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COPOLYMERIZATION OF STYRENE WITH NONIONIC SURFACTANTS: POLY(ETHYLENE OXIDE) MACROMONOMERS

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ABSTRACT

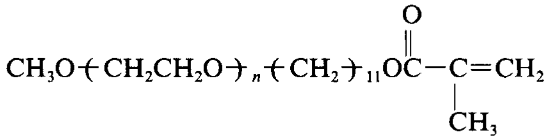
A series of macromonomers of ω-methoxy poly(ethylene oxide)$_n$ undecyl-α-methacrylate (PEO-R-MA-n, where $n = 10, 15, 40$) was synthesized. The copolymerization of styrene (M_1) with the macromonomers (M_2) was carried out in benzene solution and in an emulsion. The apparent reactivity ($1/r_1$) of the macromonomer decreased with an increase of its PEO chain length. The results are discussed in terms of the incompatibility between PEO macromonomer and polystyryl radicals. Stable emulsion latices with monodisperse particles were obtained from the copolymerization of styrene with PEO-R-MA-40. The particle sizes ranged from about 30 to 300 nm in diameter depending on the amount of styrene used and the PEO chain length of the macromonomer. The molecular weights of the copolymers produced by the emulsion copolymerization of PEO-R-MA-40 with styrene were around half a million, and their molecular weight distributions ($\overline{M}_w/\overline{M}_n$) were relatively narrow (1.6–1.9) as determined by gel-permeation chromatography.

INTRODUCTION

Since the publications on macromonomers by an ICI group [1] and Milkovich [2], much work has been done on the preparation of well-defined graft copolymers. A number of poly(ethylene oxide) macromonomers have also been synthesized and copolymerized with conventional monomers [3–14].

One of the most interesting features of PEO macromonomers is their amphiphilic nature. Moreover, the macromonomer can readily be modified to consist of a polymerizable end-group, such as methacrylate (MA) or *p*-vinylbenzyl ether (VB). The general presentations for these modified macromonomers are R-PEO-MA-*n* and R-PEO-VB-*n*, respectively. These macromonomers have been successfully homopolymerized [15, 16] and dispersionally copolymerized [17, 18] by Ito and coworkers. Owing to the existence of hydrophilic PEO, hydrophobic R, and polymerizable end-group MA or VB, the PEO macromonomers can proceed by unusually rapid homopolymerization in water due to their organization into micelles. They can also be used as soapless polymerizable surfactants in oil-in-water or water-in-oil (micro)emulsion copolymerization systems to produce stable latices.

We have recently reported [19] a new type of amphiphilic PEO macromonomer with a polymerizable group attached to a rather long hydrophobic segment (C_{11}) of the following structure:



$$CH_3O\left(CH_2CH_2O\right)_n\left(CH_2\right)_{11}O\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2$$

(n = 40, PEO-R-MA-40)

The critical micelle concentration (CMC) of this macromonomer is 6.6×10^{-5} mol/L at 25°C. The rate of its polymerization in water is extremely rapid (within 30 minutes) as compared to its solution polymerization in benzene (days). The aqueous system produced polymers with a number-average degree of polymerization (DP_n) ranging from about 130 to 160 as determined by gel-permeation chromatography (GPC), but it was very low ($DP_n \cong 7$) for the benzene system.

This paper reports the copolymerization of this macromonomer and an additional two macromonomers (PEO-R-MA-10, n = 10 and PEO-R-MA-15, n = 15) with styrene in water and in benzene.

EXPERIMENTAL

Materials

Poly(ethylene glycol) methyl ether (PEOH-10, $\overline{M}_w$ = 550, PEOH-15, $\overline{M}_w$ = 750) from Aldrich, methacryloyl chloride and 3,4-dihydro-2*H*-pyran (DHP) from Fluka, triethylamine from J. T. Baker, tetrahydrofuran (THF), methylene chloride, toluene, and benzene were dried and distilled by general methods. α,α'-Azobisisobutyronitrile (AIBN) from TCI and potassium persulfate (KPS) from Fluka were recrystallized from methanol and pure water, respectively. Water was purified by a MilliQ water purification system (resistance 18.2 kΩ). Analytical grade 11-bromoundecanol from Fluka and deuterated solvents $CDCl_3$ and C_6D_6 from Aldrich and Merck were used as received.

Synthesis of PEO Macromonomers

PEO-R-MA-40 was prepared and characterized as described before [19]. The other two macromonomers (PEO-R-MA-10 and PEO-R-MA-15) were prepared by the same method with some modifications in the purification steps. The modified procedures are described in the following sections.

ω-Methoxy Poly(Ethylene Oxide)undecyl-THP Ether (PEO-R-THP-*n*)

Bromoundecyl-THP ether [19] (0.08 mol) and the finely-ground potassium hydroxide (0.08 mol) were added to a magnetically stirred solution of poly(ethylene glycol) methyl ether (0.04 mol) in 200 mL dried THF. The reaction mixture was stirred under nitrogen atmosphere for 48 hours and then filtered. After evaporation of THF, the residue was dissolved in 280 mL of the mixed solvents of methanol and water (3/1, v/v). Hexane (120 mL) was used to extract the excess bromoundecyl-THP ether. The extraction was repeated three times. After evaporation of methanol and most of the water, the residue was dissolved in distilled chloroform. The chloroform solution was further washed with brine to remove KOH as well as the unreacted PEG, and it was dried overnight with anhydrous magnesium sulfate. After filtration, chloroform was evaporated and the yellowish product (95% yield) was further dried in a vacuum oven for 2 days at the ambient temperature.

