101%, respectively,

Table 6. Mechanical Properties of Triblock Copolymers

copolymer (composition)	tensile modulus, MPa	tensile strength, MPa	elongation, %	Izod impact strength, J/m	compression set at 70 °C for 22 h
Poly(MMA/nBuA/MMA) (20:47:33)	75	27	83	383	101
Poly(MMA/nBuA/MMA) (25:51:24)	46	22	81	390	103
Poly(MMA/nBuA/MMA) (8:72:20)	0.8	0.7	163	400	58
Poly(MMA/nBuA/MMA) (6:91:3)	0.2	0.1	246	410	97
Poly(MMA/EtA/EtMA) (26:48:26)	119	22	276	34	62

indicating that these polymers exhibit no elastic properties. Elongation of 25:51:24 triblock copolymer is 81%, while that of the 6:91:3 copolymer is 246%. Thus, a suitable ratio is required for elastic properties of these triblock copolymers.

In essentially the same way, triblock copolymerization of MMA/EtA/EtMA was performed by the addition of a mixture of EtA (9 mmol) and EtMA (4 mmol) to the growing end of living poly(MMA) (5 mmol) at 0 °C. The resulting copolymer exhibits a unimodal pattern and is composed of MMA/EtA/EtMA in 26:48:26 ratio. This copolymer shows an elongation of 276% and a compression set of 62%. Thus, this type of copolymer is also a thermoplastic elastomer.

To understand the morphology of the elastic triblock copolymers, transmission electron micrographs were measured for the 20:47:32, 8:72:20, and 6:91:3 copolymers. As illustrated in Figure 8, the 8:72:20 triblock copolymer shows the homogeneous dispersion, while 6:91:3 copolymer revealed the presence of poly(MMA) (white zone) and poly(nBuA) region (black zone). In the case of 20:47:32 copolymer, lamellar components of poly(nBuA) were observed. Thus, homogeneous mixing of the ABA triblock copolymer which results in disappearance of the phase boundary seems necessary for rubberlike elastic properties, while the elastic property was not observed when lamellar structures exist.

Block Copolymerization of Alkyl Acrylates with Lactones. As an extension of this research, block copolymerizations of alkyl acrylates with ϵ-caprolactone have been explored. The block copolymerization of EtA or nBuA followed by the polymerization of ϵ-caprolactone resulted in the formation of a mixture of at least two polymers. However, when the resulting polymer was washed with excess methanol or ether, one could obtain unimodal block copolymers in ca. 50% yield. This copolymer contains mainly caprolactone (Table 7).

Random copolymerization of alkyl acrylates with caprolactone also gave a unimodal polymer, which also contains a large quantity of lactone. In this case, no homopoly(caprolactone) was formed. NMR spectral analysis of this copolymer reveals that a block copolymer was formed exclusively. Thus, block copolymerizations of alkyl acrylates with caprolactone were for the first time realized.

