Kinetics of the Polymerizable Azo Initiator 2,2′-Azobis[*N*-(2-propenyl)-2-methylpropionamide] and Its Application to Graft Copolymerization

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ABSTRACT: The polymerizable azo initiator 2,2′-azobis[*N*-(2-propenyl)-2-methylpropionamide] (APMPA) has both vinyl groups and azo groups. To develop a new graft polymerization method, the radical polymerization kinetics of APMPA and graft polymerization with the produced macromolecular azo initiator were studied. Because the azo group of APMPA was stable below 80°C, the vinyl group of APMPA could be polymerized with 2,2′-azobis(2,4-dimethylvaleronitrile) as an initiator at 60 and 70°C. However, the homopolymerization of APMPA could not proceed because of APMPA self-circulation reactions. Using comonomers such as styrene (ST), methyl methacrylate (MMA), and vinyl acetate, we synthesized copolymers of APMPA. The ^{1}H-NMR spectra of the resulting copolymers showed the incorporation of APMPA. With the copolymer composed of ST and APMPA used as an initiator, the gel permeation chromatogram showed that the high-molecular-mass fraction of the grafted polymer increased with time. By this method, grafted copolymers having branched chains composed of ST, MMA, or an amphiphilic macromonomer were obtained. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2425–2433, 2010

Key words: azo polymers; graft copolymers; kinetics (polym.); macromonomers

INTRODUCTION

Graft copolymers have chains of one polymer attached along, or grown from, the side of a polymer chain with a different chemical composition. Unique and specific functions of graft copolymers emanate from the two different chemical compositions of polymer chains, which cannot be reproduced by ordinary random copolymerization or polymer blend methods. Hydrophobicity or hydrophilicity against the opposite property of the main chain, various optical properties, conductive properties, and chemical reactivities of graft chains are applied for industrial production and adhesives with a high adhesion strength;[1] deodorants, adsorbents,[2] and battery separators[3] have been developed. Radiation-induced polymerization[4] and polymerization with macromonomers having graft chains or chain-transfer reagents[5,6] have been the main procedures used to extend the grafted chain from the polymer backbone. In the case of radiation-induced polymerization, expensive equipment is required, and the area of irradiation is restricted. Polymerizable macromonomers having grafted chains are limited by their low reactivity during polymerization due to steric hindrance. In the case of polymerization with chain-transfer agents, the graft efficiency is dependent on chain-transfer reactions, and so the graft efficiency is quite low. Therefore, a simple and cost-effective method for graft polymerization is required for industrial application.

There has been a great interest in graft polymerization with polymerizable azo initiators.[7,8] This method can easily synthesize polymerizable azo initiators by copolymerization and does not require special polymerization equipment; only the heating of the mixture consisting of a copolymer having azo groups and a monomer are necessary to carry out the graft polymerization. Moreover, this method allows for a large amount of graft polymer to be polymerized. 2,2′-Azobis[*N*-(2-propenyl)-2-methylpropionamide] (APMPA) is one such polymerizable azo initiator,[9–12] with two vinyl groups and an azo group. By reacting the vinyl groups of APMPA with a comonomer, one can obtain a crosslinked copolymer having azo groups. The azo group of the

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produced crosslinked copolymer can concomitantly be used as an initiator for graft polymerization. The half-life of the azo group of APMPA is 10 h at 96°C.[9] Thus, when the vinyl group of APMPA reacts with radicals during copolymerization, the decomposition of azo groups is negligible at 60–80°C. Because of the high thermal stability of the azo group, APMPA is capable of producing a variety of copolymers having azo groups for the production of functional polymers.[9] Therefore, new grafted polymers that are not available through ordinary graft polymerization procedures can easily be produced with APMPA.

