Controlled Synthesis of Poly(acrylic esters) by Aluminum Porphyrin Initiators

Yasunori Hosokawa,† Masakatsu Kuroki, Takuzo Aida, and Shohei Inoue*

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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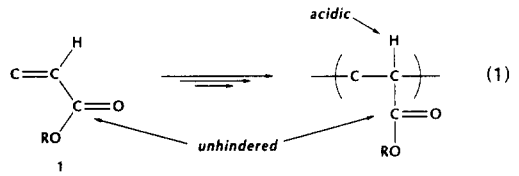
ABSTRACT: Polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) with (5,10,15,20-tetraphenylporphinato)-aluminum 1-propanethiolate ((TPP)AlSPr; **2** (X = $SCH_2CH_2CH_3$)) as initiator at −90 to +20 °C proceeded rapidly to give the polymer with M_w/M_n of 1.1–1.5. The living polymer of methyl methacrylate with a (porphinato)aluminum enolate growing terminal (**4**), prepared by the polymerization with (TPP)AlMe (**2**, X = CH_3), also brought about the polymerization of acrylic esters such as ethyl (1, R = CH_2CH_3), isobutyl (R = $CH_2CH(CH_3)_2$), and *tert*-butyl acrylates, affording the corresponding block copolymers with M_w/M_n ranging from 1.1 to 1.4. The living nature of polymerization was confirmed by the sequential two-stage polymerizations of *tert*-butyl acrylate at room temperature. The three-stage polymerizations of methyl methacrylate, *tert*-butyl acrylate, and methyl methacrylate or 1,2-epoxypropane initiated with (TPP)AlMe (**2**, X = CH_3) afforded the corresponding ABA- or ABC-type block copolymer with well-defined block lengths.

Introduction

Controlled synthesis of polymers of acrylic and methacrylic esters with well-defined architecture is of fundamental as well as practical importance. Rather recently, some new methods have been reported, which enable the synthesis of such polymers with narrow molecular weight distribution.[1,2] Group-transfer polymerization, for example, has provided a facile synthetic route to poly(methacrylic esters) with controlled molecular weight,[2a] but the results are not satisfactory in the case of acrylic esters.[2b] In the polymerization of acrylic esters, suppression of the secondary reaction is much more difficult due to the presence of acidic α-hydrogen (eq 1). Thus, the



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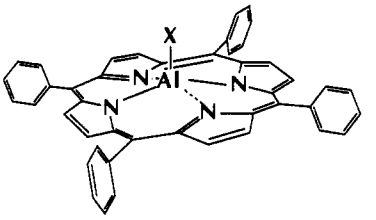
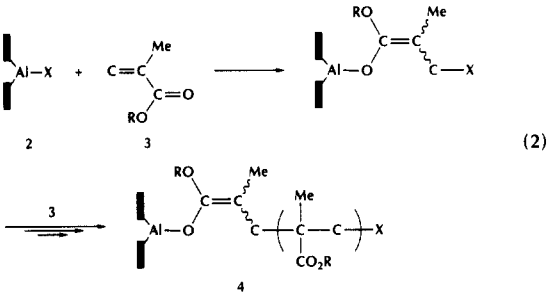
living polymerization of acrylic esters has long been unsuccessful. Teyssié and co-workers have reported that the *sec*-butyllithium/LiCl system reacted with α-methylstyrene is applicable as initiator to the living polymerization of an acrylic monomer with a bulky ester group, e.g., *tert*-butyl acrylate, at a low temperature such as −78 °C.[2f]

We have recently developed the living polymerization of methacrylic esters (**3**) initiated with methylaluminum porphyrin ((TPP)AlMe; **2** (X = CH_3)), which proceeds at room temperature under irradiation with visible light, via a (porphinato)aluminum enolate (**4**) as the growing species (eq 2).[3] In the present paper, we report results of the polymerization of acrylic esters using as initiators the aluminum porphyrins carrying alkyl, alkylthio, and enolate groups at the axial positions and its application to the synthesis of well-defined block copolymers having poly(acrylic ester) segments.



(TPP)AlX (**2**)

(TPP)AlMe (X = CH_3)
(TPP)AlSPr (X = $SCH_2CH_2CH_3$)



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Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized by the reaction of pyrrole and benzaldehyde in refluxing propionic acid and recrystallized from $CHCl_3$/MeOH.[4] Trimethylaluminum ($AlMe_3$) was fractionally distilled under reduced pressure in a nitrogen atmosphere. 1-Propanethiol was refluxed over calcium sulfate and fractionally distilled in a nitrogen atmosphere. Dichloromethane, washed successively with sulfuric acid, water, aqueous sodium bicarbonate, and water, was dried over calcium chloride overnight and then fractionally distilled in a nitrogen atmosphere. Methyl methacrylate (**3**, R = CH_3), ethyl acrylate (1, R = CH_2CH_3), and isobutyl acrylate (1, R = $CH_2CH(CH_3)_2$), obtained from commercial sources, were subjected to fractional distillation under reduced pressure over calcium hydride in a nitrogen atmosphere. *tert*-Butyl acrylate (1, R = $C(CH_3)_3$) was synthesized by the reaction of acryloyl chloride with *tert*-butyl alcohol and fractionally distilled under reduced pressure over calcium hydride in a nitrogen atmosphere. 1,2-Epoxypropane was purified by refluxing over a mixture of calcium hydride and potassium hydroxide and then fractionally distilled in a nitrogen atmosphere.

