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SYNTHESIS AND POLYMERIZATION OF SURFACE-ACTIVE SODIUM ACRYLAMIDOUNDECANOATE

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ABSTRACT

The polymerizable surfactant sodium 11-acrylamidoundecanoate (Na 11-AAU) was synthesized from acryloyl chloride and 11-aminoundecanoic acid. It had a low critical micelle concentration (CMC) of 4.3 X 10^{-4} mol/L. Polymerization of Na 11-AAU initiated by $K_2S_2O_8$ was very fast in aqueous solution, with an activation energy of only 63.2 kJ/mol. The polymerization followed first-order kinetics with respect to Na 11-AAU and one-half order with respect to $K_2S_2O_8$. The MW of poly(Na 11-AAU) was very high (1-2 million) but the MWD was rather narrow ($\bar{M}_w/\bar{M}_n$ = 1.45). Polymerization of Na 11-AAU in the micellar state may be responsible for the phenomena observed.

INTRODUCTION

Most commercially available surface-active monomers, such as sulfoethyl methacrylate, 2-acrylamido-2-methylpropane sulfonate, and styrene sulfonate, are of relatively low molecular weights. They are water soluble and only weakly surface active.

Some strongly surface-active polymerizable monomers, e.g., 10-*p*-styryl undecanoate, 9-acrylamido stearate, sodium sulfodecylstyryl ether, and styryloxyldecyltrimethylammonium bromide, have also been reported [1]. These monomers serve as stabilizers when only physically adsorbed on the particle surface, but they can be fixed on the particle surface by polymerization. This will eliminate the problems associated with adsorption/desorption which always occur in the use of conventional surfactants. Polymerization of sodium 9- (and 10-) acrylamido stearate (NaAAS) [2] adsorbed on the surfaces of a relatively unstable styrene/butadiene (60/40) copolymer latex resulted in better mechanical stability than that given by an equivalent amount of adsorbed monomeric NaAAS. This is because the charges are immobilized on the latex surface, and desorption is highly improbable.

Monolayers of vinyl stearate have been polymerized at the gas-water interface at a constant surface pressure by UV radiation [3]. The *in-situ* polymerized samples exhibited the highest compressional moduli and the lowest area per molecule. This reflects the improved packing order of the *in-situ* polymerized film.

Micellization of cationic salts of dimethylaminoethyl methacrylate quarternized with *n*-alkylbromides has also been investigated. Radical polymerizations of these monomers proceeded at a fast rate [4].

Polymerization of styrene with the surface-active comonomer undecylenic isethionate sodium salt below its CMC suggests a homogeneous nucleation mechanism [5]. Addition of salt to increase the ionic strength in the aqueous phase results in the formation of micelles which can grow to become polymer particles. The size distribution of these particles is extremely narrow. Emulsion polymerization with a polymerizable surfactant provides no emulsifier migration during film formation, excellent shear stability, and a monodisperse particle size distribution [6].

The aim of this research is to synthesize a series of surface-active monomers of acrylamidoalkanoates. This first paper deals only with sodium acrylamidoundecanoate in aqueous media. Polymerization of the related monomers in emulsion and microemulsion [7] will be reported in the future. The polymer obtained from the present investigation is one of the ionomers that have received considerable attention in recent years, as evidenced by numerous papers and several monographs [8-10].

EXPERIMENTAL

Materials

Acryloyl chloride and 11-aminoundecanoic acid from Aldrich and methanol of chromatography grade (Merck) were used as received. Superdry ethanol was prepared by treating absolute ethanol with magnesium/iodine and then distilling it. Potassium persulfate (Reachim) was recrystallized from water. Water was double distilled.

Synthesis of 11-Acrylamidoundecanoic Acid (11-AAUA) and Its Sodium Salt (Na 11-AAU)

11-Aminoundecanoic acid (10 g, 0.05 mol) was added to a 500-mL round-bottom flask containing 250 mL of 95% ethanol, 25 mL water, and 6 g (0.15 mol) NaOH. Acryloyl chloride (6 mL, 0.072 mol) was subsequently added dropwise from a separatory funnel. The reaction mixture was stirred for 1 h at 30°C and then filtered. The filtrate was acidified with dilute HCl. A white precipitate of 11-AAUA was formed when 4 L water was added. It was filtered and thoroughly washed with distilled water until the washings were free of acid. The crude 11-AAUA was repeatedly recrystallized from aqueous ethanol.

Na 11-AAU was prepared by reacting 1.6 g (0.04 mol) of NaOH with 10 g (0.04 mol) of pure 11-AAUA which was first dissolved in 500 mL superdry ethanol contained in a 1-L round-bottom flask. The reaction mixture was stirred for 24 h at room temperature before it was concentrated in a rotary evaporator. Crude Na 11-AAU was repeatedly recrystallized from superdry ethanol at 0°C.

Analysis. Calculated for $C_{14}H_{25}O_3N$: C, 65.89; H, 9.80; N, 5.49%. Found: C, 65.99; H, 9.89; N, 5.50%; mp 79.0-80.5°C. Calculated for $NaC_{14}H_{24}O_3N$: C, 60.15; H, 8.66; N, 5.05%. Found: C, 59.92; H, 8.78; N, 5.15%; mp 204-208°C.

Determination of CMC of Na 11-AAU

The CMC of Na 11-AAU was determined by surface tension measurements with a torsion balance tensiometer (White Electric Instrument Co.). The concentration at the break point of the surface tension versus concentration curve is the CMC.

Polymerization of Na 11-AAU

An aqueous solution of Na 11-AAU was purged by nitrogen before it was polymerized at 50°C with potassium persulfate initiator. The polymerization was conducted in a dilatometer which was thermostated in a 50 ± 0.1°C water bath. The open end of the dilatometer was connected to an Atmosbag under a nitrogen atmosphere. The volume contraction of the polymer solution in the dilatometer during polymerization was monitored with a cathetometer, and the monomer conversion was calculated from it. After the polymerization was complete, as evidenced by the unchanging volume in the dilatometer, the polymer was precipitated in an excess of acetone containing a small amount of benzoquinone. The precipitated polymer was filtered and washed several times with methanol.

