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Accelerated Living Polymerization of Methacrylonitrile with Aluminum Porphyrin Initiators by Activation of Monomer or Growing Species. Controlled Synthesis and Properties of Poly(methyl methacrylate-*b*-methacrylonitrile)s

Hiroshi Sugimoto,[†] **Masaaki Saika,**[‡,§] **Yasunori Hosokawa,**[‡,∥]
Takuzo Aida,[‡] **and Shohei Inoue***[,†]

Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan, and Department of Chemistry and Biotechnology, Graduate School of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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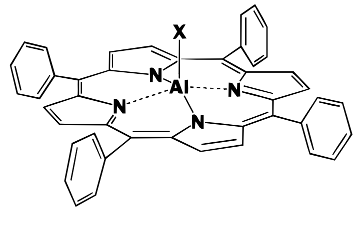
ABSTRACT: Polymerization of methacrylonitrile (MAN) with methylaluminum porphyrin (**1**) as initiator proceeded rapidly in the presence of methyaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**). The living polymer of methyl methacrylate (MMA) with a (porphinato)aluminum enolate growing terminal (**2**), prepared by the polymerization of MMA with **1**, also brought about the polymerization of MAN in the presence of **3**, affording the corresponding block copolymer with M_w/M_n ranging from 1.1 to 1.3. The living nature of polymerization was confirmed by a delayed sequential two-stage polymerization of MAN initiated with **2** (living prepolymer of MMA on aluminum porphyrin). Pyridine instead of **3** was also effective for the rapid block copolymerization of MAN from **2** to give the block copolymer of controlled molecular weight. Copolymerization of MAN and MMA initiated with **1** proceeded more rapidly in the presence of **3** or pyridine than in the absence. In the presence of **3**, the consumption of MAN was much more accelerated than that of MMA, while in the presence of pyridine, the consumptions of MAN and MMA were almost equally accelerated. The poly(MMA-*b*-MAN) obtained by the block copolymerization of MAN from the living prepolymer of MMA (**2**) was found to form micellar aggregates in organic solvents such as CHCl$_3$ and THF, depending on the composition and block length, as well as the concentration and temperature. Furthermore, a microphase separated structure was clearly observed by transmission electron microscopy for the block copolymer membrane cast from CHCl$_3$/THF.

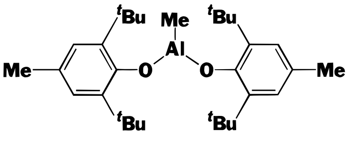
Introduction

Controlled synthesis of polymers with well-defined architecture is one of the ultimate goals of synthetic polymer chemistry. For this purpose, it is essential to select an appropriate initiator to ensure the uniform chain growth of all polymer molecules without side reactions. For the anionic polymerization of methacrylonitrile (MAN), many initiators have been developed, which include alkali-metal alkyls such as butyllithium,[1] (triphenylmethyl)sodium,[2] (phenylisopropyl)potassium,[2] the disodium salt of living α-methylstyrene tetramer,[3] alkali-metal amides,[4] alkoxides,[5] and hydroxide,[6] alkali metal in liquid NH$_3$,[7] quaternary ammonium hydroxide,[8] and silyl ketene acetal coupled with nucleophilic or Lewis acidic catalysts.[9] However, only a single example of the synthesis of PMAN with narrow molecular weight distribution can be cited, and the reported number-average molecular weights were much higher than those calculated from the stoichiometry of the butyllithium initiator.[1]

We have reported that aluminum porphyrins (**1**) initiate the living polymerizations of a wide variety of monomers such as lactones,[10] epoxides,[11] alkyl methacrylates,[12] and alkyl acrylates,[13] affording the corresponding polymers of controlled molecular weight with a narrow molecular weight distribution. Recently, we have discovered the new method "high-speed living polymerization" of methyl methacrylate, by using (enolato)aluminum porphyrin (**2**) as a nucleophilic initiator in conjunction with organoaluminum compounds, such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**),as Lewis acids.[14] On the other hand, we have reported that some reactions of aluminum porphyrin take place only when Lewis bases are added to the reaction system. For example, the addition of a Lewis base is essential for the reaction of aluminum porphyrins with carbon dioxide. We postulate that the added Lewis base coordinates to the central aluminum atom and enhances the reactivity of aluminum porphyrins.[15]



(TPP)AlX (1)



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In the present paper, we report the living anionic polymerization of methacrylonitrile by two initiating systems such as the aluminum porphrin−Lewis acid system and the aluminum porphyrin−Lewis base sys-

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[†] Science University of Tokyo.

[‡] University of Tokyo.

[§] On leave from Kansai Paint Co. Ltd., Higashiyawata, Hiratsuka, Kanagawa 254, Japan.

[∥] On leave from Kao Co., Minato, Wakayama-shi, Wakayama 640, Japan.

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tem, which enable the synthesis of poly(methyl methacrylate-*b*-methacrylonitrile)s of controlled molecular weights. Furthermore, the unique properties of the copolymers in solution and as films are discussed.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole (0.8 mol) and benzaldehyde (0.8 mol) in propionic acid (2.5 L) under reflux for 0.5 h, and the crude product, which precipitated when the reaction mixture stood overnight at room temperature, was recrystallized from $CHCl_3$/MeOH (1/2 v/v) to give $TPPH_2$ in 20% yield.[16] Trimethylaluminum (Me_3Al) was fractionally distilled under reduced pressure under a nitrogen atmosphere. 2,6-Di-*tert*-butyl-4-methylphenol and triphenylphosphine were recrystallized from hexane. Pyridine and 1-methylimidazole were dried over CaH_2 and fractionally distilled under a nitrogen atmosphere.

Methyl methacrylate (MMA) and methacrylonitrile (MAN) were fractionally distilled over CaH_2 under reduced pressure under a nitrogen atmosphere.

Dichloromethane (CH_2Cl_2) was washed successively with concentrated H_2SO_4, water, and aqueous $NaHCO_3$, dried over $CaCl_2$, and distilled over CaH_2 under a nitrogen atmosphere. Deuterated dichloromethane (CD_2Cl_2), stirred at room temperature with a small amount of triethylaluminum, was subjected to several freeze-to-thaw cycles, collected in a trap cooled in a liquid-nitrogen bath, and stored under nitrogen. Benzene (C_6H_6), deuterated benzene (C_6D_6), and hexane were distilled over sodium benzophenone ketyl under a nitrogen atmosphere. Deuterated chloroform ($CDCl_3$) and deuterated tetrahydrofuran (THF-d_8) were fractionally distilled over CaH_2 under a nitrogen atmosphere. Deuterated dimethyl sulfoxide (DMSO-d_6) was fractionally distilled over CaH_2 under reduced pressure under a nitrogen atmosphere.

Preparation of Methylaluminum 5,10,15,20-Tetraphenylporphine (1; X = Me). To a round-bottomed flask (50 mL) equipped with a three-way stopcock containing $TPPH_2$ (0.25 mmol) under dry nitrogen, were successively added CH_2Cl_2 (10 mL) and Me_3Al (1.2 equiv, 0.03 mL) by means of hypodermic syringes under a nitrogen stream, and the mixture was stirred for 1 h under a nitrogen atmosphere. Then, volatile fractions were removed from the reaction mixture under reduced pressure to leave **1** (X = Me) as a purple powder.[17]

Preparation of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3). To a 50-mL round-bottomed flask equipped with a three-way stopcock, containing 2,6-di-*tert*-butyl-4-methylphenol (25 mmol, 5.51 g), were successively added hexane (20 mL) and Me_3Al (12.5 mmol, 1.2 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h, whereupon white precipitates were formed. The white suspension was allowed to stand without stirring at room temperature, and the supernatant, upper layer (9 mL) was taken out by a syringe under a nitrogen stream. To this flask containing the wet powdery residue was added hexane at 60 °C under a nitrogen stream until the powder completely dissolved (5.5 mL), and the solution was cooled to room temperature, affording **3** as white crystals (3.7 g, 62% yield), which were dried under reduced pressure at room temperature.[18]

Polymerization. Polymerization of Methacrylonitrile Initiated with Methylaluminum Porphyrin (1; X = Me) in the Presence of Methyaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3). To a 100-mL round-bottomed flask equipped with a three-way stopcock containing a CH_2Cl_2 solution (20 mL) of (TPP)AlMe (**1**; X = Me) (0.25 mmol), was added MAN (25 mmol, 2.1 mL) by a syringe under a nitrogen stream. The mixture was irradiated with a xenon arc light (λ > 420 nm) at room temperature. After 2-h irradiation, **3** was added (10 equiv with respect to **1**) at room temperature under diffuse light. After 5 h, MeOH (5 mL) was added to the flask, and the reaction mixture was subjected to ^{1}H NMR and GPC analyses to determine the monomer conversion and to estimate the average molecular weights of the produced polymer, respectively.

