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MICELLAR POLYMERIZATION OF SODIUM 11-(*N*-ETHYLACRYLAMIDO)UNDECANOATE: KINETICS AND SOLUTION PROPERTIES

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ABSTRACT

Polymerizations of micelle-forming sodium 11-(*N*-ethylacrylamido)undecanoate (Na 11-EAAU) in water were carried out at different concentrations of the anionic monomer and potassium persulfate from 50 to 60°C. The polymerization kinetics was close to half order with respect to the initiator and first order to the monomer. With the low activation energy of only 45.7 kJ/mol, polymerization of Na 11-EAAU in the micellar aggregates proceeded very rapidly. High molecular weights ($\sim 10^6$) poly(Na 11-EAAU) could easily be obtained. The results suggest that the organized structures of the micellar monomers in aqueous solution are responsible for fast polymerization and high MW. The effect of NaCl and aging on the solution behavior of poly(Na 11-EAAU) have also been studied.

INTRODUCTION

There is increasing interest in the polymerization of surface-active monomers which are capable of forming micelles either in an aqueous medium or in organic solvents. Several studies on polymerizable anionic

or cationic surfactants have been reported recently: dodecyl-1-vinylimidazo iodide [1], allyldimethyldodecylammonium bromide [2], sodium acrylamidostearate [3], quarternary alkyl salts of dimethylaminoethyl methacrylate with different alkyl chain lengths [4, 5], sodium acrylamidoundecanoate [6], and *N,N*-didodecyl-*N*-methyl-*N*-(2-(methacryloyloxy)ethyl)ammonium chloride [7]. Most of these surfactants were polymerized in normal micelles [1, 2, 4-6], others in inverse micelles [4, 5, 7] or in an inverse microemulsion [3].

All these surfactants but allyldimethyldodecylammonium bromide [2] could readily be polymerized to high molecular weights. This is not surprising because this surfactant [2] contains an allyl group, and allyl compounds are considered to be poor monomers for free-radical polymerization because of their tendency to undergo degradative chain transfer reactions [8, 9]. In order to minimize active chain transfer reactions during polymerization, allylic hydrogens of the unsaturated fatty acid soaps (e.g., sodium 10-undecenoate) should be eliminated through some kind of structural modification. Our studies of polymerization of surfactants are based on the modifications of the unsaturated fatty acid soaps to various acrylamidoalkanoates ($\text{CH}_2=\text{CH}-\text{CONR}(\text{CH}_2)_n-\text{COONa}$). In this paper on the micellar polymerization of sodium 11-(*N*-ethylacrylamido)-undecanoate, we deal only with its polymerization kinetics and the solution properties of the polysoap.

EXPERIMENTAL

Materials

Ethylamine from Tokyo Kasei Kogyo Co. and 11-bromoundecanoic acid and acryloyl chloride from Aldrich 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 distilled twice.

Synthesis of Sodium 11-(*N*-Ethylacrylamido)undecanoate (Na 11-EAAU) Monomer

The Na 11-EAAU synthesis was based on the method [10] for preparing *N*-methacryloyl-11-alkylaminoundecanoate. It first involved the reaction of 11-bromoundecanoic acid with 70% aqueous ethylamine solution. The

resulting 11-(*N*-ethylamino)undecanoic acid (11-EAUA) was recrystallized from water in 70% yield. It was then reacted with acryloyl chloride in an aqueous ethanol solution (85 mL of 95% ethanol and 15 mL of water) at pH 10 and below 10°C to produce 11-(*N*-ethylacrylamido)undecanoic acid (11-EAAUA). The precipitate of 11-EAAUA was recrystallized from the aqueous ethanol solution at -15°C, yielding 86% of pure 11-EAAUA. The final product of Na 11-EAAU was obtained by neutralizing 11-EAAUA with anhydrous sodium carbonate in superdry ethanol. Na 11-EAAU was recrystallized from superdry ethanol and dried in a vacuum chamber at room temperature.

Elemental analysis, IR, NMR, and mass spectroscopy of 11-EAAUA and Na 11-EAAU were consistent with the expected structures of $\text{CH}_2=\text{CHCON}(\text{C}_2\text{H}_5)(\text{CH}_2)_{10}\text{COOH}$ and its sodium salt. The infrared spectra of 11-EAAUA and Na 11-EAAU in Fig. 1 show absorptions due to terminal vinyl group ($\text{CH}_2=\text{CH}-$): at 1640 and 980/950 cm^{-1} for C=C stretching and -CH out-of-plane deformation, respectively. The presence of an amide group is evidenced by C=O stretching at 1600 cm^{-1} . The