Procedures. Preparation of Aluminum Porphyrins. For the preparation of (5,10,15,20-tetraphenylporphinato)aluminum methyl ((TPP)AlMe; **2** (X = CH_3)),[5] a 100-mL round-bottomed flask equipped with a three-way stopcock containing $TPPH_2$ (1 mmol) and a Teflon-coated stirring bar was purged with dry nitrogen, and CH_2Cl_2 (40 mL) was added by a hypodermic syringe

† On leave from Wakayama Research Laboratories, Kao Corp., 1334 Minato, Wakayama-shi, Wakayama 640, Japan.

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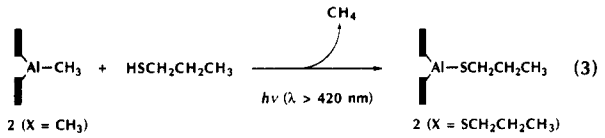
in a nitrogen stream. To this solution was added $AlMe_3$ (1.0 mmol), and the mixture was stirred for 1 h. The volatile fraction was removed from the reaction mixture under reduced pressure to leave (TPP)AlMe as purple powder. For the preparation of (5,10,15,20-tetraphenylporphinato)aluminum 1-propanethiolate ((TPP)AlSPr; 2 (X = $SCH_2CH_2CH_3$)),[6] CH_2Cl_2 (40 mL) and 1-propanethiol (HSPr; 30 mmol) were successively added to the above flask containing (TPP)AlMe (1 mmol), and the mixture was magnetically stirred for 12 h under irradiation with visible light (300-W xenon arc lamp, >420 nm), during which the color of the solution turned from bluish purple to reddish brown characteristic of (TPP)AlSPr (eq 3). Then, the reaction mixture was evaporated



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to dryness under reduced pressure at room temperature to leave (TPP)AlSPr as purple powder.

Polymerization of *tert*-Butyl Acrylate (1, R = $C(CH_3)_3$) Initiated with Aluminum Porphyrins (2). To a 50-mL flask equipped with a three-way stopcock containing a CH_2Cl_2 solution (16 mL) of (TPP)AlMe (2, X = Me; 0.025 mol/L) and a stirring bar under nitrogen atmosphere at 35 °C was added a prescribed amount of *tert*-butyl acrylate by means of a hypodermic syringe, and the mixture was exposed to visible light (300-W xenon arc lamp, >420 nm) with magnetic stirring. After 0.5 h, a small amount of methanol was added, and the reaction mixture was evaporated under reduced pressure at room temperature. The residue was weighed to determine the conversion by subtracting the amount corresponding to the initiator and subjected to gel permeation chromatography (GPC) to estimate the number- and weight-average molecular weights (M_n and M_w) of the produced polymer. The polymerization initiated with (TPP)AlSPr (1, X = $SCH_2CH_2CH_3$; 0.025 mol/L) was similarly carried out in 8 mL of CH_2Cl_2 at room temperature (~20 °C), −70 °C, or −90 °C without irradiation (under diffused light).

Block Copolymerization of Methyl Methacrylate (3, X = CH_3) and Acrylic Esters (1) Initiated with (TPP)AlMe (2, X = CH_3). To a 50-mL flask containing a CH_2Cl_2 solution (16 mL) of (TPP)AlMe (2, X = Me; 0.4 mmol, 0.025 mol/L) and a Teflon-coated stirring bar under nitrogen atmosphere was added a prescribed amount of methyl methacrylate, and the mixture was stirred magnetically at 35 °C in a nitrogen atmosphere under irradiation with visible light (300-W xenon arc lamp, >420 nm).[3] After the monomer was consumed completely, a known amount of acrylic ester (1) was added at −70 °C, room temperature (~20 °C), or +35 °C, and the second-stage polymerization was performed at the same temperature with constant stirring. After 0.5 or 1 h, a small amount of methanol was added to the polymerization system, and the mixture was evaporated to dryness under reduced pressure at room temperature. The residue was weighed to determine the conversion of the second monomer and subjected to GPC and ^1H NMR[7] analyses to evaluate the molecular weights (M_n, M_w) and composition of the produced polymer.