For isolation of the produced PMAN, the polymerization mixture was poured into a large volume of MeOH (500 mL), and the slightly colored polymer that precipitated was collected and dried in vacuo to give PMAN as a pale green powder in almost quantitative yield.

Polymerization of Methacrylonitrile Initiated with an (Enolato)aluminum Porphyrin (2) in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3) or Pyridine. A typical example is given below by the block copolymerization of MMA and MAN in the presence of methyaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate **(3).** To a 100-mL round-bottomed flask attached to a three-way stopcock, containing a CH_2Cl_2 solution (20 mL) of (TPP)AlMe (**1**; X = Me) (0.25 mmol), was added MMA (25 mmol, 2.7 mL) by a syringe under a nitrogen stream, and the mixture was irradiated with xenon arc light (λ > 420 nm) at room temperature. After 2-h irradiation, **3** was added (1 equiv with respect to **2**) to the reaction mixture at room temperature under diffuse light. After 5 min, an aliquot of the reaction mixture was taken out by a syringe under a nitrogen stream and subjected to NMR analysis to confirm the complete monomer consumption and to GPC analysis to estimate the average molecular weights of the MMA prepolymer produced. Then MAN (25 mmol, 2.1 mL) was added to the polymerization system by a hypodermic syringe under a nitrogen stream. After 3 h, MeOH (5 mL) was added to the flask, and the reaction mixture was subjected to ^{1}H NMR and GPC analyses to determine the monomer conversion and to estimate the average molecular weights of the produced polymer, respectively.

Polymerization of MAN with **2** in the presence of pyridine was carried out similarly to the above under irradiation or in the dark.

Isolation of Block Copolymers. To isolate the produced PMMA−PMAN block copolymer, the polymerization mixture was poured into a large excess of MeOH (500 mL); the polymer that precipitated was redissolved in a minimum volume of $CHCl_3$, and the solution was added dropwise into a large volume of MeOH with vigorous stirring. The slightly colored precipitates that formed were collected and reprecipitated similarly, to give the polymer as white precipitates, which were collected, dissolved in C_6H_6, and subjected to freeze−drying to give a PMMA−PMAN block copolymer as a white powder in 80% yield.

Three-Stage Polymerization of MMA, MAN, and MAN in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3). To a 100-mL round-bottomed flask attached to a three-way stopcock containing a CH_2Cl_2 solution (20 mL) of **1** (0.25 mmol) was added MMA (25 mmol, 2.7 mL) by a syringe under a nitrogen stream. The mixture was irradiated with xenon arc light (λ > 420 nm) at 35 °C. After 2-h irradiation, **3** was added (1 equiv with respect to **2**) to the polymerization system at room temperature under diffuse light. After 5 min, an aliquot of the reaction mixture was taken out by a syringe under a nitrogen stream and subjected to NMR analysis to confirm the complete monomer consumption and to GPC analysis to estimate the average molecular weights of the produced PMMA. Then MAN (12.5 mmol, 1.1 mL) was added to the polymerization system by a hypodermic syringe under a nitrogen stream. After 4 h, an aliquot of the reaction mixture was taken out by a syringe under a nitrogen stream and subjected to NMR and GPC analyses for the confirmation of the complete monomer consumption and for the estimation of the average molecular weights of the block copolymer, respectively. The polymerization mixture that remained in the flask was allowed to stand at room temperature for 15 h, and then the second part of MAN (12.5 mmol) was fed. After 6 h, MeOH (5 mL) was added to the flask, and the polymerization mixture was subjected to ^{1}H NMR and GPC analyses.

Copolymerization of Methacrylonitrile and Methyl Methacrylate. Copolymerization of methacrylonitrile (MAN) and methyl methacrylate (MMA) was carried out as follows. To a 100-mL round-bottomed flask fitted with a three-way stopcock, containing a CH_2Cl_2 solution (10 mL) of (TPP)AlMe (**1**) (0.25 mmol) under nitrogen, was added MMA (25 mmol, 2.7 mL), and the mixture was stirred at room temperature

Table 1. Block Copolymerization of Methacrylonitrile (MAN) with the Living Prepolymer of Methyl Methacrylate (MMA) (2) in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3)[a]

			prepolymer (**2**)[b]				block copolymer				
entry no.	$[MMA]_0/[\mathbf{1}]_0$	$[\mathbf{3}]_0/[\mathbf{1}]_0$	M_n[c]	M_w/M_n[c]	$[MAN]_0/[\mathbf{2}]_0$	time/h	M_n[c]	M_w/M_n[c]	M_n of PMAN block[d]		MAN/mol %[e]
1	30	4.0			100	18	11 100	1.27		(6 700)[f]	77.3
2	50	3.0	9 200	1.13	50	2	16 000	1.19	6 800	(3 400)	
3	50	4.0	6 500	1.27	50	1	11 700	1.24	5 200	(3 400)	
4	50	10.0	6 600	1.37	50	0.5	11 200	1.35	4 600	(3 400)	
5	100	3.0	10 700	1.19	50	2	16 100	1.23	5 400	(3 400)	40.1
6[g]	100	10.0	11 200	1.11	100	3	20 800	1.17	9 600	(6 700)	56.7
7[g]	100	10.0	11 100	1.19	150	3	23 600	1.35	12 500	(10 100)	62.3
8[g]	100	10.0	13 500	1.14	200	5	24 000	1.48	10 500	(13 400)	
9	200	3.0			50	3	30 300	1.18		(3 400)	19.4
10[h]	200	10.0	22 900	1.11	200	14	39 300	1.24	16 400	(13 400)	50.1

[a] In CH_2Cl_2 under nitrogen at room temperature; $[\mathbf{2}]_0 = 25$ mM, 100% conversion. [b] Prepared by the living polymerization of MMA initiated with (TPP)AlMe (**1**) in CH_2Cl_2 at 35 °C under irradiation with xenon arc light ($\lambda > 420$ nm) in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**), 100% conversion. [c] By GPC based on polystyrene standards. [d] (M_n of the block copolymer) − (M_n of the prepolymer). [e] Calculated from N content in elemental analysis. [f] Calculated from $[MAN]_0/[\mathbf{2}]_0 \times$ (MW of MAN (67)). [g] $[\mathbf{2}]_0 = 12.5$ mM. [h] $[\mathbf{2}]_0 = 6.3$ mM.

under irradiation with xenon arc light ($\lambda > 420$ nm). After 3 h, an aliquot of the reaction mixture was taken out by a syringe under a nitrogen stream and subjected to NMR analysis to determine the monomer conversion. Then an equimolar amount of MAN with respect to the unreacted MMA and 3 equiv of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) with respect to aluminum porphyrin (**2**) were successively added to the reaction mixture under diffuse light at room temperature. An aliquot of the reaction mixture was periodically taken out by a syringe under a nitrogen stream and subjected to ^1H NMR and GPC analyses.

Copolymerizations of MAN and MMA were carried out in the absence of **3** under irradiation and in the presence of pyridine under diffused light.

Conversion of Polymethacrylonitrile into Poly(methyl methacrylate). Hydrolysis of polymethacrylonitrile (0.3 g) was carried out in a 30% aqueous solution of KOH (100 mL) under reflux.[19] After 200 h, the polymer solution was acidified with 5 N HCl, and white powder was separated by filtration and dissolved in MeOH (200 mL). After insoluble KCl was filtered off, the MeOH solution was concentrated to about 20 mL and poured into ether (500 mL). The polymer that precipitated was collected by filtration, washed with ether, and dried in vacuo (0.16 g, 36%). Poly(methacrylic acid) (0.04 g) thus obtained was dissolved in MeOH (20 mL), to which was added Me_3SiCHN_2 (10% in hexane, 2 mL) for methylation.[20] The solution gradually turned heterogeneous while it was stirred for 2 h. The powdery precipitate was collected by filtration, washed with MeOH, and dried in vacuo to give poly(methyl methacrylate) as a white powder (0.20 g, 45%).

Measurements. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH Model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using tetrahydrofuran as eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes; $M_n = 2\,890\,000$ ($M_w/M_n = 1.09$), 422 000 (1.04), 107 000 (1.07), 43 900 (1.01), 16 700 (1.02), 9000 (1.06), 6200 (1.04), 4000 (1.10), and 2800 (1.05). ^1H and ^{13}C NMR measurements were performed in $CDCl_3$, CD_3OD, CD_2Cl_2, DMSO-d_6, or THF-d_8 using a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to tetramethylsilane (δ 0.00) for ^1H or CD_2Cl_2 (δ 54.0) for ^{13}C as internal standards. Turbidity measurements of the polymer solution were made with a Jasco Ubest-50 spectrophotometer using a quartz cell with optical path length of 1 cm. Calorimetric scans were obtained on a Shimadzu DSC-50 instrument at a heating rate of 12 °C/h.