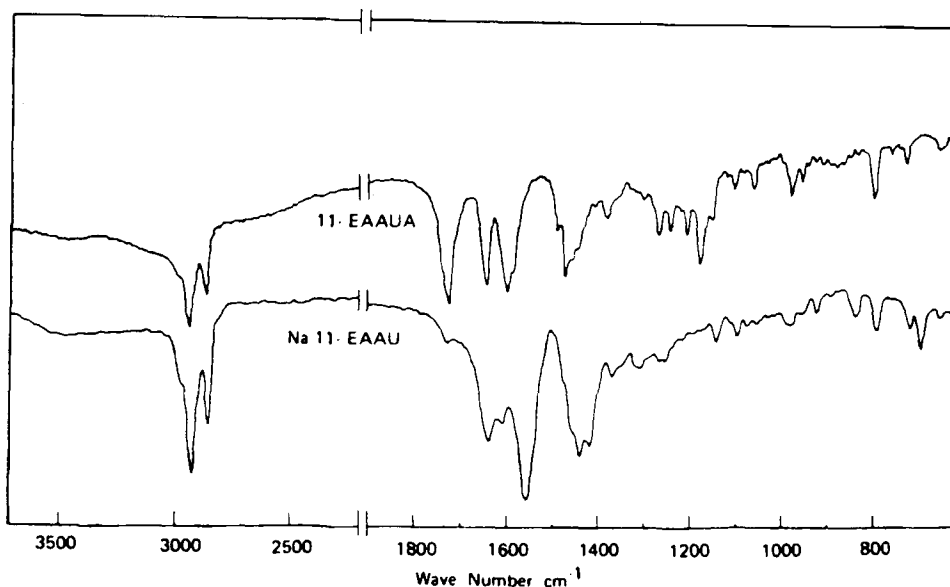


FIG. 1. Infrared spectra of 11-EAAUA and Na 11-EAAU.

broad adsorption bands at 2500–2800 and 1720 cm^{-1} are due to carboxylic acid groups ($-\text{COOH}$).

The proton-NMR spectra of 11-EAAUA and Na 11-EAAU (Fig. 2) are quite similar to those of 11-AAUA and Na 11-AAU [6]. The only difference is that the $-\text{NH}$ proton at δ 5.93 of 11-AAUA is being replaced by the $-\text{CH}_2\text{CH}_3$ protons, which appear as a side band (d) of the large peak of $-(\text{CH}_2)_8-$ and at c (see Fig. 2). The mass spectrum of 11-EAAUA in Fig. 3 shows base peaks at m/e 55 and 112 due to ion fragments $[\text{CH}_2=\text{CH}-\text{CO}]^+$ and $[\text{CH}_2=\text{CHCON}(\text{C}_2\text{H}_5)-\text{CH}_2]^+$, respectively, while the peak at m/e 284 corresponds to the molecular weight of 11-EAAUA.

Analysis. Calculated for $\text{C}_{13}\text{H}_{27}\text{O}_2\text{N}$ (11-EAAUA): C, 68.07; H, 11.87; N, 6.11. Found: C, 67.95; H, 12.55; N, 6.55. mp: 123–123.5°C.

Calculated for $\text{C}_{16}\text{H}_{29}\text{O}_3\text{N}$ (11-EAAUA): C, 67.84; H, 10.24; N, 4.94. Found: C, 67.59; H, 10.41; N, 4.80. mp: 37–39°C.

Calculated for $\text{NaC}_{16}\text{H}_{28}\text{O}_3\text{N}$ (Na 11-EAAU): C, 62.93; H, 9.24; N, 4.59; Na, 7.53. Found: C, 62.56; H, 9.33; N, 4.24; Na, 7.68. mp: 183–185°C.

Spectroscopic Measurements

Infrared (IR) spectra were recorded by a Perkin-Elmer 1310 spectrophotometer using KBr pellets. The proton NMR spectra in CDCl_3 or D_2O were obtained with a Jeol FX90Q Fourier-transform NMR spectrometer. Mass spectra were recorded by a Micromass 7035 spectrometer.

Determination of Critical Micelle Concentration

The critical micelle concentration (CMC) of Na 11-EAAU was determined by surface tension measurements by use of a torsion balance tensiometer (White Electric Instrument Co). The concentration at the break point of the surface tension versus concentration curve is taken as the CMC.

Polymerization of Na 11-EAAU

An aqueous solution of Na 11-EAAU was purged with nitrogen before it was polymerized at 50°C with potassium persulfate as initiator. The polymerization was conducted in a dilatometer placed in a $50 \pm 0.1^\circ\text{C}$ water bath. The open end of the dilatometer was connected to an Atmos-