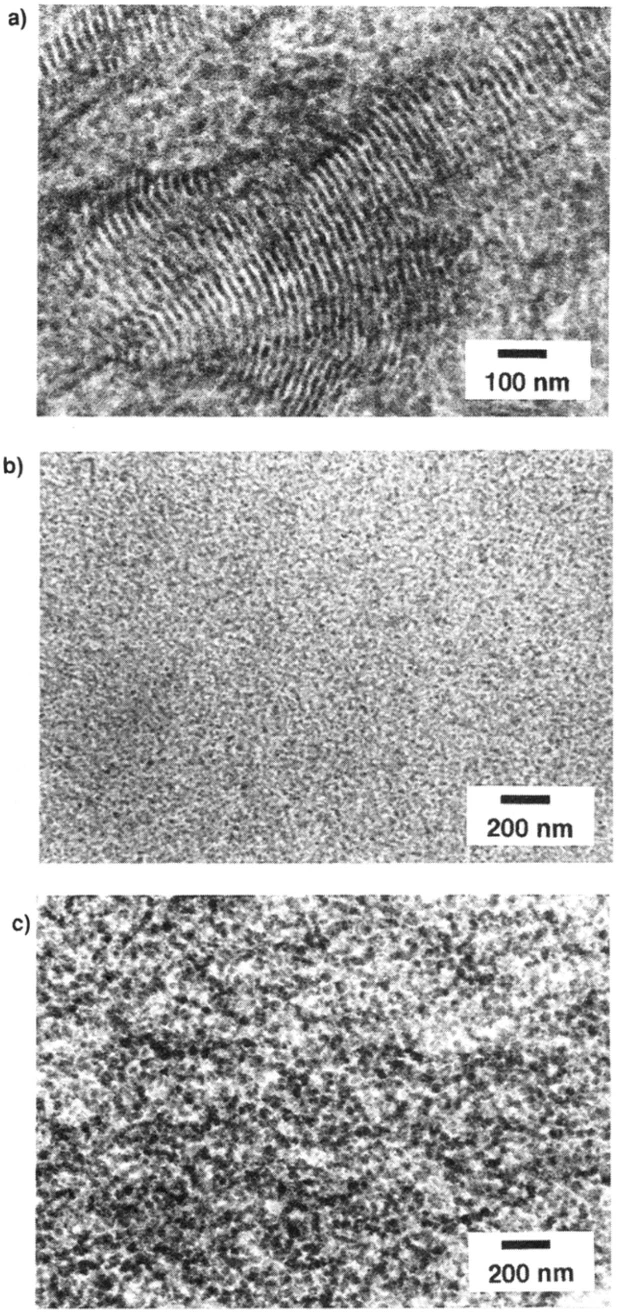


Figure 8. Transmission electron micrographs of triblock copolymers: (a) poly(MMA−*blo*−BuA−*blo*−MMA) (20:47:33), (b) poly(MMA−*blo*−BuA−*blo*−MMA) (8:72:20), and (c) poly(MMA−*blo*−BuA−*blo*−MMA) (6:91:3).

Experimental Section

General Procedures. All operations were conducted with Schlenk techniques under an argon atmosphere. Tetrahydrofuran, hexane, and toluene were dried over Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. Commercially purchased alkyl acrylates were dried over CaH_2 for 48 h, dried over activated molecular sieves of 4 Å for 5 days, and then distilled before use. Gas chromatographic analysis and separation of reaction products were made with a Yanako gas chromatograph G3810 using a column packed with Silicone DC-550 or DEGS. NMR spectra were recorded on a JEOL-EX270 or a Bruker AM-X 400wb spectrometer (400.13 MHz for ^{1}H and 100.03 MHz for ^{13}C nuclei). Chemical shifts were calibrated using benzene (δ 7.2 ppm) or chloroform (δ 7.26 ppm). Number average molecular weight and molecular weight distributions of polymers were determined by gel permeation chromatography on a Tosoh SC-8010 high speed liquid chromatograph equipped with a differential refractometer detector, using $CHCl_3$ as eluent at 40 °C. The columns used were TSK gel G5000Hxl, G4000Hxl, G3000Hxl, and G2000Hxl. The flow rate was 1.0 mL min^{-1}. The molecular weight and molecular weight distributions of polymers were calibrated by using a universal curve plotted with standard polystyrenes (whose exact M_w values were determined by light scattering methods): 8.70×10^2 ($M_w/M_n = 1.10$); 2.63×10^3 ($M_w/M_n = 1.05$); 5.97×10^3 ($M_w/M_n = 1.02$); 9.10×10^3 ($M_w/M_n = 1.02$); 3.79×10^4 ($M_w/M_n = 1.01$); 4.36×10^4 ($M_w/M_n =$