Viscosity Measurements

The reduced viscosities of polymer solutions were measured with an Ubbelohde dilution capillary viscometer (Kapenekas Laboratory Services, Akron, Ohio) thermostated in a water bath at 28 ± 0.1°C. Aqueous polymer solutions of different ionic strengths were used. The intrinsic viscosity $[\eta]_0$ was obtained by extrapolation of both the reduced viscosity (η_{sp}/c) and inherent viscosity ($\ln \eta_r/c$) to infinite dilution according to the Huggins [11]

$$\eta_{sp}/c = [\eta]_0 + k[\eta]_0^2 c$$

and Kraemer equations [12]

$$\ln \eta_r/c = [\eta]_0 + \beta[\eta]_0^2 c,$$

where k is the Huggins constant and β is the Kraemer constant.

Spectroscopic Measurements

Infrared (IR) spectra were recorded by a Perkin-Elmer 1310 spectrophotometer using KBr pellets. The proton NMR spectra were obtained in $CDCl_3$ or D_2O by a Jeol FX90Q Fourier-transform NMR spectrometer.

Molecular Weight Determination by GPC

An aqueous solution of poly(Na 11-AAU) was acidified with dilute HCl. The precipitate of poly(11-AAUA) in its acid form was filtered, followed by successive washings with water, and dried in vacuum for 24 h at 30°C. Elemental analysis confirmed that the poly(Na 11-AAU) was fully converted to poly(11-AAUA). After dissolving the poly(11-AAUA) in reagent-grade dimethylformamide (DMF), the polymer solution was filtered through a 0.5-μm filter.

The gel-permeation chromatography (GPC) measurements were performed on a Varian Vista 5500 liquid-chromatography system equipped with a RI-3 detector. A PL-gel 5-μ mix column (Polymer Loboratories) was used. The polymer solution (50 μL at a concentration of 0.5 g/L) was injected into the GPC column. The elution solvent DMF flowed at 0.3 mL/min. A calibration curve was obtained by use of polystyrene standards supplied by Polysciences Inc.

RESULTS AND DISCUSSION

Synthesis and Characterization of Na 11-AAU

Allyl compounds are traditionally considered poor monomers for free-radical polymerization because of their tendency to undergo active chain-transfer reactions [13, 14] although polymerization may occur in special cases. For example, ω-tricosenoic acid and its calcium salt have been polymerized in multilayers by means of low-energy electron beams [15], indicating that unsaturated fatty acid soaps with allylic hydrogens can be polymerized in organized systems. However, in order to avoid active chain-transfer reactions, the allylic hydrogens of unsaturated fatty acid soaps are normally eliminated through some structural modifications so that they can easily be polymerized.

Oleic acid and undecenoic acid were modified by reacting them with acrylonitrile in concentrated sulfuric acid, followed by neutralization. Such modified soaps inevitably consist of the isomer mixtures of 9- (and 10-) acrylamidostearate [7] and 10- (and 11-) acrylamidoundecanoate [16], respectively. Moreover, these modified fatty acid isomers are not only prone to prepolymerization in the strong acidic reaction medium but also difficult to separate in good yield.

The present method for synthesizing straight-chain Na 11-AAU is a modification of that reported for preparing *N*-lauroylsarcosine [17]. About 80% of 11-acrylamidoundecanoic acid (11-AAUA) could be obtained from the direct reaction of acryloyl chloride with 11-aminoudecanoic acid in an alkaline medium, i.e.,

$$\mathrm{CH_2{=}CHCOCl + H_2N(CH_2)_{10}COOH \longrightarrow CH_2{=}CHCONH(CH_2)_{10}COOH.}$$

$$\text{(11-AAUA)}$$

The elemental analyses for 11-AAUA and Na 11-AAU were in good agreement with the calculated values. However, 11-AAUA melted at 79-80.5°C, which differs from the reported value (107-108.5°C) [16]. The new evidence from IR, ^{1}H-NMR, and mass spectra confirmed that the previously reported AAUA

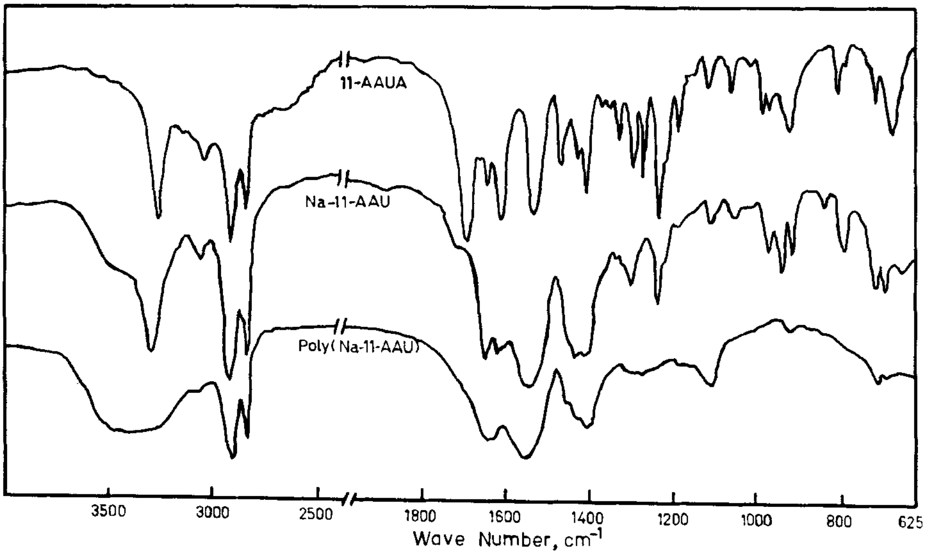

FIG. 1. Infrared spectra of 11-AAUA, Na 11-AAU, and poly(Na 11-AAU).

