Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis of Graft Polymers by Copolymerization of Macromonomer. I. Preparation of Macromonomers

Masazo Niwa[a]; Tadashi Hayashi[a]; Takahiro Matsumoto[a]
[a] Department of Applied Chemistry, Doshisha University, Kyoto, Japan

To cite this Article Niwa, Masazo , Hayashi, Tadashi and Matsumoto, Takahiro(1985) 'Synthesis of Graft Polymers by Copolymerization of Macromonomer. I. Preparation of Macromonomers', Journal of Macromolecular Science, Part A, 22: 4, 433 — 450

To link to this Article: DOI: 10.1080/00222338508056612

URL: http://dx.doi.org/10.1080/00222338508056612

J. MACROMOL. SCI.–CHEM., A23(4), 433-450 (1986)

Synthesis of Graft Polymers by Copolymerization of Macromonomer. I. Preparation of Macromonomers

MASAZO NIWA, TADASHI HAYASHI, and TAKAHIRO MATSUMOTO

Department of Applied Chemistry
Doshisha University
Karasuma-imadegawa, Kamikyo-ku, Kyoto, 602 Japan

ABSTRACT

Ethenylbenzene-terminated poly(2-acetoxyethyl methacrylate) macromonomer, 2-methyl-2-propenoate-terminated poly(2-acetoxyethyl methacrylate) macromonomer, and 2-methyl-2-propenoate-terminated poly(methyl methacrylate) macromonomer were synthesized. The number-average molecular weight of the macromonomers could be controlled by adjusting the feed composition. Comb-type polymers and graft copolymers were prepared by homopolymerization and copolymerization of macromonomer with comonomer. Unreacted macromonomer in the resulting polymers could be determined by calculating the areas of the macromonomer peaks on gel permeation chromatograms (GPC).

INTRODUCTION

Macromonomers have recently become interesting from the viewpoint of molecular design of macromolecules [1-4]. A macromonomer is constituted of a short polymer chain fitted at one end with a polymerizable double bond, and graft polymers are obtained by copolymerization of a macromonomer with suitable comonomers. The length of graft chains can be controlled by adjusting the molecular weight of the

0022-233X/86/2304-0433$3.50/0

macromonomer. In the synthesis of a macromonomer, the transformation of carboxyl-terminated prepolymer into macromonomer by the glycidyl methacrylate (GMA) method [5, 6] has been reported. We have prepared carboxyl-terminated 2-acetoxyethyl methacrylate (AEMA) prepolymer and also synthesized the macromonomer by using oxiranyl functional monomers. AEMA units in graft chains can be easily converted into hydroxy grafting sites.

The present paper describes the preparation and characterization of ethenylbenzene-terminated and 2-methyl-2-propenoate-terminated macromonomers of different molecular weights.

EXPERIMENTAL

Materials

1-Ethenyl-4-oxiranylmethoxybenzene (EOMB) was prepared by the reaction of p-vinylphenol with epichlorohydrin and distillation at a pressure of 0.1 torr at 88.0-89.0°C under purified nitrogen according to the method described by Tanimoto et al. [7]. p-Vinylphenol was synthesized by the method of Sovish [8]. AEMA was prepared in the manner described in a previous paper [9].

After reduction with zinc powder, thioglycolic acid (TGA) was distilled under purified nitrogen before use.

GMA, methyl methacrylate (MMA), 4,4'-azobis-(4-cyanovaleric acid) (ACVA), α,α'-azobisisobutyronitrile (AIBN), and polymerization solvents were purified in the usual way.

Preparation of Prepolymers

Equation (1) expresses the number-average degree of polymerization ($\overline{DP}_n$) in terms of polymer composition ($Y = ([M]_0 - [M])/([S]_0 - [S])$) and polymer yield (x),

$$\frac{1}{\overline{DP}_n} = C_s \frac{1}{y_0} \frac{\ln \dfrac{(M_s/M_m) + Y(1 - x)}{(M_s/M_m) + Y - y_0 \cdot x}}{\dfrac{(y_0 - Y)x}{(M_s/M_m) + Y - y_0 \cdot x}} \tag{1}$$

where C_s is the chain transfer constant of TGA (S) for the monomer (M), $y_0 = ([M]_0/[S]_0)$, and M_m and M_s are the molecular weights of monomer and TGA, respectively [10]. In Eq. (1), x is expressed as the weight of polymer produced per unit weight of the initial monomer. Equation (1) was utilized for design of the prepolymer. The required amounts of the monomer and TGA, calculated by Eq. (1) with $C_s = 0.22$ (AEMA [11]) or $C_s = 0.39$ (MMA [12]), were placed into a glass tube. The tube was sealed after degassing by repeated freezing and thawing cycles.