Table 7. Copolymerization of Alkyl Acrylates with ϵ-Caprolactone[a]

monomers (A/B)	charged ratio	$10^{-3}M_n$	M_w/M_n	conversion, % (reaction period, h)	A/B ratio in copolymer
MeA/CL	1/1	20.0	1.17	39 (1h)	16/84
EtA/CL	1/1	23.5	1.14	37 (2h)	10/90
	1/1	26.6[b]	1.16	35 (1h)	21/79
nBuA/CL	1/1	17.2	1.11	28 (1h)	8/92
	1/1	46.1[c]	1.19	33 (1h)	11/89

[a] Reaction conditions: initiator, $SmMe(C_5Me_5)_2(THF)$; initiator concentration, 0.2 mol %; reaction temperature, 0 °C; solvent, toluene. [b] After block copolymerization of EtA with caprolactone, resulting poly(EtA) was washed away with methanol. [c] After block copolymerization of nBuA with caprolactone, resulting poly(nBuA) was washed away with ether.

1.01); 1.90×10^5 ($M_w/M_n = 1.04$); 3.55×10^5 ($M_w/M_n = 1.02$); 7.06×10^5 ($M_w/M_n = 1.05$); 1.09×10^6 ($M_w/M_n = 1.08$); 2.89×10^6 ($M_w/M_n = 1.06$).

Preparation of $SmMe(C_5Me_5)_2(THF)$. This compound was prepared according to the procedure reported by Evans et al.[7] A THF dispersion of pentamethylcyclopentadienylpotassium (50 mmol) in 150 mL of THF was added to a stirred solution of blue-green $SmI_2(THF)_2$ (22 mmol) in 400 mL of THF. The color of the solution turned to purple immediately after the addition of C_5Me_5K, and precipitation of KI occurred. After stirring the mixture for 12 h at 20 °C, THF was removed by evaporation and 250 mL of toluene was added to the residue. The resulting solution was stirred for 12 h and was centrifuged to remove the salts. The solvent was evaporated to dryness, and the resulting $Sm(C_5Me_5)_2(THF)_2$ was recrystallized from THF/hexane at −20 °C to give purple crystals in 56% yield. To a stirred solution of $Sm(C_5Me_5)_2(THF)_2$ (4.5 g, 8.0 mmol) in 100 mL of toluene was added 5 equiv of $AlMe_3$ (4.0 mL, 41 mmol). After stirring for 12 h at 20 °C, the reaction solution gradually changed to red. Concentration of the solution followed by cooling to −20 °C gave $Me_2AlMe_2Sm(C_5Me_5)_2$ as red crystals. Recrystallization of $Me_2AlMe_2Sm(C_5Me_5)_2$ from THF/hexane afforded $SmMe(C_5Me_5)_2(THF)$ as yellow-orange crystals in 62% yield. Preparation of $YMe(C_5Me_5)_2(THF)$ was made in essentially the same way as that described for $YbMe(C_5Me_5)_2(THF)$.[8]

Preparation of $[Y(OCH{=}CH_2)(C_5H_4SiMe_3)_2]_2$. This complex was synthesized according the preparation method for $[Y(OCH{=}CH_2)Cp_2]_2$ reported by Evans et al.[16] Lithium enolate (3.5 mmol) in 7.0 mL of THF was added to the solution of $[YCl(C_5H_4SiMe_3)_2]_2$ (1.36 g, 1.71 mmol) at room temperature with magnetic stirring. Immediately after the addition, precipitation of the salt occurred. After stirring for 12 h at room temperature, THF was evaporated to dryness. The white residue was extracted 4−5 times with 40 mL of toluene. Evaporation of the solution resulted in the formation of the straw-colored solid of $[Y(OCH{=}CH_2)(C_5H_4SiMe_3)_2]_2$. M_w (cryoscopically in benzene): 830; calcd for the dimer, 812.1. ^1H-NMR (C_6D_6, ppm): δ 0.25 (s, $SiMe_3$, 18H), 4.07 (d, $OCH{=}CH_2$, 1H, $J = 10.5$ Hz), 4.28 (d, $OCH{=}CH_2$, 1H, $J = 15.2$ Hz), 6.29 (dd, $OCH{=}CH_2$, 1H), 6.39 (s, C_5H_4, 4H), and 6.78 (s, C_5H_4, 4H).