Calculated for PEO-R-THP-10 ($C_{37}H_{74}O_{13}$): C, 61.13; H, 10.26. Found: C, 60.68; H, 10.73. Calculated for PEO-R-THP-15 ($C_{47}H_{94}O_{18}$): C, 59.59; H, 10.00. Found: C, 59.13; H, 9.94.

^{1}H NMR: ($CDCl_3$), δ: 4.57t (1H, OCHO in THP), 3.89t (2H, OCH_2, in THP), 3.64m [4*n*H, $(CH_2CH_2O)_n$], 3.42–3.60t (4H, OCH_2, in chain), 3.38s (3H, OCH_3), 1.54–1.70m (10H, CH_2, two CH_2 in chain and three in THP), 1.27m [14H, $(CH_2)_7$].

ω-Methoxy Poly(Ethylene Oxide)undecanol (PEO-R-OH-*n*)

A solution of PEO-R-THP-*n* (0.035 mol) in acidified (HCl) ethanol (pH 3.0) was stirred and refluxed in an oil bath for 4 hours. After evaporation of the ethanol, the residue was dissolved in distilled chloroform. It was washed three times with saturated brine and dried overnight with anhydrous magnesium sulfate. The product (99% yield) was obtained after evaporating the chloroform and dried to a constant weight in a vacuum oven.

Calculated for PEO-R-OH-10($C_{32}H_{66}O_{12}$): C, 59.78; H, 10.35. Found: C, 59.13; H, 10.87. Calculated for PEO-R-OH-15 ($C_{42}H_{86}O_{17}$): C, 58.44; H, 10.04. Found: C, 57.98; H, 9.97.

^{1}H NMR: ($CDCl_3$), δ: 3.64m [4*n*H, $(CH_2CH_2O)_n$], 3.42–3.60t (4H, OCH_2), 3.38s (3H, OCH_3), 2.06s (1H, OH), 1.28–1.57m [18H, $(CH_2)_9$].

ω-Methoxy Poly(Ethylene Oxide)undecyl α-Methacrylate (PEO-R-MA-*n*)

To a magnetically stirred solution of PEO-R-OH-*n* (0.03 mol) and 17 mL triethylamine in 80 mL of dried CH_2Cl_2 at 0°C, methacryloyl chloride (0.12 mol) was added dropwise under nitrogen over a period of half an hour. A solid salt was immediately formed, and it was kept in an ice bath for another hour. The mixture was further stirred overnight at room temperature. After the excess methacryloyl chloride, CH_2Cl_2, and triethylamine were removed, the residue was dissolved in distilled chloroform and washed twice with saturated sodium bicarbonate solution followed by saturated brine. After evaporation of the chloroform, the residue was dissolved in 280 mL of a mixed solvent of methanol and water (2/1, v/v) and then extracted with hexan (3 × 120 mL). After evaporation of the methanol at room temperature, the residue was redissolved in distilled chloroform. The macromono-

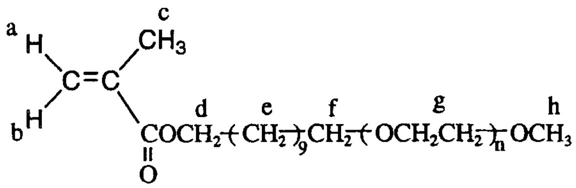


FIG. 1. Assignments of the spectra lines observed for PEO-R-MA-*n* macromonomers (see Table 1)

mer surfactant was dispersed to the chloroform phase by adding a large quantity of brine. After separation, the chloroform solution was dried and distilled. The yellowish residue (95% yield) was further dried in a vacuum oven for 5 days below 25 °C and then stored at 0°C in the dark. The ^{1}H-NMR assignments and microanalysis results of the final products are summarized in Fig. 1 and Tables 1 and 2.

Copolymerization

The copolymerization of PEO-R-MA-*n* with styrene was carried out by two methods. The first one was the solution copolymerization in deuterated benzene using AIBN as the initiator under a nitrogen atmosphere. The copolymerization was carried out in NMR tubes which were placed in a water bath at 68 °C. At different time intervals the tubes were quenched to 0 °C before they were measured by NMR at 25 °C. The extent of copolymerization was monitored by the disappearance of the corresponding terminal vinyl protons ($\delta 5.25$ and $\delta 6.17$ in PEO-R-MA-*n*; $\delta 5.09$ and $\delta 5.60$ in styrene) with reference to the ω-methoxy protons ($\delta 3.15$) by ^{1}H NMR in C_6D_6 as shown in Fig. 2. The conversions for PEO-R-MA-*n* or styrene in solution copolymerization were calculated by the following equation:

$$\text{Conversion}\,(\%) = \{1 - [(b/a)_t/(b/a)_0]\} \times 100 \qquad (1)$$

where $(b/a)_t$ and $(b/a)_0$ are the integral ratios of the peak area of the corresponding vinyl protons to that of the ω-methoxy protons at a given time (t) and at $t = 0$, respectively. The polymerization mixture, after being freeze-dried, washed with methanol, and dried in a vacuum oven, was further analyzed by ^{1} NMR and GPC.

TABLE 1. Chemical Shifts of ^{1}H-NMR Spectra Lines Observed for PEO-R-MA-*n* Macromonomers

	Chemical shifts δ, ppm							
Macromonomers	a	b	d	g	f	h	c	e
PEO-R-MA-10	6.09	5.54	4.14	3.64	3.42	3.38	1.94	1.28-1.69
PEO-R-MA-15	6.09	5.54	4.14	3.64	3.42	3.38	1.94	1.28-1.69
PEO-R-MA-40[a]	6.09	5.54	4.13	3.64	3.44	3.38	1.94	1.27-1.69

[a]Refer to Reference 19.