Free-radical polymerizations of AEMA and MMA were carried out in the presence of TGA in dioxane by using ACVA as an initiator at 50°C in the sealed tube. Polymerization was stopped at 40-60% conversion. The prepolymer was recovered by dropwise addition of the reaction mixture to a large amount of petroleum ether. The prepolymer was purified by reprecipitation from acetone solution into petroleum ether to remove unreacted monomer and into distilled water to remove unreacted TGA and ACVA. The prepolymer was dried in a vacuum oven at 60°C to constant weight.

Synthesis of Macromonomers

The macromonomers were synthesized by the reactions of prepolymers with oxiranyl vinyl monomers (50 mol% excess) at 140°C in xylene with small amounts of hydroquinone and N,N-dimethyllaurylamine, according to the method reported previously [5, 6]. The purification of macromonomers was carried out by reprecipitation, pouring the acetone solution slowly into a large excess of petroleum ether.

Measurements

Potentiometric titrations were carried out with a Hiranuma reporting titrator (Model COMTITE-7). Number-average molecular weights of macromonomers were measured with a Knauer vapor-pressure osmometer (for samples with $\overline{M}_n < 20\,000$). Molecular weight distributions of polymers were measured on samples in THF solutions at 40°C by using a Shimadzu high-speed liquid chromatograph (Model LC-3A) equipped with three columns (HSG-15, HSG-30, and HSG-50) and dual UV and RI detectors. The flow rate was 1 mL/min. The unsaturation contents of macromonomers were determined by the bromate-bromide method [13]. The IR spectrum was recorded with a Shimadzu IR-435 infrared spectrophotometer using thin film samples. The UV spectrum was recorded with a Shimadzu UV-120 spectrophotometer using chloroform solutions.

RESULTS AND DISCUSSION

Preparation of Prepolymers

The procedure employed for designing AEMA prepolymer and MMA prepolymer was based on Eq. (1). The experimental conditions and polymer yield of the prepolymers obtained are summarized in Table 1. Several samples of prepolymers were prepared with polymer yields of 40-60%. The polymerization activity of AEMA was slightly higher than that of MMA. The prepolymers from Runs 4, 3, and 1 were highly viscous liquids, soluble in methanol, acetone, chloroform, or benzene, but insoluble in distilled water or petroleum ether. Prepolymers of Runs 2, 5, and 6 were insoluble in methanol.

Table 2 lists the characteristics of the prepolymers obtained. AEMA prepolymer and MMA prepolymer are designated as CTA and CTM in this work. The number-average molecular weights of prepolymers were determined by VPO. The experimentally observed and calculated values are comparable with only a small deviation (Table 2). Figure 1 shows the IR spectra of CTM (A) and its potassium salt (B). In B, an absorption band was observed at 1 595 cm^{-1} which originates from the antisymmetric vibration of the carboxylate anion. The carboxyl-group contents of the prepolymers were determined by potentiometric titration. The number of the terminal carboxyl groups per prepolymer molecule ($\overline{N}_{COOH}$) was estimated to be 1.02-1.05 from the molecular

TABLE 1. Synthesis of the AEMA Prepolymers and MMA Prepolymers[a]

Run	Monomer	$[\text{Monomer}]_0$, mol/L	$[\text{TGA}]_0$, mol/L	y_0[b]	Polymer yield, %
3	AEMA	5.00	1.67	3.00	58.5
2			1.25	4.00	46.8
4	MMA	5.00	2.50	2.00	41.3
1			1.25	4.00	39.1
5			0.417	12.0	50.3
6			0.208	24.0	44.0

[a] Polymerization in dioxane at 50°C for 3 h; ACVA concentration, 0.01 mol/L.

[b] $y_0 = ([\text{Monomer}]_0/[\text{TGA}]_0)$.