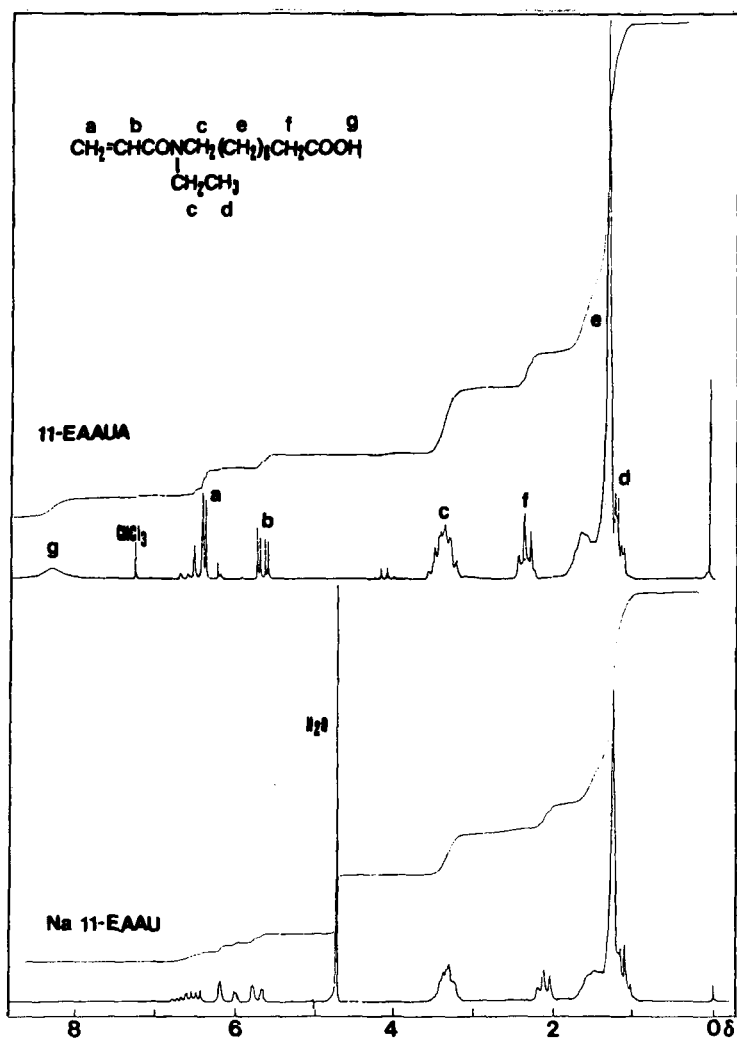


FIG. 2. Proton NMR spectra of 11-EAAUA and Na 11-EAAU.

bag under nitrogen atmosphere. The volume contraction of the solution in the dilatometer during polymerization was monitored with the help of a cathetometer. The concentration of Na 11-EAAU (mol/L) is proportional to the solution height in a dilatometer during polymerization, i.e., $[M]_0 \propto (L_0 - L_\phi)$ and $[M]_t \propto (L_t - L_\phi)$. $[M]_0$ is the initial concentration of monomer, while $[M]_t$ is its concentration at time t . The initial height of the solution in the dilatometer is denoted by L_0 , the final height by L_ϕ , and the height at any reaction time by L_t . The conversion (%) is calculated from the change of monomer concentration or the solution heights as follows:

$$\begin{aligned} \text{Polymer conversion (\%)} &= \frac{[M]_0 - [M]_t}{[M]_0} \times 100 \\ &= \frac{(L_0 - L_t)}{(L_0 - L_\phi)} \times 100. \end{aligned} \quad (1)$$

After completion of the polymerization, as evidenced by the unchanging volume of the solution 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 to remove any unreacted monomer.

Viscosity Measurements

The reduced viscosities of the polymer were measured with an Ubbelohde dilution capillary viscometer (Kapenekas Laboratory Services, Akron, Ohio) in a water bath at $23 \pm 0.1^\circ\text{C}$. Aqueous polymer solutions of different ionic strengths were measured. The intrinsic viscosity $[\eta]_0$ was obtained by extrapolation of both the reduced viscosity (η_{sp}/c) and inherent ($\ln \eta_r/c$) to infinite dilution according to the Huggins relationship [11]

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

and the Kraemer relationship [12]

$$\ln \eta_r/c = [\eta]_0 + \beta[\eta]^2c, \quad (3)$$

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

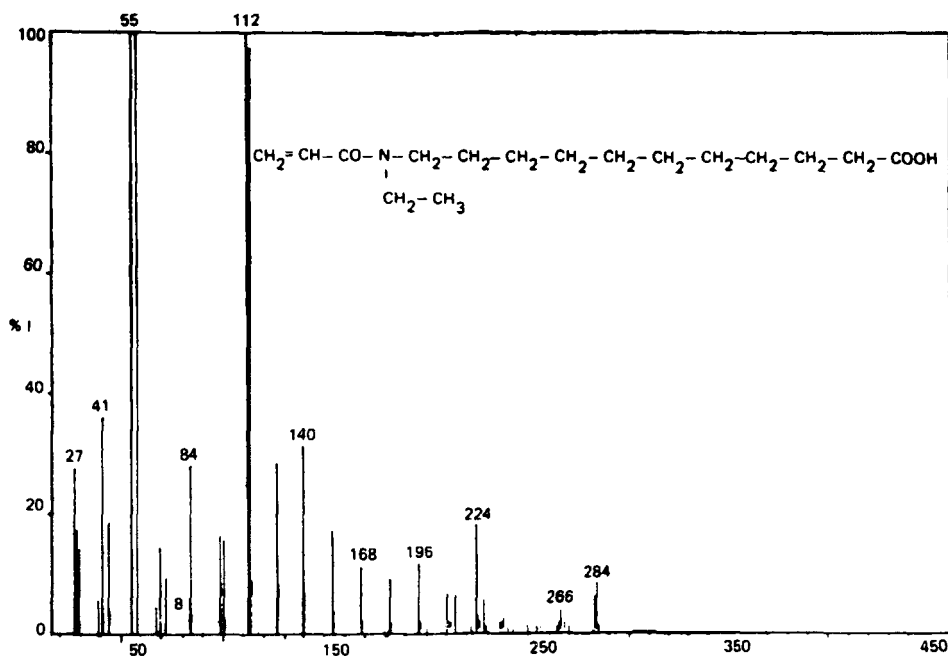


FIG. 3. Mass spectrum of 11-EAAUA.

