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Synthesis of Graft Polymers by Copolymerization of Macromonomers. II. Copolymerization Kinetics of Styrene-and Methacrylate-Terminatedpoly(2-Acetoxyethyl Methacrylate) Macromonomers

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SYNTHESIS OF GRAFT POLYMERS BY COPOLYMERIZATION OF MACROMONOMERS. II. COPOLYMERIZATION KINETICS OF STYRENE- AND METHACRYLATE-TERMINATED POLY(2-ACETOXYETHYL METHACRYLATE) MACROMONOMERS

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ABSTRACT

Styrene-terminated poly(2-acetoxyethyl methacrylate) macromonomer (EBA), methacrylate-terminated poly(2-acetoxyethyl methacrylate) macromonomer (MPA), and methacrylate-terminated poly(methyl methacrylate) macromonomer (MPM) were synthesized and subjected to polymerization and copolymerization by a free-radical polymerization initiator (AIBN). EBA and MPA were homopolymerized at various concentrations. EBA exhibited higher reactivity than styrene. The reactivity of MPA, however, was almost equal to that of glycidyl methacrylate. Cumulative copolymer compositions were determined by GPC analysis of copolymerization products. The reactivity ratios estimated were $r_a = 0.95$ and $r_b = 0.90$ for EBA macromonomer (*a*)-methyl methacrylate (*b*) copolymerization. These values were not consistent with literature values for the styrene-methyl methacrylate and *p*-methoxystyrene-methyl methacrylate systems. The reactivity ratios estimated for MPA and 2-bromoethyl methacrylate were $r_a = 0.95$ and $r_b = 0.98$; equal to the glycidyl methacrylate-2-bromoethyl methacrylate system. MPA or MPM was also copolymerized with styrene, and the reactivity ratios were $r_a = 0.40$, $r_b = 0.60$ and $r_a = 0.39$, $r_b = 0.58$, respectively. These estimates were in good agreement with the reactivity ratios for glycidyl methacrylate and styrene. Thus, no effect of molecular weight was observed for both copolymerization systems.

INTRODUCTION

Graft polymers having side chains of uniform molecular weight have been prepared via free-radical copolymerization of macromonomers with comonomers by several investigators [1, 2]. It is necessary to study the reactivity of macromonomers in copolymerization since the properties of graft polymers are dependent on the composition of the macromonomers. Recently, Ito, Usami, and Yamashita reported reactivity of radical copolymerization of methacrylate-terminated poly(stearyl methacrylate) macromonomers with methyl methacrylate [3]. More recently, Schulz and Milkovich reported the reactivity ratios of the radical copolymerization of methacrylate-terminated poly(styrene) macromonomers with several acrylates [4], but the reactivity of the macromonomers in that article was characterized by using relative reactivity ratios. Recently, we prepared styrene-terminated poly(2-acetoxyethyl methacrylate) macromonomers (EBA), methacrylate-terminated poly(2-acetoxyethyl methacrylate) macromonomers (MPA), and methacrylate-terminated poly(methyl methacrylate) macromonomers (MPM) of different molecular weights [5].

In this article these macromonomers have been copolymerized with some comonomers by radical polymerization techniques. The monomer reactivity ratios were determined by using the kinetic scheme of conventional copolymerization.

EXPERIMENTAL

Materials

EBA, MPA, and MPM macromonomers were synthesized and characterized as previously described [5].

2-Bromoethyl methacrylate was synthesized by the reaction of methyl methacrylate with 2-bromoethanol in the manner described in a previous paper [6]. Methyl methacrylate and styrene were purified by standard methods before use. Azobisisobutyronitrile (AIBN), the radical initiator, was recrystallized from methanol. Solvents were purified in the usual way.

Copolymerization of Macromonomers

The required amounts of the macromonomer, the comonomer, the initiator, and benzene were charged in a glass tube and sealed after degassing and flushing with purified nitrogen by repeated freezing and thawing cycles. The tubes were placed in a thermostatically controlled bath. Copolymerization was stopped and the contents poured into a large excess of petroleum ether. The polymer was purified by reprecipitation from acetone solution into petroleum ether to remove the unreacted comonomer and the initiator species. The resulting copolymer was dried to constant weight.