TABLE 2. Characteristics of the AEMA Prepolymer (CTA) and MMA Prepolymer (CTM)

		$\overline{M}_n \times 10^{-3}$				
Prepolymer	No.	Observed	Calculated[a]	Carboxyl groups, mmol/g	N_{COOH}[b]	Acetoxyl groups, mmol/g
CTM	1a	0.56	0.53	1.843	1.03	-
	1b	1.14	0.98	0.907	1.03	-
	1c	2.56	2.62	0.398	1.02	-
	1d	5.41	5.30	0.200	1.08	-
CTA	2a	1.57	1.81	0.659	1.03	5.433
	2b	2.29	2.59	0.460	1.05	5.580

[a] Calculated from Eq. (1).
[b] Number of carboxyl terminal groups per polymer molecule.

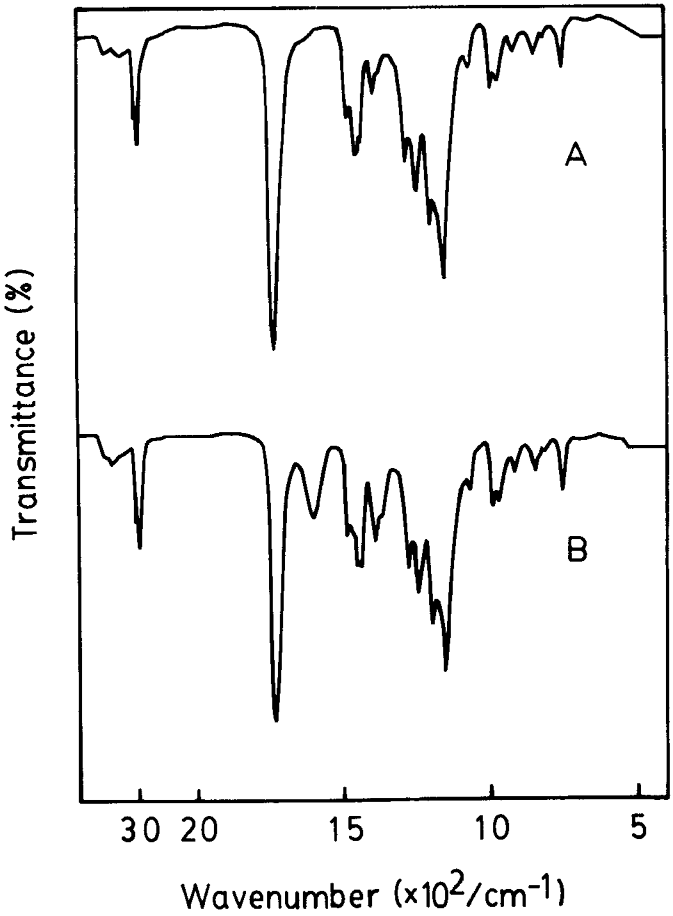


FIG. 1. IR spectra of CTM prepolymer (A) and its potassium salt (B).

weight and the carboxyl content, indicating that the prepolymers have a carboxyl group at one end. The acetoxy-group contents of CTA, determined by alkaline hydrolysis as previously described [9], were in agreement with the calculated values.

Synthesis of Macromonomers

The ethenylbenzene-terminated poly(AEMA) macromonomer (EBA) was synthesized by the reaction of CTA with EOMB. The 2-methyl-2-

TABLE 3. Synthesis and Characterization of Macromonomers

Prepolymer	–COOH, mmol/g	Functional monomer	Macromonomer	$\overline{M}_n \times 10^{-3}$	Double bonds, mmol/g	$\overline{N}_u$[a]
CTM 1b	0.907	EOMB	EBM 1b	1.32	0.773	1.02
CTA 2a	0.659	EOMB	EBA 2a	1.65	0.631	1.04
CTM 1b	0.907	GMA	MPM 1b	1.28	0.805	1.03
CTM 1d	0.200	GMA	MPM 1d	5.56	0.180	1.00
CTA 2a	0.659	GMA	MPA 2a	1.74	0.598	1.04
CTA 2b	0.460	GMA	MPA 2b	2.49	0.418	1.04

[a] Number of terminal units per macromonomer molecule.