[16, 18] was actually 10-AAUA rather than 11-AAUA isomer. The present method of synthesis produces only 11-AAUA.

The infrared spectra in Fig. 1 show that the absorption due to terminal vinyl groups ($CH_2{=}CH{-}$) appear at 3050, 1650, and 990/920 cm^{-1} for C–H, C=C stretching, and C–H out-of-plane deformation, respectively. These spectra are similar to those reported earlier, except that the previous ones [16] showed a splitting at 2930 cm^{-1} and an extra band at 2970 cm^{-1} due to the methyl group from the isomer 10-AAUA. The presence of an amide group (–CONH–) is evidenced by C=O stretching at 1620 cm^{-1} (amide I band) and N–H bending at 1533-1550 cm^{-1} (amide II band). The broad absorption bands at 2500-2800 and 1700 cm^{-1} are attributed to the carboxylic acid group (–COOH).

The ^{1}H-NMR spectra in Fig. 2 reveal the multiple peaks of vinyl protons ($CH_2{=}CH{-}$) at δ6.20 and δ5.60. The –CONH and –COOH protons of 11-AAUA, which are exchangeable with D_2O, appear at δ5.93 and δ10.10, respectively. The peak at δ0.90 next to the large peak of the $-(CH_2)_8-$ group and the multiple peaks at δ3.95, which appeared in the previously reported spectrum [16], were not observed. They can be attributed to the

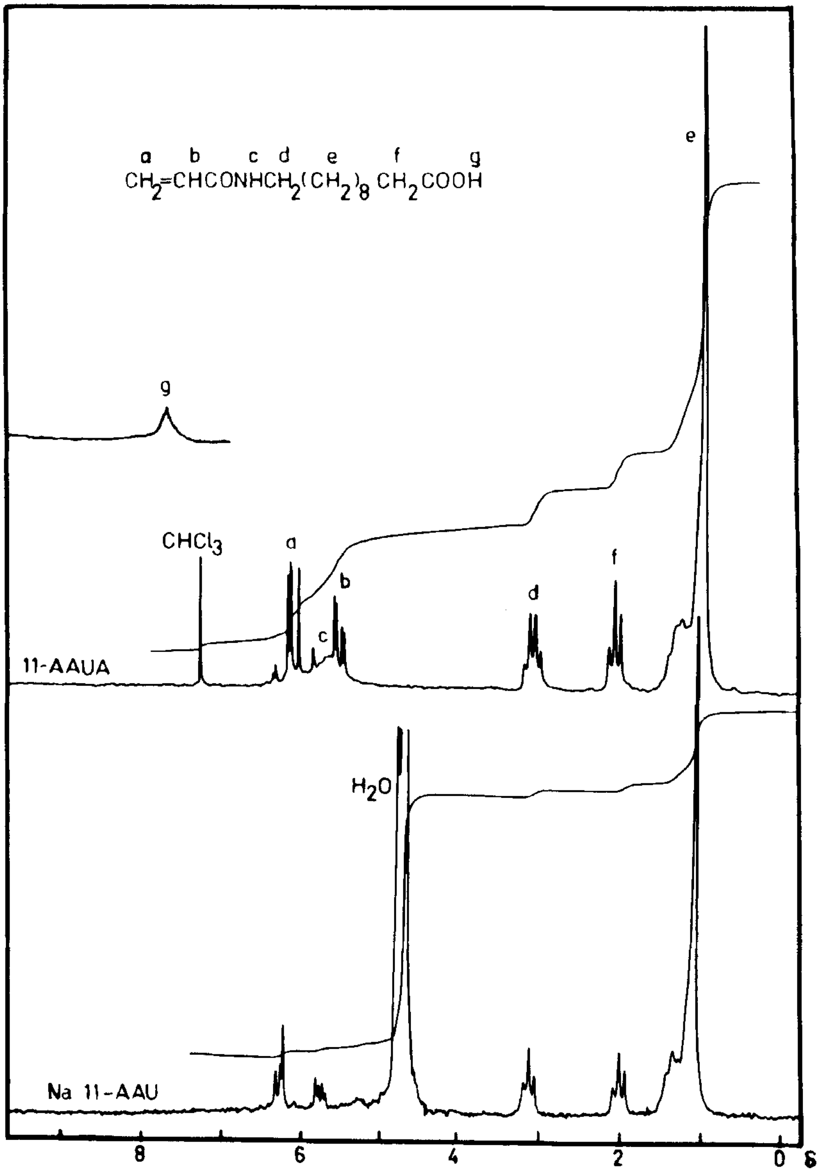

FIG. 2. Proton NMR spectra of 11-AAUA and Na 11-AAU.