Gel-Permeation Chromatography

Molecular weight distributions of the resulting polymers were measured by using a Shimadzu high-performance liquid chromatograph (model LC-3A) equipped with three columns (HSG-15, HSG-30, and HSG-50), dual UV (model SPD-2A) and RI (model Shodex RI SE-11) detectors operated at 40°C. The flow of tetrahydrofuran was maintained at 1 mL/min. A molecular weight calibration curve was obtained on the basis of the universal calibration with 12 standard polystyrene samples.

RESULTS AND DISCUSSION

Homopolymerization of Macromonomers

Macromonomers and their model monomers were homopolymerized under the same conditions in order to study the reactivity of macromonomers (Table 1). Macromonomer conversion were calculated from GPC analysis of the samples as previously described [5], and model monomer conversions were obtained by gravimetric yield.

It was found that the conversion of MPA was approximately equal to that of glycidyl methacrylate as a model monomer of MPA macromonomer, but EBA macromonomer showed a higher reactivity than styrene.

The number-average molecular weight ($\bar{M}_n$) of polymacromonomer was estimated by GPC using the standard polystyrene calibration, and number-average degrees of polymerization ($\overline{\mathrm{DP}}_n$) were calculated by using the $\bar{M}_n$ of the respective macromonomers. The $\overline{\mathrm{DP}}_n$ of poly-EBA was as high as 8.4 in benzene solution. The $\overline{\mathrm{DP}}_n$ of poly-MPA was 18-20 and bore no relation to the conversion. For MPA, the $\overline{\mathrm{DP}}_n$ was almost independent of macromonomer concentration in contrast to the model monomer. Compared to the $\overline{\mathrm{DP}}_n$ attained by their model monomers, those of the macromonomers were very small.

TABLE 1. Comparison of the Reactivities on Macromonomers and Their Model Monomers (AIBN, 1.0 wt% of monomer)

Run no.	Macromonomer,	$\bar{M}_n$ $\times 10^{-3}$	$[M]_0$, mol/L	Temperature, °C	Time, h	Conversion, %	$\bar{M}_n \times 10^{-3}$	$\overline{DP}_n$
301	EBA	1.65	0.61	80	54	62.48	13.8	8.4
401	Styrene		0.61	80	54	33.46	6.7	64.4
205	MPA	2.49	0.55	50	16	45.74	45.9	18.4
455	GMA[a]		0.50	50	16	47.99	40.7	287
207	MPA	2.49	0.18	70	48	60.55	48.9	19.5
457	GMA		0.18	70	48	85.47	4.1	29.2

[a] Glycidyl methacrylate, as a model for MPA macromonomer.

Method for the Determination of Copolymer Composition

We first examined the GPC chromatogram as a means of determining the cumulative copolymer composition and the total conversion.

The radical copolymerization of EBA with methyl methacrylate was carried out in benzene. The GPC chromatogram of the resulting copolymer shows the presence of two species (Fig. 1). The peak area, A(H), of the high molecular weight fraction increases and the peak area, A(L), of the low molecular wieght fraction decreases with increasing polymerization time. A peak attributed to unreacted macromonomer (L) has a regular UV absorption (at 263 nm) [5]; however, a peak corresponding to the graft copolymer (H) has weak UV absorption.

The area obtained with a RI detector, A_{RI}(L), is given by

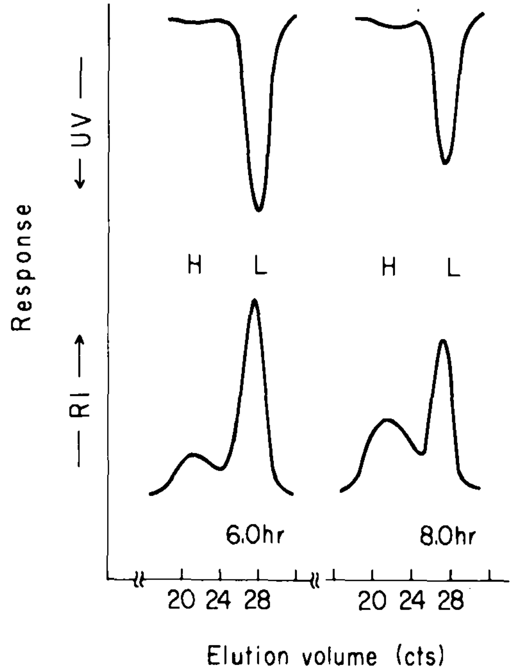

FIG. 1. GPC curves of the polymer resulting from the copolymerization of EBA macromonomer with methyl methacrylate (UV detector, λ = 263 nm).