Copolymerization of *tert*-Butyl Acrylate (1, R = $C(CH_3)_3$) and Methyl Methacrylate (3, R = CH_3) Initiated with the Living Polymer of Methyl Methacrylate (4, R = CH_3). Copolymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) and methyl methacrylate (3, R = CH_3) was carried out at room temperature (~20 °C) by adding a mixture of 1 (R = $C(CH_3)_3$) and 3 (R = CH_3) to a CH_2Cl_2 solution of 4 (R = CH_3) (M_n = 2500, M_w/M_n = 1.25; prepared by the polymerization of 3 (R = CH_3) initiated with 2 (X = CH_3) at 100% conversion under irradiation (>420 nm) with a $[3]_0/[2]_0$ of 26) ($[1]_0/[3]_0/[4]_0$ = 91/91/1). An aliquot of the polymerization mixture was periodically taken out by means of a hypodermic syringe in a nitrogen stream, diluted by $CDCl_3$, and subjected to ^1H NMR[8] and GPC analyses to determine the monomer conversion and to evaluate the molecular weights (M_n, M_w) of the produced polymer.

Block Copolymerizations of Methyl Methacrylate (3, R = CH_3), *tert*-Butyl Acrylate (1, R = $C(CH_3)_3$), and Methyl Methacrylate Initiated with (TPP)AlMe (2, X = CH_3). The block copolymerization of methyl methacrylate (3, R = CH_3) and *tert*-butyl acrylate (1, R = $C(CH_3)_3$) was carried out similarly to the above-mentioned procedure in CH_2Cl_2 using (TPP)AlMe (2, X = CH_3; 0.025 mol/L of solution) as initiator ($[3]_0/[1]_0/[2]_0$ = 41/39/1; the first stage, at 35 °C under irradiation; the second stage, at room temperature (~20 °C)). After the complete consumption of *tert*-butyl acrylate (0.5 h), 81 equiv of methyl methacrylate was added, and the mixture was stirred at 35 °C under diffused light for 40 h. Then the volatile fraction was removed under reduced pressure at room temperature, and the residue was weighed to determine the conversion and subjected to GPC and ^1H NMR[7] analyses to evaluate the molecular weights (M_n, M_w) and composition of the produced polymer.

Block Copolymerization of Methyl Methacrylate (3, R = CH_3), Isobutyl Acrylate (1, R = $CH_2CH(CH_3)_2$), and 1,2-Epoxypropane Initiated with (TPP)AlMe (2, X = CH_3). Block copolymerization of methyl methacrylate (3, R = CH_3) and isobutyl acrylate (1, R = $CH_2CH(CH_3)_2$) was carried out similarly to that above by the sequential polymerizations of the corresponding monomers with (TPP)AlMe (2, X = CH_3; 0.025 mol/L of CH_2Cl_2 solution) as initiator ($[3]_0/[1]_0/[2]_0$ = 50/48/1). After the acrylic ester was polymerized completely at −70 °C, the mixture was allowed to warm to room temperature (~20 °C). Then, 220 equiv of 1,2-epoxypropane with respect to (TPP)AlMe was added to the polymerization system, and the mixture was stirred magnetically at 35 °C. After 9 days, the volatile fractions were removed from the reaction mixture under reduced pressure at room temperature to leave a powdery mass, which was analyzed similarly by ^1H NMR[9] and GPC.

Measurements. ^1H NMR measurements were performed in $CDCl_3$ on a JEOL type GSX-270 spectrometer operating at 270.17 MHz, where the small signal due to $CHCl_3$ (δ 7.28) was used as an internal standard to determine chemical shift values. Gel permeation chromatography (GPC) was performed on a Toyo Soda Model 802A high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent at 38 °C with a flow rate of 1.1 mL·min^{-1}. The column set consisted of four Styragel columns of porosity ratings 7000–3000 (two), 3000 (one), and 2000 Å (one). The molecular weight calibration curve was obtained by using standard polystyrenes: 107 000 (M_w/M_n = 1.01), 43 900 (1.01), 39 000 (1.07), 18 000 (1.10), 16 700 (1.02), 6200 (1.04), and 2800 (1.05) (Toyo Soda Manufacturing Co., Ltd.).

Results and Discussion

Polymerization of *tert*-Butyl Acrylate (1, R = $C(CH_3)_3$) Initiated with (TPP)AlMe (2, X = CH_3) and (TPP)AlSPr (2, X = $SCH_2CH_2CH_3$). The polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) was first examined by using (TPP)AlMe (2, X = CH_3) as initiator with the initial monomer-to-initiator mole ratio ($[1]_0/[2]_0$) of 102 in CH_2Cl_2 at 35 °C. The polymerization started upon irradiation with visible light (xenon arc lamp, >420 nm) and proceeded rapidly to attain the complete consumption of the monomer within 0.5 h. The GPC chromatogram of the produced polymer showed a unimodal peak with a slight tailing (Figure 1A), from which the number-average molecular weight (M_n) and the ratio of the weight- and number-average molecular weights (M_w/M_n) were estimated by using polystyrene standards to be 66 500 and 1.38, respectively. The M_n value thus estimated is much higher than that (13 100) expected by assuming that every molecule of 2 produces one polymer molecule. This observation indicates the low efficiency of initiation (N_p/N_{Al}:[10] ratio of the number of polymer molecules to that of 2, 0.17) as a result of the slow initiation compared with the propagation.

