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SYNTHESIS AND POLYMERIZATION OF A NONIONIC SURFACTANT: POLY(ETHYLENE OXIDE) MACROMONOMER

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ABSTRACT

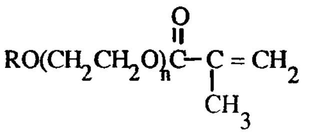
A polymerizable nonionic surfactant macromonomer, ω-methoxy poly(ethylene oxide)$_n$undecyl-α-methacrylate (n = 40) has been synthesized from poly(ethylene glycol) methyl ether, 11-bromoundecanol, and methacryloyl chloride. The critical micelle concentration of the macromonomer is 6.6×10^{-5} mol/L at 25°C. The kinetics of its polymerization in aqueous medium follows conventional solution polymerization, i.e., first and half order with respect to the concentrations of the macromonomer and $K_2S_2O_8$, respectively. The rate of its polymerization in water was extremely rapid (within 30 minutes) as compared to its solution polymerization in benzene (days). The activation energies for the macromonomer polymerization were 57 kJ/mol in water but 179 kJ/mol in benzene. The aqueous system produced polymers with a number-average degree of polymerization (DP_n) ranging from about 130 to 160, but it was much lower ($DP_n \doteq 7$) for the benzene system. The possible micellar polymerization mechanism for the macromonomer is discussed.

INTRODUCTION

The synthesis and polymerization of micelle-forming monomers have been a subject of interest for many reasons. One is to fix the labile organized systems permanently for a better description of their structures [1] and more appropriate for technological applications than their unpolymerized counterparts [2]. The polymerizable surfactants may be better used for latex stabilization via copolymerization by preventing surfactant desorption from particle surfaces [3-5].

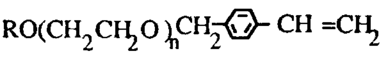
Many studies [1, 2, 6-19] have been reported on the polymerization of ionic and zwitterionic surfactants, but only a few on the homopolymerization of nonionic macromonomers [20, 21]. Most work on poly(ethylene oxide) macromonomers has been related to their copolymerization with acrylic monomers or styrene to easily form well-defined amphiphilic graft copolymers [22-36]. Owing to the existence of hydrophilic PEO side chains and hydrophobic backbones (e.g., PMMA, PSt), PEO-containing amphiphilic graft copolymers can be used as emulsifiers [37-39], surface-active agents [33, 40], phase transfer catalysts [25, 38], and solid polymer electrolytes [32, 41] after complexing with alkali salts.

Ito and coworkers [20, 21] recently reported the homopolymerization of PEO macromonomers of the following structures:



$\mathrm{RO(CH_2CH_2O)_n\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2}$

(R-PEO-MA-n)



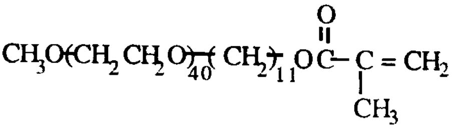
(R-PEO-VB-n)

R= H, CH_3, $C(CH_3)_3$, $nC_{18}H_{37}$

n= 24, 25, 35, 53, 67

They reported that the homopolymerization of these amphiphilic macromonomers proceeded unusually rapidly in water due to their organization into micelles. They assume that the core of the micelle is formed both from terminal segments of the ω-alkyl groups ($C \geq 4$) and the polymerizable vinyl groups, while the hydrophilic PEO chains will bend toward the core to form a looplike-shell micelle. If the alkyl group is only a short chain (e.g., $-CH_3$), the macromonomer will organize into a normal micelle where the PEO chains will extend into the aqueous phase to allow for a relatively compact arrangement of the polymerizable vinyl groups in the micellar core.

We have recently synthesized a surface-active macromonomer with the polymerizable group attached to a rather long hydrophobic segment (C_{11}) of the following structure:



$\mathrm{CH_3O(CH_2CH_2O)_{40}(CH_2)_{11}O\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2}$

(PEO-R-MA-40)

This polymerizable macromonomer is thus expected to form normal micelles easily with the polymerizable groups embedded in the relatively large hydrophobic core while long PEO groups protruded into the aqueous medium. The polymerization kinetics of this macromonomer in water and in benzene are discussed in this paper.

EXPERIMENTAL

Materials

Poly(ethylene glycol) methyl ether (PEOH-40, $\overline{M}_w$ = 2000) 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 Milli Q water purification system (resistance 18.2 KΩ). Analytical grade 11-bromoundecanol from Fluka and deuterated solvents $CDCl_3$, C_6D_6, and D_2O from Aldrich or Merck were used as received.

Synthesis of the Surface-Active Macromonomer

Bromoundecyl-THP Ether (BU-THP)

DHP (0.7 mol) was added dropwise to a magnetically stirred solution of 11-bromoundecanol (0.2 mol) and a reagent grade *p*-toluenesulfonic acid monohydrate (2 mmol) dissolved in dried THF (100 mL) at 0°C over a period of about half an hour. With further stirring for another half an hour, the solution was kept at the ambient temperature (28°C) and continuously stirred for 4 more hours. THF and the excess DHP were then removed by a rotary evaporator. The residue was dissolved in ether and washed twice with saturated brine to remove *p*-toluenesulfonic acid monohydrate. The organic layer was dried overnight with magnesium sulfate and filtered. After evaporation of the ether, the yellowish liquid (~100% yield) could be used directly for the following step, but the very pure product (60% yield) was obtained by vacuum distillation at 90°C/1 mbar.