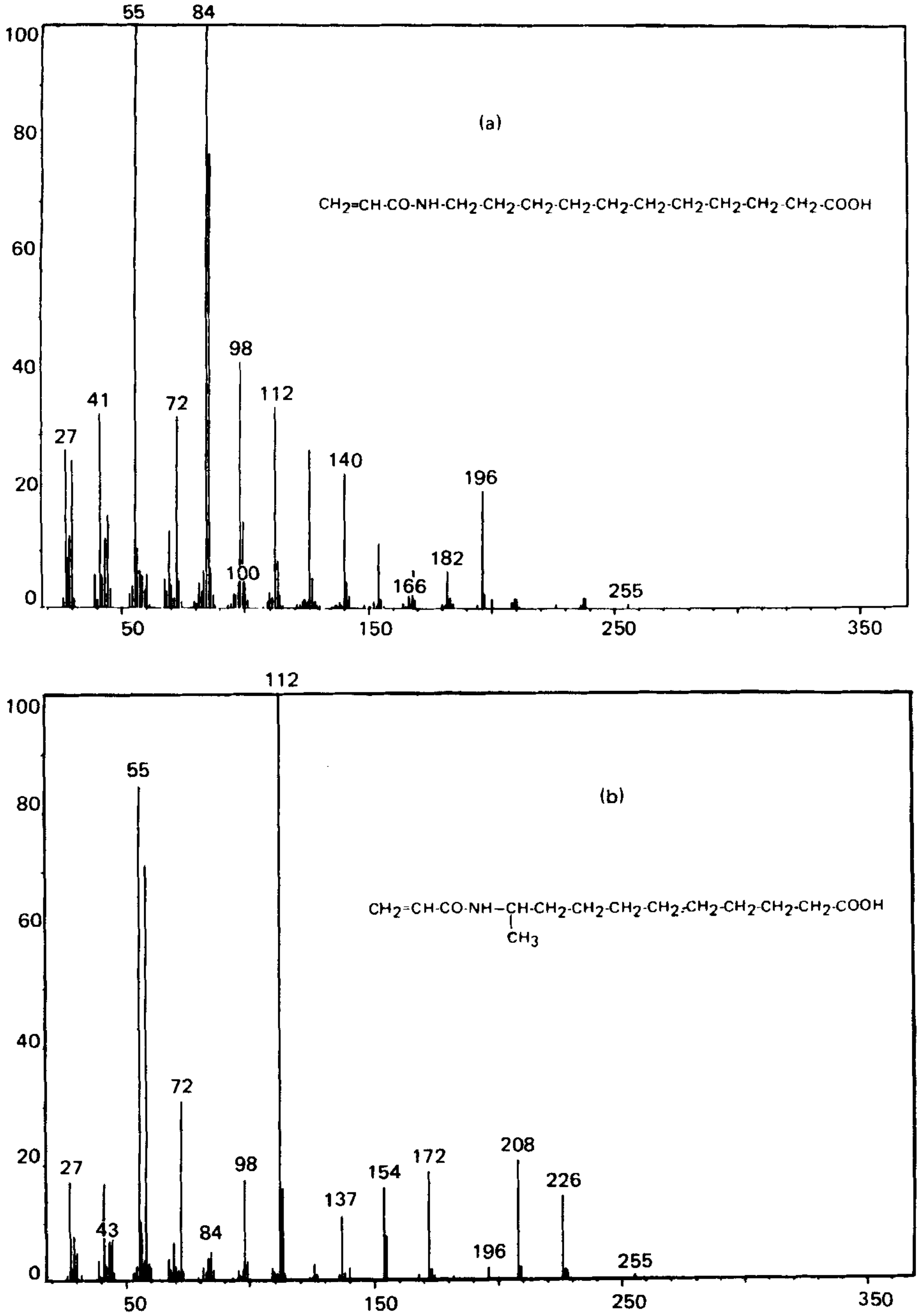

FIG. 3. Mass spectra of 11-AAUA (a) and 10-AAUA (b).

pending CH_3 protons and the methine proton of the $-NHCHCH_3$ group, respectively, of the isomer 10-AAUA.

The mass spectra of the two isomers are shown in Fig. 3. The base peaks at m/e 84 and 55 in Fig. 3(a) are due to the ion fragments $[CH_2{=}CHCONHCH_2]^+$ and $[CH_2{=}CH{-}CO]^+$, whereas the base peak in Fig. 3(b) is at m/e 112, which corresponds to the ion fragment $[CH_2{=}CH{-}CONH{=}C(CH_3)_2]^+$ arising from the cleavage of the *N*-alkyl group beta to the *N*-atom with carbocation rearrangement. From the fragmentation pattern, one can conclude that Figs. 3(a) and 3(b) are due to 11-AAUA and 10-AAUA, respectively.

Solubility of Na 11-AAU

The CMC of Na 11-AAU was 4.3×10^{-4} mol/L (0.12 g/L) as determined by surface tension measurements. This value is much smaller than those reported for the majority of fatty acid soaps.

Na 11-AAU is insoluble in most of the solvents tested, including acetonitrile and dimethylsulfoxide. It is only slightly soluble in formamide, dimethylformamide, ethanol, and ethylene glycol. Its solubilities in *n*-butyl acetate and methanol at 30°C are about 2 and 14%, respectively. Water is by far the best solvent, with a solubility of 25.5 wt% Na 11-AAU at 30°C, which can be increased further by adding a small amount of short-chain alcohol to the water. Figure 4 shows how the solubility is increased to 38% in 5% aqueous methanol or ethanol solutions and to 43% in 5% propanol solution. These solubilities remain unchanged even when the concentrations of the alcohols are further increased to about 40%, beyond which they begin to decrease. *n*-Butanol and *n*-pentanol had an effect similar to that of *n*-propanol.

The effect of alcohols on the solubility of Na 11-AAU in aqueous solution may be explained by the partial solubilization of the alcohol by micelles. It is known that the CMC is decreased by the addition of short-chain alcohols to ionic surfactant micellar solutions. The alcohol molecules can be intercalated between the ionic head groups of the surfactants. This not only increases the average distance between the charged head groups but also reduces the surface charge density of the micelle [19]. Solubilization of the surfactant may thus be favored in this stabilized system. On the other hand, alcohols of longer chain lengths may also be present in the hydrophobic core of the micelles in addition to that in the micelle palisade layer [20]. This could be why Na 11-AAU is more soluble in aqueous solutions of propanol, butanol, or pentanol than those of methanol or ethanol.

