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SYNTHESIS AND POLYMERIZATION OF A ZWITTERIONIC BETAINE SURFACTANT: ACRYLOYLUNDECYLDIMETHYLAMMONIO ACETATE

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ABSTRACT

A novel polymerizable zwitterionic betaine surfactant of acryloylundecyldimethylammonio acetate (AUDMAA) was synthesized using acryloyl chloride, 11-bromoundecanol, and glycine. Its critical micelle concentration is 9.42×10^{-3} mol/L at 24°C. The polymerization followed first-order kinetics with respect to [AUDMAA] and one-half order with respect to $[K_2S_2O_8]$. The activation energy for the micellar polymerization of AUDMAA was found to be only 50.2 kJ/mol. The $\overline{M}_w$ of poly(AUDMAA) ranged from about 3.0 to 5.0×10^4 and its MWD was rather narrow ($1.8 < \overline{M}_w/\overline{M}_n < 2.0$).

INTRODUCTION

There has been considerable interest in the synthesis and polymerization of polymerizable surfactants [1–3] because of the wide range of applications of the polyelectrolytes obtained for water treatment, soil conditioning, antistatic treatment of textiles, etc. The synthesis and polymerization of cationic vinyl monomers containing a quaternary ammonium group and anionic vinyl monomers have been extensively investigated. Some of the systems are allyldimethyldodecylammonium bromide [4], quaternary alkyl salts of dimethylaminoethylmethacrylate with different alkyl chain lengths [5, 6], and *N*,*N*-didodecyl-*N*-methyl-*N*-(2-(methacryloyloxy)ethyl)ammonium chloride [7], sodium acrylamidostearate [8], sodium acrylamidoundecanoate [9], and sodium sulfodecylstyryl ether [10].

Zwitterionic surfactants are electrically neutral compounds that possess formally charged substituent groups separated by intervening atoms. They are not salts and do not interact with ions to form salts. The hydrophilicity of zwitterionic compounds is strongly influenced by the structure and basicity of the anionic substituent group, and to a lesser degree by the length of the ion bridge that binds together these oppositely charged substituent groups [11].

Earlier work on surface-active betaine was described in considerable detail by Schwartz et al. [12, 13]. The most widely used method for preparing carboxybetaines is the quaternization of tertiary amines with sodium chloroacetate [14] or methyl chloroacetate [15]. However, very little is known about the synthesis and polymerization of polymerizable zwitterionic betaine monomers in spite of their wide applications in various areas [16].

Laschewsky and Zerbe [17] recently synthesized a series of permanently zwitterionic monomers based on sulfobetaines and their polymers. They found that the various solubilities of the polymers can be correlated with the molecular geometry of the zwitterionic monomers. On the other hand, we have recently synthesized a polymerizable betaine, acryloylundecyldimethylammonio acetate (AUDMAA). This paper discusses its synthesis, characterization, the kinetics of the micellar polymerization, and the solution properties of the polymer.

EXPERIMENTAL

Materials

Acryloyl chloride (Aldrich), 11-bromoundecanol (Fluka), glycine (Fluka), 96% formic acid (Aldrich), and formalin (Aldrich) were of analytical grades. Tetrahydrofuran (THF) was distilled over potassium metal and dried over molecular sieves of 3 Å. Superdry ethanol was prepared by refluxing absolute ethanol with magnesium in the presence of a small amount of iodine, and it was recovered by distillation. All other solvents were distilled and dried by molecular sieves of 3 Å. Water was purified by a Milli Q water purification system (resistance 18.2 kΩ). $K_2S_2O_8$[KPS] was recrystallized in pure water.

Synthesis of Dimethylglycine Sodium Salt (DMGS)

A mixture of glycine (0.6 mol), 150 mL of 96% formic acid, and 120 mL formalin was heated at 50-60°C for 10 hours and then gently refluxed for another 10 hours. When the mixture was cooled to room temperature, 60 mL concentrated hydrochloric acid was added to it. The solution was evaporated to a syrup under reduced pressure at 70°C. The crystals that appeared on cooling were recrystallized from water. About 55 g dimethylglycine hydrochloride was obtained as needle crystals (mp 189-190°C).

The dimethyglycine hydrochloride obtained was basified in ethanol with an aqueous solution of sodium hydroxide (43 wt%) at room temperature. The mixture was heated at 80°C for a while and then filtered immediately. Crystals were obtained when the filtrate was cooled to 15°C, and they were recrystallized from a mixed solvent of ethanol and water (85/15, v/v). About 40 g DMGS in the form of flakes (mp 287–288°C) was obtained.

Synthesis of Bromoundecylacrylate (BUA)

Bromoundecanol (0.32 mol) and 320 mL THF were mixed in a flask at 0°C under N_2, followed by the addition of 80 mL acryloyl chloride. The reaction system was bubbled with N_2 at room temperature for 2 hours and then left overnight. The unreacted acryloyl chloride and solvent were removed by a rotary evaporator. The yellowish brown residue was dissolved in ether and washed with a saturated sodium hydrogen carbonate solution until the aqueous layer was basic. After evaporation of the ether, a viscous yellowish liquid of BUA was obtained. It was used directly for the following quaternization step.