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

Finely-ground potassium hydroxide (0.06 mol) and bromoundecyl-THP ether (0.06 mol) were added to a magnetically stirred solution of poly(ethylene glycol) methyl ether (0.02 mol) in 200 mL of a mixed solvents of THF and benzene (1/1, v/v). The reaction mixture was stirred under nitrogen atmosphere for 24 hours and then filtered. After evaporation of THF and benzene, the residue was washed with ether to remove any excess bromoundecyl-THP ether. The white precipitate was washed with ether and then 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 magnesium sulfate. After filtration, chloroform was evaporated off and the white solid product (85% yield) was further dried in a vacuum oven for 2 days at the ambient temperature.

ω-Methoxy Poly(Ethylene Oxide) Undecanol (PEO-R-OH)

A solution of PEO-R-THP (0.015 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 by magnesium sulfate. The white solid product

(95% yield) was obtained after evaporating the chloroform and dried to a constant weight in a vacuum oven.

ω-Methoxy Poly(Ethylene Oxide)Undecyl α-Methacrylate (PEO-R-MA-40)

To a magnetically stirred solution of PEO-R-OH (0.013 mol) and 8 mL triethylamine in 80 mL of dried CH_2Cl_2 at 0°C, methacryloyl chloride (0.065 mol) was added dropwise under nitrogen over a period of half an hour. A solid salt was immediately formed, and it was kept in the 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. A solid product was recovered from the chloroform solution after rotary evaporation. The pure product of PEO-R-MA-40 (90% yield) was obtained by reprecipitating the crude product three times from chloroform and ether. Its melting point was 49.4°C. It was stored at 0°C in darkness.

Polymerization

The surface-active PEO-R-MA-40 was polymerized at different temperatures either in water with KPS or in benzene with AIBN under nitrogen atmosphere. The polymerization in the corresponding deuterated solvent was monitored by following the disappearance of the double-bond peaks in reference to the ω-methoxy peaks by ^{1}H NMR. The polymer conversions were calculated by

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

where $(b/a)_t$ and $(b/a)_0$ are the integral ratios of the peak area of the double-bond protons to that of the ω-methoxy protons at a given time (t) and at $t = 0$, respectively. Polymerization was carried out in NMR tubes which were placed in a water bath at a given temperature. At different time intervals the tubes were quickly quenched to 0°C before they were measured by NMR at 25°C. The polymerization mixture, after being freeze-dried, was also analyzed by GPC.

Measurements

Infrared (IR) and UV spectra were obtained from a Perkin-Elmer 1600 series FT-IR and a Hewlett Packard 8452A diode array spectrophotometers, respectively. Proton NMR spectra were recorded with a Bruker ACF 300 (300 MHz) spectrometer using $CDCl_3$, D_2O, or C_6D_6 as solvent and tetramethylsilane (TMS) as the internal standard. The experiments were run with a 30-seconds pulse delay time near a 75° pulse angle, and the spectra were obtained by accumulating 8 scans for the kinetic study of polymerization and 100 scans for the characterization of compounds. The ^{13}C-NMR spectra were also recorded with the same spectrometer in $CDCl_3$ solution by accumulating 16,000 scans.

Gel-permeation chromatography (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 × 7.8mm) were used in series. HPLC-grade THF was used as an eluent at a flow rate of 0.8 mL/min at 45°C. Molecular weights were obtained from the calibration line using PEO standard samples supplied by Polymer Laboratories Ltd.

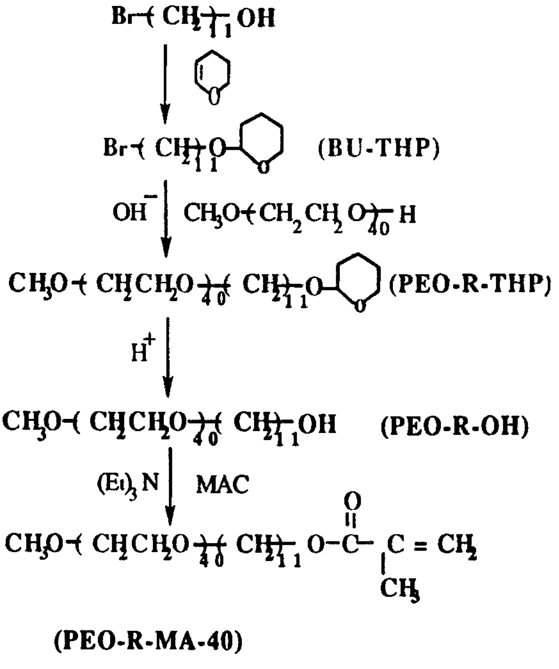
The critical micelle concentration (CMC) of the surface-active macromonomer was determined at 25°C with a torsion balance tensiometer (White Electric Instrument Co.). Its CMC was obtained from the break point of a plot of the surface tension versus log concentration of the surface-active macromonomer.

RESULTS AND DISCUSSION

Synthesis and Characterization of PEO-R-MA-40

The synthesis of the macromonomer (PEO-R-MA-40) involved four steps as shown in reaction Scheme 1. Protection of the hydroxyl group in 11-bromoundecanol by DHP was essential, and it was then reacted with poly(ethylene glycol) methyl ether by a modified Williamson reaction to give the intermediate PEO-R-THP with a yield as high as 85%. The hydrolysis of the THP-ether to the corresponding alcohol (PEO-R-OH) was achieved almost quantitatively.