Light-Scattering Measurement

Light-scattering measurements were performed with Malvern Instruments System 4700C Submicron particle analyzer. The intensities of the scattered light were measured over a range of angles from 10 to 150° by using vertically polarized light of wavelength 633 nm at 21°C. The concentration of the polymer solution in aqueous NaCl ranged from 0.2 to 0.8 g/L. All the polymer solutions were filtered through 0.45 μm disposable membrane filters (cellulose acetate) before light-scattering measurements.

The refractive index increments were determined with an Abbé 60 refractometer at the same wavelength and temperature as were used for the light-scattering measurements. A dn/dc value of 0.165 was obtained for poly(Na 11-EAAU) in 0.7 mol/L NaCl solution.

The experimental data were analyzed by the Zimm plot method [13]. The weight-average molecular weight, \bar{M}_w , of the polymer was calculated from the intercept of the plot which had been extrapolated to zero concentration and zero angle.

RESULTS AND DISCUSSION

Kinetics of Polymerization

Na 11-EAAU was soluble in water (47.8%) and in aqueous solutions of short-chain alcohols. Its critical micelle concentration (CMC) in water was only 42 $\mu\text{mol/L}$. Polymerizations of Na 11-EAAU were carried out at monomer concentrations much higher than its CMC, i.e., from 0.2 to 0.5 mol/L. Figures 4 and 5 show the rates of polymerization at three concen-

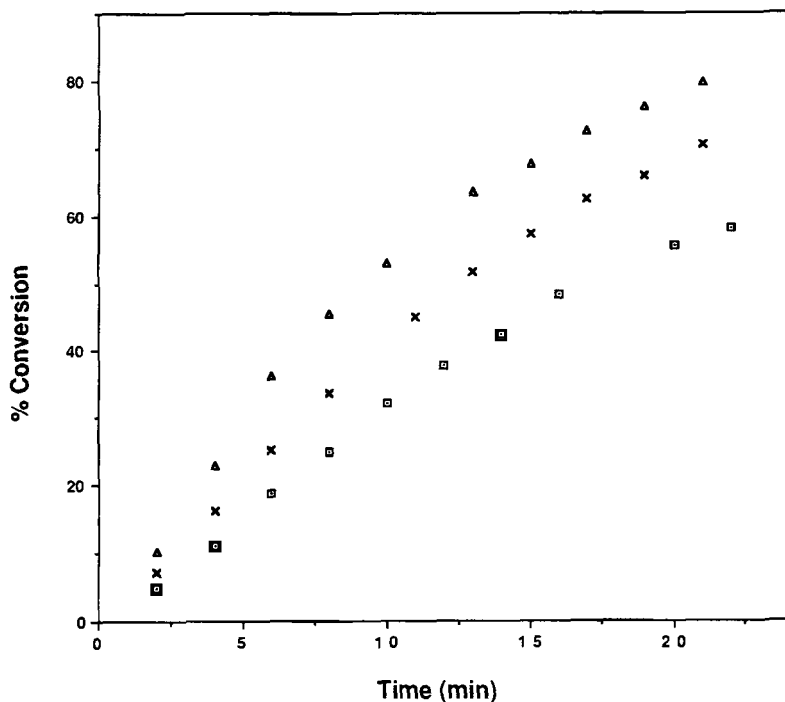


FIG. 4. Effect of concentration of Na 11-EAAU on rate of polymerization at 50°C. $[\text{K}_2\text{S}_2\text{O}_8] = 0.2 \text{ mmol/L}$; Na 11-EAAU concentration (mol/L): (\square) 0.2, (\times) 0.3, (Δ) 0.4.