Electron Microscopy. The poly(methyl methacrylate-*b*-methacrylonitrile) was cast from $CHCl_3$/THF (8/2 v/v) (1% solution) on a copper mesh with thin carbon film. The copolymer film was dried at 25 °C under atmospheric pressure for 20 h, stained with I_2 vapor, and subjected to the transmission electron micrography (TEM). Micrographs were obtained by using a JEOL JEM-100SX electron microscope operating at an accelerating voltage of 80 kV.

Results and Discussion

Polymerization of Methacrylonitrile and Methylaluminum Porphyrin (1) in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3). Polymerization of methacrylonitrile (MAN) was first attempted by using methylaluminum porphyrin (**1**) as initiator under diffuse light in CH_2Cl_2 at room temperature ($[MAN]_0/[\mathbf{1}]_0 = 100$); however, the reaction of MAN and **1** did not occur at all. However, under irradiation with visible light ($\lambda > 420$ nm) at 35 °C, the polymerization of MAN took place, accompanied by a color change from bluish purple to brownish purple. The polymerization proceeded very slowly, and the monomer conversion reached only 25% even after 1 week, affording polymethacrylonitrile (PMAN) with M_n and M_w/M_n values of 2900 and 1.31, respectively. In sharp contrast, when methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) (10 equiv with respect to **1**) was added to the above reaction mixture, the chain growth readily proceeded and was completed in 5 h. The polymerization system was homogeneous at earlier stages of the reaction but turned heterogeneous at a later stage due to the poor solubility of PMAN in the polymerization medium. The GPC profile of the PMAN finally obtained showed a unimodal but broad chromatogram ($M_w/M_n = 1.35$). The M_n value of the polymer (7800), as estimated from GPC, was close to that expected from the initial monomer-to-initiator mole ratio by assuming that every molecule of aluminum porphyrin produced one polymer molecule (6700), indicating that the added **3** could not be a new initiator for the polymerization of MAN. Actually, **3** alone did not bring about the polymerization of MAN under identical conditions.

^1H NMR in $CDCl_3$ at 55 °C of poly(methyl methacrylate) (PMMA) converted from PMAN produced as above[21] indicated that the polymer was almost atactic (I:H:S = 0.28:0.52:0.20), while PMMA prepared by the polymerization using the **2**−**3** system ($M_n = 10\,700$, $M_w/M_n = 1.19$; prepolymer in entry no. 5, Table 1) was rich in syndiotactic sequences (I:H:S = 0.02:0.37:0.61).

Block Copolymerization of Methyl Methacrylate and Methacrylonitrile with Aluminum Porphyrin (2) in the Presence of Methyaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3). The block copolymerization of MAN was attempted from a living prepolymer of MMA carrying a (porphinato)aluminum

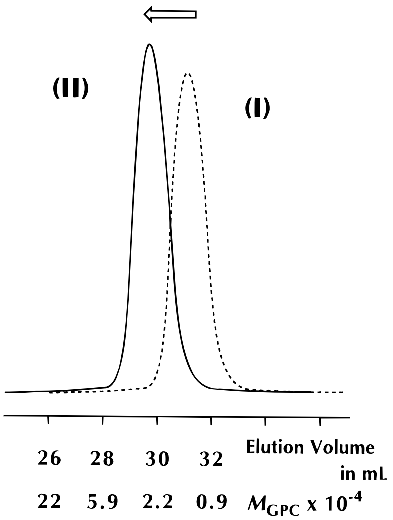
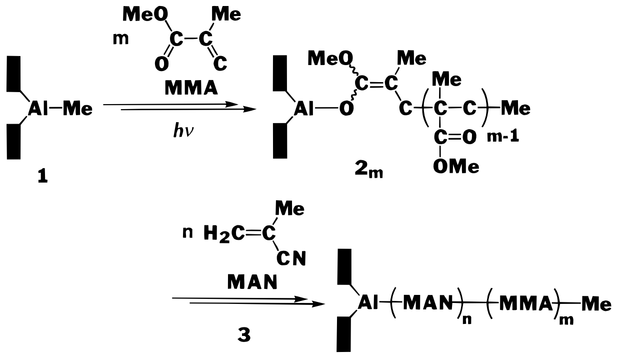


Figure 1. Block copolymerization of methyl methacrylate (MMA) and methacrylonitrile (MAN) in CH_2Cl_2 with the methylaluminum porphyrin (**1**)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system: GPC profiles of (**I**) the prepolymer of MMA ($[MMA]_0/[\mathbf{1}]_0 = 100$, under irradiation >420 nm, 35 °C, 100% conversion, $M_n = 12\ 000$, $M_w/M_n = 1.13$) and (**II**) the block copolymer of MMA and MAN (in the presence of **3**, $[MAN]_0/[\mathbf{1}]_0/[\mathbf{3}]_0 = 100/1.0/10$, room temperature, 100% conversion, $M_n = 20\ 800$, $M_w/M_n = 1.17$).

Scheme 1



enolate growing terminal (**2**) (Scheme 1); however, without **3**, the polymerization of MAN from **2** did not occur. However, when 100 equiv of MAN was added to a CH_2Cl_2 solution of **2** ($M_n = 12\ 000$, $M_w/M_n = 1.11$; prepared with $[MMA]_0/[\mathbf{1}]_0 = 100$, 100% conversion, under irradiation ($\lambda > 420$ nm)) in the presence of **3** ($[\mathbf{3}]_0/[\mathbf{2}]_0 = 10.0$, $[\mathbf{2}]_0 = 12.5$ mM) at room temperature, the polymerization of MAN started with color change of the polymerization system. The polymerization proceeded smoothly and was completed within 3 h; the polymerization mixture was homogeneous throughout the reaction.

The GPC profile provides a unimodal, sharp elution pattern for the polymer finally obtained (Figure 1 (**II**)), in which the peak due to the prepolymer of MMA (Figure 1 (**I**)) is not observed, showing that a MMA–MAN block copolymer was produced quantitatively. The M_n value of the polymer, as estimated by GPC, was 20 800 ($M_w/M_n = 1.17$), which is close to that (16 700) expected for the initial MAN-to-**2** mole ratio (entry no. 6, Table 1). Successful block copolymerization indicates that all the molecules of the growing PMMA (**2**) produced in the first stage participated in initiating the second-stage polymerization of MAN.

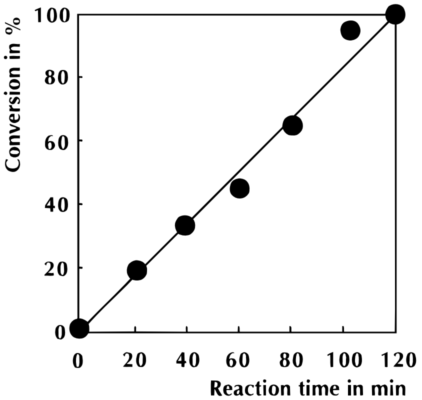


Figure 2. Polymerization of methacrylonitrile (MAN) with the living prepolymer of methyl methacrylate (MMA) (**2**; $m = 50$, $M_n = 9200$, $M_w/M_n = 1.13$)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system ($[MAN]_0/[\mathbf{2}]_0/[\mathbf{3}]_0 = 50/1.30/3.0$, $[\mathbf{2}]_0 = 22.6$ mM, CH_2Cl_2 as solvent, room temperature): conversion–time relationship.

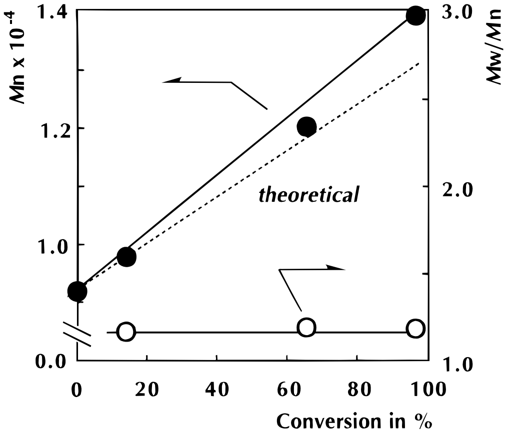


Figure 3. Polymerization of methacrylonitrile (MAN) with the living prepolymer of methyl methacrylate (MMA) (**2**; $m = 50$, $M_n = 9200$, $M_w/M_n = 1.13$)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system ($[MAN]_0/[\mathbf{2}]_0/[\mathbf{3}]_0 = 50/1.0/3.0$, $[\mathbf{2}]_0 = 22.6$ mM, CH_2Cl_2 as solvent, room temperature): relationship between M_n (●) (M_w/M_n (○)) of the polymer and conversion.

The consumption of MAN showed a linear dependence on the reaction time (Figure 2), when the polymerization of MAN using the living PMMA (**2**; $M_n = 9200$ ($M_w/M_n = 1.13$)) as initiator was carried out in the presence of **3** (3 equiv with respect to **2**) at room temperature. The M_n value of the polymer increased linearly with the conversion, giving a straight line (solid line in Figure 3), which is in good agreement with the broken line as expected from the initial mole ratio of MAN to **2** and the conversion, and the molecular weight distribution (MWD) of the block copolymer stayed narrow ($M_w/M_n = 1.1–1.2$) throughout the polymerization (Figure 3).