Preparation of $Y(OCH{=}CH_2)(C_5Me_5)_2(THF)$. $LiOCH{=}CH_2$ (3.6 mmol) in 7.2 mL of THF was added to the solution of $YCl(C_5Me_5)_2(THF)$ (0.91 g, 1.95 mmol) at room temperature. After stirring for 12 h, the white precipitate was removed by centrifugation and the solution was evaporated to dryness. The resulting white residue was extracted with 40 mL of toluene, and evaporation of the solvent yielded the straw-colored solid of $Y(OCH{=}CH_2)(C_5Me_5)_2(THF)$. M_w (cryoscopically in benzene): 480; calcd for the monomer, 473.9. ^1H-NMR (C_6D_6, ppm): δ 1.31 (m, THF), 2.20 (s, C_5Me_5, 30H), 3.53 (m, THF), 3.93 (d, $OCH{=}CH_2$, 1H, $J = 15.2$ Hz), 4.02 (d, $OCH{=}CH_2$, 1H, $J = 10.5$ Hz), 6.92 (dd, $OCH{=}CH_2$, 1H).

Preparation of $Sm(OEt)(C_5Me_5)_2(OEt_2)$. This compound was synthesized according to the procedure reported by Evans et al.[17] An orange powder of $[SmH(C_5Me_5)_2]_2$ (0.71 g, 0.84 mmol) was dissolved in 20 mL of diethyl ether. Immediately after mixing, the color of the solution turned to pale-yellow. After the mixture was held at 20 °C for 30 min, volatiles were evaporated by flash distillation to result in the formation of yellow powder. The powder was extracted with 20 mL of hexane, and the hexane solution was concentrated and cooled to −20 °C to induce the precipitation of $Sm(OEt)(C_5Me_5)_2(OEt_2)$; yield, 42% (0.30 g).

Preparation of $[YOMe(C_5H_5)_2]_2$. A mixture of $YCl(C_5H_5)_2(THF)$ (0.68 g, 2.10 mmol) and NaOMe (0.13 g, 2.4 mmol) was dissolved in 30 mL of THF with magnetic stirring. Stirring was continued for 36 h, and the solution was evaporated to dryness. The resulting solid was extracted with toluene. Evaporation of toluene resulted in the formation of $[YOMe(C_5H_5)_2]_2$; yield, 29%. EIMS, m/z (relative intensity): 219 [$(C_5H_5)_2{}^{89}Y^+$, 18.8], 435 [$(C_5H_5)_3{}^{89}Y_2(OMe)_2{}^+$, 100], 469 [$(C_5H_5)_4{}^{89}Y_2(OMe)^+$, 7.0], 500 [$(C_5H_5)_4{}^{89}Y_2(OMe)_2{}^+$, 64.6]. ^1H-NMR (C_6D_6, ppm): δ 2.88 (s, OMe, 6H), 6.19 (s, C_5H_5, 20H). ^{13}C-NMR (C_6D_6, ppm): δ 51.8 (OMe), 111.7 (C_5H_5).

Living Polymerization of MeA by $SmMe(C_5Me_5)_2(THF)$. A catalyst, $SmMe(C_5Me_5)_2(THF)$ (0.01 g, 0.02 mmol), was dissolved in 1.0 mL of toluene. The catalyst concentration was adjusted by diluting an appropriate amount of the solution with 20 mL of toluene. To the diluted solution was added 0.9 mL of MeA (10 mmol) with a syringe at 0 °C with vigorous magnetic stirring. The stirring was continued for 10 min at 0 °C. Then the mixture was poured into excess MeOH, and the resulting polymer was dried in vacuo; typical yield, 99%.