TABLE 2. Elemental Analysis and Melting Points of Macromonomers

Macromonomers	mp, °C[a]	%C		%H	
		Calcd	Found	Calcd	Found
PEO-R-MA-10 ($C_{36}H_{70}O_{13}$)	15.0	60.82	60.25	9.93	9.85
PEO-R-MA-15 ($C_{46}H_{90}O_{18}$)	27.0	59.33	59.70	9.74	9.69
PEO-R-MA-40[b] ($C_{96}H_{190}O_{43}$)	49.4	56.73	56.13	9.42	9.54

[a] Measured by DSC.

[b] Refer to Reference 19.

The second method was emulsion copolymerization using KPS as the initiator under a nitrogen atmosphere. The copolymerization was undertaken at 60°C with magnetic stirring around 700 rpm. A certain amount of the reaction mixture was precipitated at different time intervals in a large quantity of methanol. The product was washed repeatedly with methanol and dried in a vacuum oven at 30°C for 24 hours. Each product was confirmed by GPC to be free of the unreacted macromonomers, and the composition was analyzed by ^1H NMR. A typical ^1H-NMR spectrum of the styrene-macromonomer copolymer is shown in Fig. 3. The mole fraction of styrene in the copolymer, x, was calculated from the peak area of phenyl protons relative to that of oxyethylene protons as follows:

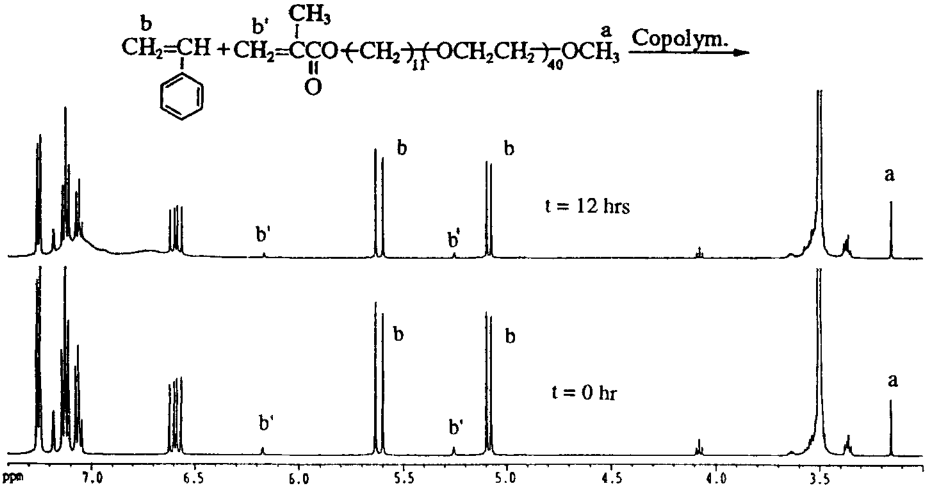


FIG. 2. The ^1H-NMR spectra for the copolymerization of styrene and PEO-R-MA-40 in benzene at t = 0 hours and t = 12 hours.

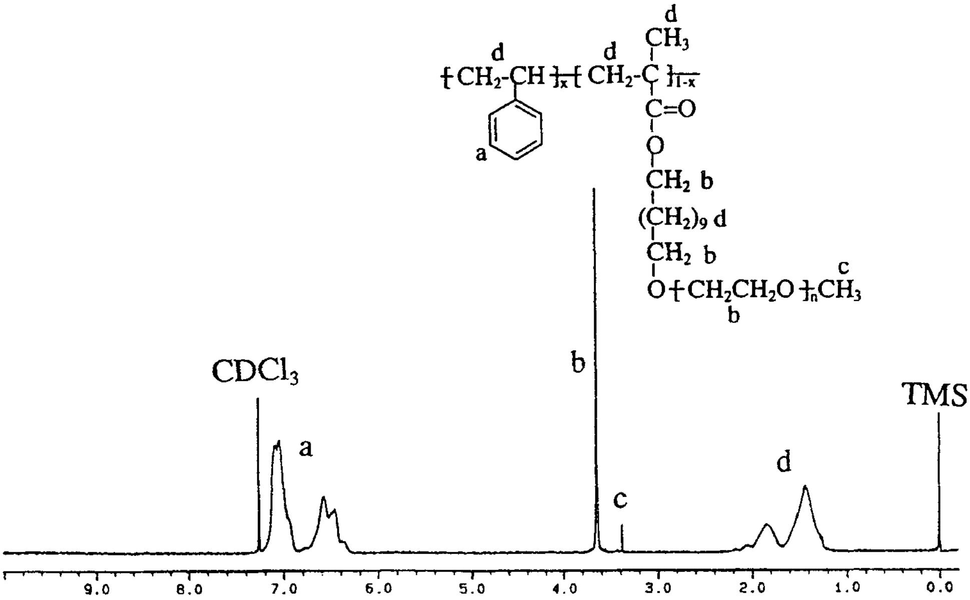


FIG. 3. ^{1}H-NMR spectrum of a copolymer by emulsion copolymerization of styrene and PEO-R-MA-*n*.

$$\frac{5x}{(4n + 4)(1 - x)} = \frac{\text{area of phenyl protons at } \delta 6.3\text{-}7.2}{\text{area of } OCH_2CH_2O \text{ protons at } \delta 3.64} \tag{2}$$

and its molar ratio ($d[M_1]/d[M_2]$) in the copolymer should be $x/(1 - x)$.