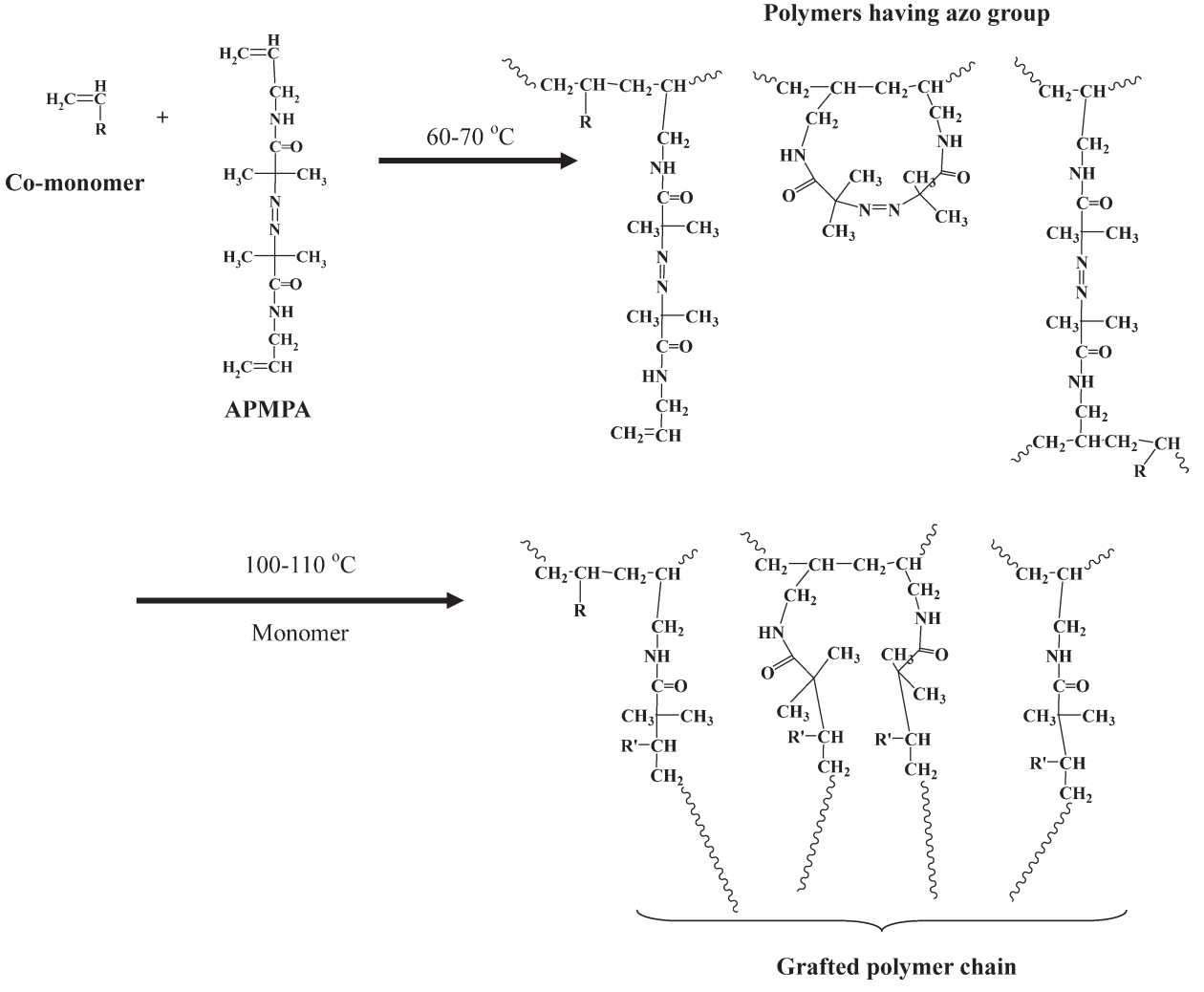
Some studies concerning the reactivity of the vinyl groups of APMPA with styrene (ST) and vinyl benzoate have been published.[9–12] However, in these studies, the copolymerization of the vinyl groups of APMPA with other monomers and graft polymerization with the produced copolymer having azo groups were insufficient for industrial applications.

The objective of this study was to develop a new industrial graft polymerization method with APMPA. For this purpose, the homopolymerization of APMPA, the decomposition properties of the azo group of APMPA, and its copolymerization with ST, methyl methacrylate (MMA), and vinyl acetate (VA) were studied. Furthermore, the grafted polymers composed of ST, MMA, 2-[*p*-(1,1,3,3-tetramethyl butyl) phenoxy polyethoxy] ethyl methacrylate macromonomer (MAX-*n*, where *n* is the mean numbers ethylene oxide units, and *n* is 1.27, 4.39, or 9.27), and *N*-isopropyl acrylamide (NIPAAm) were synthesized with the polymeric azo initiator. Scheme 1 depicts the APMPA copolymerization with the comonomer and the graft polymerization with the polymeric azo initiator.

EXPERIMENTAL

Materials

2,2′-Azobisisobutyronitrile, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN), 2,2′-azobis[*N*-(2-propenyl)-2-



Scheme 1

TABLE I
Composition of the Reaction Mixture for the Solution Copolymerization of APMPA with the Comonomers

Component	Amount (mol)
Comonomer (ST, MMA, or VA)	3.6×10^{-2}
APMPA	4.0×10^{-3}
ADVN	4.0×10^{-4}
Toluene or 1,4-dioxane[a]	20 mL

[a] Toluene (St or MMA) or 1,4-dioxane (VA) was used for a solvent.

methyl propionamide] (APMPA), divinyl benzene (55 mol % of a 2 : 1 mixture of *m*-divinylbenzene and *p*-divinylbenzene and 45% ethylvinylbenzene), ST, *n*-hexane, methacrylic acid (MA), MMA, and NIPAAm were purchased from Wako Pure Chemical Industries, Ltd.(Osaka, Japan). Acetone, ethanol, hydrochloric acid, chloroform, *N,N′*-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine, diethyl ether, sodium hydrogen carbonate, tetrahydrofuran (THF), toluene, methanol, anhydrous magnesium sulfate, VA, *p*-xylene, and dichloromethane were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). 2-[*p*-(1,1,3,3-Tetramethyl butyl) phenoxy polyethoxyl] ethanol (Triton X) was purchased from Sigma-Aldrich Co. (St. Louis, MO). Deuterated chloroform containing 1% v/v tetramethylsilane (TMS) was purchased from SCETI K. K. (Saint Aubin, France).