Synthesis of Acryloylundecyldimethylammonio Acetate (AUDMAA)

Dimethylglycine sodium salt (0.32 mol) was quaternized by reaction with BUA (0.30 mol) in a mixed solvent of water (100 mL) and isopropanol (360 mL) at 30°C under N_2 atmosphere for a week in the presence of an inhibitor, 2,6-di-*tert*-butyl-*p*-cresol (0.5 g). The reaction was checked constantly by TLC. At the completion of the reaction, the solvents were removed by a rotary evaporator. The dried solid residue was redissolved in about 140 mL superdry ethanol. Any insoluble salt was filtered off, and the filtrate was mixed with 700 mL ethyl acetate at 5°C. The precipitate obtained was dried and recrystallized three times with a mixed solvent of ethanol and ethyl acetate (1/8, v/v). The yield of AUDMAA (mp 170–171°C) was about 35 to 40%.

The elemental analysis for AUDMAA was found to be 66.12% C, 10.11% H, and 4.30% N, values which are in good agreement with the calculated ones: 66.03% C, 10.15% H, and 4.28% N.

Determination of the Critical Micelle Concentration and Krafft Point of AUDMAA

The CMC of AUDMAA was determined by surface tension measurements with a torsion balance tensionmeter (White Electric Instrument Co.). The surface tensions (γ) of a series of AUDMAA solutions of different concentrations (16 samples) were measured at 24°C. The CMC of AUDMAA was obtained from a plot of the surface tension vs the ln concentration as usual, i.e., CMC at the break point of the plot.

The Krafft point of AUDMAA was determined by gradually cooling a 1.0% aqueous solution of AUDMAA to a turbid state, which was then heated in a water bath at the rate of 1°C/min. The temperature at which the solution turned clear again was taken as the Krafft point of AUDMAA.

Polymerization of AUDMAA

Aqueous solutions of AUDMAA of different concentrations were polymerized with potassium persulfate initiator at different temperatures. The solutions were first degassed at about 10 torr for one freeze-thaw cycle. The polymerization was monitored by dilatometry. The dilatometer consists of a 15-mL Erlenmeyer flask with an attached 40 cm long capillary of 2 mm diameter as described elsewhere [3]. When the polymerization was completed, as evidenced by the unchanging volume in the dilatometer, the polymer was precipitated in an excess amount of acetone.

Spectroscopic Measurements

Infrared (IR) spectra were recorded by a Shimadzu IR-470 spectrophotometer using KBr pellet. The ^{1}H- and ^{13}C-NMR spectra were obtained in $CDCl_3$ and D_2O by a Brucker AMX500 NMR spectrometer. Chemical shifts were measured in ppm downfield from the internal standard tetramethylsilane (TMS).

Viscosity Measurements

Measurements of solution viscosity were conducted in an Ubbelohde dilution capillary viscometer (Kapenekas Laboratory Services, Akron, Ohio) in a water bath at 27 ± 0.1°C. The apparent relative viscosity η_r was obtained from the flow item of a polymer solution relative to that of pure water. The reduced viscosity (η_{sp}/c) and inherent viscosity ($\ln \eta_r/c$) were obtained according to the methods of Huggins [18] and Kraemer [19], respectively.

Molecular Weight Determination of GPC

The gel-permeation chromatography (GPC) measurements were performed on a Waters 600E liquid-chromatography system equipped with a RI-3 detector. TSKG4000PW and G2000PW columns were used. Milli Q purified water was used as an eluent. The polymer solution (50 μL at a concentration of 0.5 mg/L) was injected into the GPC columns. The eluent water flowed at 1.0 mL/min. A calibration curve was obtained using polyethylene oxide supplied by Toyo Soda Co.

RESULTS AND DISCUSSION

Synthesis and Characterization of AUDMAA

The zwitterionic surfactant was prepared in three stages with modifications from those reported earlier [17, 20]. The sodium dimethylaminoacetate was first prepared by reacting glycine with formaldehyde and formic acid:

$$H_2NCH_2COOH + HCHO + HCOOH \rightarrow (CH_3)_2NCH_2COOH \xrightarrow{NaOH} (CH_3)_2NCH_2COONa\ (DMGS) \qquad (1)$$

The polymerizable moiety was then prepared by reacting 11-bromoundecanol with acrylol chloride under N_2 atmosphere:

$$\begin{gathered}\mathrm{BrCH_2(CH_2)_9CH_2OH + CH_2{=}CHCOCl \rightarrow} \\ \mathrm{BrCH_2(CH_2)_9CH_2OOCCH{=}CH_2\ (BUA)}\end{gathered} \tag{2}$$

Finally, the zwitterionic surfactant AUDMAA was obtained by quaternization of the DMGS with the polymerizable alkyl bromide BUA:

$$\begin{gathered}\mathrm{BrCH_2(CH_2)_9CH_2OOCCH{=}CH_2 + (CH_3)_2NCH_2COONa \rightarrow} \\ \mathrm{CH_2{=}CHCOOCH(CH_2)_9CH_2N^+(CH_3)_2CH_2COO^-\ (AUDMAA)}\end{gathered} \tag{3}$$

The synthesis was carried out at near room temperature in order to avoid or minimize premature polymerization. The selection of mixed solvents of isopropanol and water as the reaction medium was not only to prevent the hydrolysis of the ester linkage, but also to provide a homogeneous reaction system.