Measurements

UV spectra were obtained from a Hewlett-Packard 8452A diode array spectrophotometer. Proton NMR spectra were recorded with Bruker AMX 500 (500 MHz) spectrometer using $CDCl_3$ or C_6D_6 as a solvent and tetramethylsilane (TMS) as an internal standard. The experiments were run with a 45-second pulse delay time at a nearly 75° pulse angle, and the spectra were obtained by accumulating 8 scans for the kinetic study of copolymerization and 100 scans for the characterization of compounds.

GPC measurements were performed on a Waters 600E liquid-chromatography system equipped with a Waters 410 differential refractometer as a detector. Two 10μ Phenogel columns (500A and linear, 300 × 7.8 mm) were used in series. HPLC-grade THF which contained 0.25 wt% 2,6-di-*tert*-butyl-*p*-cresol as a stabilizer was used as an eluent at a flow rate of 0.8 mL/min at 45°C. The molecular weights of macromonomers were obtained from the calibration line using PEO standard samples (0.15 mg/mL in THF) supplied by Polymer Laboratories Ltd and polystyrene standard samples supplied by Polyscience to establish the molecular weights of the copolymers.

The copolymer latices were examined by a JOEL JEM-100CX electron microscope. One drop of the latex was added to 2 mL of a 0.2% phosphotungstic acid

(PTA) aqueous solution, and the mixture was well mixed with a Vortex mixer. A drop of this mixture was then put on a copper grid coated with a thin layer of Formvar. The particle diameters were measured directly from each transmission electron micrograph (TEM). The number-average diameter ($\overline{D}_n$) and weight-average diameter ($\overline{D}_w$) were calculated from the following equation [20]:

$$\overline{D}_n = \frac{\sum N_i D_i}{\sum N_i}$$

$$\overline{D}_w = \frac{\sum N_i D_i^4}{\sum N_i D_i^3} \tag{3}$$

At least 300 particles (N) were counted for each calculation. The polydispersity of particle size is expressed as $\overline{D}_w/\overline{D}_n$.

RESULTS AND DISCUSSION

Characterization of PEO-R-MA-*n*

The structures of the synthesized macromonomers and their purities have been determined by ^{1}H-NMR spectroscopy and microanalysis. Figure 1 and Table 1 give the assignments and chemical shifts of the different spectral lines observed for the three macromonomers. Their melting points and the weight percentages of carbon and hydrogen from microanalysis are listed together with the theoretical values in Table 2. The results are in very good agreement.

Table 3 lists the molecular weights of three macromonomers (PEO-R-MA-*n*) and their molecular weight distributions ($\overline{M}_w/\overline{M}_n$) as determined by ^{1}H NMR and by GPC using PEO standards. The number of double bond per macromonomer as

TABLE 3. Characterization of PEO-R-MA-*n* Macromonomers

	GPC			NMR,[a]	Number of double bonds/per macromonomer	
Macromonomers	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	NMR[b]	UV[c]
PEO-R-MA-10	680	720	1.06	710	1.00	0.99
PEO-R-MA-15	960	1037	1.08	930	1.00	1.01
PEO-R-MA-40	2110	2330	1.10	2030	1.00	0.99

[a] Determined by ^{1}NMR from the integral values of peak areas of different protons.

[b] Determined by ^{1}H NMR from the integral ratio of peak areas of $-OCH_3$ and $-CH_3$ of PEO-R-MA-*n*.

[c] Number of double bonds per macromonomer = C_s/C_0, where C_s (mol/L) was obtained from the calibration line by UV measurements and

$$C_0 = \frac{\text{weight of PEO-R-M-}n}{\overline{M}_{n(GPC)}} \div \text{volume of solvent}$$

determined by a UV method [19] is also shown in Table 3. The results confirm that the synthesized macromonomers have a unity functionality and are free from polymerized by-products.

Reactivity of PEO-R-MA-*n* in Radical Copolymerization

Figure 4 shows the conversions of macromonomers in the copolymerization with styrene in benzene solution as a function of time. It generally required about 30 hours of polymerization at 68°C to attain about 50% conversion. The rate of copolymerization was faster for the macromonomer with a shorter PEO chain length. The percentage conversions of PEO-R-MA-40 macromonomer obtained from the freeze-dried method (FDM) are in good agreement with those measured directly from NMR tubes up to 20% conversion. This provides a convenient way to analyze the copolymer compositions directly from ^{1}H-NMR measurements and to calculate the reactivity ratios of PEO-macromonomers and styrene at their conversions below 20%.

The monomer reactivity ratios can be evaluated from the methods developed by Fineman-Ross [21] and Kelen-Tüdös [22]. The equation of Kelen-Tüdös methods is

$$\eta = (r_1 + r_2/\alpha)\ \xi - r_2/\alpha \qquad (4)$$

where $\eta = G/(\alpha + F)$, $\xi = F/(\alpha + F)$ and $\alpha = (F_{\min} \cdot F_{\min})^{1/2}$; $G = x(y - 1)/y$, $F = x^2/y$; $x = [M_1]/[M_2]$, $y = d[M_1]/d[M_2]$.