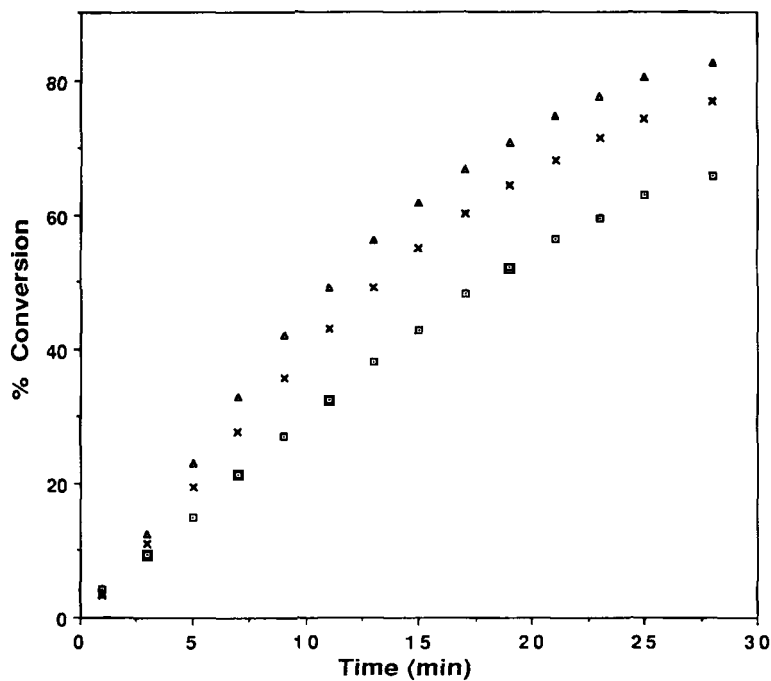


FIG. 5. Effect of concentration of $K_2S_2O_8$ on rate of polymerization of Na 11-EAAU at $50^\circ C$. $[Na\ 11-EAAU] = 0.2\ mol/L$; $K_2S_2O_8$ concentration (mol/L): (\square) 0.2, (\times) 0.4, (\triangle) 0.5.

trations of Na 11-EAAU and potassium persulfate at $50^\circ C$. The polymer formed was completely soluble in the reaction medium, and its viscosity increased with the progress of polymerization. This homogeneous polymerization proceeded very rapidly, indicating that Na 11-EAAU monomer is very reactive in the state of micellar aggregates. This fast polymerization could be due to accelerated propagation of the highly dense aggregation of acrylamido groups in the cores of the micelles, as was also observed in other surfactant systems [4].

The rate of polymerization (R_p) is expressed in terms of the rate of polymer conversion (%/min) as calculated from Eq. (1). The initial rates of polymerization (R_{p_i}) were obtained from the initial slopes of the polymerization curves (Figs. 4 and 5). Figure 6 shows both linear plots of log

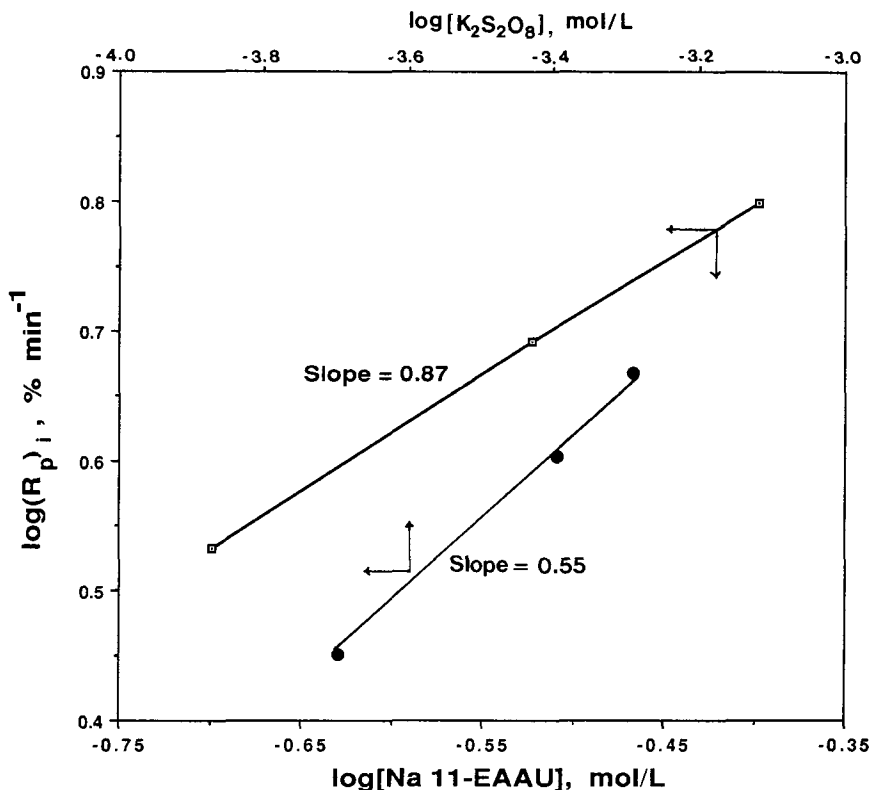


FIG. 6. Logarithmic plots of initial rate of polymerization against the initial concentration of monomer and initiator.