When the amount of **3** was increased from 3.0 to 10.0 equiv with respect to **2**, the polymerization of MAN proceeded more rapidly (Figure 4). However, the M_n value of the PMAN sequence obtained at 100% conversion was almost constant, irrespective of the ratio of **3** to **2** (entry nos. 2–4, Table 1). These results indicate that the added **3** did not serve as an initiator but served as an accelerator for the polymerization of MAN.

When the initial mole ratio of MAN to the prepolymer of MMA (**2**) was increased from 50 to 200, the M_n value of the PMAN sequence increased almost proportionally from 5400 to 16 400, with the ratio M_w/M_n remaining in the range of 1.2–1.3 (entry nos. 5–7, 10, Table 1; Figure 5). Since PMMA–PMAN block copolymers with longer PMMA sequences were more soluble, the polym-

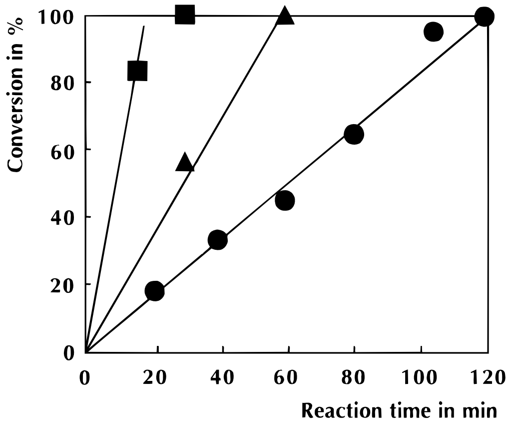


Figure 4. Polymerization of methacrylonitrile (MAN) with the living prepolymer of methyl methacrylate (MMA) (**2**)−methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system ($[MAN]_0/[\mathbf{2}]_0 = 50$, $[\mathbf{2}]_0 = 22.6$ mM, CH_2Cl_2 as solvent, room temperature, initial ratios of **3** to **2** = 3.0 (●), 4.0 (▲), and 10 (■)): effect of the amount of Lewis acid (**3**) on the rate of polymerization.

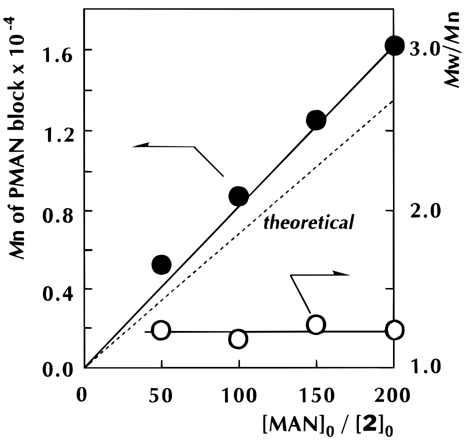


Figure 5. Polymerization of methacrylonitrile (MAN) with the living prepolymer of methyl methacrylate (MMA) (**2**)−methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system in CH_2Cl_2 at room temperature. Relationship between M_n of the PMAN block (●) (M_w/M_n (○)) of the polymer formed at 100% conversion and the initial monomer-to-initiator mole ratio ($[MAN]_0/[\mathbf{2}]_0$).

erization mixture was homogeneous throughout the polymerization of MAN, even when a block copolymer with a long PMAN sequence was formed, and the MWD of the produced block copolymer was narrow (entry nos. 8 and 10, Table 1).

The polymerization of MAN with **2** in the presence of **3** proceeded with living character. Clear evidence for this was given by the sequential two-stage polymerization of MAN initiated with the system of (enolato)-aluminum porphyrin **2** (living PMMA; $M_w = 13\,200$, $M_w/M_n = 1.22$; Figure 6 (**I**)) in the presence of **3** (1/3), where 50 equiv of MAN with respect to **2** was polymerized up to 100% conversion (4 h) at the first stage and, after a 16-h interval at room temperature, 50 equiv of MAN was charged to the mixture. In spite of a long interval between the completion of the first-stage polymerization and the second monomer feed, the second-stage polymerization ensued and was complete within 6 h. The GPC profile of the product (the block copolymer) shows a clear increase in molecular weight from 17 500 (the first stage: Figure 6 (**II**)) to 20 700 (the second stage (**III**)) with a shift in the sharp peak (M_w/M_n from 1.21 to 1.29).

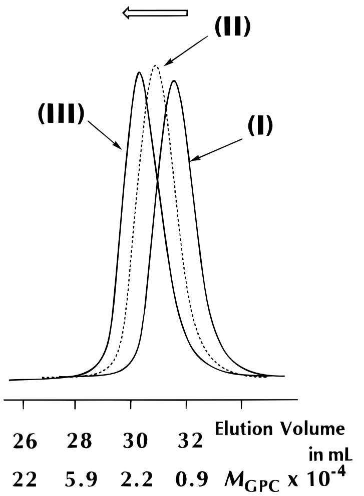


Figure 6. Sequential three-stage polymerization of methyl methacrylate (MMA), methacrylonitrile (MAN), and MAN in CH_2Cl_2 at room temperature with methylaluminum porphyrin (**1**)−methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system: GPC profiles of the polymers formed at the first stage (**I**; $[MMA]_0/[\mathbf{1}]_0 = 100$, 100% conversion, $M_n = 13\,200$, $M_w/M_n = 1.22$), the second stage (**II**; $[MAN]_0/[\mathbf{1}]_0 = 50$, 100% conversion, $M_n = 17\,500$, $M_w/M_n = 1.21$), and the third stage (**III**; $[MAN]_0/[\mathbf{1}]_0 = 50$, 100% conversion, $M_n = 20\,700$, $M_w/M_n = 1.29$).

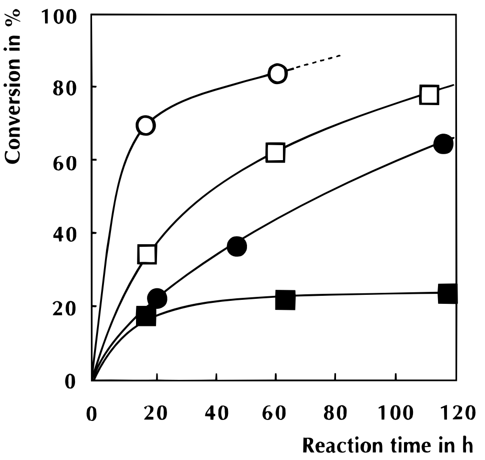


Figure 7. Polymerization of methacrylonitrile (MAN) with the living prepolymer of methyl methacrylate (MMA) (**2**)−pyridine system ($[\mathbf{2}]_0 = 20.7$ mM, CH_2Cl_2 as solvent, room temperature, $[MAN]_0/[\mathbf{2}]_0 = 100$, $[pyridine]_0/[\mathbf{2}]_0 = 0.6$ (■, □), 10 (●, ○)) under diffuse light (■, ●) and under irradiation of visible light ($\lambda > 420$ nm) (□, ○): conversion−time relationship.

Block Copolymerization of Methyl Methacrylate and Methacrylonitrile with Aluminum Porphyrin (2) in the Presence of Pyridine. Pyridine in place of methylaluminum bis(2,6-di-*tert*-4-methylphenolate) (**3**) was also effective for the polymerization of MAN from the living PMMA (**2**). An example is shown by the polymerization of MAN under irradiation with the **2** ($M_n = 4000$, $M_w/M_n = 1.09$, prepared with $[MMA]_0/[\mathbf{1}]_0 = 40$, 100% conversion)−pyridine system at an initial mole ratio $[MAN]_0/[\mathbf{2}]_0/[pyridine]_0$ of 100/1.0/0.6. MAN was polymerized up to 63% conversion in 65 h (Figure 7 (□)), where the GPC peak of the polymer formed was observed to shift clearly toward the higher molecular weight region ($M_n = 7600$), retaining the narrow MWD ($M_w/M_n = 1.26$) (Figure 8), and the peak corresponding to the prepolymer of MMA was not observed. These facts clearly demonstrate the successful polymerization of MAN from **2**, affording a PMMA−PMAN block copolymer. In sharp contrast to the polymerization of

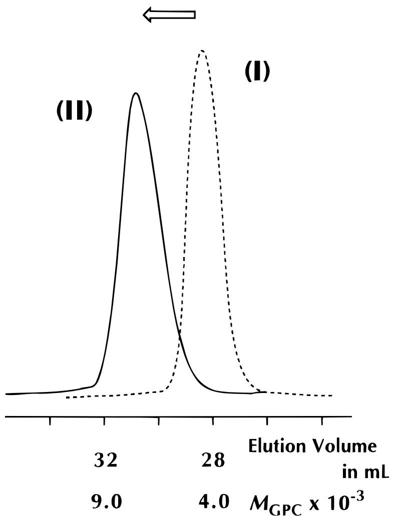


Figure 8. Block copolymerization of methyl methacrylate (MMA) and methacrylonitrile (MAN) in CH_2Cl_2 with the methylaluminum porphyrin (**1**)−pyridine system: GPC profiles of (**I**) the prepolymer of MMA ($[MMA]_0/[\mathbf{1}]_0 = 40$, under irradiation > 420 nm, 35 °C, 100% conversion, $M_n = 4000$, $M_w/M_n = 1.09$) and (**II**) the block copolymer of MMA and MAN (in the presence of pyridine, $[MAN]_0/[\mathbf{1}]_0/[pyridine]_0 = 100/1.0/0.6$, room temperature, 63% conversion, $M_n = 7600$, $M_w/M_n = 1.26$).