In the case of the conventional monomer (M_1) and macromonomer (M_2), difficulty arises from the necessity that the ratio of M_1 to M_2 must usually be around 1/3 to 3/1 on a weight basis for both analytical and preparative purposes. However,

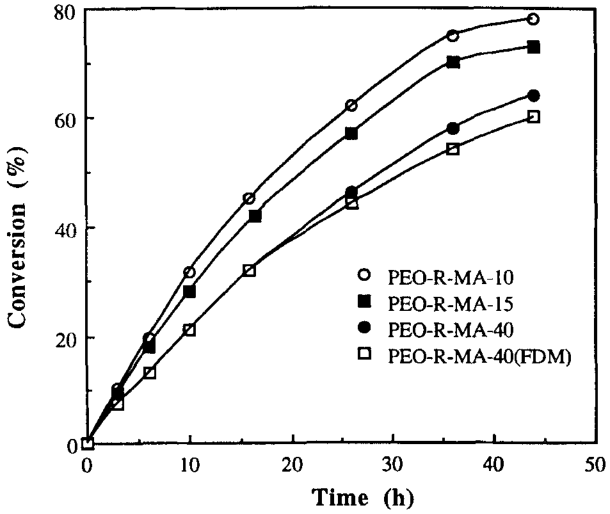


FIG. 4. The conversions of macromonomers in copolymerization with styrene in benzene at 68°C as a function of polymerization time. Total monomers: 20 wt% in benzene, [styrene]/[PEO-R-MA-*n*] = 10, [AIBN] = 0.5 mM.

the monomer ratio has a very wide range based on the molar basis. The molar composition of the copolymer is thus very insensitive to the value of r_2. This is because the conventional copolymerization Eq. (5) will be reduced to Eq. (6) in the limiting condition of $[M_1]/[M_2] \gg 1$ [23]:

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + r_1[M_1]/[M_2]}{1 + r_2[M_2]/[M_1]} \tag{5}$$

$$\frac{d[M_1]}{d[M_2]} = r_1\frac{[M_1]}{[M_2]} \tag{6}$$

This situation is equivalent to dealing with only two of the four conventional propagation reactions:

$$\sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim M_1\bullet \tag{7}$$

$$\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim M_2\bullet \tag{8}$$

with

$$r_1 = k_{11}/k_{12}$$

It also implies that the other cross-propagation

$$\sim M_2\bullet + M_1 \xrightarrow{k_{21}} \sim M_1\bullet \tag{9}$$

should occur with a rate equal to that of Reaction (8) at the steady state, i.e.,

$$k_{12}\,[\sim M_1\bullet][M_2] = k_{21}\,[\sim M_2\bullet][M_1] \tag{10}$$

Hence, Eq.(6) may be used for the determination of r_1 [9] at the condition $[M_1]/[M_2] \gg 1$.

The r_1 thus determined should approximate most simply to the relative reactivities of the monomers M_1 and M_2 in competition reactions with the M_1-ended radical. In addition, the reciprocal of r_1 values obtained by copolymerization of a common monomer (M_1), styrene in the present case, with various monomers (M_2) may be taken as a measure of the relative reactivities of the macromonomers M_2 [9], i.e.,

$$1/r_1 = k_{12}/k_{11} \tag{11}$$

Table 4 lists the feed molar ratios ($[M_1]/[M_2]$) of styrene (M_1) and PEO-macromonomers (M_2) and the copolymer compositions ($d[M_1]/d[M_2]$). The feed and copolymer compositions were very rich in styrene on a molar basis, but $d[M_1]/d[M_2]$ could be satisfactorily determined directly by ^{1}H NMR measurements. The reactivity ratios of styrene (r_1) were calculated from the approximate Eq. (6). On the other hand, when the Kelen-Tüdös method was used, the reactivity ratios obtained were $r_1 = 0.93$ and $r_2 = 0.91$ for styrene (M_1) and PEO-R-MA-40 (M_2), respectively. According to the method of error analysis, $\Delta r_1 = \pm 0.05$ and $\Delta r_2 = \pm 1.27$ were obtained. As expected, the value of r_2 involved too much error to be reliable. On the other hand, the r_1 value is in good agreement with that ($r_1 =$

TABLE 4. Solution[a] Copolymerization of Styrene (M_1) and PEO-R-MA-*n* (M_2) in Benzene

M_2	$[M_1]/[M_2]$, mol/mol	Conversion, wt%	$d[M_1]/d[M_2]$, mol/mol	r_1	Average r_1
PEO-R-MA-10	8.75	9.7	6.17	0.71	
	10.00	10.17	7.30	0.73	
	17.96	10.69	12.56	0.70	0.73 ± 0.03
	28.58	12.87	21.68	0.76	
	39.10	14.60	29.33	0.75	
PEO-R-MA-15	10.00	9.2	8.3	0.83	
	12.80	9.3	10.51	0.82	
	13.10	9.8	10.53	0.80	0.80 ± 0.03
	15.52	10.2	12.57	0.81	
	38.72	13.2	29.81	0.77	
PEO-R-MA-40	10.00	7.5	9.60	0.96	
	17.84	8.4	16.79	0.94	
	24.61	9.2	22.60	0.92	0.94 ± 0.02
	31.34	10.1	29.46	0.94	
	40.56	11.6	38.53	0.95	

[a]Total monomers, 20 wt% in benzene; AIBN, 0.5 mM; temperature, 68°C; polymerization time, 3 hours for each sample.

0.94 ± 0.02) obtained by the use of Eq. (6). This justifies the application of the approximate Eq. (6) to the present copolymerization of styrene and PEO-R-MA-*n* macromonomers. Similar conclusions have also been drawn in many other macromonomer systems [2, 9, 24].

The values of r_1 shown in Table 4 are consistent within the composition range investigated for each system. The average r_1 values for styrene in copolymerization with the PEO-R-MA-*n* increased with increasing PEO chain length (*n*). This implies that the effect of the PEO polymer chain will reduce the reactivity of the terminal vinyl group of the macromonomers ($1/r_1$). The similar reduction in $1/r_1$ was also observed by Ito et al. [9] for the macromonomer R-PEO-MA-*n*. It is attributed to the different nature of the PEO macromonomer and the polystyrene radical. Since these polymers are incompatible and interact repulsively, they should interpenetrate in the solution with a greater difficulty, especially for macromonomers with longer PEO chains, than in the case of the same polymers. Thus, a corresponding decrease in the relative reactivity ($1/r_1$) for the macromonomers was observed.