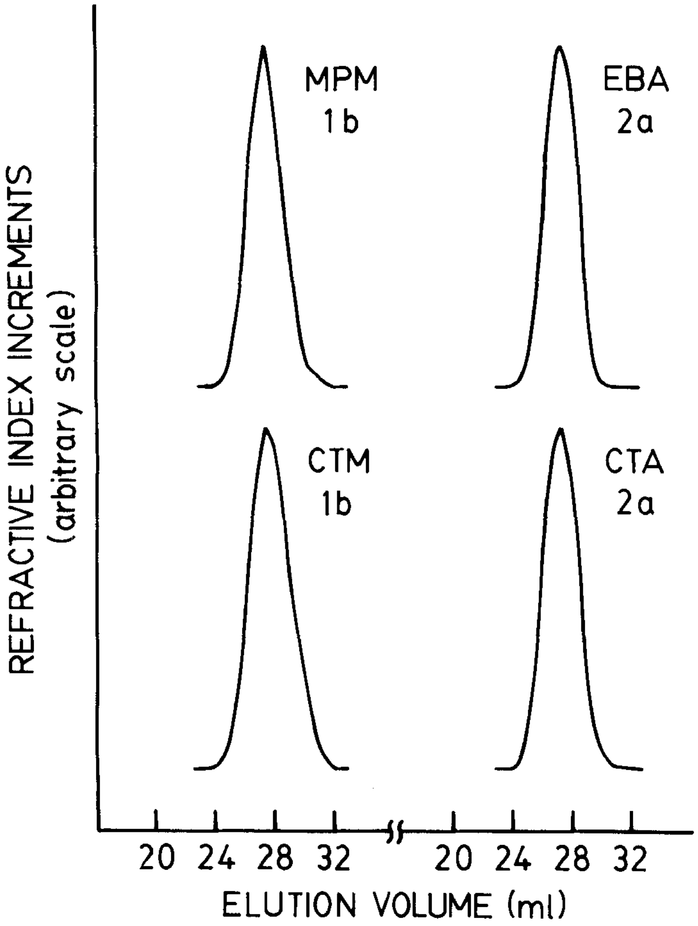


FIG. 2. GPC chromatograms of macromonomers (EBA 2a, MPM 1b) and their raw prepolymers (CTA 2a, CTM 1b).

propenoate-terminated poly(AEMA) macromonomer (MPA) and the 2-methyl-2-propenoate-terminated poly(MMA) macromonomer (MPM) were synthesized by the reaction of CTA and CTM with GMA, respectively. Table 3 summarizes the synthesis and characterization of the macromonomers. The reaction was complete as confirmed by the absence of titrable carbonyl groups. The completion of reaction was also confirmed by IR spectroscopy. The characteristic absorption bands at 680 (ν_{CH}) and 1630 ($\nu_{C=C}$) cm^{-1} appeared.

The molecular weight distribution was measured by GPC chromatography of the macromonomer and the prepolymer. Figure 2 illustrates the typical GPC chromatograms of macromonomer (EBA 2a,

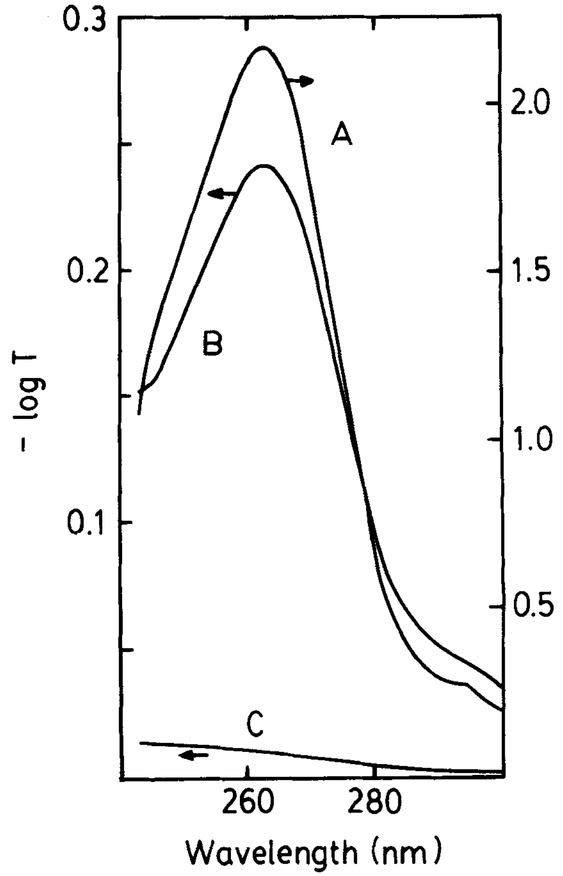


FIG. 3. UV spectra of EOMB (A), macromonomer (EBA 2a) (B), and prepolymer (CTA 2a) (C) in chloroform (0.025 g/L).