To purify ST, MMA, and VA, these monomers were added to 300-mL distillation flasks, and the polymerization inhibitor was subsequently removed from the monomers by vacuum distillation with a rotary evaporator (N-1000, Eyela Co., Ltd., Tokyo, Japan). Other reagents were of the highest grade and were used without purification.

Synthesis of the macromonomer

Several kinds of MAX-*n* ($n = 1.27$–40.5) were synthesized from MA and Triton X with various *n* values by esterification with DCC as a dehydrating reagent. In a four-necked, 500-mL glass flask, 3.44 g (40 mmol) of MA, 0.49 g (4 mmol) of 4-dimethylaminopyridine, 40 mmol of Triton X, and 70.0 g of dichloromethane were placed under a dry nitrogen atmosphere and stirred at 4°C and 100 rpm. To this flask, a mixture of 8.24 g (40 mmol) of DCC and 70.0 g of dichloromethane was added gradually for 1 h under nitrogen. After the addition of the mixture, the reaction mixture was stirred for 48 h at room temperature and 100 rpm. The produced 1,3-dicyclohexylurea, which was insoluble in dichloromethane, was removed by filtration with a fritted glass funnel. To the filtrate, 200 mL of a 0.5*N* hydrochloric acid solution was added. Unreacted Triton X, MA, and DCC were removed by repeated extractions with a 0.5*N* hydrochloric acid solution and an aqueous solution saturated with sodium hydrogen carbonate. The synthesized MAX-*n* was recovered from the dichloromethane solution by the evaporation of dichloromethane in a rotary evaporator at 30°C.

Polymerization and purification of the polymers

In the case of the homopolymerization of APMPA, 4.0×10^{-3} mol of APMPA and 4.0×10^{-4} mol of AVDN were added to 20 mL of toluene in a 50-mL polypropylene screw-cap tube at 60°C for 12 h. To compare the polymerization and copolymerization kinetics, the reaction mixture shown in Table I was prepared in a 50-mL polypropylene screw-cap tube. To purify produced polymers, 2 mL of the reaction solutions were dropped in 40 mL of *n*-hexane. The precipitated polymer was recovered with a centrifugal separator (2010, Kubota Co., Tokyo, Japan). The collected polymer was dissolved in 1 mL of THF and poured into 40 mL of *n*-hexane again. These series of precipitation and dissolution were repeated three times, and the samples were subsequently dried *in vacuo* at room temperature for more than 24 h.

Graft polymerization with ST–APMPA copolymer as the initiator

APMPA (6.00×10^{-3} mol) and ST (1.94×10^{-1} mol) were added to 100 mL of toluene in a 200-mL glass flask and polymerized at 60°C for 12 h. The produced polymer was purified and dried at room temperature. In a 15-mL glass tube, 0.20 g of the produced polymeric initiator and 20 g of monomer were added to 5 mL of solvent. Toluene (100°C) or *p*-xylene (110°C) was used as a solvent for the graft copolymerization of ST and MMA. In other cases, 1,4-dioxane was used.

Conversion and characterization of the polymers

The conversions of ST, MMA, and VA were measured by the mass method.[13] The conversion of APMPA was measured by gas chromatography (GC-8A, Shimadzu Co., Kyoto, Japan). The conversions of NIPAAm and MAX-*n* were measured by the decrease of the hydrogen peak of the vinyl group with a 200-MHz NMR spectrometer (Gemini 2000, Varian, CA). A small portion of the reaction mixture was added to $CDCl_3$ and poured into glass tubes (4.20 mm in diameter and 178 mm in length, 507-PP, Wilmad-Labglass, Buena). The incorporation of APMPA in the copolymer was identified from the ^{1}H-NMR spectrum of the purified copolymer.

Molecular mass and its distribution

To measure the molecular mass and its distribution, the purified and dried polymers were dissolved in THF, and the molecular masses were subsequently measured with gel permeation chromatography (GPC;

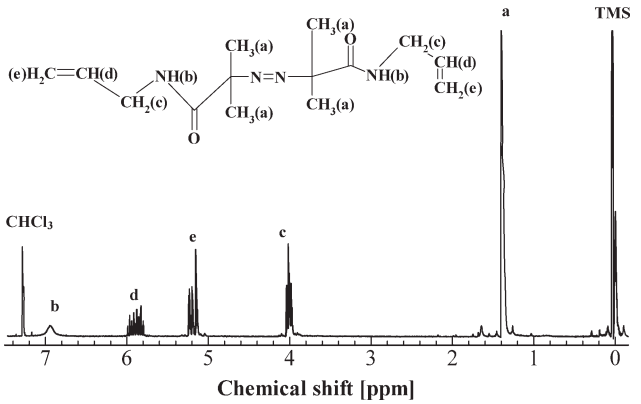


Figure 1 ^{1}H-NMR spectrum of APMPA.

GPC8020 system, Tosoh Co., Tokyo, Japan) attached with TSKgel G5000H_{HR} and TSKgel G3000H_{HR} columns. THF was used as a mobile phase, and the polymers were detected by both UV (at 265 nm) spectroscopy and refractive-index detectors. Polystyrene (pST) standards with molecular masses of 9.86×10^3, 5.46×10^3, 2.95×10^3, 1.3×10^3, and 5.8×10^2 [weight-average molecular weight (M_w)/number-average molecular weight (M_n) = 1.02–1.15; GL Sciences, Inc., Torrance, CA] were used as standards and yielded molecular masses relative to linear pST.