$$A_{\mathrm{RI}}(\mathrm{L}) = c(K_{am}(\mathrm{RI})W_{am}), \tag{1}$$

where K_{am} (RI) is the instrument constant of the RI detector for the macromonomer, W_{am} is the weight fraction of unreacted macromonomer in the resulting polymer, and c is the concentration of GPC sample in milligrams per gram. On the other hand, the area for the RI detector, A_{RI} (H), and the area for the UV detector, A_{UV} (H), are given by

$$A_{\mathrm{RI}}(\mathrm{H}) = c(K_a(\mathrm{RI})W_a + K_b(\mathrm{RI})W_b), \tag{2}$$

$$A_{\mathrm{UV}}(\mathrm{H}) = c(K_a(\mathrm{UV})W_a + K_b(\mathrm{UV})W_b), \tag{3}$$

where W_a and W_b are the weight fractions of polymerized macromonomer and comonomer in a sample, respectively, K_a and K_b are the instrument constant of polymacromonomer and polycomonomer, and (RI) and (UV) identify the detector.

From Eqs. (1), (2), and (3), the mole fraction conversion of macromonomer, X_a, defined as $X_a = W_a/(W_a + W_{am})$, is given by

$$X_a = \frac{\dfrac{A_{\mathrm{UV}}(\mathrm{H})}{K_b(\mathrm{UV})} - \dfrac{A_{\mathrm{RI}}(\mathrm{H})}{K_b(\mathrm{RI})}}{\dfrac{A_{\mathrm{UV}}(\mathrm{H})}{K_b(\mathrm{UV})} - \dfrac{A_{\mathrm{RI}}(\mathrm{H})}{K_b(\mathrm{RI})} + \left(\dfrac{K_a(\mathrm{UV})}{K_b(\mathrm{UV})} - \dfrac{K_a(\mathrm{RI})}{K_b(\mathrm{RI})}\right)\dfrac{A_{\mathrm{RI}}(\mathrm{L})}{K_{am}(\mathrm{RI})}}. \tag{4}$$

The cumulative, or average, copolymer composition (mole ratio), F, defined as $F = (W_a/M_a)/(W_b/M_b)$, where M_a and M_b are the molecular weights of macromonomer and comonomer, respectively, is given by

$$F = \frac{M_b}{M_a}\left(\frac{A_{\mathrm{UV}}(\mathrm{H})\cdot K_b(\mathrm{RI}) - A_{\mathrm{RI}}(\mathrm{H})\cdot K_b(\mathrm{UV})}{A_{\mathrm{RI}}(\mathrm{H})\cdot K_a(\mathrm{UV}) - A_{\mathrm{UV}}(\mathrm{H})\cdot K_a(\mathrm{RI})}\right). \tag{5}$$

As F can be expressed as $F = f_0\ (X_a/X_b)$ in terms of the mole ratio feed composition f_0 ($= f_{a,\mathrm{o}}/(1 - f_{a,\mathrm{o}})$, where $f_{a,\mathrm{o}}$ is the mole fraction of macromonomer in the feed), the mole fraction conversion of comonomer, X_b, leads to

$$X_b = \frac{f_0 \cdot X_a}{F}. \tag{6}$$

Total conversion in weight fraction, X_w, and mole fraction of macromonomer in the graft copolymer, F_a, can be calculated from X_a, X_b, and F:

$$X_w = \frac{M_a \cdot f_{a,0} \cdot X_a + M_b(1 - f_{a,0})X_b}{M_a \cdot f_{a,0} + M_b(1 - f_{a,0})}, \tag{7}$$

$$F_a = \frac{F}{F + 1}. \tag{8}$$

K_{am} (RI) was reported previously [5]. In this section, we used new instrument constants K_a (RI) and K_a (UV) of polymacromonomer, K_b (RI) and K_b (UV) of polycomonomer, determined by the method described previously [5] and shown in Table 2.