The infrared spectrum of AUDMAA (Fig. 1) shows that the absorption due to the terminal vinyl group ($\mathrm{CH_2{=}CH{-}}$) appears at 3050 and 959/920 cm^{-1} for C—H stretching and C—H out-of-plane deformation, respectively. The C=C stretching is observed at 1620 cm^{-1} as a shoulder of the strong absorption at 1633 cm^{-1} due to the asymmetric stretching of the carboxylate anion ($-\mathrm{COO^-}$). The symmetric stretching appears at 1400 cm^{-1}. The absorption bands at 1710 and 1273/1196 cm^{-1} are attributed to C=O and C—O stretchings of the ester group, respectively, while C—N stretching appears at 1005 and 1063 cm^{-1}. The absorptions

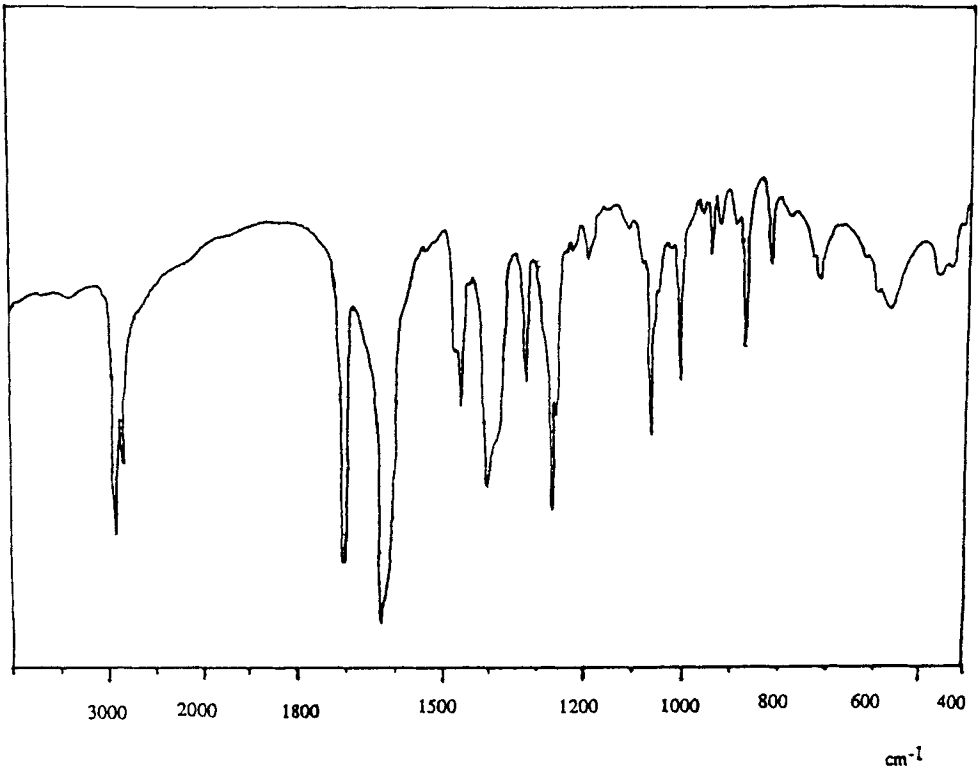

FIG. 1. Infrared spectrum of AUDMAA.

at 1479 and 1465 cm^{-1} are due to the $(CH_3)_2{-}N$ group and $-CH_2-$ scissor vibration, respectively. They are inconsistent with the reported values for saturated alkyl betaine [21].

Figure 2 shows assignments of the ^{1}H-NMR spectrum of DMGS, BUA, and AUDMAA. Three multiple peaks of vinyl protons $(CH_2{=}CH-)$ appear at 6.40, 6.10, and 5.80 ppm. The chemical shift of $(CH_3)_2)N-$ protons changes from 2.23 ppm in DMGS to 3.16 ppm in AUDMAA. The chemical shift of $N{-}CH_2{-}COO^-$ protons also changes substantially from 2.99 ppm in DMGS to 3.79 ppm in AUDMAA. The downfield shifts of these protons are clearly due to the change of the nature of N from tertiary to quaternary. A similar observation was also reported for saturated alkyl betaine surfactants [22].

The ^{13}C-NMR spectrum of AUDMAA in $CDCl_3$ and the assignment are shown in Fig. 3. The peaks of vinyl group appear at 130.52 ppm $(\underline{C}H_2{=}CH-)$ and 128.60 ppm $(CH_2{=}\underline{C}H-)$. The peaks at 167.45 and 166.34 ppm are attributed to $-\underline{C}OO^-$ and $-\underline{C}OOCH_2-$, respectively. The chemical shifts for $-N{-}\underline{C}H_2{-}COO^-$ (65.89 ppm), $-\underline{C}H_2{-}O-$ (64.83 ppm), $-\underline{C}H_2{-}N-$ (65.28 ppm), and $(\underline{C}H_3)_2N-$ (50.10 ppm) are also observed. The group of peaks at 22.82 to 29.50 ppm, which are not well resolved, corresponds to $-(CH_2)_9-$. Similar assignments have also been reported for a similar structure of cationic surfactant [23].

Solubility and CMC of AUDMAA

AUDMAA is very soluble in water, methanol, ethanol, and ethylene glycol, sparingly soluble in chloroform and DMSO, but insoluble in acetone, ether, THF, and DMF. The Krafft point of AUDMAA in an aqueous solution is 8°C.