Nomenclature of the synthesized polymers

In this study, MMA, ST, and VA were selected as comonomers to investigate the copolymerization kinetics of APMPA. The produced copolymers were labeled poly{methyl methacrylate-*co*-2,2′-azobis[*N*-(2-propenyl)-2-methylpropionamide]} [p(MMA-*co*-APMPA)], poly{styrene-*co*-2,2′-azobis[*N*-(2-propenyl)-2-methylpropionamide]} [p(ST-*co*-APMPA)], and poly{vinyl acetate-*co*-2,2′-azobis[*N*-(2-propenyl)-2-methylpropionamide]} [p(VA-*co*-APMPA)], respectively. In the case of the grafted polymers, when p(ST-*co*-APMPA) was used for the graft polymerization of NIPAAm, MMA, MAX-*n*, or ST, the resulting grafted polymers were named grafted poly(*N*-isopropyl acrylamide) from p(ST-*co*-APMPA) [pSTA-g(pIPA)], grafted poly(methyl methacrlate) from p(ST-*co*-APMPA) [pSTA-g(pMMA)], grafted poly(MAX-*n*) from p(ST-*co*-APMPA) [pSTA-g(pMAX-*n*)], and grafted poly(styrene) from p(ST-*co*-APMPA) [pSTA-g(pST)], respectively.

RESULTS AND DISCUSSION

Polymerization of the vinyl groups of APMPA and polymerization of the vinyl monomers with APMPA as an initiator

APMPA's two vinyl groups acted as monomers in the presence of another initiator. It was expected that the produced polymer had not only crosslinking networks but also an azo group, which could act as initiator at high temperatures, as shown in Scheme 1. Because the half-life of the azo group of APMPA was 10 h at 96°C,[9] the Arrhenius constant and activation energy of azo group decomposition were 4.77×10^{14} s^{-1} and 1.37×10^5 J/mol, respectively. Using the Arrhenius equation and applying a first-order decomposition reaction of APMPA, we found the conversion of the azo group of APMPA to be almost 5% in 4 h at 80°C. This result indicates that the azo group of APMPA was stable at temperatures below 80°C. When ADVN was used as an initiator for APMPA homopolymerization, the conversion of APMPA at 12 h was almost zero and found to be within the experimental error. GPC analysis indicated that the reacting mixture had almost the same molecular mass as the monomer solution. In the ^{1}H-NMR spectrum of APMPA in $CDCl_3$, as shown in Figure 1, five hydrogen peaks of δ (ppm) = 1.3–1.4 (H_a: methyl), 3.8–4.2 (H_c: *N*-methylene), 5.1–5.3 (H_e: methylene of allyl group), 5.8–6.1 (H_d: methine of allyl group), and broad 6.9–7.1 (H_b: NH) were observed. After polymerization, only the hydrogen peaks of δ = 5.1–5.3 and 5.8–6.1 ppm were slightly decreased over time; this indicated that the vinyl group of APMPA was available for reaction with radical molecules. Therefore, GC–mass measurements of the reacting mixture were performed and showed that the small dimer and trimer peaks of APMPA appeared. A similar result[9] was reported, which concluded that the APMPA polymer could not be obtained because of ring-forming polymerization between two intermolecular vinyl groups of APMPA. Therefore, to synthesize a polymer having azo groups available as initiators for graft polymerization, other comonomers have to be used.

To check the decomposition properties of the azo group of APMPA, ST or MMA was polymerized in toluene (100°C) or *p*-xylene (110°C) with APMPA as the initiator. Figure 2 shows the time-dependent conversion of ST and MMA. As shown in Figure 2, the conversions increased over time. The reaction rate at 110°C was faster than that at 100°C; this indicated that the azo group of APMPA could be used for polymerization at 100–110°C.

With the well-established kinetics for radical polymerization,[14] the initiator efficiency (*f*) of APMPA was evaluated:

$$R_i = 2k_d f[I] = R_t = R_{tc} + R_{td} = 2(k_{tc} + k_{td})[\mathrm{R}\cdot]^2 \quad (1)$$

where R_i is the initiation rate, k_d is the decomposition rate constant of the azo group of APMPA, [I] is the initiator concentration, R_t is the termination rate, R_{tc} is the termination rate caused by combination, R_{td} is the termination rate caused by disproportionation, k_{tc} is the combination rate constant, k_{td} is the disproportionation reaction constant, and [R·] is the