In this way we obtained the copolymerization results for three macromonomers shown in Table 3. The resulting polymers were fractionated with methanol to extract the unreacted macromonomers which are completely soluble in methanol. The isolated unreacted macromonomer was weighted to determine the conversion, X_a. On the other hand, X_b was calculated from the total weight of the feed monomers and that of the resulting polymer.

There is good agreement in X_a and X_b determined by the two methods. It appears obvious that this GPC method is applicable to the determination of both the copolymer composition (F_a) and the total conversion (X_w) of samples containing unreacted macromonomer.

Copolymerization of Macromonomers

These macromonomers copolymerization studies were pursued to evaluate the monomer reactivity ratios and the resulting graft copolymer compositions in free-radical systems. Copolymerizations of EBA (A) with methyl methacrylate (B) were conducted in benzene at 60°C. The total concentration of monomers was 1.0 mol/L. Table 4 shows the relationship between mole fraction of EBA macromonomer in the feed ($f_{a,0}$) and in the graft copolymer (F_a) at various conversions (X_w). Number-average molecular weights ($\bar{M}_n$) of graft copolymer are also shown in Table 4. Figure 2 shows the relationship between cumulative copolymer composition (F_a) and conversion from experimental results. In order to compare the reactivities of EBA macromonomer and the model monomers in the copolymerization system, styrene and p-methoxystyrene were selected as model monomer.

TABLE 2. Instrument Constants of Polymacromonomer and Polycomonomer by GPC

	Constant, count·g/mg, × 10^{-3}		
Homopolymer of	K_a (RI)	K_a (UV)	λ, nm
EBA	10.31	19.71	263
MPA	11.80	10.77	254
MPM	12.93	13.83	254
	K_b (RI)	K_b (UV)	λ, nm
MMA[a]	14.75	0.37	263
Styrene	31.80	60.40	254
BEMA[b]	15.11	1.18	254

[a] Methyl methacrylate.

[b] 2-Bromoethyl methacrylate.

The monomer reactivity ratios utilized were $r_a = 0.52$ and $r_b = 0.46$ for styrene (*a*)-methyl methacrylate (*b*) copolymerization [7], and $r_a = 0.32$ and $r_b = 0.29$ for *p*-methoxystyrene (*a*)-methyl methacrylate (*b*) copolymerization [8]. The theoretical F_a-conversion curves calculated by using the integral expression for binary copolymerization derived by Alfrey and Goldfinger [9] are shown in Fig. 2. All experimental plots are lower than the theoretical dashed and broken lines at each feed composition.

The monomer reactivity ratios in the EBA-methyl methacrylate system were determined by fitting experimental data to theoretical F_a-conversion curves plotted from the integral expression. The reactivity ratios estimated were $r_a = 0.95$ and $r_b = 0.90$. These values are not consistent with literature values for styrene-methyl methacrylate and *p*-methoxystyrene-methyl methacrylate. The above results predict that the reactivity of EBA macromonomer is significantly different from that of the model monomers.

We have also estimated the relative reactivity ratio of methyl methacrylate (r_b(rel)), which is calculated from Eq. (9) using these experimental values of X_a and X_b. This equation was derived by Schulz and Milkovich [4] and Fukutomi and coworkers [10]:

TABLE 3. Comparison between Conversions of Macromonomer (X_a) and Comonomer (X_b) Obtained by GPC (A) and Gravimetric (B) Techniques

Run no.	Macromonomer	Comonomer	$f_{a,o}$[a]	Temperature, °C	Time, h	X_a, mol% A	X_a, mol% B	X_b, mol% A	X_b, mol% B
101	MPM	Styrene	0.200	50	24	3.54	3.52	11.10	11.04
102			0.200	70	24	19.30	19.39	60.39	60.39
201	MPA	BEMA	0.050	50	8	11.61	11.65	37.90	37.86
202			0.072	50	8	29.30	29.34	35.78	33.92
203			0.301	50	24	33.05	33.01	48.28	48.20
204			0.499	50	24	35.40	37.80	47.02	49.46
302	EBA	MMA	0.152	60	8	47.36	47.37	47.57	47.49
304			0.234	60	8	46.77	46.80	38.70	39.90

[a] Mole fraction of macromonomer in monomers.