On the other hand, the polymerization using (TPP)AlSPr (2, X = $SCH_2CH_2CH_3$) as initiator at −70 °C proceeded even without irradiation to give the polymer with a much narrower molecular weight distribution. An example is shown by the polymerization in CH_2Cl_2 with

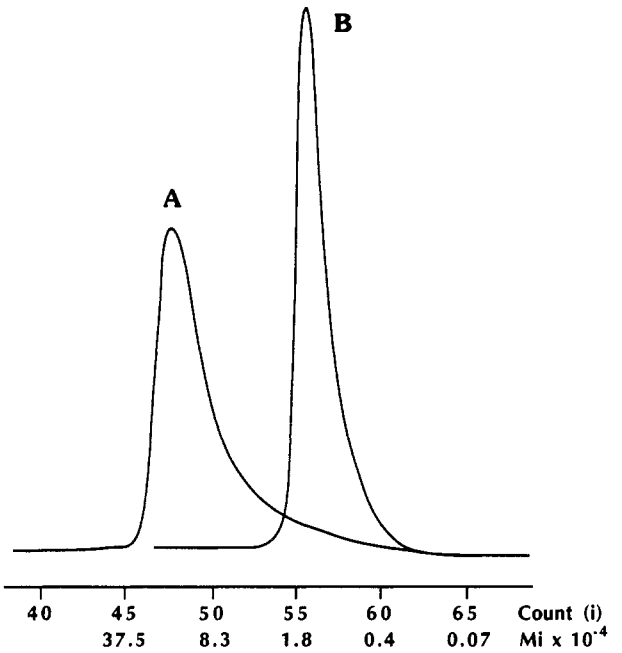

Figure 1. Polymerizations of *tert*-butyl acrylate (1, R = $C(CH_3)_3$)) initiated with aluminum porphyrins in CH_2Cl_2. GPC chromatograms of the polymers formed with (TPP)AlMe (2, X = CH_3) ($[1]_0/[2]_0$ = 102, 35 °C, under irradiation >420 nm, 0.5 h, 100% convn) (A) and (TPP)AlSPr (1, X = $SCH_2CH_2CH_3$) ($[1]_0/[2]_0$ = 52, −70 °C, under diffused light, 0.5 h, 100% convn) (B).

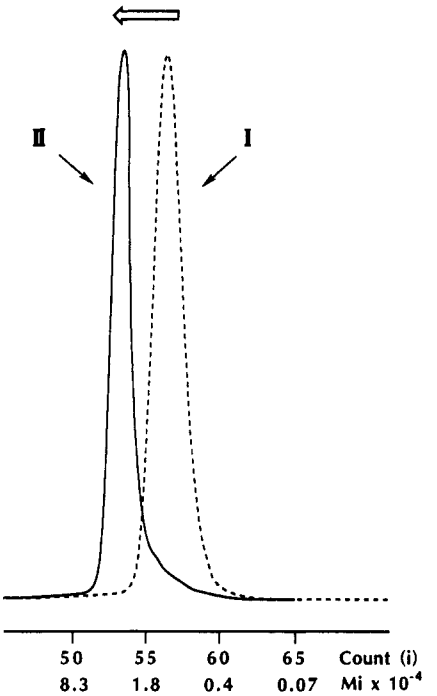

Figure 2. Polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) initiated with the living prepolymer of methyl methacrylate (4 (R = CH_3), M_n = 9580, M_w/M_n = 1.09), $[1]_0/[4]_0$ = 100, in CH_2Cl_2 at room temperature (~20 °C) under diffused light. GPC chromatograms of the prepolymer (I) and the final product (II) (M_n = 22 400, M_w/M_n = 1.12).

the initial mole ratio $[1\ (R = C(CH_3)_3)]_0/[(TPP)AlSPr]_0$ of 52 at −70 °C under diffused light, which proceeded rapidly and was completed within 0.5 h. As shown in Figure 1B, the produced polymer exhibited a unimodal, sharp GPC chromatogram, from which the M_n and M_w/M_n values were estimated by using polystyrene standards to be 10 000 (N_p/N_{Al} = 0.67) and 1.14, respectively. A similar result was obtained for the polymerization carried out at −90 °C with the initial mole ratio $[1\ (R = C(CH_3)_3)]_0/[(TPP)AlSPr]_0$ of 48, which was also completed in 0.5 h to give the polymer with M_n and M_w/M_n, respectively, of 12 200 (N_p/N_{Al}[10] = 0.5) and 1.13. The polymerization attempted at room temperature (20 °C) under similar conditions ($[1\ (R = C(CH_3)_3)]_0/[(TPP)AlSPr]_0$ = 100) also proceeded to 100% conversion (0.5 h) to give the polymer with a M_n of 11 600 (polystyrene standards), which is close to that expected from the monomer-to-initiator mole ratio (12 800) (N_p/N_{Al}[10] = 1.1), but the molecular weight distribution was not narrow as indicated by the ratio M_w/M_n of 1.48.