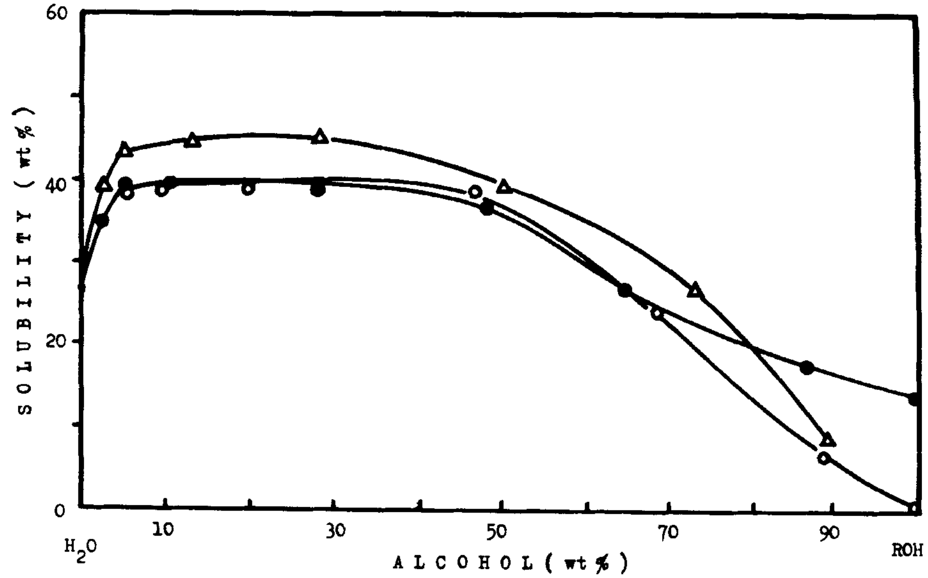

FIG. 4. Solubility of Na 11-AAU in the aqueous alcoholic solutions. (△) Propanol, (○) ethanol, (●) methanol.

Polymerization

The polymer conversion curves are shown in Figs. 5 and 6. The polymers formed were completely soluble in the aqueous reaction medium, whose viscosity increased continuously as the polymerization proceeded. The polymerizations were very rapid, as observed in the other surfactant system [4]. Some of the polymerizations were completed within 15 min. This suggests that the surface-active Na 11-AAU was very reactive in the micellar aggregates. It is conceivable that the polar heads of the anionic surfactant molecules were distributed over the outer surfaces of the micelles, while their acrylol groups were aggregated in the cores of the micelles. The close proximity of these reactive acrylol groups would thus accelerate the polymerization.

The rate of polymerization (R_p) is normally expressed as the rate of decrease of monomer concentration (mol/(L•s)). If one is not concerned with the absolute value of the reaction rate constant, R_p can also be expressed in terms of the rate of polymer conversion (%/min), which we use here for establishing the orders of reaction with respect to initiator and monomer. The

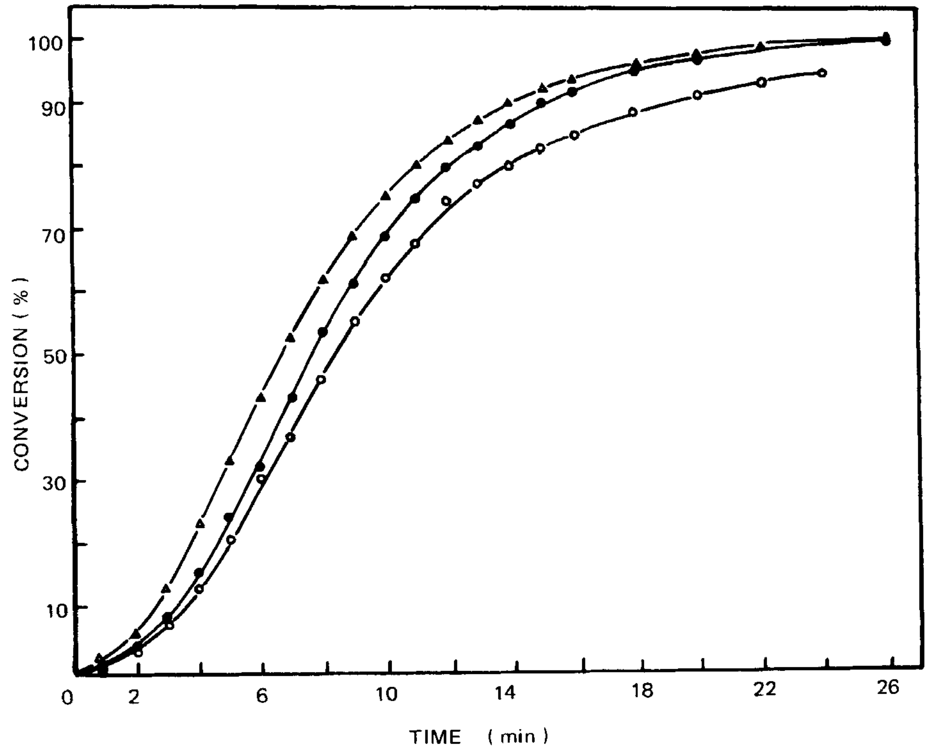

FIG. 5. Polymer conversion curves for different monomer concentrations. [Na 11-AAU]: (△) 0.20, (●) 0.15, (○) 0.10 mol/L. [$K_2S_2O_8$]: 2 mmol/L. Temperature: 50°C.

initial rates of polymerization $(R_p)_i$ were obtained from the slopes of the polymerization curves (Figs. 5 and 6) up to about 5% conversion. At this early stage of the polymerization, the concentrations of initiator and monomer can be approximated to their initial values, $[\mathrm{I}]_0$ and $[\mathrm{M}]_0$. Figure 7 shows that linear plots were obtained of log $(R_p)_i$ vs log $[\mathrm{I}]_0$ and log $[\mathrm{M}]_0$ with slopes of 0.54 and 0.99, i.e., R_p is proportional to the 0.54 power of [$K_2S_2O_8$] and 0.99 power of [Na 11-AAU]. These are in good agreement with general kinetic expression for radical polymerization, as given by [21]

$$R_p = k_p[\mathrm{M}]\left\{\frac{fk_d[\mathrm{I}]}{k_t}\right\}^{1/2}, \qquad (1)$$