TABLE 4. Copolymerization of EBA Macromonomer (M_a = 1 650) with Methyl Methacrylate in Benzene at 60°C[a]

f_a,o, %	X_a, %	$F \times 10^2$	X_b, %	X_w, wt%	F_a	$\bar{M}_n \times 10^{-3}$
4.00	6.97	6.496	4.47	5.49	6.10	7.42
	6.98	3.412	8.53	7.90	3.30	15.44
	18.57	3.412	22.67	21.00	3.32	15.44
	26.68	2.880	38.58	33.73	2.80	12.01
	44.34	4.112	45.52	45.03	3.90	15.22
15.20	19.39	17.79	19.52	19.42	15.12	13.62
	21.32	21.51	17.98	20.48	17.70	15.91
	30.56	19.90	27.48	29.78	16.60	18.25
	51.27	19.92	46.17	49.98	16.62	26.00
23.41	19.25	31.06	18.88	19.20	23.71	26.78
	25.14	32.98	23.31	24.84	24.80	30.87
	47.60	33.32	43.62	46.94	25.02	27.88
	49.68	21.36	70.81	53.19	17.60	44.92

[a] Concentration of total monomers, 1.0 mol/L.

$$r_b(\text{rel}) = \frac{\log(1 - X_b)}{\log(1 - X_a)} . \qquad (9)$$

The r_b(rel) values obtained by using 15.20 and 23.41% for feed compositions are quite close to the value of r_b.

MPA (A) was copolymerized with 2-bromoethyl methacrylate (B) in benzene using feed compositions (f_a,o) of 2.40, 6.32, 27.0, and 45.8 mol% macromonomer (Table 5).

In Figs. 3 and 4, cumulative copolymer compositions (F_a) are plotted versus the corresponding conversion (X_w) values. These figures also illustrate F_a as a function of conversion as dashed lines for the model monomer, glycidyl methacrylate (a)-2-bromoethyl methacrylate (b) (BEMA) copolymeriza-

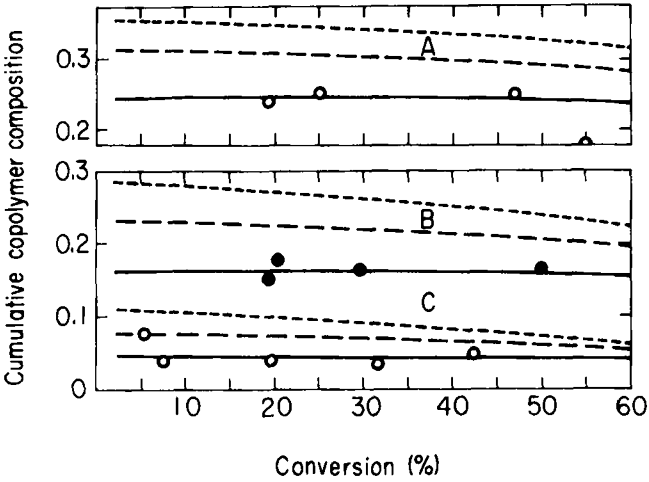

FIG. 2. Cumulative copolymer composition (F_a) and conversion for the copolymerization of EBA macromonomer with methyl methacrylate at 60°C. EBA macromonomer (mol%) in feed (f_a,o): 23.41 (A), 15.20 (B), and 4.00 (C). Estimated values (r_a = 0.95 and r_b = 0.90) of the EBA macromonomer-methyl methacrylate system shown as solid lines. Dashed and broken lines denote calculated values for styrene (r_a = 0.52)-methyl methacrylate (r_b = 0.64) and *p*-methoxystyrene (r_a = 0.32)-methyl methacrylate (r_b = 0.29), respectively.

tion, where the reactivity ratios were r_a = 0.95 and r_b = 0.98 [11]. In all feed composition, these plots show good fits to the dashed lines. Therefore, the reactivity of the methacrylate double bond in this macromonomer is unaffected in the present system.