Polymerization of Acrylic Esters (1) Initiated with (TPP)Al Enolate (4). Synthesis of Methacrylic Ester–Acrylic Ester Block Copolymers. Polymerizations of acrylic esters (1) were attempted with the living prepolymer of methyl methacrylate bearing a (porphinato)aluminum enolate growing terminal (4, R = CH_3), prepared by the visible light induced polymerization of methyl methacrylate with (TPP)AlMe (2, X = CH_3; 0.025 mol/L) (eq 2).[3] A typical example is shown by the polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) with the initial mole ratio of 1 to 4 (M_n = 9580, M_w/M_n = 1.09) of 100 in CH_2Cl_2 at room temperature (~20 °C), which proceeded without irradiation to attain 100% conversion within 0.5 h. The GPC analysis of the polymer finally produced showed a unimodal, sharp chromatogram with M_n and M_w/M_n, as estimated by GPC using polystyrene standards to be 22 400 and 1.12, respectively (Figure 2). The absence of the prepolymer (I) in the final product (II) indicates the quantitative initiation of the polymerization from the living terminal ((porphinato)aluminum enolate) of the prepolymer (4, R = CH_3), to form the methyl methacrylate–*tert*-butyl acrylate block copolymer. The M_n value of the block copolymer (M_n = 22 400, polystyrene standards) is exactly the same as the expected value by assuming that every molecule of 4 produces one molecule of the block copolymer. The time course was examined for the polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) in CH_2Cl_2 at room temperature using the living polymer 4 (M_n = 3280, M_w/M_n = 1.10) as initiator, where the monomer was consumed very rapidly with heat evolution to attain 67, 92, and 100% conversion in only 2, 3, and 4 min, respectively. As shown in Figure 3, M_n of the block copolymer was observed to increase with conversion to provide a straight line, which is very close to the line expected by assuming the quantitative initiation from every molecule of the prepolymer (4). It should also be noted that the ratio M_w/M_n remained almost constant in a range 1.1–1.2 throughout the polymerization, indicating the uniformity of the molecular weight of the poly(acrylic ester) block. The content of the unit from *tert*-butyl acrylate in the block copolymer finally obtained (M_n = 15800, M_w/M_n = 1.16), as determined by ^1H NMR,[7] was 75%, which is close to that calculated from the mole ratio of the two monomers reacted (77%) and from the M_n values of the two blocks estimated by GPC (75%). The results of the polymerizations of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) with varying mole ratios to 4 (R = CH_3) at 100% conversion are shown in Table I (runs 8–10), which clearly demonstrate a linear dependence of the molecular weight of the poly(acrylic ester) block (M_n of poly(1) block) on $[1]_0/[4]_0$ with the ratio M_w/M_n in a range from 1.1 to 1.2. Thus, the controlled synthesis of methyl methacrylate–*tert*-butyl acrylate block copolymer was achieved at room temperature by the sequential polymerizations of the corresponding monomers using (TPP)AlMe (2, X = CH_3) as initiator.

Table I
Polymerization of Acrylic Esters (1) Initiated with the Living Polymer of Methyl Methacrylate (4; R = CH_3)[a]

		prepolymer (4)[b]						block copolymer			
run	1: R	M_n[c]	M_w/M_n[c]	$[1]_0/[4]_0$	temp, °C	time, h	convn, %	M_n[c]	M_w/M_n[c]	M_n of poly(1)	block[d]
1	CH_2CH_3	4700	1.15	119	−70	0.5	100	14 100	1.43	9 400	(11 900)[e]
2		5000	1.10	208	−70	0.5	49	16 200	1.42	11 200	(10 200)
3	$CH_2CH(CH_3)_2$	5300	1.09	48	−70	0.5	100	11 500	1.25	6 200	(6 100)
4		4600	1.09	100	−70	0.5	100	18 800	1.29	14 200	(12 800)
5		5200	1.10	147	−70	1.0	100	24 500	1.39	19 300	(18 800)
6		5200	1.09	204	−70	1.0	90	27 900	1.43	22 700	(23 500)
7		10100	1.09	109	35	0.5	60[f]	19 000	1.25	8 900	(8 400)
8	$C(CH_3)_3$	4800	1.09	48	rt[g]	0.5	100	11 000	1.11	6 200	(6 100)
9		3300	1.10	100	rt	0.5	100	15 800	1.16	12 500	(12 800)
10		3800	1.09	147	rt	0.5	100	22 300	1.27	18 500	(18 800)