The CMC of AUDMAA in an aqueous solution at 24°C is 9.42×10^{-3} mol/L as determined by surface tension measurements. This value is slightly higher than that of normal alkyl betaine surfactants, such as tetradecyldimethylammonio acetate (1.8×10^{-4} mol/L at 23°C) [24]. The presence of the polar ester group in the hydrophobic tail of AUDMAA may contribute to a higher CMC. However, the CMC of carboxybetaines is dependent on pH [21] as they may exist as either zwitterionic or cationic surfactants.

Based on the plot of surface tension vs ln concentration of the AUDMAA solution, the maximum surface excess concentration (Γ_2) and the area per molecule occupied at the saturated surface (σ) were calculated from Eqs. (4) and (5) [25], respectively, as follows:

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\delta\gamma}{\delta \ln C}\right)_T \tag{4}$$

$$\sigma = \frac{1}{\Gamma_2 N_A} \tag{5}$$

where C = solution concentration of the surfactant
N_A = Avagardro's number

The values obtained for Γ_2 and σ are 2.36×10^{-6} $mol{\cdot}m^{-2}$ and 7.0×10^{-19} $m^2{\cdot}molecule^{-1}$, respectively. The value of σ is larger than that ($\sigma = 6.1 \times 10^{-20}$ $m^2{\cdot}molecule^{-1}$) of a corresponding carbon chain length tetradecyltrimethylammon-

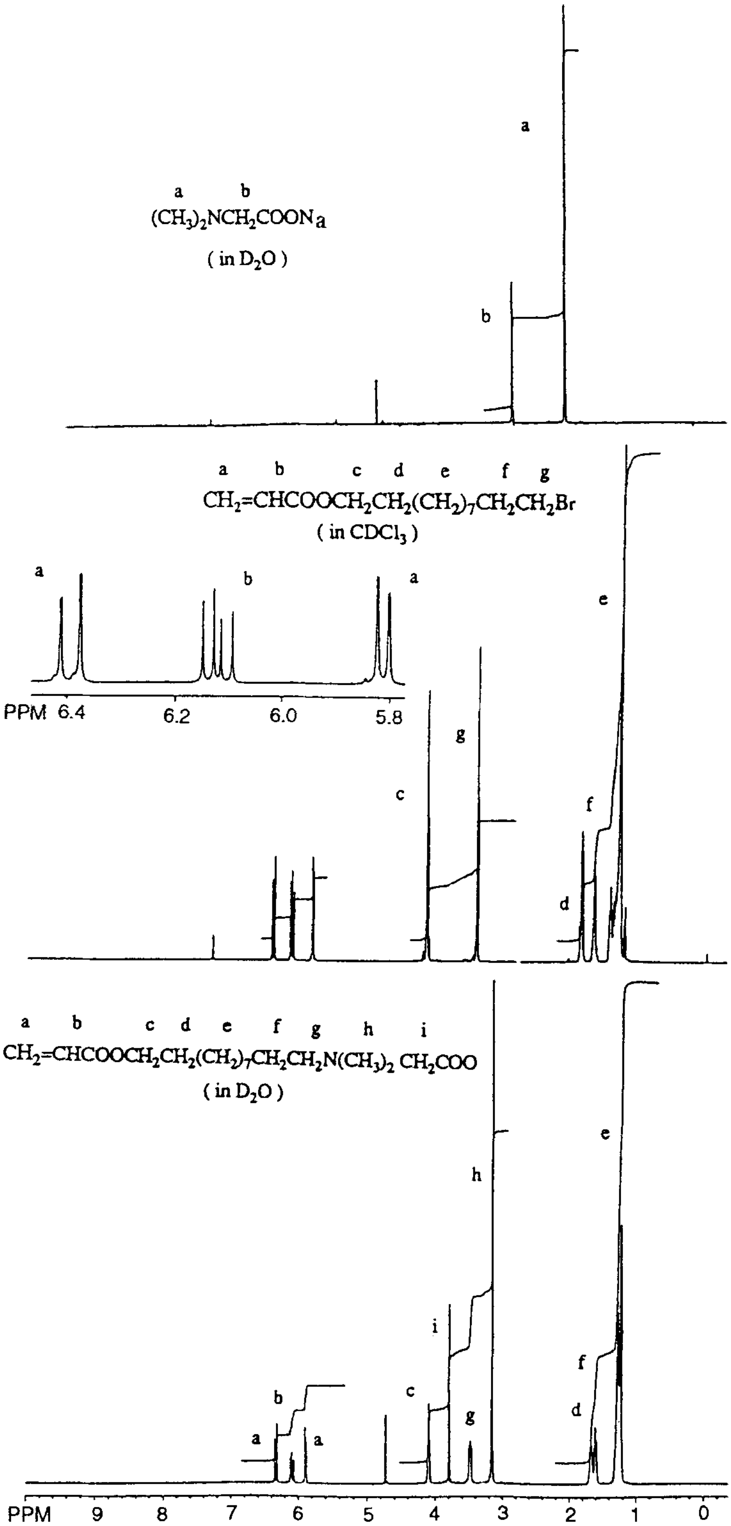

FIG. 2. ^{1}H-NMR spectra of DMGS, BUA, and AUDMAA.