Free-radical copolymerizations of MPA macromonomer (A) with styrene (B) were carried out at 50°C (Table 5). Figure 5 shows the relationship between cumulative copolymer composition (F_a) and conversion. From these experimental data, monomer reactivity ratios were estimated by fitting to the integral expression of the copolymerization equation, giving r_a = 0.40 and r_b = 0.60 for the copolymerization of MPA and styrene. Relationships between cumulative copolymer composition and conversion were calculated by using the estimated reactivity ratios and are illustrated in Fig. 5 with solid lines. Dashed lines in Fig. 5 denote the copolymer composition-conversion curves of glycidyl methacrylate-styrene system using r_a = 0.44 and r_b = 0.53 [12]. The solid lines are quite close to the dashed lines.

TABLE 5. Copolymerizations of MPA Macromonomer (M_a = 1 650) and MPM Macromonomer (M_a = 2 740) at 60°C

MPA-BEMA[a]			MPA-styrene			MPM-styrene		
$f_{a,0}$, %	X_w, wt%	F_a, %	$f_{a,0}$, %	X_w, wt%	F_a, %	$f_{a,0}$, %	X_w, wt%	F_a, %
2.40	18.29	2.10	10.00	4.40	16.80	2.80	5.19	4.20
	27.91	1.50		13.79	15.00		8.02	4.70
	38.56	1.30		21.39	11.20		31.68	4.50
	49.12	2.80		29.64	11.30		47.00	4.50
6.30	17.64	6.50		44.97	15.00	5.30	6.71	7.30
	24.30	5.90	23.40	12.81	27.50		16.71	7.80
	35.50	7.30		20.04	28.00		36.50	8.00
	47.08	5.70		30.02	27.04	25.00	22.20	29.30
27.00	12.02	28.10		53.40	27.30		36.46	29.20
	26.53	28.50					60.83	27.82
	29.62	26.50				30.00	12.60	33.50
	44.85	27.20					28.50	31.90
45.80	15.50	46.30					30.78	33.80
	37.37	43.00					42.27	33.00
	38.71	43.90				50.00	16.59	47.50
	54.50	45.30					25.87	48.50
							55.48	47.52

[a] 2-Bromoethyl methacrylate.

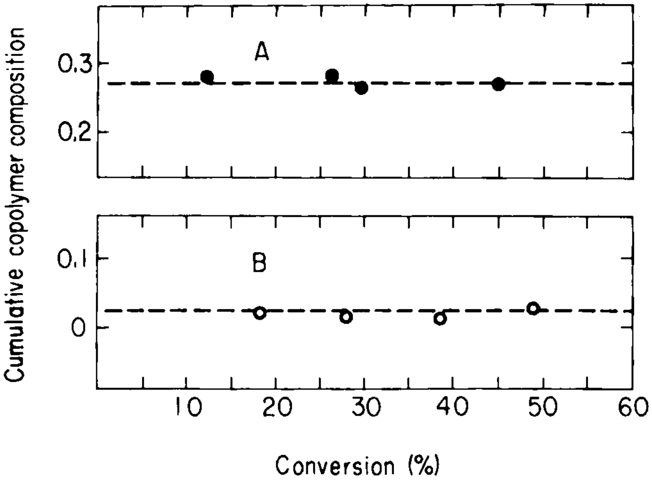

FIG. 3. Relationship between cumulative copolymer composition and conversion for the copolymerization of MPA macromonomer with 2-bromoethyl methacrylate. MPA macromonomer (mol%) in feed: 27.00 (A) and 2.40 (B). Dashed lines denote calculated values of glycidyl methacrylate-2-bromoethyl methacrylate with $r_a = 0.95$ and $r_b = 0.98$.