Table 5 shows r_1 values of styrene (M_1) copolymerized with PEO-R-MA-*n* (M_2) in O/W emulsion system. The PEO-R-MA-*n* with a higher PEO chain length also exhibited a lower relative reactivity ($1/r_1$) in emulsion copolymerization as for solution copolymerization in benzene. But the relative reactivity ($1/r_1$) of each PEO-R-MA-*n* in an emulsion copolymerization was always correspondingly higher than its copolymerization in benzene. It is known that water-soluble PEO-R-MA-*n*

TABLE 5. Copolymerization of Styrene (M_1) and PEO-R-MA-*n* (M_2) in O/W Emulsion[a]

M_2	$[M_1]/[M_2]$, mol/mol	Conversion, wt%	R_{app}, wt%·h^{-1}	$d[M_1]/d[M_2]$, mol/mol	r_1	Average r_1
PEO-R-MA-10	38.81	3.9	7.8	24.04	0.62	
	59.34	4.7	9.4	35.88	0.60	
	75.19	4.9	9.8	44.00	0.58	0.60 ± 0.02
	83.58	4.1	8.2	49.72	0.59	
	94.83	5.2	10.4	56.64	0.60	
PEO-R-MA-15	30.07	4.3	8.6	19.91	0.66	
	68.46	4.8	9.6	43.04	0.63	
	75.19	5.3	10.3	47.18	0.63	0.64 ± 0.04
	84.34	7.4	14.8	55.25	0.66	
	95.68	8.7	17.4	57.60	0.60	
PEO-R-MA-40	40.56	5.3	10.6	30.43	0.75	
	75.19	6.8	13.6	53.40	0.71	
	91.60	7.9	15.8	68.04	0.74	0.74 ± 0.03
	118.41	8.1	16.2	90.06	0.76	
	140.03	9.4	18.8	102.66	0.73	

[a] Total weight emulsion, 50 g; PEO-R-MA-*n*, 1.5 wt%; [KPS], 5 mM; temperature, 60°C.

macromonomers can form micelles [19] in water with the terminal vinyl groups concentrated in the cores which can be swollen by monomer styrene. Due to the preference of monomer partition in micelles and swollen micelles, the compositions of the comonomers at the polymerization site (micelles and swollen micelles) were different from the feed composition. The r_1 values were only "apparent" ones, not the real parameter $(r_1)_{true}$. This is because the same method (Eq. 6) was used for emulsion copolymerization as for solution copolymerization. This only reflects the corresponding change in the monomer composition ("effective" monomer composition $([M_1]/[M_2])_{eff}$) near the polymerization sites. With this consideration, the "apparent" higher reactivity ($1/r_1$) of PEO-R-MA-*n* in emulsion copolymerization as compared to the solution system (Table 6) implies that the polymerization may proceed preferentially at the site between the cores and shells of the micelles or the particles. It is envisaged that the vinyl groups of macromonomers were concentrated and styrene solubilized in the micellar cores which were surrounded by the PEO chains extended into the aqueous phase to form the shells. This situation will effectively remove the repulsion between polystyryl radicals and the PEO chains, which retarded the polymerization observed in the solution system.

Table 6 shows the comparative results of $1/r_1$ between the macromonomers of C_{12}-PEO-M-*n*. The only difference between these two types of macromonomers is that the R group for the former is situated at one of the terminals, while it is inserted between PEO chain and the vinyl terminal for the latter. It is noted that the apparent reactivity ($1/r_1$) for both types of macromonomers is comparable for solution copolymerization with styrene. But the values of $1/r_1$ were generally smaller for PEO-C_{11}-

TABLE 6. Monomer Reactivity Ratio of Styrene (M_1) in Copolymerization with PEO-R-MA-*n* (M_2) Macromonomers

M_2		Medium[a]	r_1	$1/r_1$	*T*, °C	Reference
$C_{12}MA$, *n* = 0		Solution	0.56 ± 0.02	1.79	60	10
C_{12}-PEO-MA-*n*,	*n* = 9	Solution	0.79 ± 0.05	1.27	60	10
	n = 20	Solution	0.82 ± 0.02	1.22	60	10
	n = 25	Solution	1.04 ± 0.04	0.96	60	10
	n = 9	Emulsion	0.15 ± 0.42	6.67–2.38	60	17
	n = 20	Emulsion	0.43 ± 0.03	2.33	60	17
PEO-C_{11}-MA-*n*,	*n* = 10	Solution	0.73 ± 0.03	1.37	68	This work
	n = 15	Solution	0.80 ± 0.03	1.25	68	This work
	n = 40	Solution	0.94 ± 0.02	1.06	68	This work
	n = 10	Emulsion	0.60 ± 0.02	1.67	60	This work
	n = 15	Emulsion	0.64 ± 0.04	1.54	60	This work
	n = 40	Emulsion	0.74 ± 0.03	1.35	60	This work

[a] AIBN was used in benzene solution while KPS was used in the emulsion system. 4,4′-Azobis (4-cyanovaleric acid) was used in the Reference 10 emulsion system.