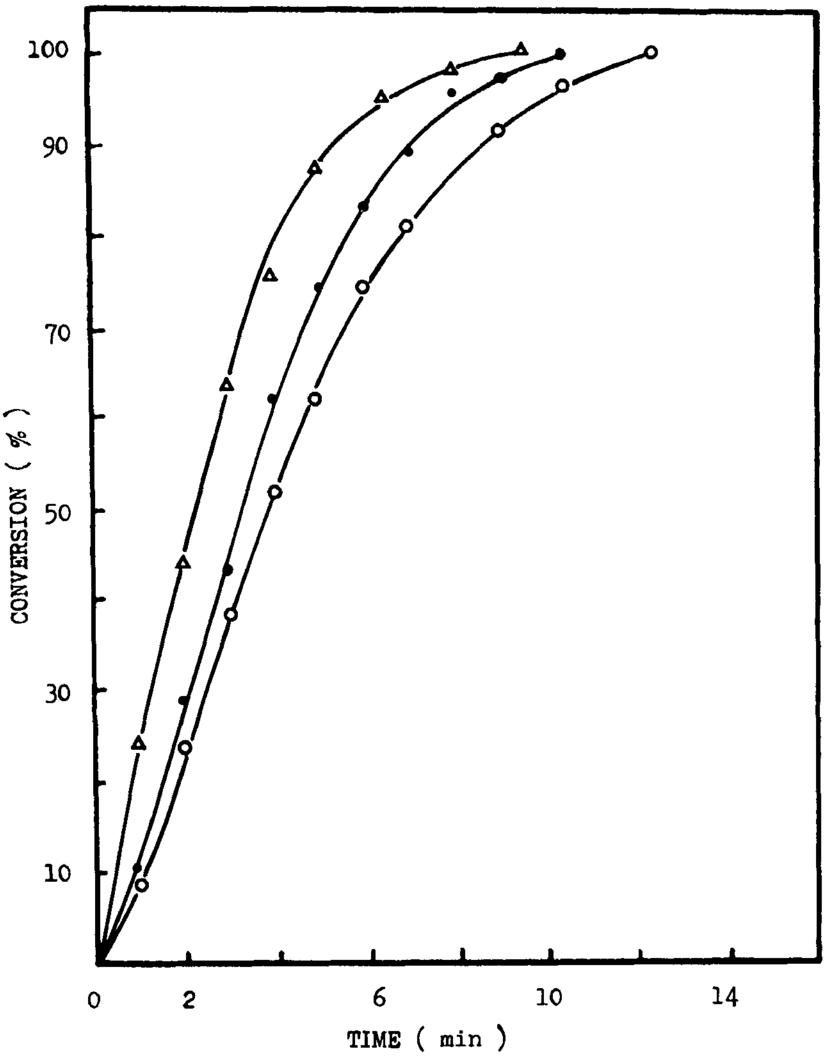

FIG. 6. Polymer conversion curves for different initiator concentrations. [Na 11-AAU] : 0.3 mol/L. $[K_2S_2O_8]$: (△) 4.0, (●) 3.0, (○) 2.0 mmol/L. Temperature: 50°C.

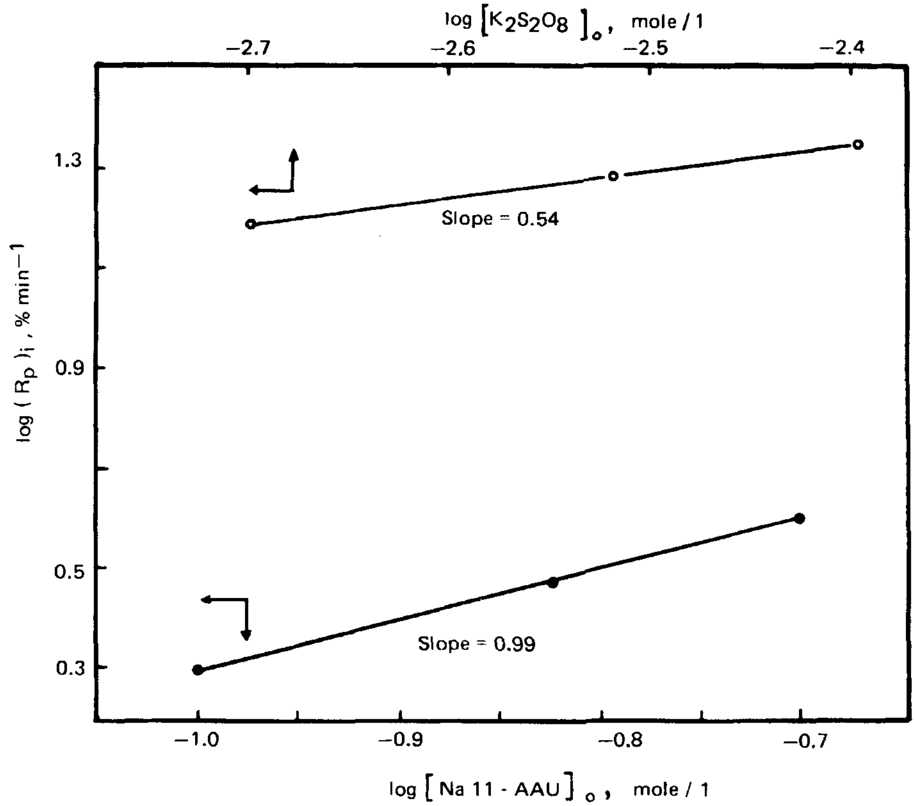

FIG. 7. Logarithmic plots of initial rate of polymerization versus the initial concentrations of monomer and initiator.