$(R_p)_i$ versus $\log [I]_0$ and $\log (R_p)_i$ versus $\log [M]_0$. The slopes indicate that R_p is proportional to the 0.55 power of $[K_2S_2O_8]$ and the 0.87 power of $[Na\ 11\text{-EAAU}]$. This is in fairly good agreement with the theoretical values of half order with respect to initiator and first order to monomer for free-radical polymerization in solution based on the general kinetic expression [14]

$$R_p = k_p[M] \left\{ \frac{fk_d[I]}{k_t} \right\}^{1/2}, \quad (4)$$

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

The effect of temperature on the rate of polymerization of Na 11-EAAU (0.2 mol/L) is shown in Fig. 7. The initial rates of polymerization ($(R_p)_i$) at various temperatures calculated from the initial slopes of these curves are plotted according to the Arrhenius equation (Fig. 8), which gave an overall activation energy of 45.7 kJ/mol. This linear plot has the relationship

$$\ln (R_p)_i = \ln C - E_a/RT, \quad (5)$$

where $C \propto (f[I])^{1/2}[M]_0$ and

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

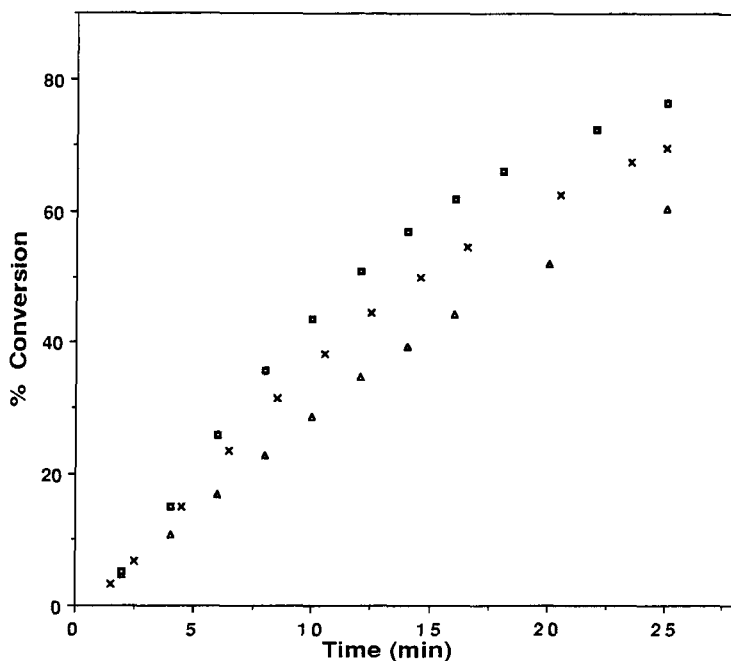


FIG. 7. Effect of temperature on rate of polymerization of Na 11-EAAU. $[\text{Na 11-EAAU}] = 0.2 \text{ mol/L}$, $[\text{K}_2\text{S}_2\text{O}_8] = 0.2 \text{ mmol/L}$. Temperature ($^{\circ}\text{C}$): (Δ) 50, (\times) 55, (\square) 60.

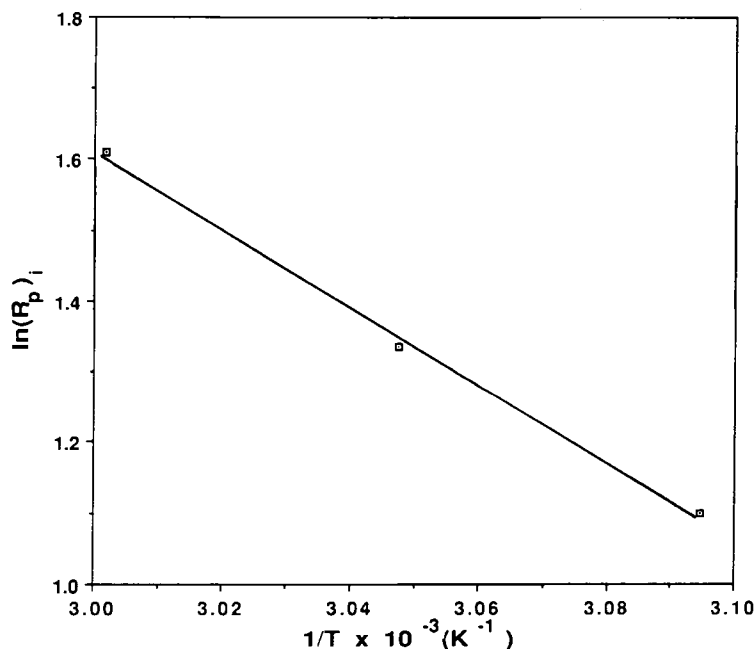


FIG. 8. Arrhenius plot of initial rate of polymerization.

The observed activation energy, 45.7 kJ/mol, is much lower than that of most radical polymerizations initiated by thermal decomposition of radical initiators (80–90 kJ/mol). With this low activation energy, polymerization of Na 11-EAAU in the micellar state was very rapid, as was also observed in the system of micelle forming Na 11-AAU [6].