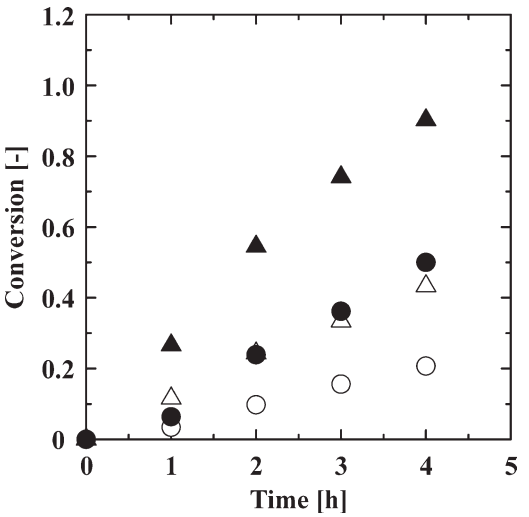


Figure 2 Time course of the conversion on the solution polymerization. APMPA was used as an initiator: (○) ST at 100°C, (△) ST at 110°C, (●) MMA at 100°C, and (▲) MMA at 110°C.

concentration of radical molecules. From this equation, [R·] can be expressed as

$$[\mathrm{R}\cdot] = \{2k_d f[\mathrm{I}]/(k_{tc} + k_{td})\}^{1/2} \quad (2)$$

The polymerization rate (R_p) is then expressed as

$$R_p = -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}][\mathrm{R}\cdot] \quad (3)$$

where k_p is the propagation rate constant and [M] is the monomer concentration. When a ratio x of disproportionation to termination reaction is defined, $x = 0$ is equivalent to combination and $x = 1$ corresponds to disproportionation. With x and eqs. (2) and (3), f can be given as

$$f = \frac{2k_{td} + k_{tc}}{k_p^2[\mathrm{M}]^2}\frac{R_p^2}{k_d[\mathrm{I}](1+x)} \qquad x = \frac{k_{td}}{k_{td} + k_{tc}} \quad (4)$$

It is known that combination termination is the dominant termination mechanism in ST ($x = 0$), whereas for MMA, disproportionation also occurs simultaneously. Therefore, it was assumed that MMA had a lower f than ST because of its termination mechanism. With the kinetic parameters of ST[15] and MMA,[16] the initiator efficiencies of APMPA in the ST polymerization at 100 and 110°C were found to be 0.260 and 0.297, respectively. Corresponding values in the MMA polymerization were found to be 0.063 and 0.097, respectively. At high temperatures, disproportionation was predominant in the polymerization of MMA.[15] Therefore, the f of MMA was quite small. Moreover, the low f may have been due to the simultaneous polymerization reaction of the vinyl group of APMPA, which left the monomer supply to the azo group incorporated into the polymer insufficient for polymerization at high temperatures.

Copolymerization reactivity of APMPA

Because the homopolymer of APMPA could not be obtained because of coupling reactions between intramolecular vinyl groups, the copolymerizations of APMPA with ST, MMA, and VA were studied with ADVN as an initiator. Figure 3 shows the ^{1}H-NMR spectrum of the copolymer of APMPA and ST in $CDCl_3$. As shown in this spectrum, the hydrogen peaks of broad methylene groups (δ = 1.2–1.6) and methine groups (δ = 1.7–2.1) in the main chain and phenyl groups (δ = 6.4–6.7, 6.9–7.2) of pST were present. A small amount of hydrogen peaks of APMPA [δ = 1.3–1.4 (H_a: methyl), 4.0 (H_c: *N*-methylene), 5.1–5.3 (H_e: methylene of allyl group), and 5.8–6.1 (H_d: methine of allyl group)] also existed in the copolymer spectrum. In the spreading segment shown in Figure 3, there were broad and small peaks of methylene groups incorporated into polymer chain. However, this peak amount was quite small. Therefore, the majority fraction of vinyl groups from APMPA did not form crosslinks and, thus, remained as shown in Scheme 1.

Figures 4(a–c) shows the time-dependent copolymerization conversions of ST and APMPA, MMA and APMPA, and VA and APMPA, respectively. Here, the reactivity of the radical against APMPA was found to be higher than that against comonomers. Because the homopolymerization conversion of APMPA at 12 h was almost zero, the homopolymerization of APMPA did not occur. This result was indicated by the observation that the reaction of APMPA against the APMPA radical terminal was negligible and that k_{22} was almost zero. k_{22} is the rate coefficient for propagation of the radical

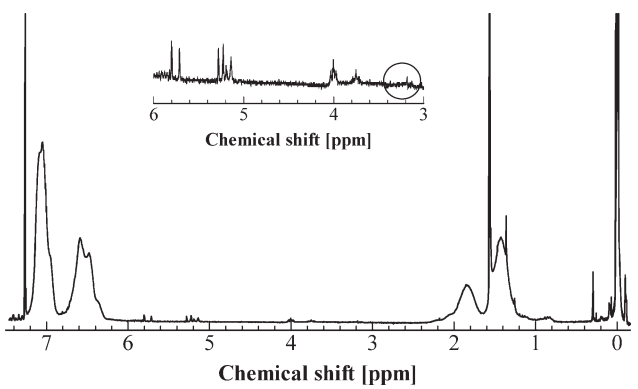


Figure 3 ^{1}H-NMR spectrum of the p(ST-*co*-APMPA) copolymer. The copolymerization was conducted at 60°C for 12 h, and the molar fraction of APMPA in the monomer was 4.5 mol %.