[a] In CH_2Cl_2 under nitrogen atmosphere. [b] Prepared by the polymerization of methyl methacrylate (3, R = CH_3) initiated with (TPP)AlMe (2, X = CH_3) in CH_2Cl_2 at 35 °C under irradiation with xenon arc lamp ($\lambda > 420$ nm) under nitrogen atmosphere. [c] Estimated by GPC using polystyrene standards. [d] M_n of the block copolymer (M_n of the prepolymer). [e] Calculated from $[1]_0/[4]_0$(convn/100)MW of 1. [f] No more monomer was consumed in the prolonged reaction. [g] At ~20 °C.

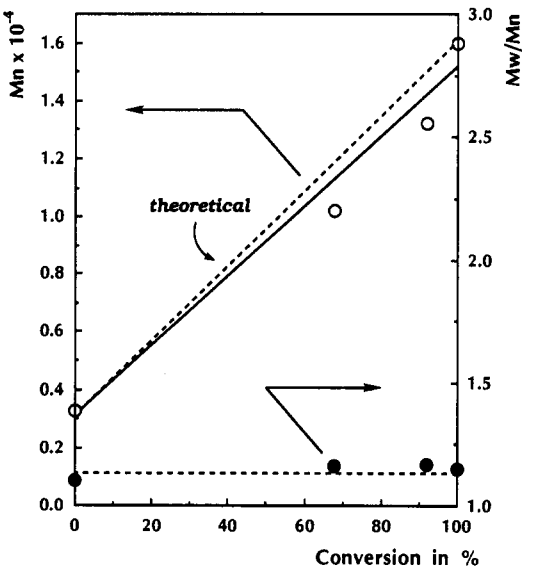

Figure 3. Polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) initiated with the living prepolymer of methyl methacrylate (4 (R = CH_3), M_n = 3280, M_w/M_n = 1.10), $[1]_0/[4]_0$ = 100, in CH_2Cl_2 at room temperature (~20 °C) under diffused light: M_n (○) (M_w/M_n (●)) versus conversion.

In order to confirm the living nature of the polymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$), 48 equiv of 1 (R = $C(CH_3)_3$) was once polymerized at room temperature up to 100% conversion (0.4 h) from 4 (R = CH_3; M_n = 4800, M_w/M_n = 1.09) to prepare the prepolymer (block copolymer, M_n = 11 000, M_w/M_n = 1.11), and 110 equiv of *tert*-butyl acrylate was further added. In this case, the polymerization of *tert*-butyl acrylate ensued at the third stage and was completed within 0.4 h. The GPC profile of the polymerization showed that the peak corresponding to the prepolymer shifted toward the higher molecular weight region to provide a unimodal, sharp peak with M_n and M_w/M_n, respectively, of 24 000 (M_n(expected)= 25 500) and 1.25. Thus, the polymerization of *tert*-butyl acrylate initiated with aluminum porphyrin proceeds essentially with living character at room temperature.

The results of the polymerizations of other acrylic esters (1) such as ethyl acrylate (R = CH_2CH_3) and isobutyl acrylate (R = $CH_2CH(CH_3)_2$) from the living poly(methyl methacrylate) 4 are summarized in Table I (runs 1–7), where the block copolymers with fairly narrow molecular weight distribution were obtained from isobutyl acrylate. As a typical example, given in run 3 is the polymerization of isobutyl acrylate at −70 °C, which proceeded rapidly and afforded at 100% conversion (0.5 h) the block copolymer with M_n and M_w/M_n, respectively, of 11 500 (M_n(expected)= 11 400) and 1.25. When the mole ratio of isobutyl acrylate to the prepolymer (4) was increased from 48 to 100, 147, and 204 (runs 4–6), the M_n of the poly(acrylic ester) block was increased almost proportionally from 6200 to 14 200, 19 300, and 22 700, with a slight broadening of the molecular weight distribution (M_w/M_n from 1.25 to 1.43). The polymerization of isobutyl acrylate attempted at 35 °C with the initial mole ratio to 4 (M_n = 10 100, M_w/M_n of 1.09) of 109 also proceeded rapidly to attain 60% conversion in 0.5 h, but no further polymerization ensued. The polymerization of ethyl acrylate (1, R = CH_2CH_3) from 4 attempted at −70 °C also proceeded rapidly to afford the corresponding block copolymer having the expected M_n from the ratio $[1]_0/[4]_0$ and the M_w/M_n ratio of about 1.4 (runs 1 and 2).