Molecular Weights of the Polymers

The molecular weights of poly(Na 11-EAAU) could not be obtained by gel permeation chromatography (GPC) measurements owing to adsorption of the anionic polymers onto the columns. Hence, they were determined from Zimm plots of the light-scattering measurements. Table 1

TABLE 1. Molecular Weight of Poly(Na 11-EAAU)

Polymerization ^a		Molecular weights		
[Na 11-EAAU], mol/L	Temperature, °C	$\bar{M}_w \times$ 10^{-5}	$\overline{DP}^b \times$ 10^{-3}	$\langle \bar{s}^2 \rangle^{1/2, c}$ nm
0.2	50	8.68	2.84	34.6
0.2	55	8.38	2.74	31.6
0.2	60	7.31	2.39	32.8
0.3	50	10.51	3.43	40.1
0.5	50	10.12	3.31	38.2

^aK₂S₂O₈ (04 mmol/L) for all systems.

^bThe average degree of polymerization, \overline{DP} , was calculated from \bar{M}_w .

^cRadius of gyration.

shows that high molecular weights of about 1 million could easily be obtained at 50°C. As expected, the molecular weights decreased with increasing polymerization temperature, as is generally observed for radical polymerization. The average \overline{DP} was found to be in the range of 2400 to 3400. It has been reported that the \overline{DP} for the dimethylaminoethyl methacrylate system [5] is also in the 1000 to 10 000 range. Since the aggregation number of a Na 11-EAAU micelle is not known, it is not possible to state definitely at present whether the polymerization of Na 11-EAAU proceeded solely in single micelles or/and involved intermicellar polymerization. This aspect of our investigation is now under way.

The double logarithmic plot in Fig. 9 shows a good linear relationship that can be expressed in the form of the Mark-Houwink empirical equation:

$$[\eta] = 3.63 \times 10^{-5} \bar{M}_w^{0.69}, \quad (6)$$

where $[\eta]$ is expressed in dL/g in 0.7 mol/L aqueous NaCl at 23°C. The value of the exponent ($a = 0.69$) lies between the theoretical values of 0.5 to 0.8 for randomly coiled linear polymers [15a]. The lower limit applies to the tightly coiled chains in θ -solvents, and the upper limit to the highly swollen polymers in very good solvents. The stiffness of polymer molecules is related to an increasing value of a .

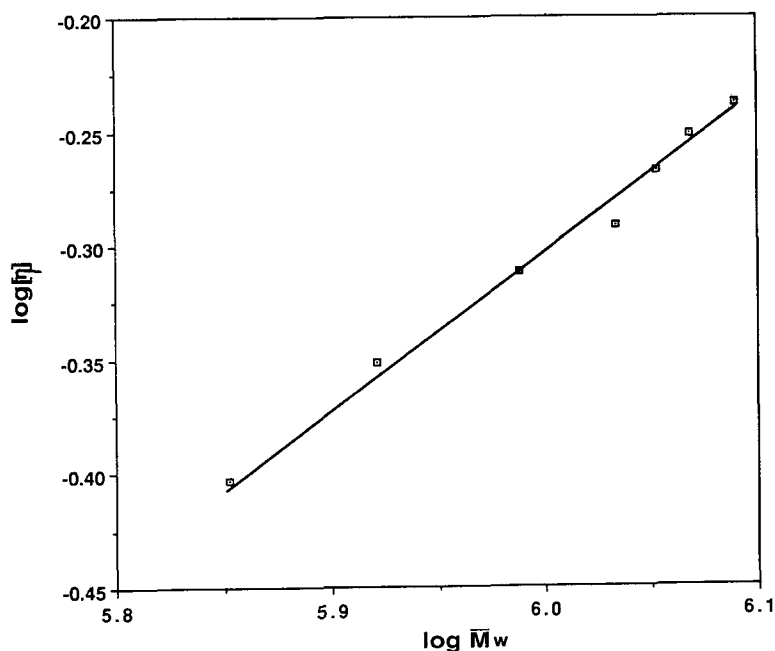


FIG. 9. Double logarithmic plot of intrinsic viscosity $[\eta]$ and weight-average molecular weight (M_w) for poly(Na 11-EAAU) in 0.7 mol/L NaCl solution at 23°C.

Solution Properties

Poly(Na 11-EAAU) is an anionic polyelectrolyte, readily soluble in water. The surface tension measurements indicate that it does not seem to form micellar structures at concentrations even up to 1 g/L. The surface tension only changed slightly and gradually up to 1 g/L. At low polymer concentrations, its reduced viscosity η_{sp}/c underwent a marked increase with dilution, as shown in Fig. 10. When $(\eta_{sp}/c)^{-1}$ is plotted against $c^{1/2}$, a nearly straight line is obtained, which is the characteristic of a polyelectrolyte solution [15b].