TABLE 7. Particle Sizes of Latices from Emulsion[a] Copolymerization of Styrene (M_1) and PEO-R-MA-*n* (M_2)

M_2	$[M_1]/[M_2]$, mol/mol	St (M_1), wt%	$\overline{D}_n$, nm	$\overline{D}_w/\overline{D}_n$	Symbols for TEM in Figs. 4 and 5
PEO-R-MA-40	75.19	5.79	31.1	1.14	a
	91.60	7.05	39.6	1.09	b
	118.41	9.09	63.4	1.02	c
	140.03	10.78	90.2	1.01	d
PEO-R-MA-15	75.19	12.61	250.9	—	e
PEO-R-MA-10	75.19	16.52	299.3	—	f

[a] Total weight of emulsion, 50 g; PEO-R-MA-*n*, 1.5 wt%; KPS, 5 mM; temperature, 60°C; conversion, nearly 100%.

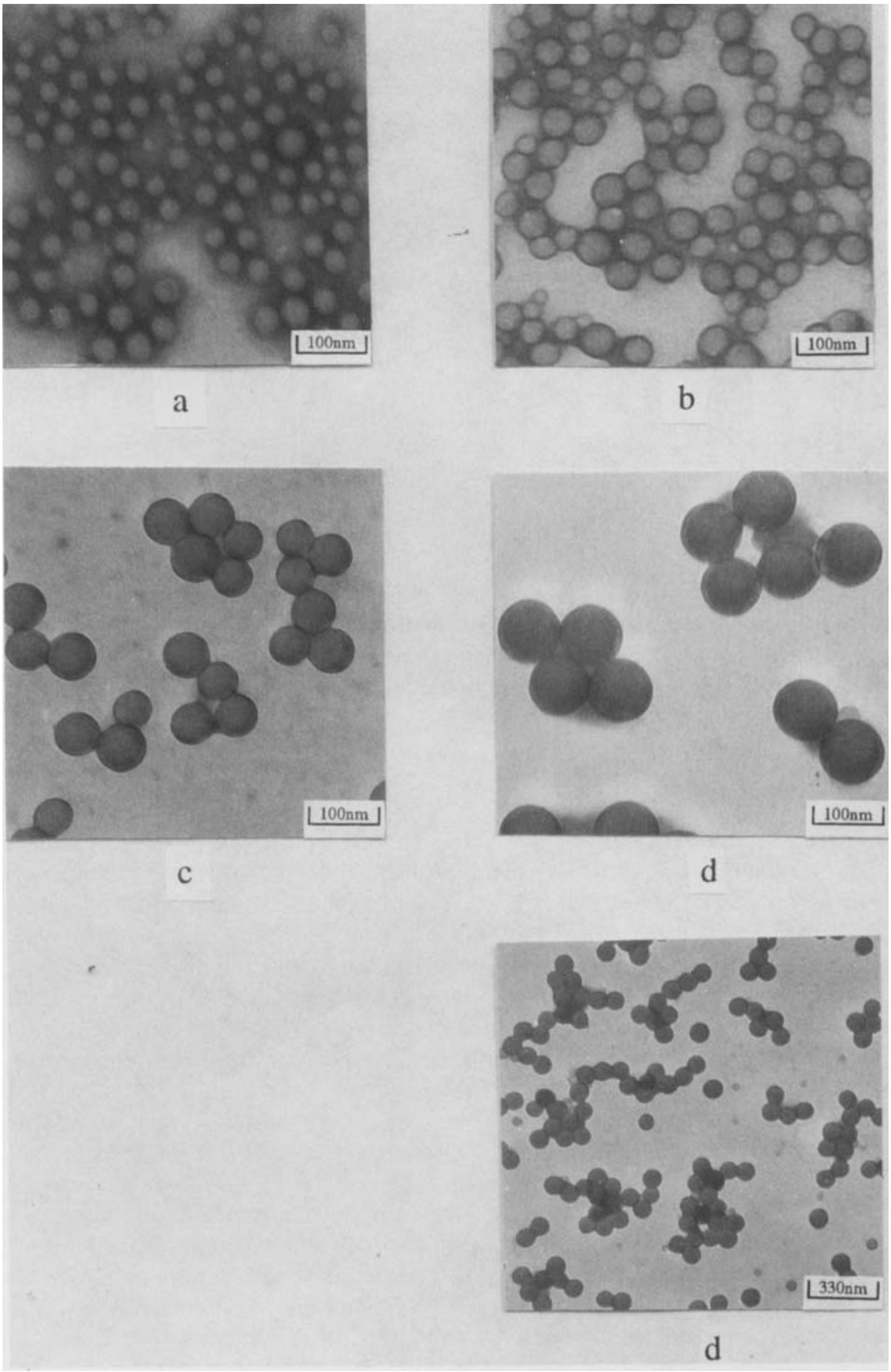


FIG. 5. TEM of latex particles from emulsion copolymerization of styrene and PEO-R-MA-40. The symbols a, b, c, and d (low and high magnification) are identical to those in Table 7.