MAN, polymerization of MMA with aluminum porphyrin (**2**) was retarded by pyridine. For example, in the presence of 2 equiv of pyridine with respect to **2**, the polymerization of 100 equiv of MMA proceeded very slowly to attain 25% conversion in 18 h under irradiation, while in the basence of pyridine, the polymerization of MMA with **2** was complete within 12 h under otherwise identical conditions.

When the amount of pyridine was increased from 0.6 to 10 equiv with respect to the living PMMA (**2**) ($[MAN]_0/[\mathbf{2}]_0 = 50$), the polymerization of MAN under visible light irradiation proceeded more rapidly (Figure 7 (○)), where the M_n value of the produced polymer increased linearly with conversion, retaining the ratio M_w/M_n in the range of 1.1−1.3. A good agreement between the observed and expected M_n values of the polymer (solid and broken lines, respectively) again indicates quantitative initiation from every molecule of the living PMMA (**2**) (Figure 9).

It is particularly noteworthy that a dramatic acceleration by irradiation with visible light was observed in the presence of pyridine for the polymerization of MAN initiated with the living PMMA (**2**) (Figure 7; ■, ● → □, ○).[22] For example, the polymerization of MAN with **2** ($[MAN]_0/[\mathbf{2}]_0/[pyridine]_0 = 100/1.0/10$) proceeded rapidly up to 67% conversion in 18 h under visible light irradiation ($\lambda > 420$ nm) (○), while under diffused light under otherwise identical conditions, the conversion of MAN after 20 h was only 22% (●). All the block copolymers produced under irradiation and under diffused light were of narrow MWD.

When 1-methylimidazole was used as a Lewis base (10 equiv with respect to aluminum porphyrin, in the dark) under otherwise identical conditions, the polymerization proceeded more rapidly, up to 28 and 90% conversion in 9 and 116 h, respectively. However, in this case, the GPC profile of the produced polymer showed a bimodal, broad elution pattern, where the peak due to the prepolymer of MMA remained. In contrast, when triphenylphosphine (10 equiv) was used, a narrow MWD copolymer was obtained, although the polymerization proceeded rather slowly even under visible light irradiation (13% conversion in 40 h).

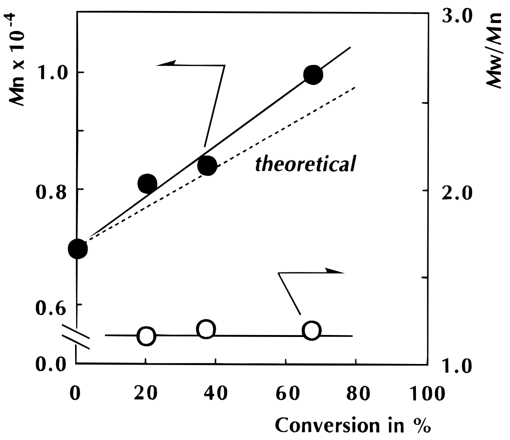


Figure 9. Polymerization of methacrylonitrile (MAN) with the living prepolymer of methyl methacrylate (MMA) (**2**; $m = 60$, $M_n = 6900$, $M_w/M_n = 1.10$)−pyridine system ($[MAN]_0/[\mathbf{2}]_0/[pyridine]_0 = 100/1.0/10$, $[\mathbf{2}]_0 = 20.7$ mM, CH_2Cl_2 as solvent, room temperature): relationship between M_n (●) (M_w/M_n (○)) of the polymer and conversion.

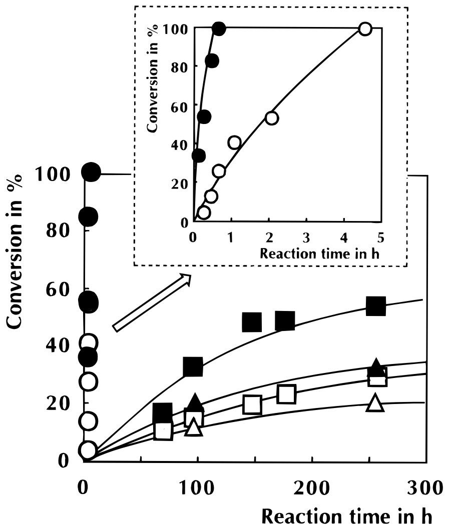


Figure 10. Copolymerization of methacrylonitrile (MAN) and methyl methacrylate (MMA) with the living prepolymer of MMA (**2**; $m = 10$) ($[\mathbf{2}]_0 = 17.5$ mM, CH_2Cl_2 as solvent, room temperature, $[MAN]_0/[MMA]_0/[\mathbf{2}]_0 = 90/90/1.0$) under irradiation of visible light ($\lambda > 420$ nm) (▲, △), in the presence of methylaluminum bis (2,6-di-*tert*-butyl-4-methylphenolate) (**3**) ($[\mathbf{3}]_0/[\mathbf{2}]_0 = 3.0$) (●, ○) and in the presence of pyridine ($[pyridine]_0/[\mathbf{2}]_0 = 3.0$) (■, □): conversion−time (MAN, ▲, ●, ■; MMA, △, ○, □) relationships.

Copolymerization of Methyl Methacrylate and Methacrylonitrile with Aluminum Porphyrin (2). In the copolymerization under irradiation with visible light at room temperature ($[MMA]_0/[MAN]_0/[\mathbf{2}]_0 = 90/90/1.0$), the reactions of MAN and MMA took place very slowly, and the conversions of monomers were only 48 and 35%, respectively, in 1250 h (Figure 10 (▲, △)). On the other hand, by the addition of **3**, both MMA and MAN were polymerized more rapidly; the conversions of MAN and MMA were 97 and 25% in 30 min (Figure 10 (●, ○)). Pyridine also accelerated the copolymerization of MAN and MMA to attain 56 and 27% conversion in 255 h (Figure 10 (■, □)). It is of interest to note that the consumption of MMA in the copolymerization with MAN initiated with **1** was accelerated by pyridine, while the homopolymerization of MMA was decelerated by pyridine.

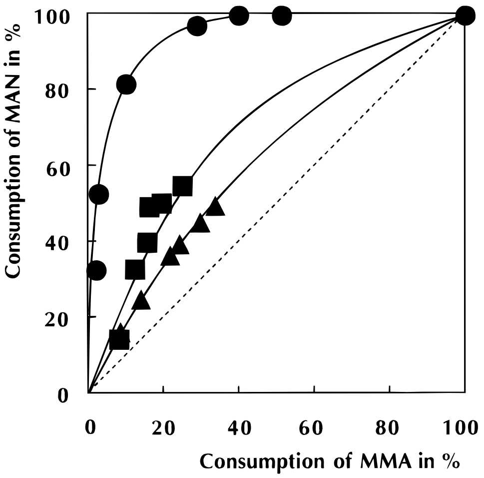


Figure 11. Copolymerization of methacrylonitrile (MAN) and methyl methacrylate (MMA) with the living prepolymer of MMA (**2**; $m = 10$): plots of MAN consumptions versus MMA consumptions under irradiation of visible light (■), in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) (●) and in the presence of pyridine (▲) (for reaction conditions, see Figure 10).

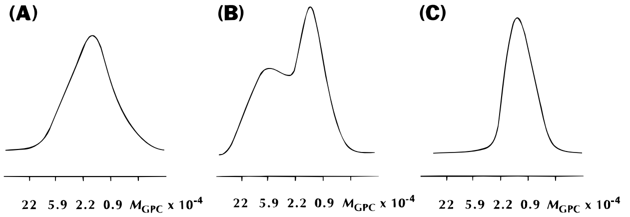


Figure 12. Copolymerization of methacrylonitrile (MAN) and methyl methacrylate (MMA) with the living prepolymer of MMA (**2**; $m = 10$): GPC profiles of the polymers formed (A) under irradiation of visible light, (B) in the presence of methylaluminum bis (2,6-di-*tert*-butyl-4-methylphenolate) (**3**), and (C) in the presence of pyridine (for reaction conditions, see Figure 10).