MPM 1b) and prepolymer (CTA 2a, CTM 1b). The GPC distribution curve of the macromonomer was similar to that of the raw prepolymer. It is obvious from Fig. 2 that polymerization did not occur during synthesis of macromonomer. The number-average molecular weight of macromonomer was determined by VPO, and the result agreed with the sum of the molecular weights of prepolymer and oxiranyl monomer. As shown in Table 3, macromonomer has a double-bond content corresponding to the carboxyl-group content of prepolymer. The unsaturation per molecule ($\overline{N}_u$) was estimated to be 1.02-1.04.

Figure 3 shows the UV spectra of EBA 2a, EOMB, and CTA 2a. CTA 2a is the starting material for EBA 2a. This figure shows that the spectrum of EBA macromonomer has an absorption peak at 263 nm due to

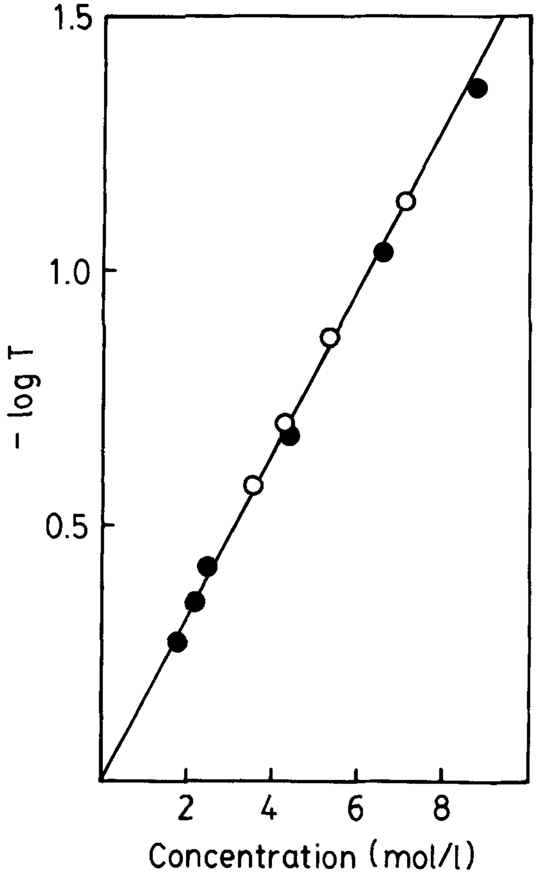


FIG. 4. Relationship between -log T and molar concentration for macromonomer (EBA 2a) (●) and EOMB (○) (263 nm).

the EOMB group. This absorption band is due to the resonance of the double bond and benzene ring. This absorption is negligible in CTA prepolymer.

The quantity -log T at 263 nm was plotted against molar concentration, which was calculated from c (g/L) and the molecular weight (for macromonomer, $\overline{M}_n$ was used). The plot of EBA and EOMB in Fig. 4 gave the same straight line. There is good agreement in the number-average molecular weight determined by VPO and by endgroup determination by UV spectroscopy.

If the prepolymer consists of hydroxyl-pendant polymer, this method cannot be used because there is a possibility of competitive attack by the hydroxyl group on the oxiranyl group. This side reaction was avoided by capping the hydroxyl groups with acetic acid.

The macromonomers synthesized in this work are summarized in Table 4.

Preparation of the Poly(macromonomer)

Homopolymerizations of EBA and MPA macromonomer were carried out in benzene by using AIBN under various conditions in a sealed tube (Table 5). If the macromonomer has polymerizable vinyl groups at both chain ends, crosslinked polymers are formed during the polymerization. In this work, gelation was not observed during the polymerization. The resulting polymer, which contained unreacted macromonomer, was soluble in benzene, acetone, chloroform, THF, and DMF. The GPC chromatogram of the resulting polymer (Run 301) shows bimodality, as shown in Fig. 5. The peak (L) at low molecular weights is due to the unreacted macromonomer and the peak (H) at high molecular weights is due to the homopolymer. The macromonomer conversion (X_a) was calculated by using the RI area (RL) of the peak L. Defining $W_{am,0}$ and W_{am} as the weights of initial macromonomer and unreacted macromonomer, respectively, W_{am} can be written as $W_{am} = (RL/K_{am}(RI))(W_{am,0}/c)$, where $K_{am}(RI)$ is the instrument constant and c is the concentration of the GPC sample present in milligram per gram. X_a is given by $1 - (W_{am}/W_{am,0})$. Thus X_a can be expressed as