The final introduction of a methacrylate group to PEO-R-OH produced the macromonomer (PEO-R-MA-40) with an α-polymerizable group located at the "tail" of the molecule. The yield was as high as 90%. The microanalytical results for the intermediates and the macromonomer are in good agreement with the calculated ones listed in Table 1. Their proton NMR spectra and the peak assignments are shown in Fig. 1. The peaks at δ6.09 and δ5.54 ppm indicate the presence of the



SCHEME 1.

TABLE 1. Microanalysis of PEO-R-MA-40 and Its Intermediates

	Microanalysis					
	% C		% H		% Br	
Compound	Calcd.	Found	Calcd.	Found	Calcd.	Found
BU-THP ($C_{16}H_{31}O_2Br$)	57.31	57.70	9.32	9.25	23.83	23.62
PEO-R-THP ($C_{97}H_{194}O_{43}$)	56.86	55.27	9.55	9.54		
PEO-R-OH ($C_{92}H_{186}O_{42}$)	56.24	55.83	9.54	9.43		
PEO-R-MA-40 ($C_{96}H_{190}O_{43}$)	56.73	56.17	9.42	9.54		

$=CH_2$ group (Fig. 1D). From the integral ratio of $-OCH_3$ (δ3.38) and $-CH_3$ (δ1.94) groups, the number of double bond per macromonomer (the end-group functionality) was calculated to be unity, as expected. The molecular weights of the precursor PEOH-40 and the macromonomer (PEO-R-MA-40) were also determined by ^{1}H NMR from the integral values of different proton peaks or by GPC using PEO standards. As shown in Table 2, their molecular weight distributions ($\overline{M}_w/\overline{M}_n$) are almost about the same, i.e., 1.09 for PEOH-40 and 1.10 for PEO-R-MA-40.

UV spectrophotometry was also used to calculate the double bonds of the macromonomer. Absolute ethanol was used as the solvent, and different mixtures of pure MMA and PEO-R-OH were used as the standards for the calibration line. No UV absorption peak was found for PEO-R-OH in the concentration range investigated. The addition of PEO-R-OH to the standard solution was used to maintain a similar refractive index and other physical properties related to the macromonomer solution. However, the macromonomer exhibits a strong absorption at 209 nm as for MMA, indicating that the unsaturated end group of the macromonomer is derived from MMA reacted with PEO-R-OH. The number of double bonds per macromonomer was calculated from the calibration line to be 0.99, which is in good agreement with the unity value found by ^{1}H-NMR measurements.

The FT-IR spectrum of the macromonomer (Fig. 2) shows strong absorption peaks at 2865 and 1111 cm^{-1} due to the vibrations of CH_2 and $C-O-C$, respectively. The presence of the unsaturated methacryloyl group is also evidenced from the stretchings of $C=O$ at 1717 cm^{-1} and $C=C$ at 1635 cm^{-1}.

Assignments of the ^{13}C-NMR spectrum of the macromonomer in $CDCl_3$ are shown in Fig. 3. Peaks for $C=CH_2$ are observed at 136.46 and 125.04 ppm while those for $C=O$, $(CH_2CH_2O)_{40}$, and $(CH_2)_9$ appear at 166.80, 70.44, and 25.90–29.37 ppm, respectively. The other peaks occur at 64.74 ppm for CH_2-OOC, 58.59 ppm for CH_3O, $OCH_2(CH_2)_9$, and 18.22 ppm for CH_3.

Solubility and CMC of PEO-R-MA-40

PEO-R-MA-40 is a nonionic polymerizable surfactant and is very soluble in a variety of polar and nonpolar solvents, such as water, short-chain alcohols, THF, chloroform, toluene, and benzene. This unique property is unmatched by most the