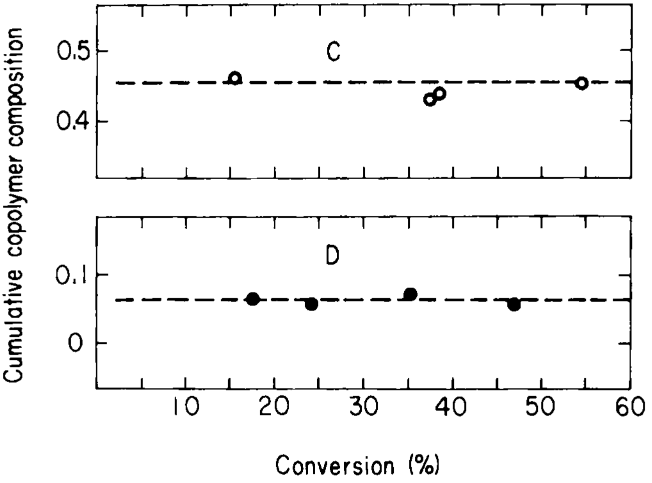

FIG. 4. Relationship between cumulative copolymer composition and conversion for the copolymerization of MPA macromonomer with 2-bromoethyl methacrylate. MPA macromonomer (mol%) in feed: 45.80 (C) and 6.30 (D). Dashed lines denote values calculated for $r_a = 0.95$ and $r_b = 0.98$.

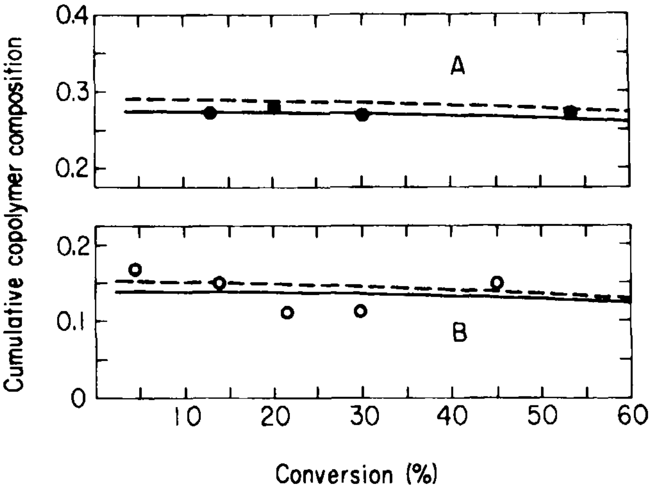

FIG. 5. Plots of experimental data of 23.40 (A) and 10.00 (B) mol% in the feed for the copolymerization of MPA macromonomer and styrene. Solid lines are calculated for $r_a = 0.40$ and $r_b = 0.60$, the values estimated. Dashed lines are for the glycidyl methacrylate ($r_a = 0.44$)-styrene ($r_b = 0.53$) system.

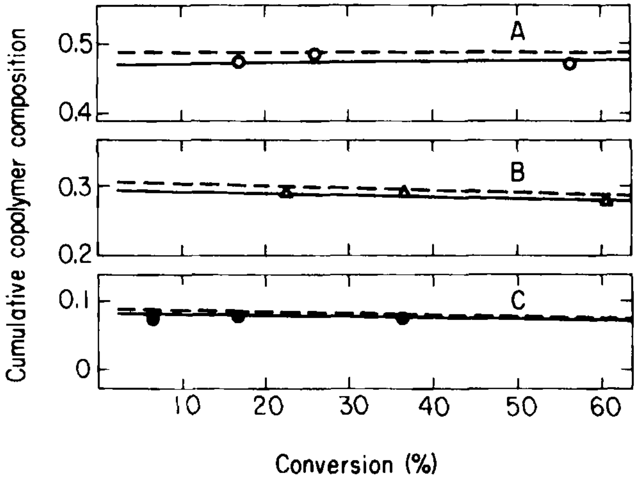

FIG. 6. Cumulative copolymer composition (F_a) calculated as a function of conversion for MPM macromonomer-styrene ($r_a = 0.39$ and $r_b = 0.58$; solid lines) and glycidyl methacrylate-styrene ($r_a = 0.44$ and $r_b = 0.53$; dashed lines). Experimental data for feed compositions of 50.0 mol% (A), 25.0 mol% (B), and 5.30 mol% (C).