Competitive Polymerizations (Copolymerization) of Methacrylic and Acrylic Esters from Poly(methacrylic ester) Growing Terminal (4). In order to evaluate the difference in the polymerizabilities of acrylic and methacrylic esters with aluminum porphyrin initiator, copolymerization of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) and methyl methacrylate (3, R = CH_3) was investigated by using living poly(methyl methacrylate) (4 (R = CH_3), M_n = 2500, M_w/M_n = 1.25) with the mole ratio $[1]_0/[3]_0/[4]_0$ of 91/91/1 in CH_2Cl_2 at room temperature (~20 °C). As shown in Figure 4, *tert*-butyl acrylate was polymerized much more rapidly than methyl methacrylate and consumed completely in 1 h, while only 6% of methyl methacrylate was consumed.[8] Although the polymerization of residual methyl methacrylate further proceeded, the reaction was very slow (e.g., after 300 h, 79% conversion). This observation clearly indicates a large polymerizability gap between acrylic and methacrylic esters. The GPC chromatogram of the produced copolymer was sharp and unimodal throughout the copolymerization (e.g., at 100% conversion of 1 (R = $C(CH_3)_3$) and 79% conversion of 3 (R = CH_3), M_w/M_n = 1.08 (M_n = 19 500)).

Block Copolymerization of Methacrylic Ester or Epoxide from Poly(acrylic ester) Growing Terminal. The nucleophilic reactivity of the growing species of the polymerization of acrylic ester (1) is generally thought to be lower than that of methacrylic ester (3) due to the absence of the electron-donating methyl group, and therefore the controlled synthesis of their block copolymer starting from the polymerization of acrylic ester is of much difficulty.[2b] But the sharp and unimodal GPC profile of the copolymer of 1 (R = $C(CH_3)_3$) and 3 (R = CH_3), as

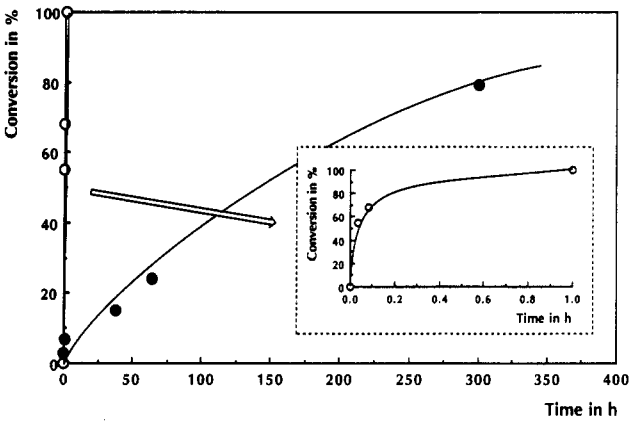

Figure 4. Competitive polymerization (copolymerization) of *tert*-butyl acrylate (1, R = $C(CH_3)_3$) and methyl methacrylate (3, R = CH_3) with the living polymer of methyl methacrylate (4, M_n = 2500, M_w/M_n = 1.25; formed at 100% conversion by the polymerization of 3 (R = CH_3) with 2 (X = CH_3) with the mole ratio of 26) with the initial mole ratio $[1]_0/[3]_0/[4]_0$ of 91/91/1 in CH_2Cl_2 at room temperature (~20 °C). Time–conversion relationships for 1 (R = $C(CH_3)_3$) (○) and 3 (R = CH_3) (●).

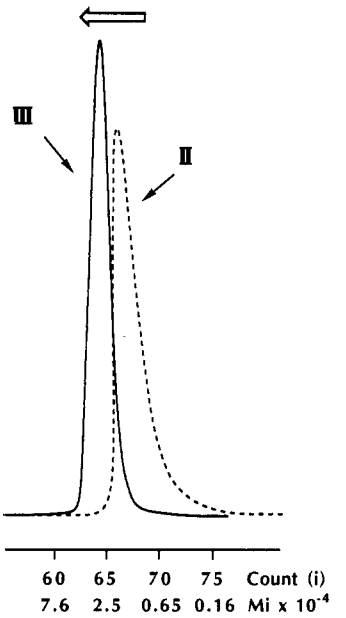

Figure 5. Sequential three-stage polymerizations of methyl methacrylate (3, R = CH_3) (41 equiv, 35 °C, under irradiation >420 nm, 20 h, 100% convn, M_n = 3500, M_w/M_n = 1.27), *tert*-butyl methacrylate (1, R = $C(CH_3)_3$) (39 equiv, room temperature (~20 °C), under diffused light, 0.5 h, 100% convn), and methyl methacrylate (81 equiv, 35 °C, under diffused light, 40 h, 100% convn) initiated with (TPP)AlMe (2, X = CH_3) in CH_2Cl_2. GPC chromatograms of the polymers formed at the second (II; M_n = 9900, M_w/M_n = 1.23) and third stages (III; M_n = 20 200, M_w/M_n = 1.11).