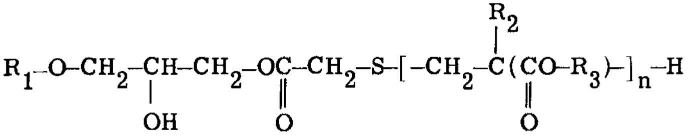
$$X_a = 1 - \frac{RL}{K_{am}(RI)\cdot c} \tag{2}$$

Initially, the $K_{am}(RI)$ values of the macromonomers were determined. By injecting macromonomer solutions of known concentrations into GPC, integrated areas of the macromonomer peak detected by RI and UV were plotted against c, in Fig. 6. The plots are linear. The values of K_{am} calculated from the slopes of these plots are given in Table 6.

Values of X_a were calculated by Eq. (2) using $K_{am}(RI)$, shown also in Table 5. In the case of Run 301, unreacted macromonomer could be separated sufficiently from the resulting polymer by precipitation in methanol, and the conversion obtained gravimetrically was 62.39%, which agreed well with the value X_a (62.48%) in this GPC method.

Molecular weights of the poly(macromonomer) were estimated from

TABLE 4. Structural Formulas of the Macromonomers Synthesized:



$$R_1{-}O{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_2{-}O\underset{\underset{O}{\|}}{C}{-}CH_2{-}S{-}[-CH_2{-}\overset{\overset{R_2}{|}}{C}(\underset{\underset{O}{\|}}{C}O{-}R_3){-}]_n{-}H$$

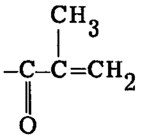
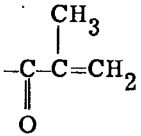
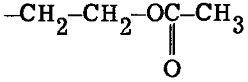
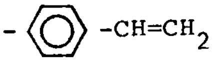
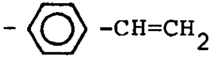
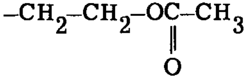
Macromonomer	No.	R_1	R_2	R_3	n
MPM–	1a	 $-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$	$-CH_3$	$-CH_3$	5
	1b				10
	1c				25
	1d				53
MPA–	2a	 $-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$	$-CH_3$	 $-CH_2-CH_2-O\underset{\underset{O}{\|}}{C}-CH_3$	9
	2b				13
EBM–	1b	 -CH=CH$_2$	$-CH_3$	$-CH_3$	10
	1c				25
EBA–	2a	 -CH=CH$_2$	$-CH_3$	 $-CH_2-CH_2-O\underset{\underset{O}{\|}}{C}-CH_3$	9
	2b				13

TABLE 5. Homopolymerization of Macromonomers in Benzene[a]

Run	Macromonomer	$\overline{M}_n \times 10^{-3}$	$[M]_0$ mol/L	Temperature, °C	Time, h	X_a,[b] %	$\overline{M}_n$,[c] $\times 10^{-3}$	$\overline{DP}_n$
301	EBA 2a	1.65	0.61	80	54	62.48	13.8	8.4
206	MPA 2b	2.49	0.18	50	48	39.56	46.4	18.6
207	MPA 2b	2.49	0.16	70	48	60.55	48.9	19.6
106	MPM 1d	5.56	0.55	50	16	45.74	81.0	14.6

[a] AIBN, 1.0 wt% of monomer.

[b] Calculated by Eq. (2) from GPC data.

[c] Estimated from GPC using standard polystyrene calibration.