Plots of the consumptions of MAN against those of MMA indicated that the rates of consumption of two monomers were rather close to each other under irradiation in the absence of **3** and pyridine (Figure 11 (■)), although the homopolymerization of MMA initiated with methylaluminum porphyrin (**1**) proceeded much faster than that of MAN. This tendency is almost unchanged under accelerating conditions in the presence of pyridine, where the relative consumption of MAN to MMA was slightly higher than that observed in the copolymerization under irradiation (Figure 11 (▲)). However, much more notably, the polymerization of MAN proceeded much more rapidly than that of MMA in the presence of **3** (Figure 11 (●)).

The copolymer obtained by the copolymerization in the presence of **3** showed a ^{1}H NMR spectrum very similar to that of the block copolymer. In contrast, the copolymers formed in the copolymerizations under irradiation or in the presence of pyridine gave different spectra, where the signals due to the copolymer were complicated.

The copolymers produced under irradiation (MAN, 48% conversion; MMA, 35% conversion) and in the presence of pyridine (MAN, 56% conversion; MMA, 27% conversion) exhibited unimodal, broad GPC chromatograms (Figure 12A,C), from which the M_n (M_w/M_n) values were estimated as 9900 (2.61) and 9800 (1.38), respectively. On the other hand, the GPC chromatogram for the polymer produced in the presence of **3** (MAN, 100% conversion; MMA, 10% conversion) exhibited a bimodal MWD consisting of a broad peak with a sharp shoulder on the low-molecular-weight side ($M_n = 24\,800$, $M_w/M_n = 4.24$) (Figure 12B). This is probably due to the low initiation efficiency of the homopolymerization of MMA from the living PMAN and the rapid chain growth of PMAN. In this relation, when MMA was added to the living block copolymer of PMMA−PMAN ($M_n = 14\,500$, $M_w/M_n = 1.30$) in the presence of 10 equiv of **3**, a rapid polymerization took place to attain 100% conversion within 10 min. The GPC showed a bimodal elution pattern ($M_n = 23\,200$, $M_w/M_n = 2.32$). The peak in the lower molecular weight region corresponds to PMMA−PMAN, indicating that only a part of the prepolymer took part in the third-stage polymerization of MMA.

All the above results lead to the following conclusions. Addition of **3** or pyridine under diffused light results in the accelerated consumptions of comonomers. In the presence of pyridine, the consumptions of MAN and MMA are almost equally accelerated, compared with the case using irradiation in the absence of pyridine. In that instance, the addition of **3** accelerates the consumption of MAN much more than that of MMA.

Interactions between Monomers and Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (3). NMR Studies. In the ^{1}H NMR spectrum of a mixture of **3** and MAN (0.9/1.0) in CD_2Cl_2 at 25 °C, all the signals of MAN protons clearly shifted downfield (CH_2, δ 6.16 and 6.11; CH_3, 2.03) from those of MAN alone (CH_2; δ 5.79 and 5.71, CH_3; 1.96) (Figure 13). When the mole ratio of **3** to MAN was changed from 0.2 to 1.8, the downfield shifts became more remarkable; for example, the signal due to CH_2 and CH_3 groups appeared at δ 6.21 and 6.17 ppm and at δ 2.08 ppm, respectively.

The signals due to $C{\equiv}N$ (δ 118.7), $CH_2{=}C$ (δ 119.6), and CH_3 (δ 21.2) of MAN in the ^{13}C NMR spectrum were broadened and shifted upfield to δ 114.9, 119.0, and 19.6, respectively, in the presence of 1.8 equiv of **3**. When the mole ratio of **3** to MAN was increased, the upfield shift became more remarkable, particularly for the signal due to CN. Each signal due to MAN was broadened with an increase in the ratio of **3** to MAN, and the broadening was also most remarkable in the signal due to CN. As for the signals of **3**,[23] the C−O signal of the phenolate ligands shifted most remarkably from δ 152.8 to 154.0 ($[\mathbf{3}]_0/[\mathrm{MAN}]_0 = 1.8$). These observations indicate the occurrence of coordination of the CN group in MAN to **3**.

The ^{13}C NMR of an equimolar mixture of MAN and MMA in the presence of 1.5 equiv of **3** in CD_2Cl_2 at 25 °C showed a shift for the $C{\equiv}N$ signal of MAN from δ 118.7 to δ 115.9, while the MMA $C{=}O$ signal was only slightly shifted (0.4 ppm), although a large shift (2.7 ppm) was observed for a mixture of MMA and **3** (2.0/1.0) under similar conditions.

Mechanistic Aspects. To summarize the above results, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) accelerates the polymerization of MAN with aluminum porphyrin. Together with the results of the NMR investigations, the accelerated polymerization of MAN with the **2**−**3** system is concluded to be the result of activation of MAN through the coordination to **3** for the nucleophilic attack of aluminum porphyrin (electrophilic activation of monomer by Lewis acid). As also indicated by ^{13}C NMR studies, **3** interacts more preferably with MAN than with MMA. Thus, in the

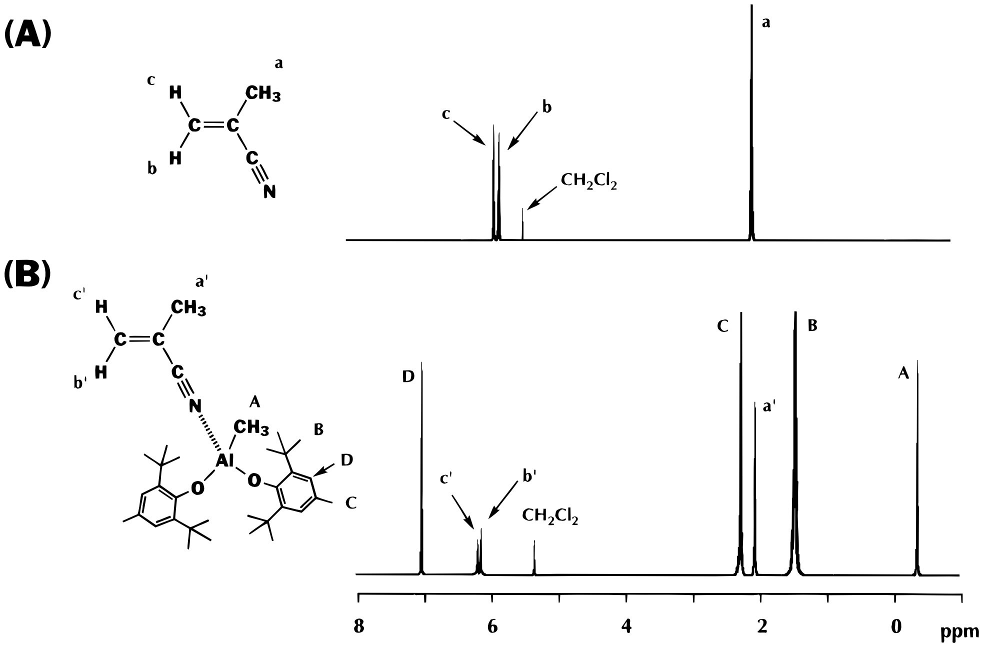


Figure 13. ^{1}H NMR spectra in CD$_2$Cl$_2$ at 25 °C of (A) methacrylonitrile (MAN) (B) a mixture of MAN and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) (1/0.9).

copolymerization of MAN and MMA, the homopolymerization of MAN takes place at an early stage, on account of the preferential activation of MAN by **3**.

On the other hand, it is well demonstrated that Lewis bases coordinate to aluminum porphyrin to form a six-coordinated complex[15,24] and enhance the reactivity of aluminum porphyrins.[15] Therefore, the rapid polymerization of MAN with the **2**−pyridine system is a consequence of the coordinative activation of the aluminum porphyrin by pyridine (nucleophilic activation of the growing species by Lewis base). Due to the activation of the growing species by pyridine, the consumption of MAN and MMA in the copolymerization was almost equally accelerated.

It was difficult to determine by ^{1}H NMR whether the structure of the active end of the growing PMAN was (TPP)Al−C(Me)(CN)−CH$_2$−polymer or (TPP)Al−N=C=C(Me)−CH$_2$−polymer because the spectrum obtained for the living PMAN was very complicated.

Chacterization of Poly(methyl methacrylate-*b*-methacrylonitrile)s. For the estimation of the composition, the PMMA−PMAN block copolymers synthesized with the living prepolymer of the MMA (**2**)−methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system were isolated by repeated precipitations from CHCl$_3$/MeOH and subjected to elemental analysis. On the basis of the analytical value for nitrogen, the lengths of the PMAN block were calculated to be in good agreement with those expected by the initial MAN-to-MMA comonomer feed ratios (entry was 1, 5−7, 9, and 10, Table 1). The estimation by ^{1}H NMR gave different values of the PMAN block content, depending upon the solvent and the temperature used for measurement.