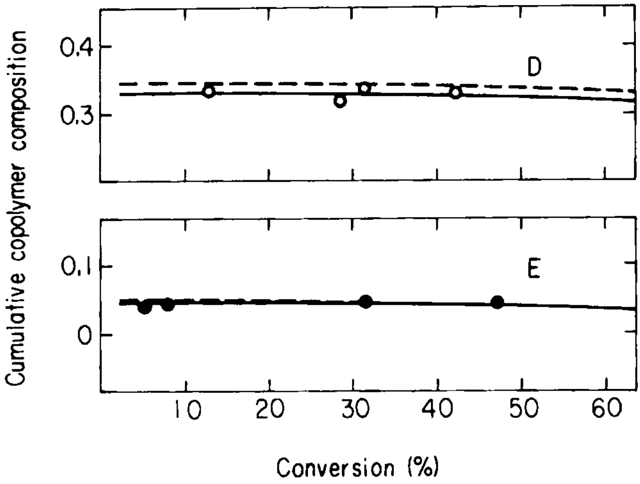

FIG. 7. Cumulative copolymer composition (F_a) calculated as a function of conversion for MPM macromonomer-styrene ($r_a = 0.39$ and $r_b = 0.58$; solid lines) and glycidyl methacrylate-styrene ($r_a = 0.44$ and $r_b = 0.53$; dashed lines). Experimental data for feed compositions of 30.0 mol% (D) and 2.80 mol% (E).

Free-radical copolymerization studies of MPM (A) with styrene (B) were carried out at 50°C, and the results are also shown in Table 5. Figures 6 and 7 show the relationship between F_a and conversion. Monomer reactivity ratios were found to be $r_a = 0.39$ and $r_b = 0.58$ from these experimental results. Comparison of the F_a-conversion relations for the MPM-styrene system and their model system ($r_a = 0.44$ and $r_b = 0.53$) are illustrated in Figs. 6 and 7 with solid and dashed lines, respectively.

These results establish that the reactivities of the MPA macromonomer and the MPM macromonomer which have the same methacrylate double bond are the same as the reactivity of glycidyl methacrylate. The length of side chains had little or no effect on the reactivity ratios but had a pronounced effect in acrylate monomers [13].

The number of graft chains (macromonomer) on each graft copolymer molecule (N_g) are defined by

$$N_g = \frac{F_a \cdot \overline{M}_n}{F_a \cdot M_a + (1 - F_a)M_b}. \tag{10}$$

TABLE 6. Number of Graft Chains of the Copolymer Molecule (N_g), Cumulative Copolymer Composition (F_a), and Number-Average Molecular Weight ($\bar{M}_n$) for the Copolymers of EBA Macromonomer with Methyl Methacrylate (MMA) and MPA Macromonomer with 2-Bromoethyl Methacrylate (BEMA)[a]

	f_a,o, mol%	Conversion, wt%	F_a, mol%	$\bar{M}_n \times 10^{-3}$	N_g
EBA-MMA	4.00	33.73	2.80	12.01	2.2
	15.20	29.78	16.60	18.25	8.4
	23.41	24.84	24.80	30.87	15.7
MPA-BEMA	2.40	38.56	1.30	90.33	5.2
	6.30	35.50	7.30	44.10	8.5
	27.00	29.62	26.20	36.78	11.2
	45.80	37.37	43.00	36.25	12.1

[a] Molecular weight of macromonomer (M_a), 1 650 (EBA) and 2 740 (MPA).

where $\bar{M}_n$ is the number-average molecular weight of the graft copolymer. Table 6 shows the N_g-F_a and N_g-$\bar{M}_n$ relations for the copolymers of EBA and methyl methacrylate and those of MPA and 2-bromoethyl methacrylate. In this table, graft copolymers at similar conversions (25-39%) are summarized since the cumulative copolymer composition (F_a) varied gradually as conversion increased in both systems. This indicates that the $\bar{M}_n$ of EBA-methyl methacrylate copolymers increases with increasing F_a, and the $\bar{M}_n$ of MPA-2-bromoethyl methacrylate copolymer decreases markedly with increasing F_a. Nevertheless, N_g increased as the feed mole fraction of macromonomer increased in both copolymerization systems.

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