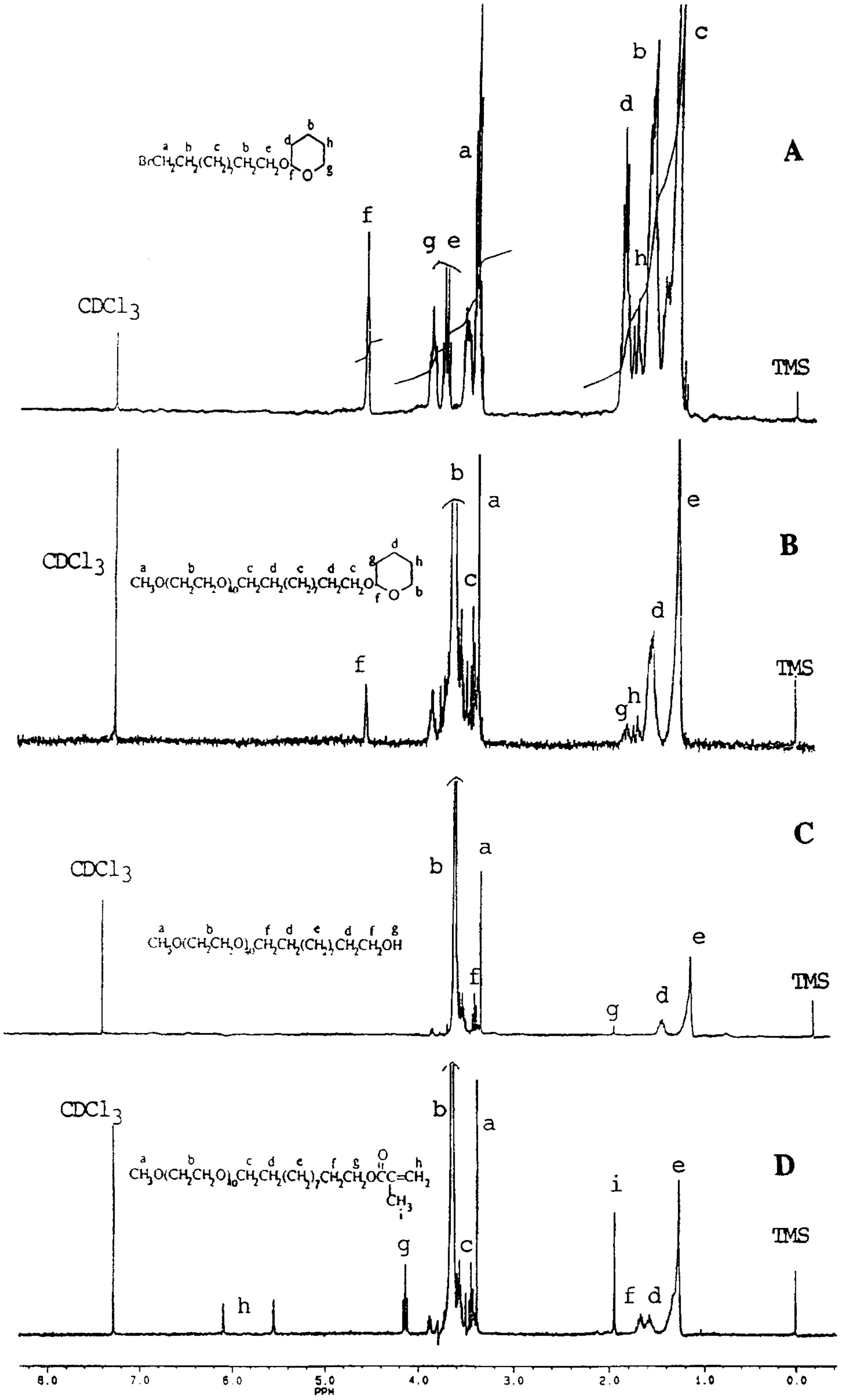


FIG. 1. ^{1}H-NMR spectra of the intermediate compounds and PEO-R-MA-40.

TABLE 2. Characterization of the Surface-Active Macromonomer and Its Precursor

Macromonomer and its precursor	GPC			NMR[a]	Number of double bonds/per macromonomer	
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	NMR[b]	UV[c]
PEOH-40	1780	1940	1.09	1790		
PEO-R-MA-40	2110	2330	1.10	2030	1.00	0.99

[a] Determined by ^{1}H 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-40.

[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

$$C_0 = \frac{\text{weight of PEO-R-MA-40}}{M_n\ (2110) \times \text{volume}}$$

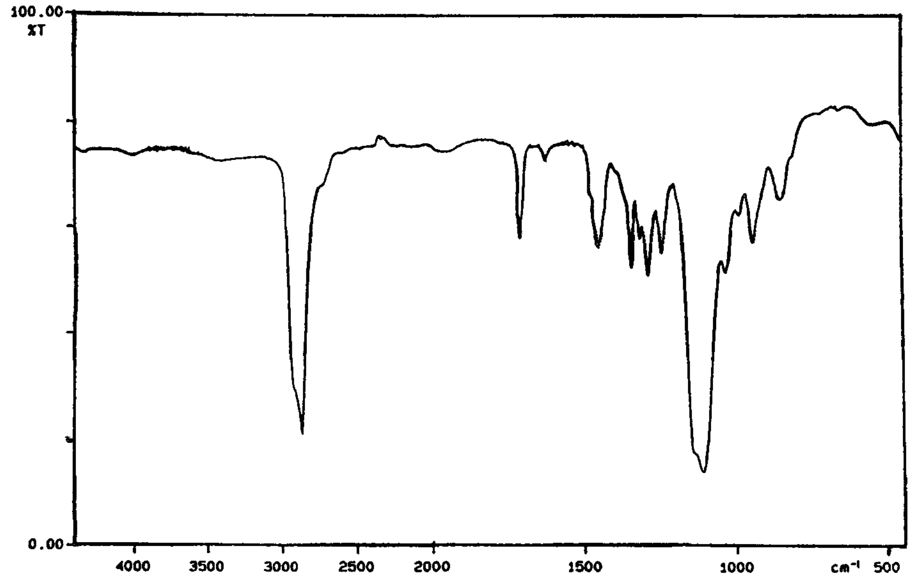


FIG. 2. FT-IR spectrum of PEO-R-MA-40.