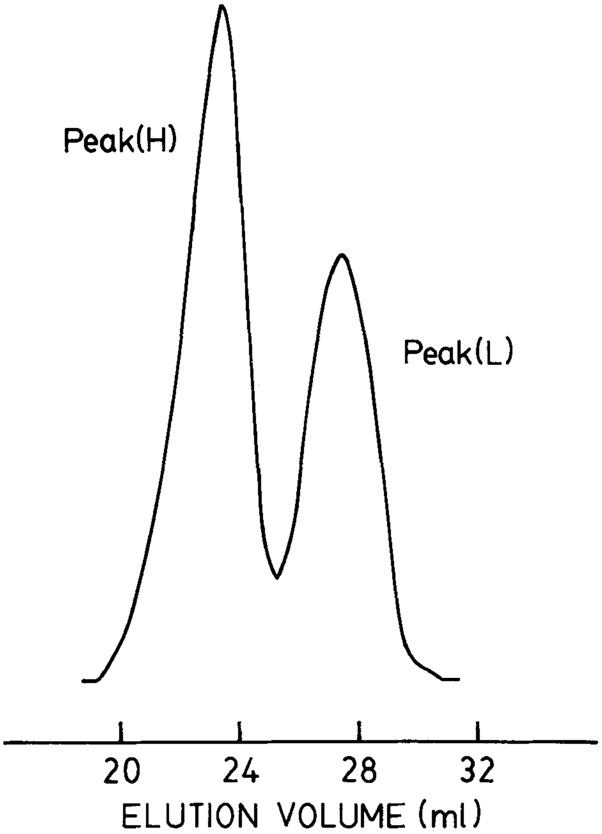


FIG. 5. GPC chromatogram of the polymer (Run 301) prepared by homopolymerization of EBA 2a macromonomer.

the areas of peak (H) of the GPC traces using the standard polystyrene calibration. Number-average molecular weight ($\overline{M}_n$) of MPA homopolymers was in the range of $4.6\text{-}4.9 \times 10^4$, that of EBA homopolymer was 1.4×10^4, and that of MPM macromonomer was 8.1×10^4. It is clear that $\overline{M}_n$ of the poly(macromonomer) was smaller than that of the homopolymer of the conventional vinyl monomer.

EBA macromonomer showed a spectral change during polymerization: the appearance of a new absorption band at 278 nm with a decrease in absorbance at 263 nm. This spectral change was also utilized to follow the polymerization of macromonomers.

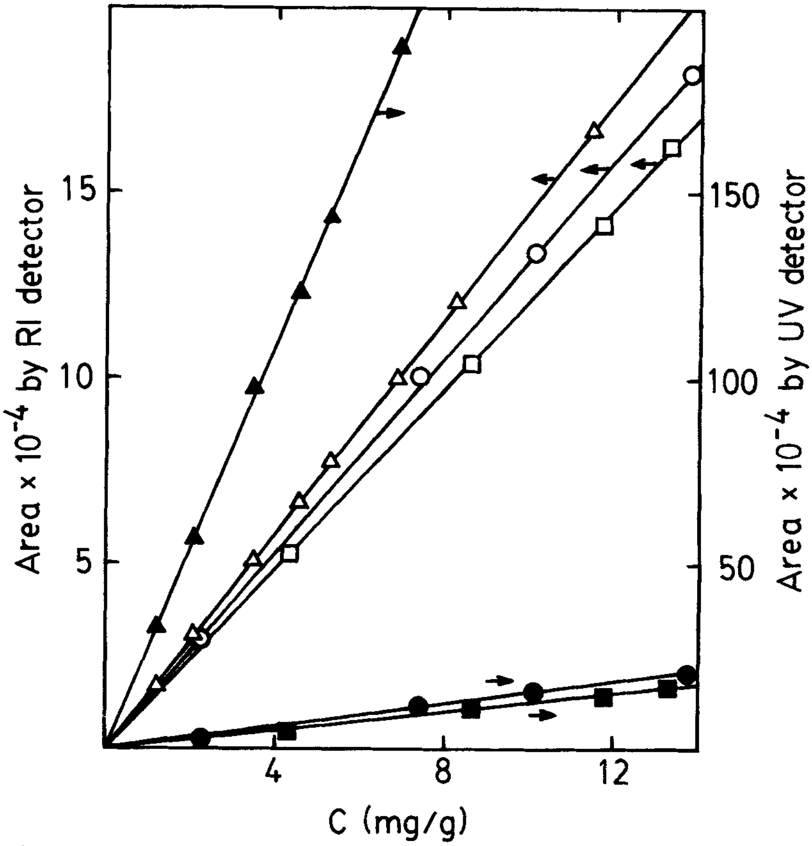


FIG. 6. Plots of the integrated area detected by RI or UV and the concentration for EBA 2a macromonomer (△, ▲), MPA 2b macromonomer (□, ■), and MPM 1b macromonomer (○, ●).