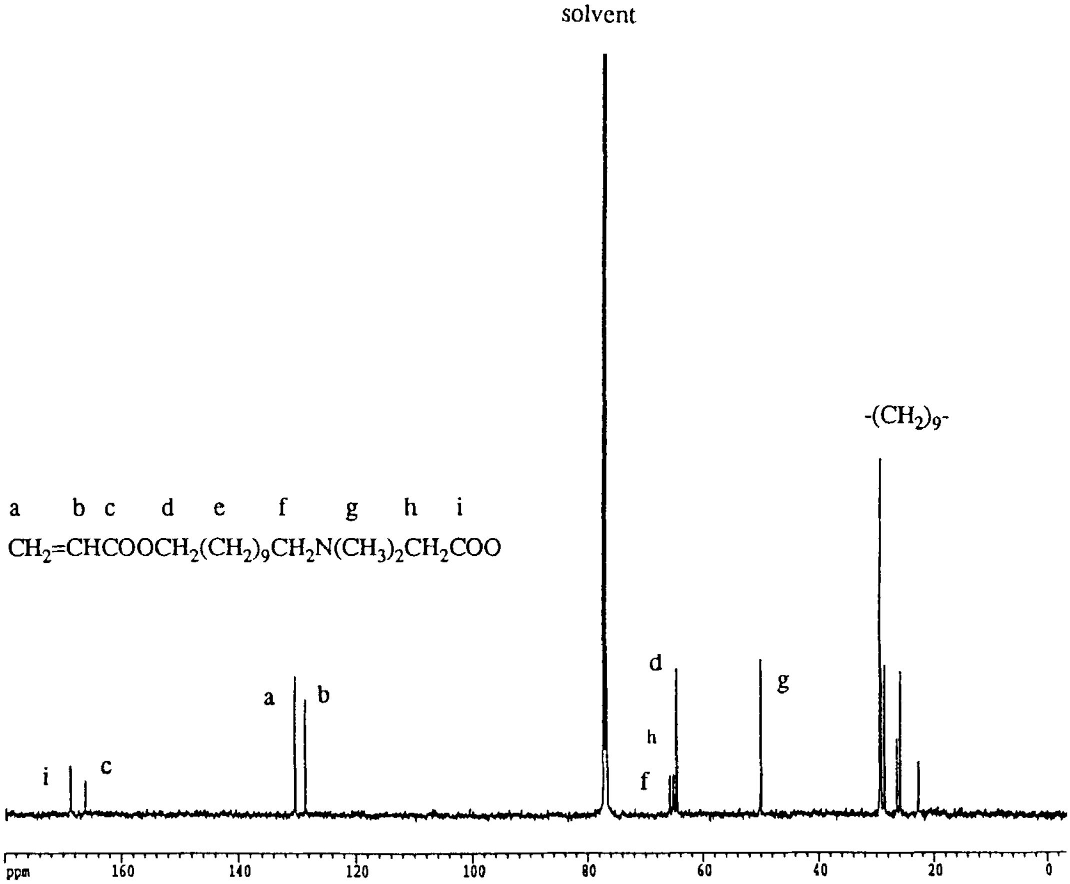

FIG. 3. ^{13}C-NMR spectrum of AUDMAA.

ium bromide [26], indicating that AUDMAA possesses a large hydrophilic head group.

Kinetics of Polymerization

All the polymerizations of AUDMAA in aqueous solutions were carried out at 50 to 60°C using monomer concentrations higher than its CMC. Potassium persulfate was used as the initiator. The polymer conversion curves are shown in Figs. 4 and 5. The polymers formed were completely soluble in the aqueous reaction medium, whose viscosity increased continuously as the polymerization proceeded. The polymerizations were very rapid, and some were even completed within 15 minutes. It is thought that the big polar heads of the zwitterionic surfactant molecules were distributed over the outer surfaces of the micelles, while their reactive acryloyl groups of AUDMAA were aggregated in the cores of micelles. The polymerization of AUDMAA via acryloyl groups in such a small micellar environment would be facilitated.

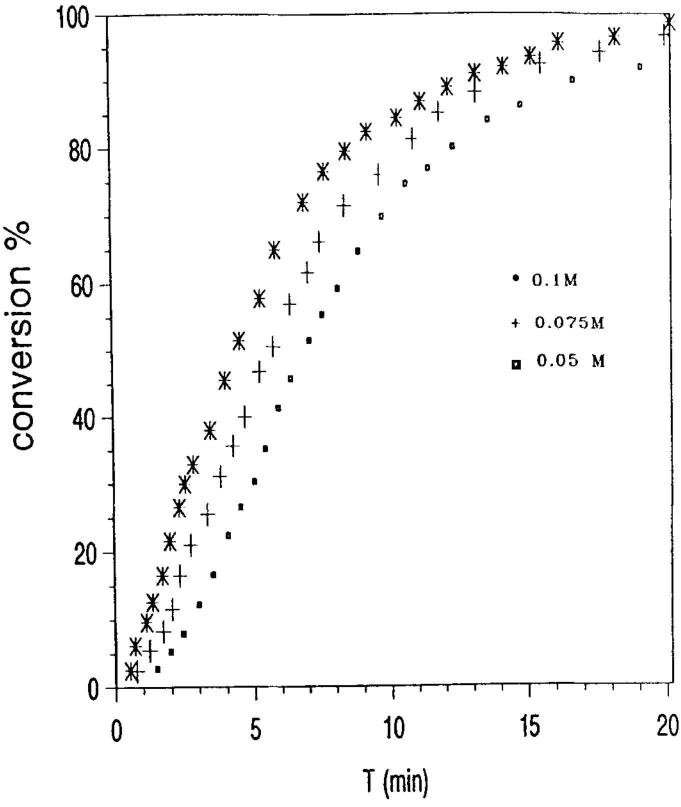

FIG. 4. Polymer conversion curves for different monomer concentrations at 0.3 mM KPS and 55°C.