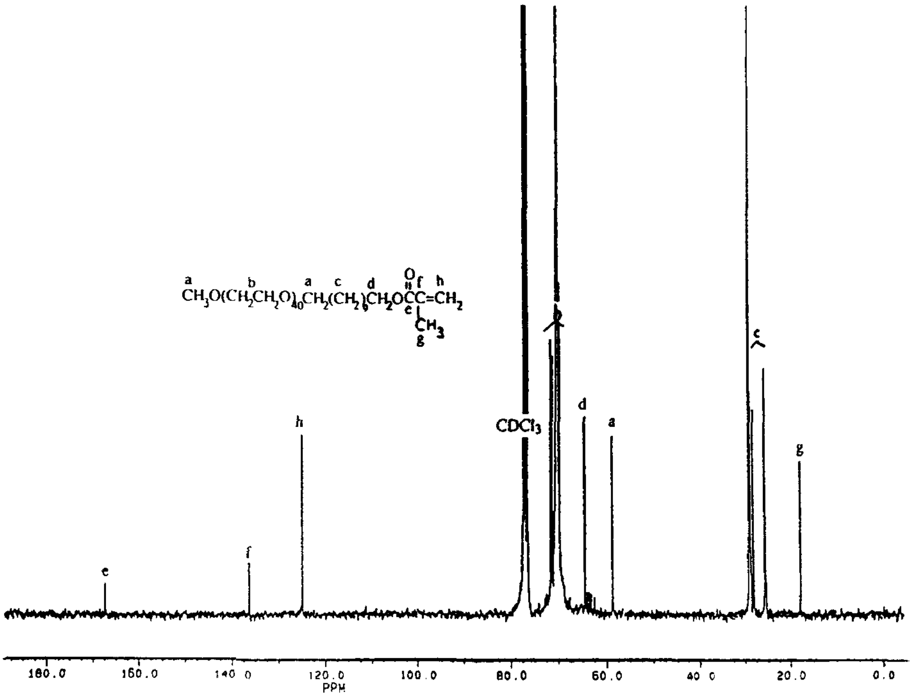


FIG. 3. ^{13}C-NMR spectrum of PEO-R-MA-40.

conventional monomers and ionic polymerizable surfactants. Figure 4 shows two plots of the surface tension versus log concentration of the macromonomer in water and in benzene at 25°C. The CMC of PEO-R-MA-40 in water was found to be 6.6 $\times 10^{-5}$ mol/L from the breakpoint of the plot. However, no CMC could be detected from benzene solutions of the macromonomer.

Kinetics of Polymerization

The polymerization of PEO-R-MA-40 in water was initiated by KPS; AIBN was used in the benzene solution system. The progress of polymerization was monitored by ^{1}H-NMR measurements. The polymerizations of PEO-R-MA-40 in water and in benzene as a function of time at different temperatures are shown in Figs. 5 and 6, respectively. The polymerization carried out in water was extremely rapid; it was completed within half an hour at 50°C. In contrast to the aqueous system, the polymerization of PEO-R-MA-40 in benzene did not exceed 80% conversion even after 4 days of polymerization at 68°C. The striking difference in the polymerization kinetics between the two systems is attributed to the formation of macromonomer micelles in water but not in benzene. The different kinetics cannot be due to the different types of initiators used (i.e., KPS versus AIBN) because the decomposition rate constant (k_d) at 60°C for AIBN in benzene (9.15×10^{-6} S^{-1}) [42] is larger than that of KPS in water (5.78×10^{-6}) [43]. The ability of PEO-R-MA-40 to form micelles in an aqueous phase is responsible for its extremely fast rate of micellar polymerization. The micellar environment not only provides a higher con-

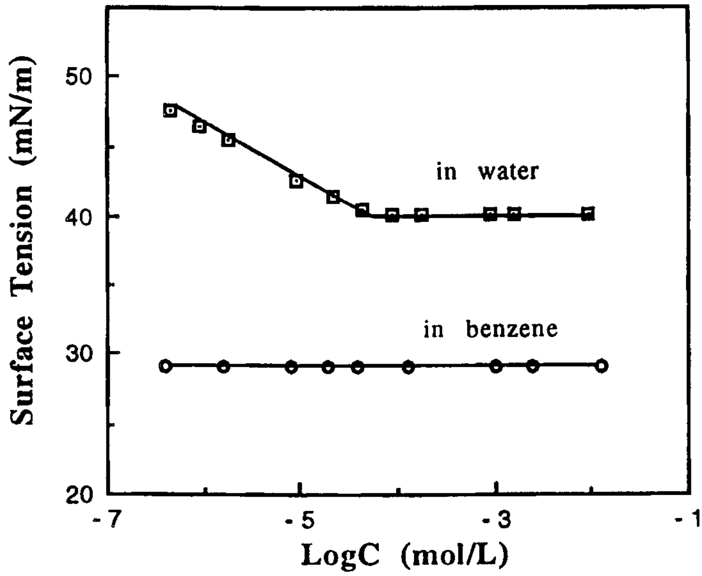


FIG. 4. The plot of the surface tension vs log[PEO-R-MA-40] in water and in benzene at 25 °C.

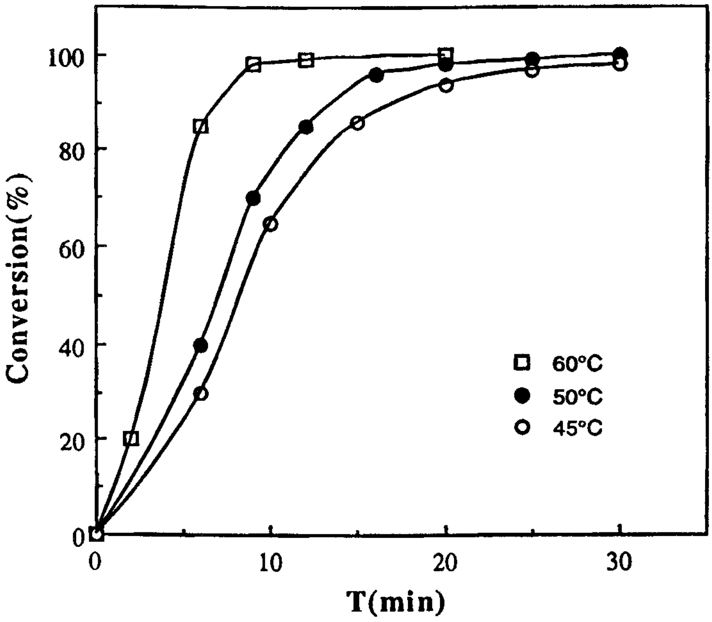


FIG. 5. The polymerization of the macromonomer in water as a function of time at different temperatures. [M] = 0.04 M, [KPS] = 0.20 mM.