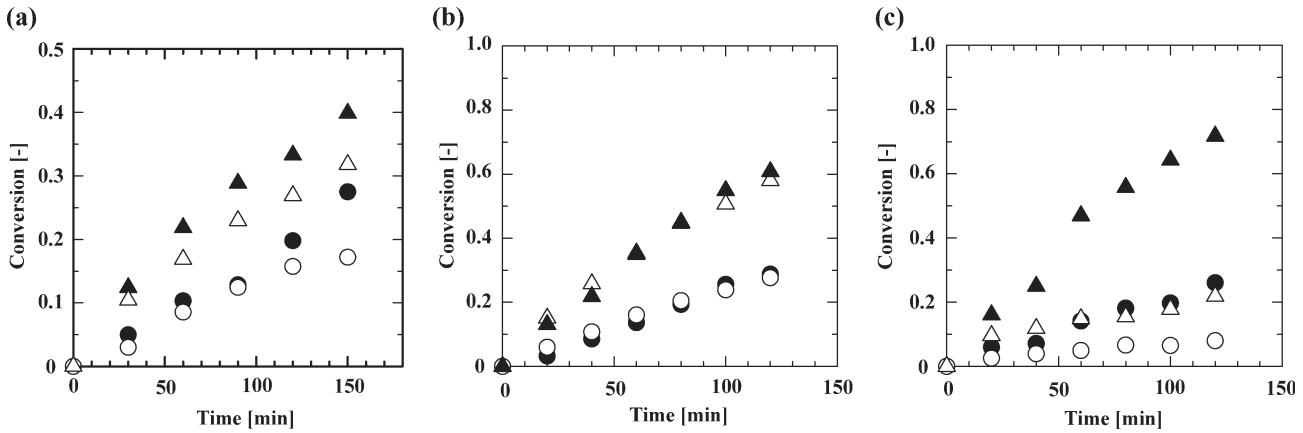


Figure 4 Time courses of the conversion of the solution copolymerization of (a) ST and APMPA [(○) ST at 60°C, (△) ST at 70°C, (●) APMPA at 60°C, and (▲) APMPA at 70°C], (b) MMA and APMPA [(○) MMA at 60°C, (△) MMA at 70°C, (●) APMPA at 60°C, and (▲) APMPA at 70°C], and (c) VA and APMPA [(○) VA at 60°C, (△) VA at 70°C, (●) APMPA at 60°C, and (▲) APMPA at 70°C].

(APMPA terminal) against APMPA. Therefore, we assumed that k_{22} was approximately equal to zero, and from the results shown in Figure 4, the reactivity ratio was estimated. Table II shows the calculated reactivity ratios (r_1's). The calculated r_1 was arranged in ascending order as VA, ST, and MMA, respectively. It is well-known that the resonance effect is influenced as a first-order factor and the polar effect is influenced as a second-order factor against the propagation reaction in addition polymerization.[17] In the case of VA copolymerization, the resonance effect affects the copolymerization reactivity.[15] Therefore, we estimated that r_1 of the conjugated monomer of ST and MMA was larger than that of unconjugated VA.

Molecular mass and its distribution of p(ST-*co*-APMPA), p(MMA-*co*-APMPA), p(VA-*co*-APMPA), pST, poly(methyl methacrylate) (pMMA), and poly(vinyl acetate) (pVA)

Table III shows the molecular masses and their distributions of p(ST-*co*-APMPA), p(MMA-*co*-APMPA), and p(VA-*co*-APMPA). The molecular masses of these copolymers were compared to those of pST, pMMA, and pVA. As shown in Table III, the M_n and M_w values of the copolymers were lower than those of the homopolymers. Particularly, M_w of p(VA-*co*-APMPA) was significantly lower than that of pVA. This was because VA was an unconjugated monomer, and VA reactivity against the terminal radical was lower than for ST and MMA.

Effect of the APMPA-to-ST monomer ratio on the copolymerization

Figure 5 shows the time development of the conversion of ST and APMPA on the copolymerization at 60°C. Here, the concentration of APMPA in monomer was changed from 3 to 10 mol %. The conversions of ST and APMPA were found to increase monotonically when the APMPA concentration was 3 mol %. However, in the case of the 10 mol % APMPA concentration, the conversion of APMPA reached a threshold value of 0.3 and remained constant, whereas the conversion of ST increased with time. This suggested that, in the presence of an excess of APMPA, intramolecular terminal reactions of APMPA occurred. Bartlett and Oliwa[18] reported that the polymerization reactivity of diallyl monomer was lost because of a transfer of radicals to one allyl group of the monomer, followed by intramolecular reaction with the other allyl group. The produced ring radical molecules had little reactivity. In the case of APMPA, allyl radicals may have proceeded with the chain-transfer reaction and formed dimer or trimer molecules, which exhibited high steric hindrances and little reactivity with the radicals.

Figure 6 shows the effect of the APMPA molar fraction in the monomer on the molecular mass. As shown, the molecular mass of the copolymer decreased with increasing molar fraction of APMPA. This was because the polymerization reactivity of APMPA decreased via chain-transfer reactions. The distribution index of p(ST-*co*-APMPA) increased slightly.