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

Polymerizations of Na 11-AAU (0.2 mol/L) initiated by $K_2S_2O_8$ (2 mM/L) were carried out at 50, 55, and 60°C. They were faster at higher temperature, as expected (Fig. 8). The effect of temperature on the polymerization rate depends on the ratio of three rate constants of $k_p(k_d/k_t)^{1/2}$. Relating these rate

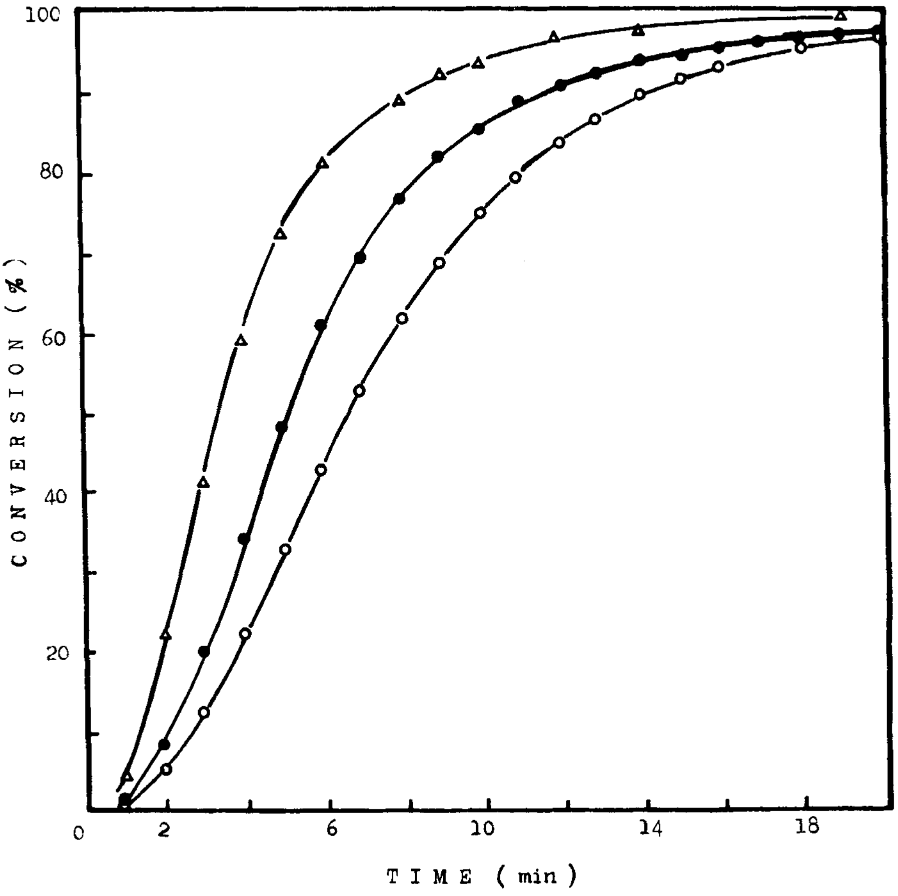

FIG. 8. Polymer conversion curves at different temperatures: (△) 60°C, (●) 55°C, (○) 50°C. [Na 11-AAU]$_0$: 0.2 mol/L. [$K_2S_2O_8$]: 2.0 mmol/L.

constants with three separate Arrhenius-type equations, in accordance with Eq. (1), one obtains

$$\ln (R_p)_i = \ln C - E_a/RT, \tag{2}$$

where C is proportional to $(f[I])^{1/2}$ $[M]_0$, and

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

$(R_p)_i$ is the initial polymerization rate (%/min) obtainable from Fig. 8, and E_a is the overall activation energy for polymerization. The straight-line plot in Fig. 9 gives an E_a of 63.2 kJ/mol, which is lower than the 80-90 kJ/mol for most of the polymerizations initiated by thermal decomposition of initiators.