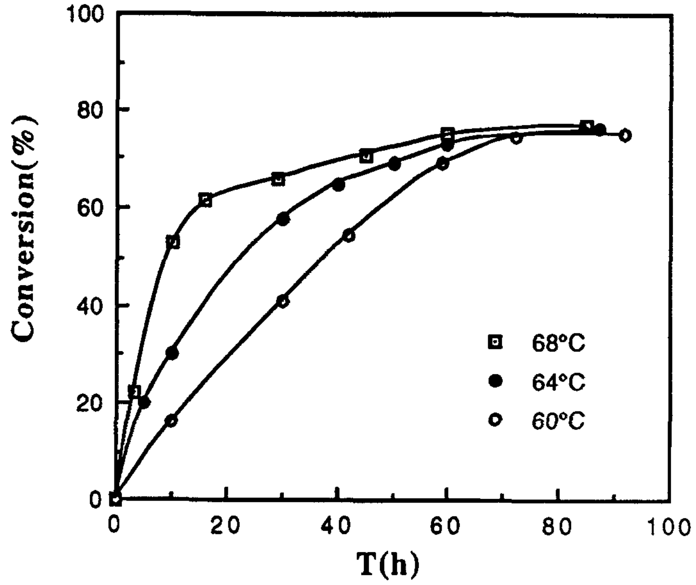


FIG. 6. The polymerization of the macromonomer in benzene as a function of time at different temperatures. [M] = 0.04 M, [AIBN] = 1.0 mM.

centration of the hydrophobic polymerizable groups for fast propagation polymerization but also a slower rate for diffusion-controlled bimolecular termination due to the highly crowded segments.

It is interesting to compare the rate of polymerization between the reported aqueous system [20] of R-PEO-MA-24 and our aqueous system of PEO-R-MA-40. The former required about 5 hours to be completed as compared to only about half an hour for the latter. This strongly indicates the important effect of the location of the alkyl group (R) within the macromonomer on its polymerization rate. The insertion of the hydrophobic alkyl R group in between the hydrophilic PEO chain and the polymerizable methacryloyl group favors the formation of a normal micelle of PEO-R-MA-40 with the polymerizable groups concentrated in the core of the micelle, as depicted in Fig. 7. Once the radicals generated from the aqueous medium diffuse into the cores of the macromonomer micelles, polymerization proceeds rapidly due to a higher concentration of methacryloyl groups congregated in the relatively small micellar cores. However, additional macromonomers may also be recruited from the uninitiated micelles to the growing polymerized micelles. As for R-PEO-MA-24, the formation of a micelle would require the bending of R and MA groups [20] to the micellar core. The concentration of the polymerizable MA group is thus diluted by the presence of the R group in the micellar core. This may be responsible for its much slower polymerization rate compared to PEO-R-MA-40. The dilution effect of the polymerizable methacryloyl group on the rate of polymerization is more striking in solution polymerization of the macromonomer in benzene. In this case the diluted polymerizable groups are randomly dispersed in the solution, resulting in a very slow rate of polymerization.

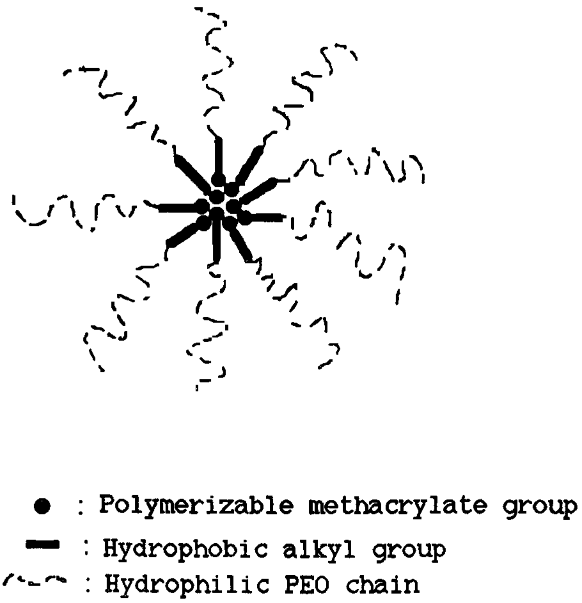


FIG. 7. Schematic representation of a macromonomer micelle.

The initial rate of polymerization of PEO-R-MA-40 in the aqueous system was found to be the 0.51 power of [KPS] and the 1.0 power of the concentration of the macromonomer. These are in good agreement with the general kinetic expression for radical polymerization [44] as given by

$$R_p = k_p(2f k_d/k_t)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2} \tag{2}$$

where f, k_d, k_p, and k_t are the initiator efficiency and the constants for initiator decomposition, propagation, and termination, respectively.