TABLE II
r_1 Values for the Copolymerization of APMPA with the Comonomers

	Temperature (°C)	
Comonomer	60	70
ST	1.10	1.30
MMA	1.60	1.60
VA	0.37	0.43

TABLE III
Molecular Mass of the Produced Polymers

Temperature (°C)	Polymer	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n
60	pST	5.8	11.0	1.8
	p(ST-*co*-APMPA)	5.2	10.0	1.9
70	pST	6.3	12.0	1.9
	p(ST-*co*-APMPA)	5.3	12.0	2.2
60	pMMA	6.3	15.0	2.3
	p(MMA-*co*-APMPA)	6.1	14.0	2.3
70	pMMA	6.1	12.0	2.0
	p(MMA-*co*-APMPA)	5.2	12.0	2.3
60	pVA	3.8	8.6	2.3
	p(VA-*co*-APMPA)	3.0	5.1	1.7
70	pVA	3.1	7.1	2.3
	p(VA-*co*-APMPA)	2.0	4.0	2.1

Graft polymerization of MAX-*n*, ST, MMA, and NIPAAm with p(ST-*co*-APMPA) as an initiator

To evaluate the effect of the polymeric initiator on graft polymerization, ST and APMPA were copolymerized for 12 h at 60°C, and the molar fraction of APMPA was fixed at 4.5 mol %. With the produced p(ST-*co*-APMPA) as initiator, the graft polymerization of ST and MMA was studied. Figure 7 shows the GPC chromatograms of the grafted polymers of ST and MMA. A UV detector was used to measure the phenyl groups of pST. The average molecular mass of p(ST-*co*-APMPA) was found to be about 10,000 (0 h). In the case of the graft polymerization of ST at 100°C [Fig. 7(a)], the peak of the produced grafted copolymer of ST appeared in the range from 6×10^4 to 6×10^5, with the initiator peak intensity of p(ST-*co*-APMPA) decreasing with time. The area of each peak around from 6×10^4 to 6×10^5 at 110°C [Fig. 7(b)] at 1–4 h and 110°C was larger than that at 100°C. This was attributed to the increased rates of monomer propagation and azo group decomposition at 110°C. In Figure 7(c, upper left inset), the chromatogram with a refractive index detector is shown; it indicates the high-molecular-mass peak of the MMA graft copolymer at 110°C. The peak area of the grafted copolymer was the same as that shown in Figure 7(b). However, in Figure 7(c), a small fraction with a high molecular mass is shown. This was due to a lack of absorbance at 265 nm for the grafted acryl ester group of MMA, and so the absorbance of the grafted copolymer molecule was reduced by a factor of 10 with increasing estimation of molecular mass. The production of a high-molecular-mass copolymer with UV absorbance was the evidence of the production of grafted MMA chains from the p(ST-*co*-APMPA) main chain.

Next, the graft copolymer of p(ST-*co*-APMPA) with the macromonomer (MAX-1.27, MAX-4.39, MAX-9.20, MAX-40.5) ST, MMA, or NIPAAm was

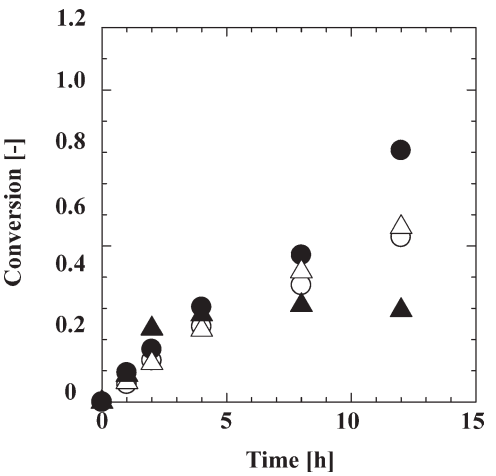


Figure 5 Time course of the conversion of the solution copolymerization of ST and APMPA. The molar fractions of APMPA in the monomer were 3 and 10 mol %, respectively: (○) ST (3 mol % APMPA), (△) ST (10 mol % APMPA), (●) APMPA (3 mol % APMPA), and (▲) APMPA (10 mol % APMPA).

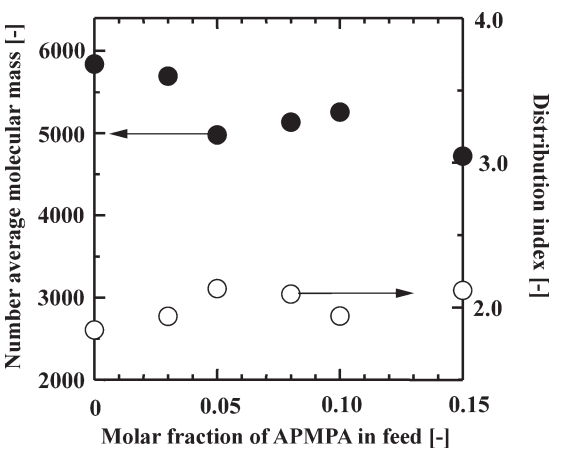


Figure 6 Relationship between the molar fraction of APMPA in the feed and the molecular mass or dispersion index on the ST–APMPA copolymerization: (○) distribution index and (●) M_n.