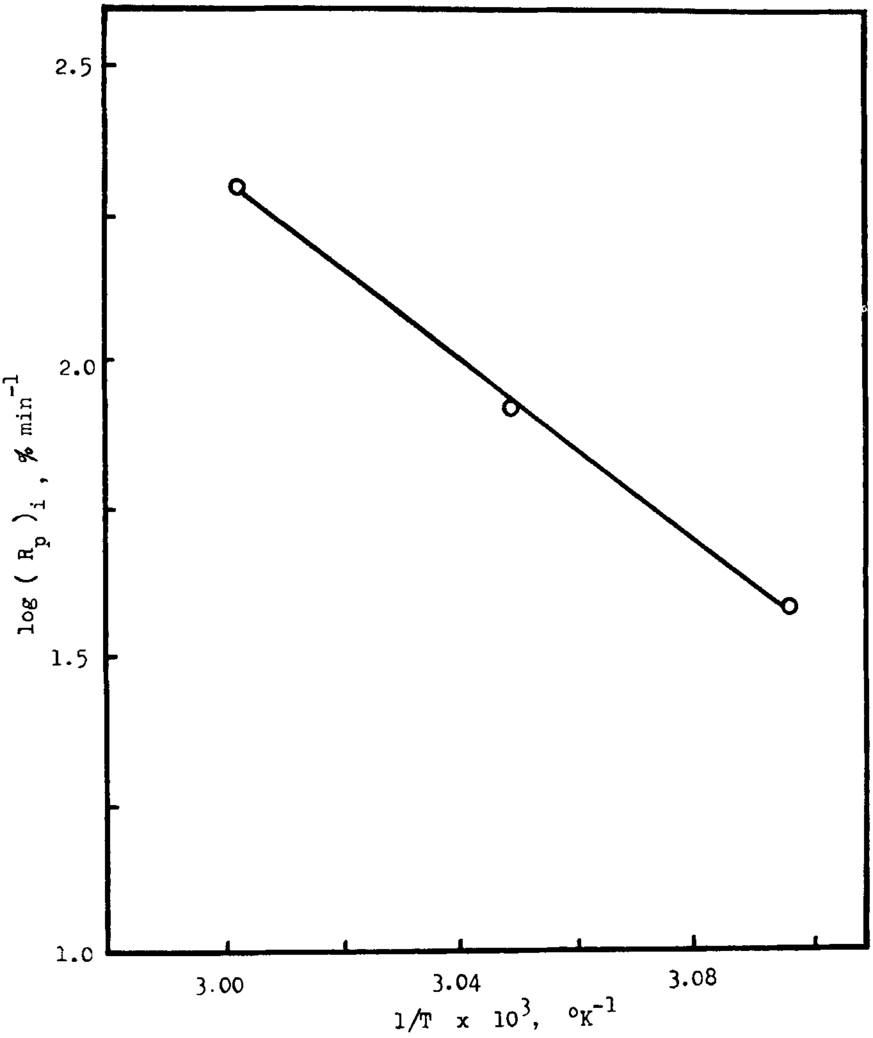

FIG. 9. Dependence of the initial rate of polymerization on temperature. [Na 11-AAU]; 0.2 mol/L. [$K_2S_2O_8$]: 2.0 mmol/L.

Viscosity

Poly(Na 11-AAU) is readily soluble in water. The clear polymer solution at about 18% became very viscous (gel-like). However, the reduced viscosity underwent a marked increase with dilution at low polymer concentration. This effect is related to ionization of ionic groups of the polymer and is typical for most polyelectrolytes [22]. Because of the electrostatic repulsion between its charged groups in dilute polymer solution, poly(Na 11-AAU) expands its hydrodynamic volume, causing the increase in viscosity. The viscosity of dilute polyelectrolyte solution is interrelated with hydrodynamic volume, counterion concentration, and site binding of the polyelectrolyte molecules [23]. Addition of sodium chloride to dilute poly(Na 11-AAU) solution lowers the reduced viscosity markedly. Figure 10 shows the effect

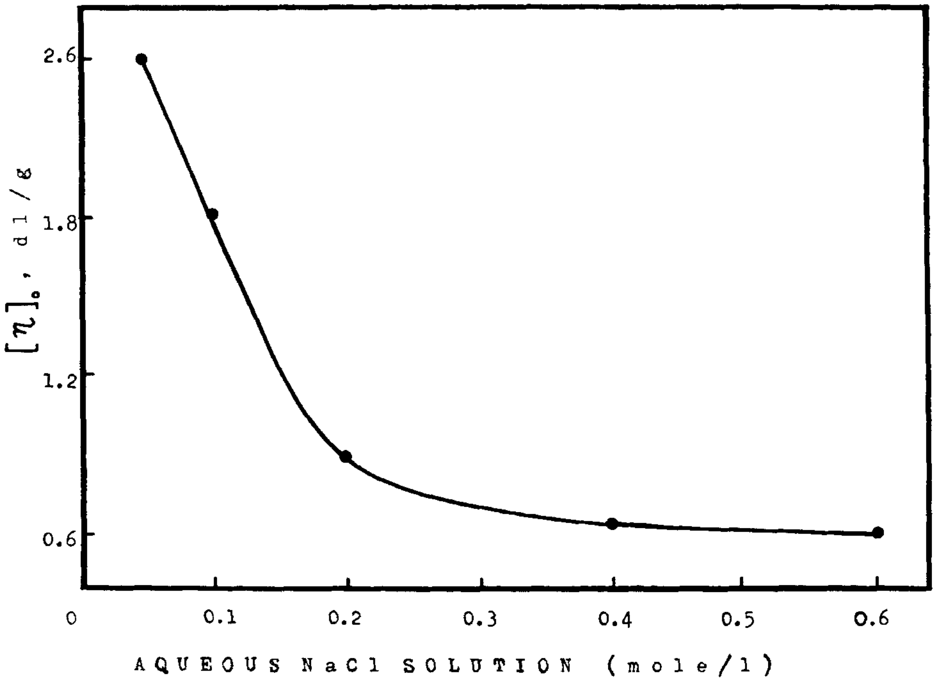

FIG. 10. Effect of sodium chloride on the intrinsic viscosity at 28°C of poly(Na 11-AAU) prepared from 0.3 mol/L Na 11-AAU and 4.0 mmol/L $K_2S_2O_8$ at 50°C.

TABLE 1. Molecular Weights of Poly(11-AAUA)[a]

Polymer	Polymerization temperature, °C	Polymerization time, min	$\bar{M}_w \times 10^{-6}$	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
p-50	50	22	1.6	1.1	1.45
p-60	60	14	1.2	0.8	1.50

[a] Na 11-AAU (0.2 mol/L) and $K_2S_2O_8$ (2 mmol/L).

of sodium chloride on the intrinsic viscosity. The polyelectrolyte effect vanished when the sodium chloride concentration exceeded 0.4 mol/L.

Molecular Weights

The molecular weight of poly(Na 11-AAU) could not be successfully determined directly by GPC because no suitable column was available for this water-soluble polyelectrolyte due to extensive adsorption. Thus poly(Na 11-AAU) was converted to its acid form poly(11-AAU) which is soluble in DMF.

Table 1 shows that the molecular weights of poly(11-AAUA) were very high, i.e., Na 11-AAU could be easily polymerized to $\bar{M}_w$ 1.6 × 10^6 at 50°C. At 60°C, $\bar{M}_w$ decreased to 1.2 × 10^6. This is consistent with the general kinetics of radical polymerization. However, their molecular weight distributions are rather narrow ($\bar{M}_w/\bar{M}_n$ 1.45) for a radical polymerization system. This value might not be surprising in some radical polymerization systems since it depends on the mode of termination, but in our system the polymerizations were carried out in aqueous micellar solutions. Therefore, the narrow molecular weight distributions may be related to the polymerization of Na 11-AAU in a state of aggregation (micelles). More work on this aspect is in progress, and the polymerization mechanism will be discussed in another paper.

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