mentioned above, implies the possibility of the successive polymerizations of acrylic ester and methacrylic ester in this order to give the block copolymer. Therefore, the polymerization of methyl methacrylate (81 equiv) was attempted from the growing species of the polymerization of *tert*-butyl acrylate, which was prepared by the polymerization of methyl methacrylate (3, R = CH_3) with (TPP)AlMe (2, X = CH_3; 0.025 mol/L of CH_2Cl_2 solution) ($[3]_0/[2]_0$ = 41, 35 °C, under irradiation: $\lambda > 420$ nm, 20 h, 100% conversion, M_n = 3500, M_w/M_n = 1.27) followed by *tert*-butyl acrylate (1, R = $C(CH_3)_3$) ($[1]_0/[2]_0$ = 39, room temperature (~20 °C), under diffused light, 0.5 h, 100% conversion, M_n = 9900, M_w/M_n = 1.23, content of 3 (R = CH_3) was 48% as determined by ^1H NMR[7]). In this case, the third-stage polymerization of methyl methacrylate actually took place at 35 °C from the prepolymer (AB-type block copolymer, peak II in Figure 5) to attain 100% conversion after 40 h and gave the corresponding ABA-type block copolymer (peak III) with M_n and M_w/M_n, respectively, of 20 200 and 1.11 (content of 3 (R = CH_3) was 73%[7]).

The attempted polymerization of 1,2-epoxypropane (220 equiv) at 35 °C from the methyl methacrylate–isobutyl acrylate block copolymer, prepared similarly to that above (prepolymer (4, R = CH_3), M_n = 5300, M_w/M_n = 1.09; block copolymer of 3 (R = CH_3) and 1 (R = $CH_2CH(CH_3)_2$), M_n = 11 500, M_w/M_n = 1.25), was also successful to give at 39% conversion (9 days) the corresponding ABC-type polyvinyl–polyether block copolymer with M_n and M_w/M_n, respectively, of 15 300 and 1.23. The contents of the units from methyl methacrylate, isobutyl acrylate, and 1,2-epoxypropane in the block copolymer, as determined by ^1H NMR,[9] were 30, 30, and 40%, respectively.

These two successful examples of the block copolymerizations demonstrate that the growing species of the polymerization of acrylic ester with aluminum porphyrin initiator is reactive enough to attack the double bond of methacrylic ester and epoxide ring.

Conclusion

A novel methodology for the controlled polymerization of acrylic esters has been developed by using aluminum porphyrin initiators (TPP)AlMe (2, X = CH_3), (TPP)Al-SPr (2, X = $SCH_2CH_2CH_3$), and (TPP)Al enolate (4, the living polymer of methyl methacrylate prepared with (TPP)AlMe). With respect to the initiation efficiency, (TPP)-Al enolate as initiator gave the best result, where the polymerization of *tert*-butyl acrylate with living character was attained even at room temperature, affording the polymer of expected molecular weight with narrow molecular weight distribution. (TPP)AlSPr, which is a new entry as initiator, also enabled the formation of poly(acrylic ester) with narrow molecular weight distribution at a low temperature such as −70 °C, but the molecular weight was higher than expected. The block copolymers of methacrylic and acrylic esters with narrow molecular weight distribution were synthesized by starting from the polymerization of either methacrylic ester or acrylic ester, although the latter way is generally of much difficulty.

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(7) ^{1}H NMR ($CDCl_3$): for $-(CH_2C(CH_3)(CO_2CH_3))-$, δ 1.7 (CH_2), 0.75–1.2 (CH_3), 3.65 (OCH_3); for $-(CH_2CH(CO_2C(CH_3)_3))-$, δ 1.55 (CH_2), 2.25 (CH), 1.45 (CH_3).

(8) The conversion of methyl methacrylate (**3**, R = CH_3) was determined by ^{1}H NMR from the relative intensity of the signals due to OCH_3 of **3** (R = CH_3) (δ 3.75 ppm) and its polymeric unit (δ 3.65). The conversion of *tert*-butyl acrylate (**1**, R = $C(CH_3)_3$) was also determined by ^{1}H NMR based on the sum of the intensities of the signals due to the vinyl group (δ 6.28 and 5.70 (CH_2=CH) and 6.03 (CH_2=C*H*) of **1** (R = $C(CH_3)_3$) relative to the sum of those of the signals due to OCH_3 of **3** (R = CH_3) and its polymeric unit.

(9) ^{1}H NMR ($CDCl_3$): for $-(CH_2C(CH_3)(CO_2CH_3))-$, see ref 7; for $-(CH_2CH(CO_2CH_2CH(CH_3)_2)-$, δ 1.65 (CH_2), 2.35 (CH), 3.85 (OCH_2), 1.95 ($CHMe_2$), 0.95 (CH_3); for $-(CH_2CH(CH_3)O)-$, δ 3.6 (CH_2), 3.4 (CH), 1.15 (CH_3).

(10) N_p/N_{Al}, calculated from $([\text{monomer}]_0/[2]_0)(\text{convn}/100)M_n(\text{GPC})^{-1}$.