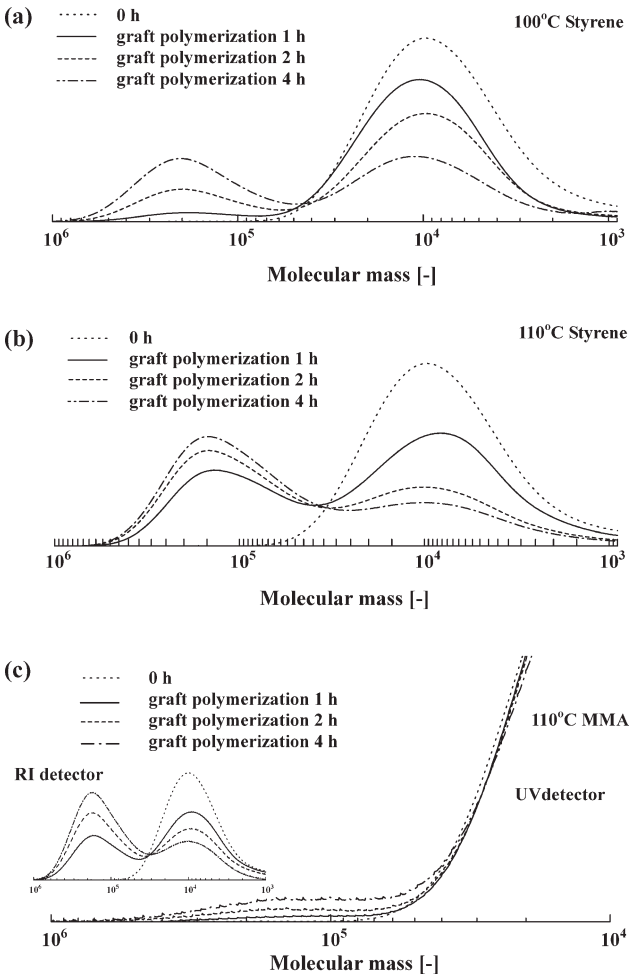


Figure 7 GPC chromatogram of the grafted copolymer measured by a UV detector (265 nm): graft copolymerization of (a) ST at 100°C, (b) ST at 110°C, and (c) MMA at 110°C [(· · ·) p(ST-*co*-APMPA) used for an initiator (0 h), (—) reaction time = 1 h, (- - -) reaction time = 2 h, and (– · –) reaction time = 4 h.

polymerized for 8 h at 100°C. In our study, we simply estimated their molecular masses measured by GPC under the assumption that the grafted copolymers were of linear conformation. Table IV shows molecular mass of the grafted copolymers. St and MMA were grafted onto p(ST-*co*-APMPA), and the polymerization degrees of the graft chains were estimated to be 910 and 1700, respectively. The molecular mass of the branched polymer was smaller than that of the linear polymer. Therefore, the degree of polymerization of the branched chain from the main ST–APMPA chain was higher than about 1000. In the case of NIPAAm, the graft polymer could not be obtained, and only the NIPAAm homopolymer was precipitated. This was because hydrophilic NIPAAm could not approach the hydrophobic initiator polymer chain, and the chain-transfer reaction of radicals against NIPAAm monomer mainly took place.

In the case of the graft polymerizations of MAX-1.27, MAX-4.39, and MAX-9.20, the M_n values of the obtained graft polymers were 11, 280, and 18, respectively. However, MAX-40.5 could not be polymerized with p(ST-*co*-APMPA). MAX-40.5 could not approach the polymer chain because of its steric hindrance. Yasuda[13] reported that the number of n (number of polyethoxy groups) controlled the reactivity by the gel effect in the solution polymerization of MAX-n, and their R_p values increased at a high n. Because the steric hindrance of polymer with an azo group and R_p was balanced, the molecular mass of graft polymer of MAX-4.39 was the highest of those tested in this study.

CONCLUSIONS

A polymerizable azo initiator, APMPA, with two vinyl groups and one azo group was used to produce graft copolymers. To develop a new graft polymerization method, the radical polymerization kinetics of APMPA and graft polymerization with produced macromolecular azo initiator were studied. The homopolymerization of APMPA could not proceed because of APMPA self-circulation reactions. The copolymerization of APMPA with ST, MMA, or VA with ADVN was shown to be successful. With the produced macromolecular azo initiator, graft polymers of ST, MMA, or an amphiphilic macromonomer was synthesized. In the case of NIPAAm, the homopolymer of NIPAAm precipitated.

TABLE IV
Molecular Mass of the Graft Polymers

Grafted polymer	M_n (g/mol)	M_w (g/mol)	Degree of polymerization[a]
p(ST-*co*-APMPA)	5.7×10^3	1.1×10^3	–
pSTA–g(pST)	1.0×10^5	1.2×10^5	910
pSTA–g(pMMA)	1.8×10^5	2.1×10^5	1700
pSTA–g{p[MAX(n = 1.27)]}	9.3×10^3	1.7×10^4	11
pSTA–g{p[MAX(n = 4.39)]}	1.3×10^5	1.7×10^5	280
pSTA–g{p[MAX(n = 9.27)]}	1.8×10^4	3.8×10^4	18

[a] Estimated value calculated on the assumption that the grafted copolymer was linear.

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