The initial rates of polymerization $(R_p)_i$, were obtained from the slopes of the polymerization curves (Figs. 4 and 5) up to about 5% conversion. At this early stage of the polymerization, the concentrations of initiator and monomer may be approximated to their original concentrations. Figure 6 shows linear plots of $\log(R_p)_i$ vs $\log[I]_0$ and $\log[M]_0$. R_p is proportional to the 0.52 power of [KPS] and the 0.98 power of [AUDMAA]. These are in good agreement with the general kinetic expression for radical polymerization [27] as given by

$$R_p = k_p[M]\left\{\frac{fk_d[I]}{k_t}\right\}^{1/2} \tag{6}$$

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

Effect of Temperature of Polymerization

The polymer conversion curves for AUDMAA (0.1 M) initiated by KPS (0.3 mM) at 50, 55, and 60°C are shown in Fig. 7. The effect of temperature on the initial polymerization rate depends on the ratio of three rate constants of

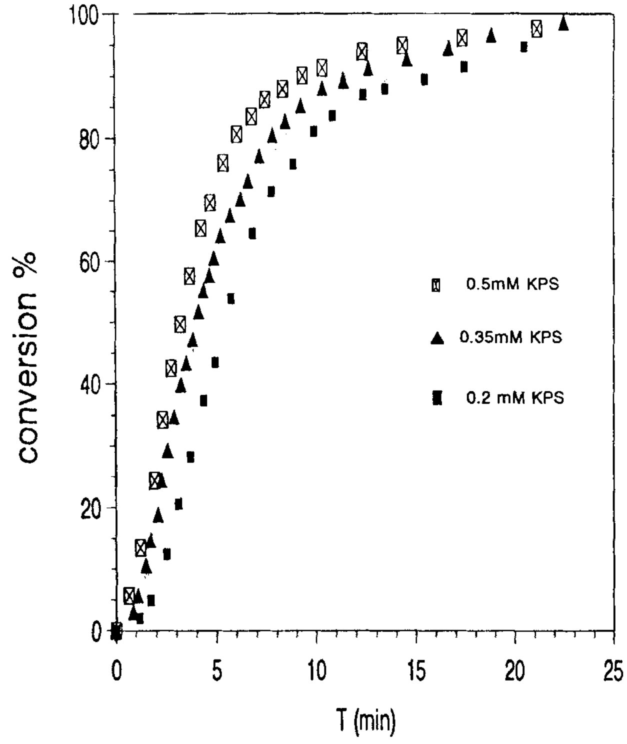

FIG. 5. Polymer conversion curves for different initiator concentrations at 0.1 M AUDMAA and 55°C.

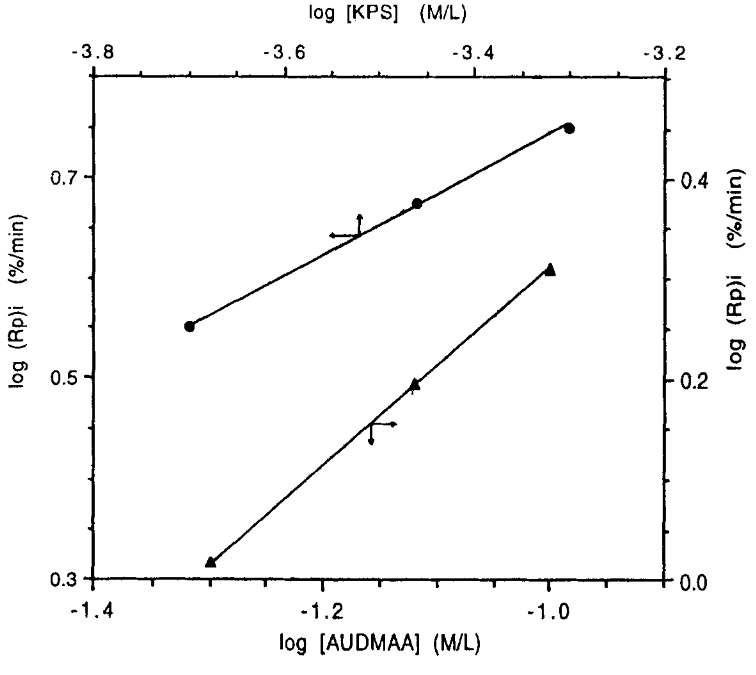

FIG. 6. Plots of initial rate of polymerization vs initial concentrations of monomer and initiator.