Determination of the Apparent Rate of Polymerizations. The apparent rates of polymerizations of MeA, EtA, and nBuA (10 mmol) were examined by using $SmMe(C_5Me_5)_2(THF)$ (0.01 g, 0.02mmol) or $YMe(C_5Me_5)_2(THF)$ (0.01 g, 0.02mmol) as the initiator in toluene (20 mL) at −78 or 0 °C. At 30-s intervals, toluene solution (1 mL) was taken out and was poured into excess MeOH (100 mL). The precipitated polymer was dried under reduced pressure and weighed. The accuracy of the observed apparent rate of polymerizations involves an error of 0.5% for polymerization at 0 °C and an error of 1.2% for polymerization at −78 °C.

Measurement of Monomer Reactivity Ratio. A mixture of MeA and EtA (monomer ratio, 10:90, 25:75, 50:50, 75:25, 90:10; in total 10 mmol) or a mixture of MeA and nBuA was polymerized with $SmMe(C_5Me_5)_2(THF)$ (0.01 g, 0.02mmol) in 20 mL of toluene, and the polymerization was terminated prior to 25% conversion. The respective monomer ratio of MeA and EtA units in the resulting random polymers was determined by ^1H-NMR spectra using the MeO group at 3.65 ppm and the $MeCH_2$ group at 1.2 ppm. In the case of random copolymerization of EtA and nBuA, the respective polymer ratio was determined on the basis of ^1H-NMR using the $MeCH_2$ group (1.2 ppm) and the $MeCH_2CH_2CH_2$ group at 4.06 ppm. In the case of random copolymerization of MMA with nBuA, the respective monomer ratio in the polymer was determined by ^1H-NMR spectra using the MeO group (3.58 ppm) of MMA and the $MeCH_2CH_2CH_2$ group (4.06 ppm) of nBuA.

Diblock Copolymerization of MMA with nBuA. MMA (1.07 mL, 10 mmol) was added to the toluene solution (20 mL) of $SmMe(C_5Me_5)_2(THF)$ (0.01 g, 0.02mmol) at 0 °C with vigorous magnetic stirring. The stirring was continued for 10 min, and then nBuA (1.40 mL, 10 mmol) was added at 0 °C. After the mixture was stirred for 10 min, the reaction mixture was poured into excess MeOH to induce the precipitation of copolymer; typical polymer yield, 99%.

Triblock Copolymerization of MMA/nBuA/MMA. Method A. After completion of the diblock copolymerization of MMA with nBuA (5.0 mmol) in 30 min, freshly distilled MMA (0.5 mL, 5.0 mmol) was added at 0 °C and stirring was continued for a further 30 min. Then the mixture was poured into MeOH (50 mL) and the precipitated polymer was filtered.

Method B. After completion of living polymerization (30 min) of MMA (5.0 mmol) with $SmMe(C_5Me_5)_2(THF)$ (0.05 g, 0.1 mmol) at 0 °C, a mixture of nBuA (10.0 mmol) and MMA (5.0 mmol) was added at once at 0 °C and magnetic stirring was continued for 30 min. The mixture was poured into excess MeOH to induce the precipitation of the polymer.

Triblock Copolymerization of MMA/EtA/EtMA. MMA (0.53 mL, 5.0 mmol) was added to the toluene solution (25 mL) of $SmMe(C_5Me_5)_2(THF)$ (0.05 g, 0.1 mmol) at 0 °C with vigorous magnetic stirring. The stirring was continued for 30 min, and then a mixture of EtA (1.73 mL, 16 mmol) and EMA (0.50 mL, 4.0 mmol) was added at once at 0 °C. The stirring was continued for 30 min. Then the resulting polymer was poured into excess MeOH.