The effect of temperature on the initial rate of polymerization depends on the ratio of the three rate constants $k_p(k_d/k_t)^{1/2}$. Relating these rate constants with three separate Arrhenius-type equations, one obtains

$$\ln(R_p)_i = \ln C - E_a/RT \tag{3}$$

where C is proportional to $[\mathrm{I}]_0^{1/2}[\mathrm{M}]_0$. The overall activation energy for polymerization (E_a) is related to the activation energies for propagation (E_p), termination (E_t), and decomposition of initiator (E_d) as follows:

$$E_a = E_p + E_d/2 - E_t/2 \tag{4}$$

The initial polymerization rates $(R_p)_i$ at different temperatures were obtained from the initial slopes of the plots shown in Figs. 5 and 6. By plotting $\ln(R_p)_i$ against $1/T$, as in Fig. 8, the activation energies of polymerization (E_a) were obtained from the gradients of the linear plots. The E_a for the aqueous system was found to be 57 kJ/mol, but it is triple that value (179 kJ/mol) for the benzene system. The low E_a value of 57 kJ/mol is quite expected for general micellar polymerization. It is comparable to those of other micellar polymerizations: sodium acrylamidoundeca-

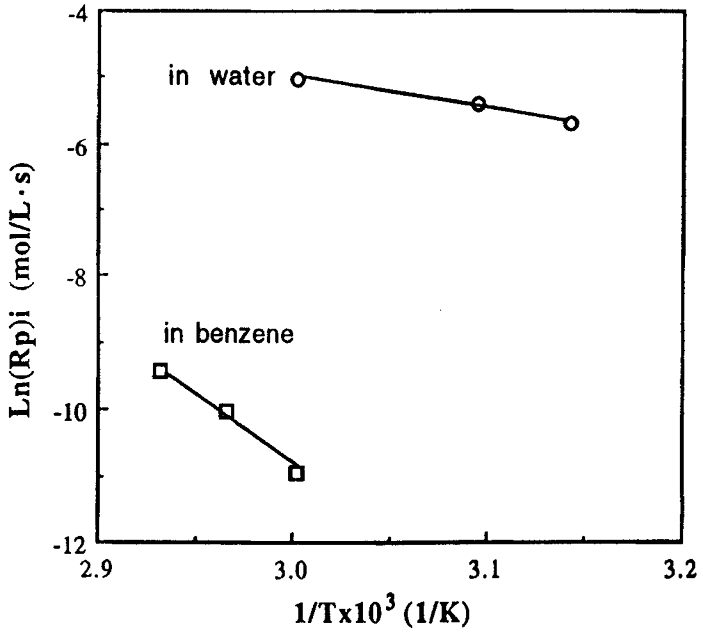


FIG. 8. The temperature dependencies on the initial rates of polymerization of PEO-R-MA-40 in water and in benzene.

noate (63 kJ/mol) [9], acryloyl undecyldimethylammonio acetate (50 kJ/mol) [19], and sodium 11-(*N*-ethylacrylamido)undecanoate (46 kJ/mol) [10]. On the contrary, a very high E_a is required for the benzene solution polymerization of PEO-R-MA-40 due to the absence of any aggregated structures.

Molecular Weights of Poly(PEO-R-MA)

Table 3 summarizes some of the molecular weights of poly(macromonomer)s obtained by free radical polymerization at different conditions. The number-average degree of polymerization (DP_n) was only about 7 from benzene solution polymerization, indicating the difficulty of macromonomer polymerization in a nonstructured medium. However, its DP_n increased by about 15 to 20-fold for the micellar polymerization of the macromonomer in water. The DP_n varied only moderately (130–160) by the effect of the concentrations of the macromonomer and the initiator as well as of the temperature. This implies that the polymerization of PEO-R-MA-40 may proceed mainly within micelles with some additional macromonomers from the surrounding area.

CONCLUSION

A new surface-active and polymerizable macromonomer (PEO-R-MA-40) was synthesized in mild conditions with high yields. This amphiphilic macromonomer can be polymerized much faster in water than in benzene. Its polymerization in an

TABLE 3. Molecular Weights of Poly(Macromonomer)s

°C	Solvent	[I], mM	[PEO-R-MA-40], M	$\overline{M}_n$[a] × 10^5	$\overline{M}_w/\overline{M}_n$[a]	DP_n[b]
50	H_2O	0.20	0.04	3.32	1.63	164
50	H_2O	0.20	0.03	3.25	1.74	160
50	H_2O	0.20	0.02	3.04	1.99	150
50	H_2O	0.20	0.01	2.83	1.59	139
50	H_2O	0.40	0.02	2.66	1.82	131
50	H_2O	0.50	0.02	2.57	2.19	127
60	H_2O	0.50	0.03	2.57	1.93	127
60	C_6H_6	1.00	0.04	0.16	1.33	7.8
68	C_6H_6	1.00	0.04	0.14	1.48	6.9

[a] Determined by GPC.
[b] $DP_n = \overline{M}_n$ of polymacromonomer/$\overline{M}_n$ of macromonomer (2030).

aqueous solution follows first-order kinetics with respect to [PEO-R-MA-40] and one-half-order with respect to [$K_2S_2O_8$]. The activation energy for the polymerization in water was 57 kJ/mol as compared to 179 kJ/mol in the benzene solution polymerization. The number-average degree of polymerization for the former system ranged from about 130 to 160; it was around 7 for the latter. The results suggest that organized structures and compact cores of macromonomer micelles are responsible for the unusually rapid polymerization in aqueous solution.

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REFERENCES

[1] U. Kammer and H. G. Slias, *Kolloid-Z. Z. Polym., 250,* 344 (1972).

[2] C. M. Paleos and A. Malliaris, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys., C28,* 403 (1988).

[3] B. W. Greene, D. P. Sheety, and T. D. Fishes, *J. Colloid Interface Sci., 32,* 90 (1970).