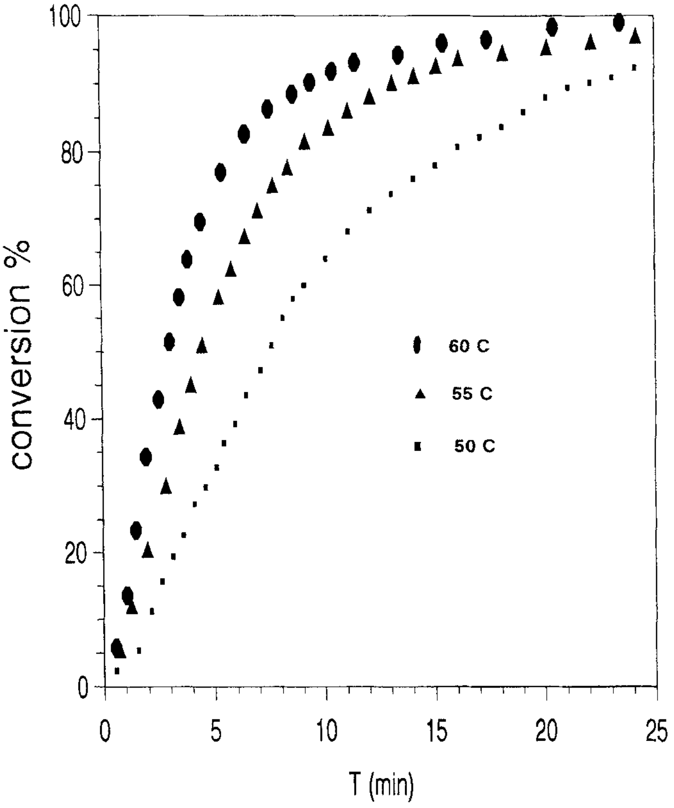

FIG. 7. The effect of temperature on polymerization at 0.1 M AUDMAA and 0.3 mM KPS.

$k_p(k_d/k_t)^{1/2}$. By relating these rate constants with three separate Arrhenius-type equations, one obtains

$$\ln(R_p)_i = \ln C - E_a/RT \tag{7}$$

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

$$E_a = E_p + E_d/2 - E_t/2$$

The initial polymerization rates $(R_p)_i$ were found to be 3.99, 5.39, and 7.29%·min^{-1} at 323, 328 and 333 K, respectively. A good linear relationship was observed for a plot of $\ln(R_p)_i$ vs $1/T$. An E_a of 50.2 kJ/mol was calculated from the gradient of the plot. This value of E_a is slightly lower than that of 63.2 kJ/mol for the polymerization of sodium acrylamidoundecanoate [9], but it is comparable to that (45.7 kJ/mol) for the polymerization of sodium 11-(*N*-ethylacrylamido)undecanoate [3]. With this low activation energy, polymerization of AUDMAA in the micellar state was very rapid, as was also observed for other micellar polymerization systems [3, 9].

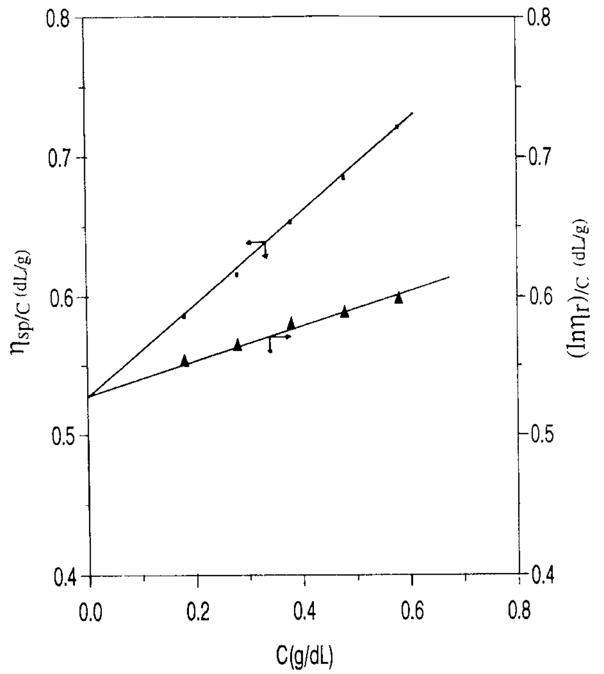

FIG. 8. Huggins and Kraemer plots of poly(AUDMAA) in aqueous solution at 27°C.

Viscosity of Poly(AUDMAA) Solution

At low concentrations of poly(AUDMAA) in aqueous solutions, their reduced viscosities η_{sp}/c and inherent viscosities $(\ln \eta_r)/c$ decreased linearly with the decrease of polymer concentrations C (g/dL) as shown in Fig. 8. This indicates that the behavior of poly(AUDMAA) in an aqueous solution is not different from that of an uncharged polymer solution.

When the polymer solution is in acidic conditions, the reduced viscosities do not change linearly with the concentration of poly(AUDMAA), as shown in Fig. 9. For poly(AUDMAA) dissolved in either 0.5 M or 0.1 M HCl solution, η_{sp}/c de- it increased with further dilution. The reversal of this phenomenon of η_{sp}/c at higher dilutions resembles the typical behavior of a polyelectrolyte solution. If this is the case, it is due to the conversion of carboxylate ion into the carboxylic acid form of poly(AUDMAA) at low pH, resulting in the formation of a typical polyelectrolyte. In addition, the effect of breaking inter- and intrasegmental interactions of polymer at low pH may also affect the viscosity.