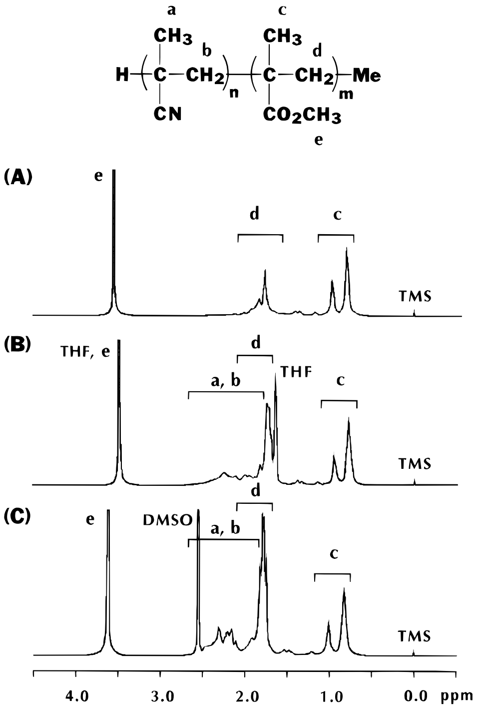


Figure 14. ^{1}H NMR spectra in CDCl$_3$ (A), THF-d_8 (B), and DMSO-d_6 (C) of the poly(methyl methacrylate-*b*-methacrylonitrile) (M_n = 39 300, M_w/M_n = 1.24, MAN content by elemental analysis 51.0%) obtained with the (enolato)aluminum porphyrin (**2**)−methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3**) system (entry no. 10, Table 1).

Solution Properties of Poly(methyl methacrylate-*b*-methacrylonitrile)s. (1) Micelle Formation in Organic Solvent. In general, PMMA is highly soluble in common organic solvents such as benzene, toluene, CHCl$_3$, THF, and DMSO. In sharp contrast, PMAN is dissolved in limited solvents such as DMSO, DMF, and trifluoroacetic acid. Therefore, in a particular organic solvent, PMMA−PMAN block copolymers are expected to form micelle-like aggregation because of the different solubilities of the segments.[25] For the investigation as to this expectation, narrow MWD PMMA−PMAN block copolymers were synthesized by the sequential polymerization of MMA and MAN with aluminum porphyrin (**2**) in the presence of Lewis acid (**3**) or Lewis base (pyridine). Figure 14B,C shows the ^{1}H NMR spectra (δ −0.5 to +4.5 ppm) of the block copolymer (entry no. 10 in Table 1) at 25 °C in THF-d_8 and in DMSO-d_6 (20 mg/mL), respectively, where the signals due to the CH_3 (δ 1.5−1.9) and CH_2 groups (δ 2.0−2.5) in the PMAN segment are observed: the relative

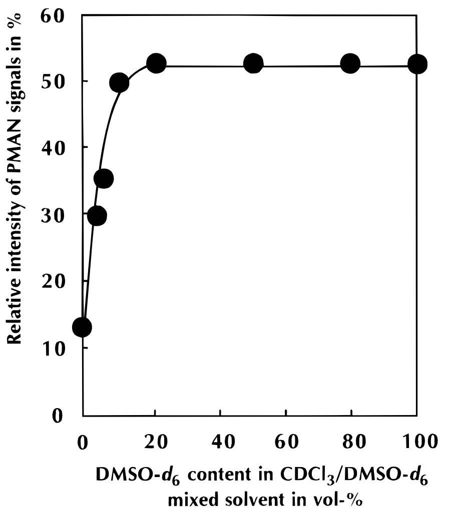


Figure 15. ^{1}H NMR of poly(methyl methacrylate-*b*-methacrylonitrile) ($M_n = 39\,300$, $M_w/M_n = 1.24$) (entry no. 10, Table 1) in $CDCl_3$/DMSO-d_6 mixed solvent at 25 °C ([polymer] = 20 mg/mL): relationships between relative intensities of the signals due to polymethacrylonitrile sequence in the block copolymer and the solvent composition.

intensity ratio of the signals due to the PMAN segment in the block copolymer (entry no. 10), as calculated from the intensities of the signals due to the CH_2 groups in the PMAN and PMMA segments and that due to the CH_3 group in the PMAN segment, was 52.6%, which was very close to that determined from the elemental analysis (51.0%). On the other hand, in $CDCl_3$, the signals due to the PMAN segment were very weak, where the relative intensity of the PMAN signals was only 12.3% (Figure 14A). In $CDCl_3$ containing DMSO-d_6 (20/1 v/v), the peaks due to the PMAN segment in the block copolymer (entry no. 10) were larger than in $CDCl_3$ alone. When the amount of DMSO-d_6 in the $CDCl_3$/DMSO-d_6 mixed solvent was increased, the signals due to the PMAN segment were sharper and more enhanced. The calculated value for the relative intensity of the PMAN segment increased with the amount of DMSO-d_6 and reached 52.6% in $CDCl_3$/DMSO-d_6 (8/2), which is the same as that calculated from the spectrum in DMSO-d_6 (Figure 15). These facts indicate that the block copolymer molecule is dispersed in DMSO-d_6 and in THF-d_8, while in $CDCl_3$, the PMAN segments associate to form a micelle.

In $CDCl_3$ at higher temperature, the signals due to the PMAN segment in block copolymer (Table 1, entry no. 10) became larger (Figure 16 (■)). Thus, the micelle was considered to be broken into dispersion by elevating the temperature. The spectrum of the block copolymer (entry no. 10) in DMSO-d_6 was almost unchanged at 25−90 °C (Figure 16 (●)). However, quite unexpectedly, in THF-d_8, the signals due to the PMAN segment became smaller as the temperature was elevated (Figure 16 (▲)). This change is opposite to the behavior in $CDCl_3$, showing that the block copolymer formed a micelle at high temperature in THF-d_8. This fact indicates that the PMAN segments aggregate by desolvation at higher temperature.

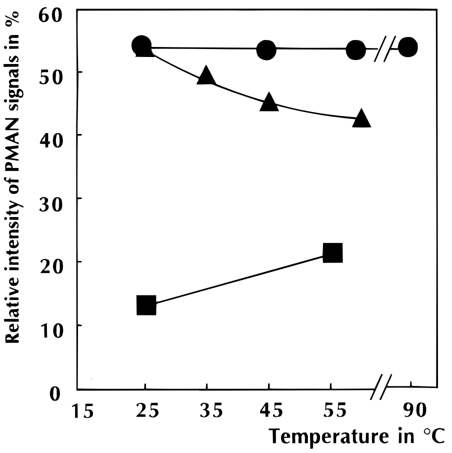


Figure 16. ^{1}H NMR of poly(methyl methacrylate-*b*-methacrylonitrile) ($M_n = 39\,300$, $M_w/M_n = 1.24$) (entry no. 10, Table 1) in $CDCl_3$ (■), DMSO-d_6 (●), or THF-d_8 (▲) ([polymer] = 20 mg/mL): relationships between relative intensities of the signals due to polymethacrylonitrile sequence in the block copolymer and temperature.

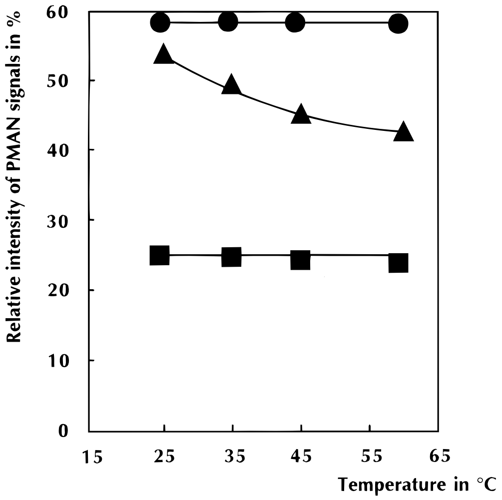


Figure 17. ^{1}H NMR of poly(methyl methacrylate-*b*-methacrylonitrile)s in THF-d_8 ([polymer] = 20 mg/mL): relationships between relative intensities of the signals due to polymethacrylonitrile sequence in the block copolymer and temperature (block copolymers entry no. 9 in Table 1 (■), entry no. 6 (●), and entry no. 10 (▲)).

The micelle formation in THF at high temperature depends on the MAN content and the M_n value of the copolymer. In comparison with the block copolymer (entry no. 10) (Figure 17 (▲)), a block copolymer with almost the same M_n value and a lower MAN content (entry no. 9) and a block copolymer with a lower M_n value and almost the same MAN content (entry no. 6) do not form micellar aggregates, as shown by the constant relative intensity of the PMAN signals irrespective of the temperature (Figure 17 (■ and ●)). A block copolymer with a shorter PMMA segment and a longer PMAN segment (entry no. 1, Table 1) forms a micellar aggregate in THF even at room temperature, which was demonstrated by the ^{1}H NMR analysis at 25 °C, giving a lower integral ratio for the PMAN signals (70%) than the MAN content given by the elemental analysis (77%).