[4] M. B. Urquiola, V. L. Dimonic, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Polym. Chem. Ed., 30,* 2619 (1992).

[5] J. Dickstein, US Patent 4,075,411 (1978).

[6] E. D. Sprague, D. C. Duecker, and C. E. Larrahee, *J. Am. Chem. Soc., 103,* 6797 (1981).

[7] K. Arai, Y. Maseki, and Y. Ogiwara, *Makromol. Chem., Rapid Commun., 8*, 563 (1987).

[8] K. W. Yeoh, C. H. Chew, L. M. Gan, and L. L. Koh, *Polym. Bull., 22*, 123 (1989).

[9] K. W. Yeoh, C. H. Chew, L. M. Gan, L. L. Koh, and H. H. Teo, *J. Macromol. Sci.—Chem., A26*, 663 (1989).

[10] K. W. Yeoh, C. H. Chew, L. M. Gan, and L. L. Koh, *Ibid., A27*(1), 63 (1990).

[11] C. M. Paleos, P. Dais, and A. Malliaris, *J. Polym. Sci., Polym. Chem. Ed., 22*, 3383 (1984).

[12] K. Nagai, Y. Ohishi, M. Inaba, and S. Kudo, *Ibid., 23*, 1221 (1985).

[13] S. M. Hamid and D. C. Sherrington, *Polymer, 28*, 325 (1987).

[14] B. Lerebours, B. Perly, and M. P. Pileni, *Chem. Phys. Lett., 147*, 503 (1988).

[15] B. Durairaj and F. D. Blum, *Langmuir, 5*, 370 (1989).

[16] D. Y. Chu and J. K. Thomas, *Macromolecules, 24*, 2212 (1991).

[17] A. Laschewsky and I. Zerbe, *Polymer, 32*, 2070 (1991).

[18] D. Cochin, F. Candau, and R. Zana, *Macromolecules, 26*, 5755 (1993).

[19] C. H. Chew, T. D. Li, and L. M. Gan, *J. Macromol. Sci.—Pure Appl. Chem., A32*(2), 211 (1995).

[20] K. Ito, K. Tanaka, H. Tanaka, G. Imai, S. Kawaguchi, and S. Itsuno, *Macromolecules, 24*, 2348 (1991).

[21] K. Ito, K. Hashimura, S. Itsuno, and E. Yamada, *Ibid., 24*, 3977 (1991).

[22] K. Ito, H. Tsuchida, A. Hayashi, T. Kitano, E. Yamade, and T. Matsumoto, *Polym. J., 17*, 827 (1985).

[23] P. Rempp, P. Lutz, P. Masson, and E. Franta, *Makromol. Chem., Suppl., 8*, 3 (1984); *13*, 47 (1985).

[24] W. W. Shulz, J. Kaladas, and D. W. Shulz, *J. Polym. Sci., Polym. Chem., Ed., 22*, 3795 (1984).

[25] T. Hamaide, M. Marriaggi, J. L. Foureys, P. Lepercechec, and A. Guyot, *Ibid., 22*, 3091 (1984).

[26] T. Suzuki and T. Tomono, *Ibid., 22*, 2829 (1984).

[27] S. Kobayashi, M. Kaku, T. Mizutani, and T. Saegusa, *Polym. Bull., 9*, 169 (1983).

[28] S. Kobayashi, T. Mizutani, and T. Saegusa, *Mackromol. Chem., 185*, 441 (1984).

[29] K. Ito, S. Yokoyama, F. Arakawa, Y. Yukawa, T. Iwashita, and Y. Yamasaki, *Polym. Bull., 15*, 425 (1986); *16*, 337 (1986).

[30] H. Q. Xie, J. Liu, and H. Li, *J. Macromol. Sci.—Chem., A27*, 725 (1990).

[31] Y. Tsukahara, K. Ito, H. C. Tasi, and Y. Yamashita, *J. Polym. Sci., Polym. Chem. Ed., 27*, 1099 (1989).

[32] D. W. Xia and J. Smid, *J. Polym. Sci., Polym. Lett. Ed., 22*, 617 (1984).

[33] I. Nwankwo, D. W. Xia, and J. Smid, *J. Polym. Sci., Polym. Phys. Ed., 26*, 581 (1988).

[34] C. M. F. Oliveira and E. F. Lucas, *Polym. Bull., 24*, 363 (1990).

[35] L. A. Schechtman, *Stud. Polym. Sci., 11*, 23-41 (1992).

[36] H. Uyama, Y. Honda, and S. Kobayashi, *J. Polym. Sci., Polym. Chem. Ed., 31*, 123 (1993).

[37] B. Wesslen and K. B. Wesslen, *Ibid., 27*, 3915 (1989).

[38] H. Q. Xie, J. Liu, and D. Xie, *Eur. Polym. J., 25*(11), 1119 (1989).
[39] G. Bo, B. Wesslen and K. B. Wesslen, *J. Polym. Sci., Polym. Chem. Ed., 30*, 1799 (1992).
[40] K. Ito, S. Yokoyama, and F. Arakawa, *Polym. Bull., 16*, 345 (1986).
[41] H. Q. Xie, D. Xie, and J. Liu, *Polym.-Plast. Technol. Eng., 28*(4), 355 (1989).
[42] J. Brandrup and E. H. Immergut (Eds.), *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.
[43] D. C. Blackley, *Emulsion Polymerization*, Applied Science, England, 1975, p. 163.
[44] G. Odian, *Principles of Polymerization*, McGraw-Hill, New York, 1981, pp. 198, 250.

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