Molecular Weights of Poly(AUDMAA)

Table 1 summarizes some of the molecular weights of poly(AUDMAA) obtained by free radical polymerization at different concentrations of monomer and KPS in the temperature range between 50 and 60°C. Although the rates of

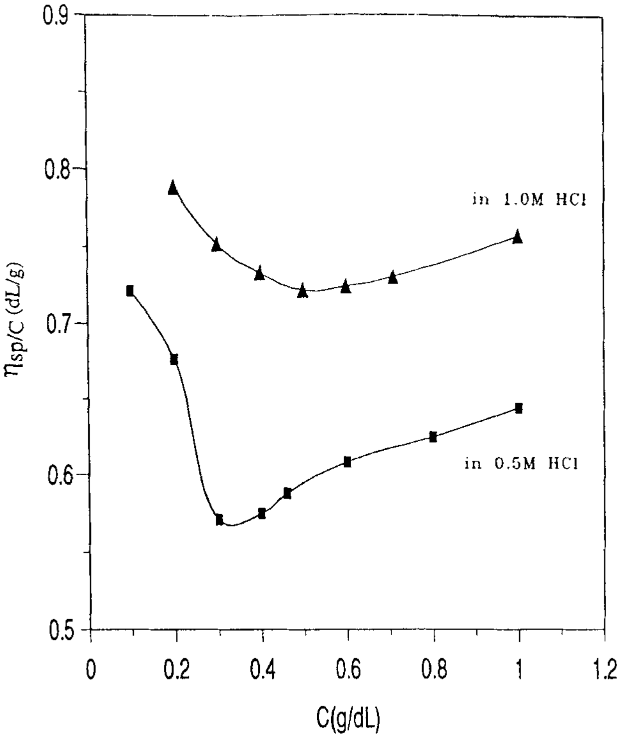

FIG. 9. The plots of reduced viscosities of poly(AUDMAA) in acidic solutions.

polymerization for all samples were relatively fast, the molecular weights of poly(AUDMAA) obtained were rather low, i.e., $\overline{M}_n = 1.7$ to 2.6×10^4. Moreover, $\overline{M}_n$ was less sensitive to the concentration change of monomer and KPS, but it decreased slightly from 2.6 to 2.1×10^4 as the polymerization temperature was raised from 50 to 60°C. The order of magnitude of these $\overline{M}_n$ values is similar to that reported [28] for another type of polymerizable zwitterionic surfactant $CH_2{=}C(CH_3)COO(CH_2)_{11}N^+(CH_3)_2(CH_2)_3SO_3^-$, i.e., $\overline{M}_n$ was about 1×10^4. It was

TABLE 1. Molecular Weights of Poly(AUDMAA)

°C	KPS, 10^{-4}	AUDMAA, M	$\overline{M}_w \times 10^4$	$\overline{M}_n \times 10^4$	$\overline{M}_w/\overline{M}_n$
55	2	0.10	3.04	1.69	1.80
55	3	0.10	3.65	1.98	1.84
55	3	0.15	3.72	2.00	1.87
55	3	0.20	3.90	2.02	1.93
50	4	0.10	4.78	2.60	1.84
55	4	0.10	4.29	2.24	1.92
60	4	0.10	3.71	2.06	1.80

calculated that the number-average degree of polymerization ($\overline{P}_n$) for poly(AUDMAA) decreased from about 80 to 60 as the temperature was increased from 50 to 60°C.

It is interesting to note that the molecular weight distributions are about the same ($\overline{M}_w/\overline{M}_n \cong 1.80$) for all samples shown in Table 1. Such a molecular weight distribution is considered to be relatively narrow for polymers prepared by a free radical mechanism. It seems to approach the theoretical value ($\overline{M}_w/\overline{M}_n = 2.0$) obtained from a linear stepwise polymerization mechanism. The fast polymerization rate of AUDMAA and the relatively narrow molecular weight distribution of poly(AUDMAA) may be characteristic for micellar polymerization where the polymerizable vinyl groups are aggregated within micelles.

It has been reported [29] that the average aggregation number (n) per micelle for alkyldimethylammonio acetates ($RN^+(CH_3)_2CH_2COO^-$) zwitterionic surfactant was about 60 to 90 where R is C_{11} and C_{13}, respectively. As for AUDMAA ($R'N^+(CH_3)_2CH_2COO^-$), R′ is $CH_2{=}CHCOO(CH_2)_{11}{-}$, which is not a normal alkyl chain (R). Hence, no strict comparison of n can be made for the two types of surfactants. However, it may be reasonable to assume that n for AUDMAA may not be too much different from the value quoted for $RN^+(CH_3)_2CH_2COO^-$. If this is the case, the values of $\overline{P}_n$ (50 to 80) for poly(AUDMAA) may be viewed to be closely related to n for AUDMAA before polymerization. This implies that each poly(AUDMAA) chain might be formed mainly within a micelle. In other words, it is envisaged that the micellar aggregation of AUDMAA might remain about the same before and after polymerization. This is quite likely because AUDMAA molecules consist of both positively and negatively charged groups. Besides intra-interactions, the charged groups might also interact with neighboring molecules through coulombic forces in close proximity within a micelle.

CONCLUSION

A new polymerizable zwitterionic betaine surfactant of acryloylundecyldimethylammonio acetate was synthesized in mild conditions and polymerized under micellar conditions. The polymerization of AUDMAA initiated by $K_2S_2O_8$ was very fast in aqueous solution with an activation energy of only 50.2 kJ/mol. It follows first-order kinetics with respect to [AUDMAA] and one-half order with respect to $K_2S_2O_8$. The $\overline{M}_w$ of poly(AUDMAA) was of the order of 10^4 and its MWD was rather narrow (<2.0). The results suggest that the organized structures of the micellar monomers in aqueous solution are responsible for fast polymerization and the narrow distribution of $\overline{M}_w$ of poly(AUDMAA). The viscosity of a dilute solution of poly(AUDMAA) at low pH resembles that of a polyelectrolyte solution.

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