(II) Aggregation by Elevating Temperature. When the temperature was elevated, the THF solution of the block copolymer (entry no. 1) became turbid. As shown in Figure 18 (●), the transmittance of visible light (λ = 500 nm) through the THF solution of th block copolymer (entry no. 1, 2 mg/mL) in a quartz cell (optical path length 1 cm) became smaller as the solution was heated. The copolymer solution turned apparently homogeneous as the temperature was lowered (Figure 18 (○)), indicating that this phenomenon was reversible. On the other hand, the solution of a block copolymer with a lower MAN content (entry no. 6, Table 1) looked

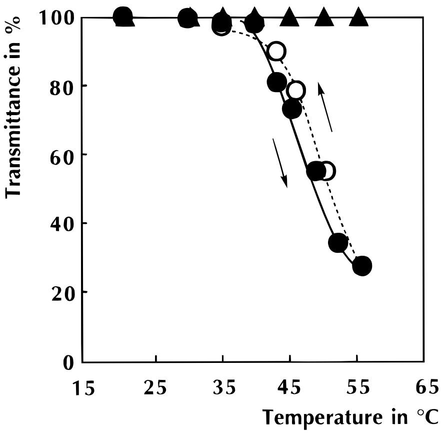


Figure 18. Change of the turbidity of the THF solutions of poly(methyl methacrylate-*b*-methacrylonitrile)s (entry no. 1 in Table 1, ●, ○; entry no. 6, ▲): relationships between transmittance ($\lambda = 500$ nm) of the THF solutions and temperature in the quartz cell (optical path length 1 cm, [copolymer] = 2 mg/mL).

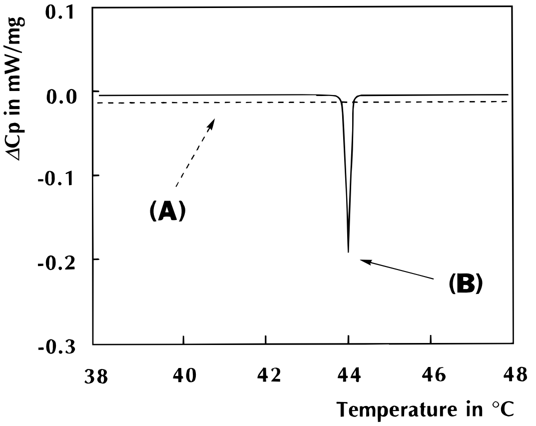


Figure 19. Calorimetric scans for the THF solutions of poly(methyl methacrylate-*b*-methacrylonitrile)s (entry no. 10 in Table 1 (A) and entry no. 1 (B); $[\text{polymer}]_0 = 2$ mg/mL, heating rate 12 °C/h; ΔCp = the change in specific heat capacity at constant pressure).

homogeneous throughout the observation in the same range of temperature (Figure 18 (▲)). These results show that when the PMAN segments are relatively longer, the block copolymer molecules associate into large aggregates on account of the quite strong interaction between the PMAN segments resulting from desolvation at high temperature.

In this relation, the DSC profile for the THF solution of the block copolymer (entry no. 1, 2 mg/mL) showed an endothermic peak at 44.1 °C (Figure 19B), and this temperature is close to the cloud point as observed above. In contrast, no peak was observed in the DSC profile for the block copolymer (entry no. 10) having a longer PMAN block with a lower MAN content (Figure 19A).

Microphase Separation in Membrane. Block copolymers tend to form a microphase-separated structure in the solid state similarly to the micellar formation in solution.[26] This is also the case for the PMMA–PMAN block copolymers synthesized in the present study. The film of the PMMA–PMAN block copolymer (entry no. 10), cast from $CHCl_3$/THF (8/2 in v/v) at 25 °C and stained with I_2 vapor, was subjected to transmission electron microscopy (TEM). Figure 20A shows a micrograph of the block copolymer (entry no. 10) in which the microphase-separated structure is clearly observed. Since the TEM photograph for the block copolymer (entry no. 10) is darker than that for the block copolymer (entry no. 9) with the lower MAN content, the dark, uniformly scattered circles are the domains from the PMAN segment, while the light region shows

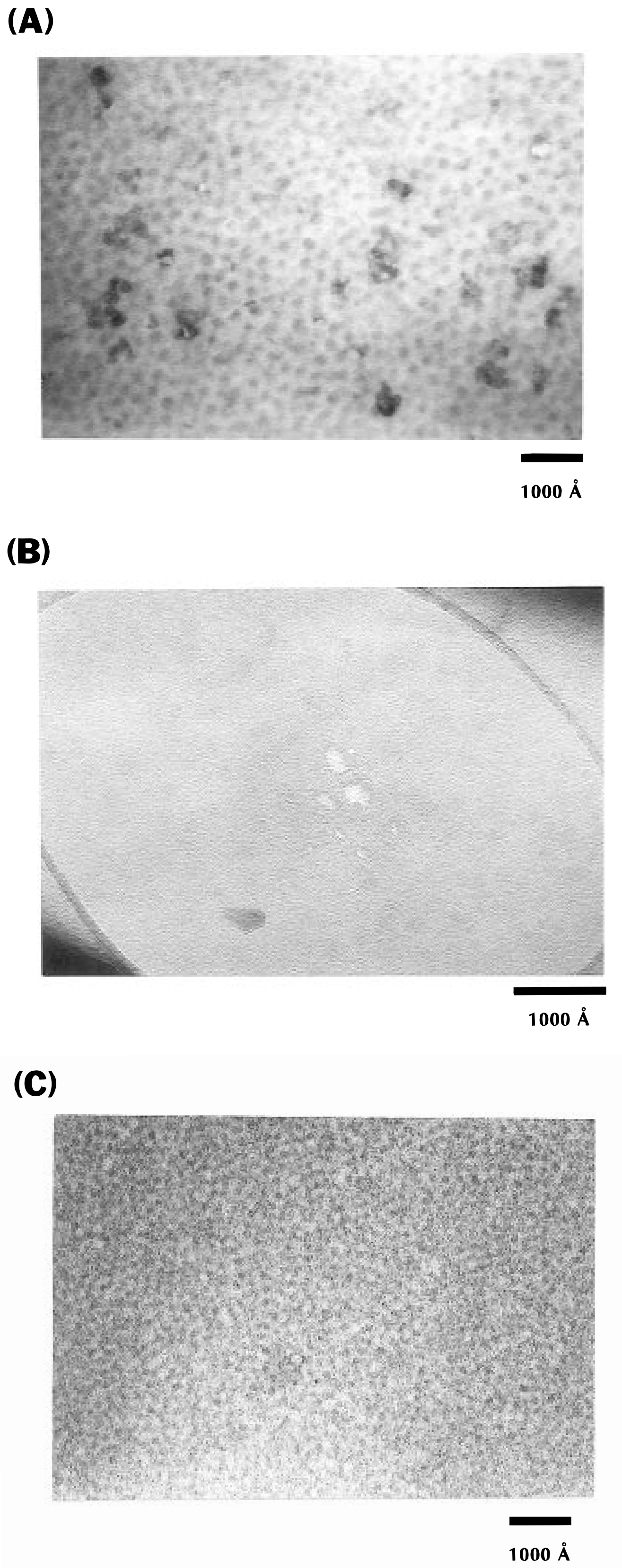


Figure 20. Transmission electron microscopic views of poly(methyl methacrylate-*b*-methacrylonitrile) (entry no. 10 in Table 1): cast samples from $CHCl_3$/THF (8/2) at 25 °C (A), THF at 25 °C (B), and THF at 60 °C (C).

the domains from the PMMA segment. Thus, the morphology with the PMAN domains in a matrix of PMMA was formed in a film of the block copolymer (entry no. 10). When the film of the block copolymer (entry no. 10) was cast from THF alone at 25 °C, the micrograph exhibited no clear phase separation (Figure 20B), while the polymer membrane sample cast from THF at 60 °C showed clear phase separation again (Figure 20C). The block copolymer (entry no. 9), which has a relatively shorter PMAN chain, showed no clear phase separation in micrographs irrespective of the casting conditions. These results are quite consistent with the solution behavior that the block copolymer with a long enough PMAN segment forms micelles in $CHCl_3$ at room temperature or in THF at higher temperature, while the block copolymer with a shorter PMAN segment does not aggregate under similar conditions.

Conclusion

A novel living polymerization of methacrylonitrile was developed by using as initiator the living polymer of methyl methacrylate having an (enolato)aluminum porphyrin at the growning terminal (**2**). The presence of an electrophilic activator for the monomer (methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate (**3**)) or nucleophilic activator for the growing species (pyridine) was essential for the rapid and clean chain growth in the polymerization of methacrylonitrile with **2**.

On the basis of the living polymerization of methacrylonitrile from the living prepolymer of methyl methacrylate, (methyl methacrylate-*b*-methacrylonitrile)s with controlled molecular weights were synthesized.

The poly(methyl methacrylate-*b*-methacrylonitrile)s carrying two segments with different solubilities in organic solvents reveal microphase separation in solution as well as in the solid state. Furthermore, this block copolymer is the first example of the formation of micelle-like aggregation of a polymer in an organic solvent upon elevating temperature.

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