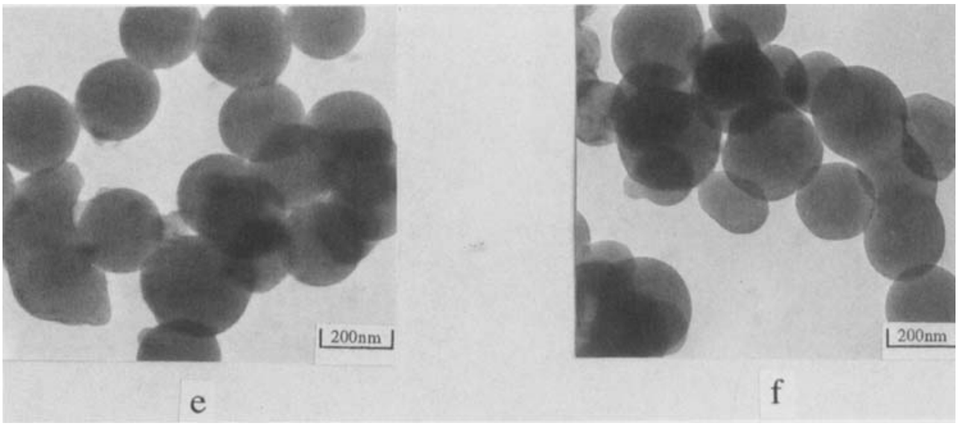


FIG. 6. TEM of latex particles from emulsion copolymerization of styrene and PEO-R-MA-15 or PEO-R-MA-10. The symbols e and f are identical to those in Table 7.

MA-*n* than those of C_{12}-PEO-MA-*n* for emulsion copolymerization with styrene. This may be due to the formation of slightly different micellar structures that affect the different monomer partitions in different emulsion systems. This will result in different effective feed compositions in micelles or particles and different compositions in the copolymers.

Particle Sizes and Molecular Weights of Copolymers

Stable latices with rather monosized particles could easily be prepared by emulsion copolymerization of styrene and PEO-R-MA-*n*. Table 7 shows some information about the latex particles. It was found that the PEO-R-MA-40 emulsion system could produce very small and uniform latex particles. The average particle diameter ($\overline{D}_n$) increased from about 31 to 90 nm, and their polydispersities ($\overline{D}_w/\overline{d}_n$) decreased from about 1.14 to 1.01 with increasing styrene concentration from 5.79 to 10.78 wt% based on the total weight of the emulsion. Their size variations can be better seen from the TEM pictures in Fig. 5. On the other hand, the latex particles produced by PEO-R-MA-10 or PEO-R-MA-15 were much larger ($\overline{D}_n \cong 250$–300 nm), as can be seen from Fig. 6. This is due to the larger amounts of styrene used in the latter systems although their molar ratios of styrene to PEO-R-MA-*n* were fixed at 75.19.

Table 8 summarizes some of the molecular weights of the copolymers as estimated by GPC calibrated with linear polystyrene standard samples. As pointed out by Ito [25], the apparent molecular weights and also the $\overline{M}_w/\overline{M}_n$ of this type of branched polymers as determined by GPC might be underestimated due to their compact conformations as compared to the expanded coil conformation of the linear polystyrene standard. In general, $\overline{M}_w$s obtained from solution copolymerization were much lower than those from emulsion copolymerization, indicating the copolymerization was less readily achieved in the nonstructured solution medium. It is noted that a higher $\overline{M}_w$ and a relatively narrow polydispersity ($\overline{M}_w/\overline{M}_n = 1.6$–

TABLE 8. Molecular Weights of Copolymers of Styrene (M_1) and PEO-R-MA-*n* (M_2)

M_2	$[M_1]/[M_2]$, mol/mol	Medium[a]	$\overline{M}_w$ (10^5)	$\overline{M}_w/\overline{M}_n$
PEO-R-MA-10	17.96	Solution	0.30	1.61
	39.10	Solution	0.35	1.77
	38.81	Emulsion	1.12	3.56
	75.19	Emulsion	1.34	3.28
	94.83	Emulsion	1.42	2.96
PEO-R-MA-15	15.52	Solution	0.21	1.38
	38.72	Solution	0.47	2.12
	30.07	Emulsion	1.07	3.98
	75.19	Emulsion	1.19	3.13
	95.68	Emulsion	1.68	2.73
PEO-R-MA-40	31.34	Solution	0.46	1.17
	40.56	Solution	0.50	1.95
	40.56	Emulsion	2.87	1.92
	75.19	Emulsion	3.34	1.83
	91.60	Emulsion	4.07	1.75
	118.41	Emulsion	5.28	1.64
	140.03	Emulsion	6.13	1.59

[a] Emulsion: total weight, 50 g; PEO-R-MA-*n*, 1.5 wt%; [KPS], 5 mM; temperature, 60°C. Solution: total monomers, 20 wt% in benzene; [AIBN], 0.5 mM; temperature, 68°C.

1.9) were obtained from the emulsion copolymerization of styrene with PEO-R-MA-40. Moreover, $\overline{M}_w$ increased but its $\overline{M}_w/\overline{M}_n$ decreased slightly with an increasing concentration of styrene. This implies that the copolymerization of styrene with PEO-R-MA-40 might proceed mainly within micelles or particles which were sterically well protected, and thus forms a very stable latex. On the other hand, latices produced from PEO-R-MA-10 or PEO-R-MA-15 were less stable.

CONCLUSION

PEO macromonomers with three different PEO chain lengths have been successfully copolymerized with styrene in benzene solution and in oil-in-water emulsions. The apparent reactivities ($1/r_1$) of the macromonomers decreased with an increase of their PEO chain lengths for both copolymerization systems. The copolymerization in the solution was faster for the macromonomer with a shorter EO chain length. On the other hand, the rate of copolymerization in the emulsion was much higher than that in the solution due to the ease with which copolymerization proceeded in the micellar environment. Stable copolymer latices with monodisperse particles ($\bar{D}_w/\bar{d}_n$ = 1.01) were obtained from the copolymerization of 1.5 wt% PEO-R-MA-40 with about 10 wt% styrene in emulsions. Moreover, the emulsion copolymerization produced copolymers of relatively high molecular weights ($\bar{M}_w > 10^5$) with a relatively narrow molecular weight distribution as determined by GPC.

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