Synthesis of Graft Copolymers

Radical copolymerizations of macromonomers were carried out in benzene solution with AIBN as initiator. Initial concentration of total monomers was maintained 1.00 mol/L. All of the graft copolymers were soluble in solvent for the homopolymer. $\overline{M}_n$ was estimated by GPC by use of the standard polystyrene calibration. Macromonomer conversion (X_a) was determined as previously described.

TABLE 6. Evaluation of Constants (K_{am}) of the Macromonomers

Macromonomer	$\overline{M}_n \times 10^{-3}$	λ, nm	Instrument constant × 10^{-3} K_{am}(RI)	 K_{am}(UV)
EBA 2a	1.65	263	14.68	272.7
MPA 2b	2.49	254	12.17	12.29
MPM 1b	1.28	254	13.24	14.52
MPM 1d	5.56	254	13.20	14.51

EBA macromonomer was copolymerized with MMA using feed compositions (f_a,o) or 0.152 and 0.234 mole fraction macromonomer. It was found that the total conversion (X_w) after 8 h (Runs 303 and 305) was 45 wt%, independent of f_a,o (see Table 7). Cumulative composition ($\overline{F}_a$) of copolymer obtained with the same feed composition (Runs 304 and 305) decreased with increasing conversion. The numbers of poly(AEMA) branches in the graft copolymers, calculated on the basis of $\overline{F}_a$ and $\overline{M}_n$ of the graft copolymer, were 16.5 and 10.6, respectively.

MPM macromonomer was copolymerized with styrene at the same feed composition of 0.200 (f_a,o) at 50 and 70°C. It was found that the total conversion at 70°C was about 5.5 times that at 50°C, and both the copolymer composition and number-average molecular weight increased with increasing polymerization temperature.

REFERENCES

[1] R. Milkovich, Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem., 21, 40 (1980) and references therein.
[2] S. R. Palit and B. M. Mandal, J. Macromol. Sci.–Rev. Macromol. Chem., C2, 225 (1972).
[3] J. P. Kennedy, Polym. J., 12, 609 (1980).
[4] P. Ferruti, E. Martuscelli, L. Nicholais, M. Palma, and F. Riva, Polymer, 18, 387 (1977).
[5] K. Ito, N. Usami, and Y. Yamashita, Macromolecules, 13, 216 (1980).

TABLE 7. Copolymerizations of the Macromonomer with Vinyl Monomers in Benzene

Run	Macromonomer	$\overline{M}_n \times 10^{-3}$	Comonomer	f_a,o	Temperature, °C	Time, h	X_w, %	$\overline{F}_a$	$\overline{M}_n \times 10^{-3}$[a]
303	EBA 2a	1.65	MMA	0.152	60	8	45.01	0.180	26.0
304	EBA 2a	1.65	MMA	0.234	60	6	23.07	0.308	30.9
305	EBA 2a	1.65	MMA	0.234	60	8	45.62	0.255	20.6
101	MPM 1b	1.28	ST	0.200	50	24	5.37	0.100	8.65
102	MPM 1b	1.28	ST	0.200	70	24	29.40	0.160	17.8

[a] Calculated from GPC by the use of standard polystyrene.

[6] D. J. Walbridge, Dispersion Polymerization in Organic Media (K. E. Barrett, ed.), Wiley, London, 1975, Chap. 3.

[7] S. Tanimoto, J. Horikawa, M. Okano, and R. Oda, Yukigosei Kagaku, 26, 1102 (1968).

[8] R. C. Sovish, J. Org. Chem., 24, 1345 (1959).

[9] K. Noma, M. Niwa, S. Iida, and U. Nakazato, Kobunshi Ronbunshu, 32, 189 (1975).

[10] M. Niwa and T. Matsumoto, Sci. Eng. Rev. Doshisha Univ., 23, 222 (1983).

[11] M. Niwa and T. Hayashi, Unpublished Data.

[12] K. Roy, D. Pramanick, and S. Palit, Makromol. Chem., 153, 71 (1972).

[13] S. Siggia, Quantitative Organic Analysis via Functional Groups, 3rd ed., Wiley, New York, 1963, p. 301.

Received March 4, 1985