Block Copolymerization of Alkyl Acrylates with Lactones. EtA (0.62 mL, 5.0 mmol) was added to the toluene solution (25 mL) of $SmMe(C_5Me_5)_2(THF)$ (0.1 mmol) at 0 °C with vigorous magnetic stirring, and stirring was continued for 30 min. Then caprolactone (5.0 mmol) was added to the resulting solution, and stirring was continued for 1 h. The mixture was poured into excess MeOH to induce the precipitation of the copolymer. Thus, the homopolymer of EtA was soluble in MeOH, and the copolymer of EtA and caprolactone was insoluble in MeOH. In the case of copolymerization of nBuA and caprolactone, the resulting polymer was washed with excess diethyl ether [poly(nBuA) is soluble in diethyl ether].

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on the Priority Area of Reactive Organometallics No. 05236104 from the Ministry of Education, Science and Culture. We are also indebted to the Mitsubishi Petrochemical Co. Ltd. for measurement of mechanical properties of ABA triblock coploymers and to the Sumitomo Chemical Co. Ltd. for measurement of transmission electron micrographs of triblock copolymers.

References and Notes

(1) Kitano, T.; Fujimoto, T.; Nagasawa, M. *Polymer J.* **1977**, *9*, 153.

(2) (a) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (b) Lochmann, L.; Janata, M.; Machova, L.; Vlcek, P.; Mitera, J.; Müller, A. H. E. *Polym. Prepr. Am. Chem. Soc.* **1988**, *29*, 29. (c) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1990**, *191*, 2253. (d) Kunkel, D.; Müller, A. H. E.; Janata, M.; Lochmann, L.; *Polym. Prepr. Am. Chem. Soc.* **1991**, *32*, 301. (e) Janata, M.; Lochmann, L.; Vlcek, P.; Dybal, J.; Müller, A. H. E. *Makromol. Chem.* **1992**, *193*, 101. (f) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442.

(3) (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (b) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473. (c) Yu, H.; Choi, W.; Lim, K.; Choi, S. *Macromolecules* **1988**, *21*, 2893.

(4) Hosokawa, Y.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1991**, *24*, 824.

(5) (a) Hautekeer, J. P.; Varshney, S. K.; Fayt, R.; Jacobs, C.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 3893. (b) Jacobs, C.; Varshney, S. K.; Hautekeer, R.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 4024. (c) Varshney, S. K.; Jacobs, C.; Hautekeer, J. P.; Bayard, Ph.; Jérôme, R.; Fayt, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 4997.

(6) Boffa, L. S.; Novak, B. M. *Macromolecules* **1994**, *27*, 6993.

(7) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.

(8) Watson, P. L.; Herskovitz, T. *ACS. Symp. Ser.* **1983**, *212*, 459.

(9) (a) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134. (b) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097.

(10) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.

(11) Matsuzaki, K.; Kanai, T.; Kawamura, T.; Matsumoto, S.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 861.

(12) Brandrup, J.; Immergut, E. H. *Polym. Handb.* **1975**, III–144.

(13) (a) Bevington, J. C.; Harris, D. O. *Polym. Lett.* **1967**, *5*, 799. (b) Shima, M.; Kotera, A. *J. Polym. Sci.* **1963**, *A1*, 1115. (c) Zubov, V. P.; Valuev, L. I.; Kabanov, V. A.; Kaegin, V. A. *J. Polym. Sci.* **1971**, *A9*, 833. (d) Madruga, E. L.; Roman, J. S.; Rodriguez, M. J. *J. Polym. Sci., Polym. Chem. Ed.*, **1983**, *21*, 2739.

(14) Suchoparek, M.; Spvacek, J. *Macromolecules* **1993**, *26*, 102.

(15) Holden, G.; Bishop, E. T.; Legge, N. R. *J. Polym. Sci.* **1969**, *C26*, 37.

(16) Evans, W. J.; Dominguez, R; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291.

(17) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

MA9465183