The intrinsic viscosities of the polymer were obtained according to the methods of Huggins and Kraemer (Eqs. 2 and 3). The methods of Martin

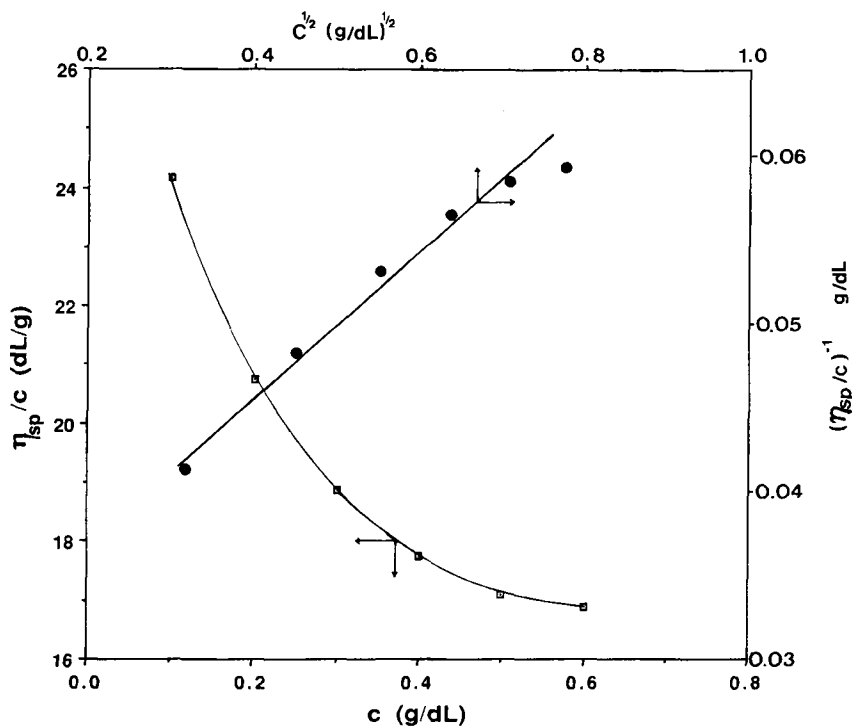


FIG. 10. Dependence of reduced viscosity on concentration of poly(Na 11-EAAU) in water at 23°C.

[16], Schulz-Blaschke [17], and Fedors [18] are also included for comparison according to the following respective equations:

$$\ln (\eta_{sp}/c) = \ln [\eta] + k_M[\eta]c \quad (7)$$

$$\eta_{sp}/c = [\eta] + k_{S-B}[\eta]\eta_{sp} \quad (8)$$

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{-1}{[\eta]c_m} + \frac{1}{[\eta]c} \quad (9)$$

where η_{sp} is the specific viscosity, η_r is the relative viscosity, c is the polymer concentration (g/dL), and c_m is the concentration to which the particles can pack.

Figures 11–13 show the dependence of viscosity on concentration of poly(Na 11-EAAU) according to the five methods. Deviations from linearity are observed for all cases at polymer concentrations above 0.4 g/dL, except for Eq. (9). Hence, all the intrinsic viscosities reported here were determined from polymer concentrations below 0.4 g/dL. It appears from Table 2 that the Schulz-Blaschke method yields the highest $[\eta]$ value, which decreases slightly in the Martin and Huggins methods, in accordance to the conclusions of Sakai [19].

The dependence of $[\eta]$ on the NaCl concentration in Fig. 14 exhibits two straight lines of different slopes, which intersect at about 0.22 mol/L

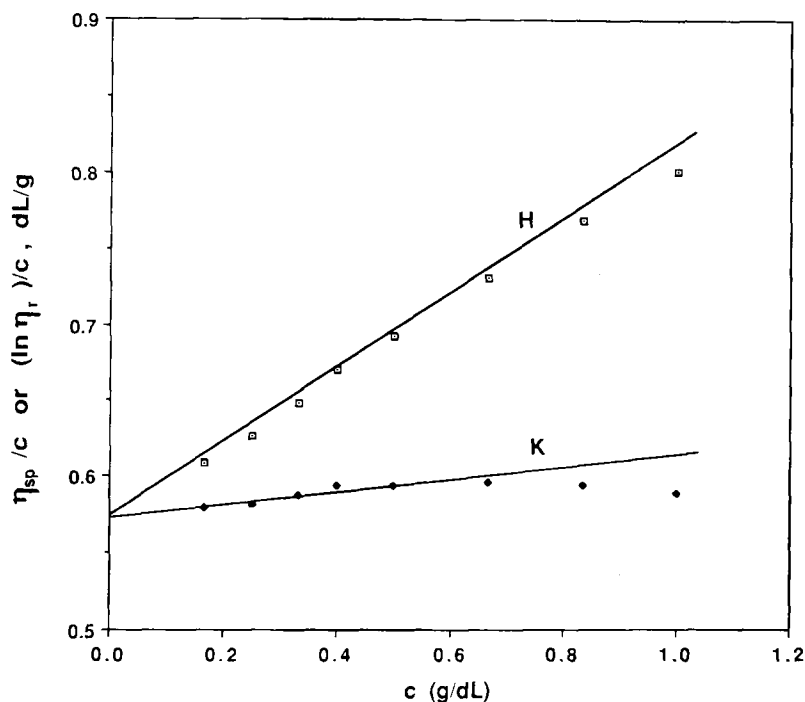


FIG. 11. Huggins and Kraemer plots of poly(Na 11-EAAU) in 0.5 mol/L NaCl aqueous solution at 23°C.

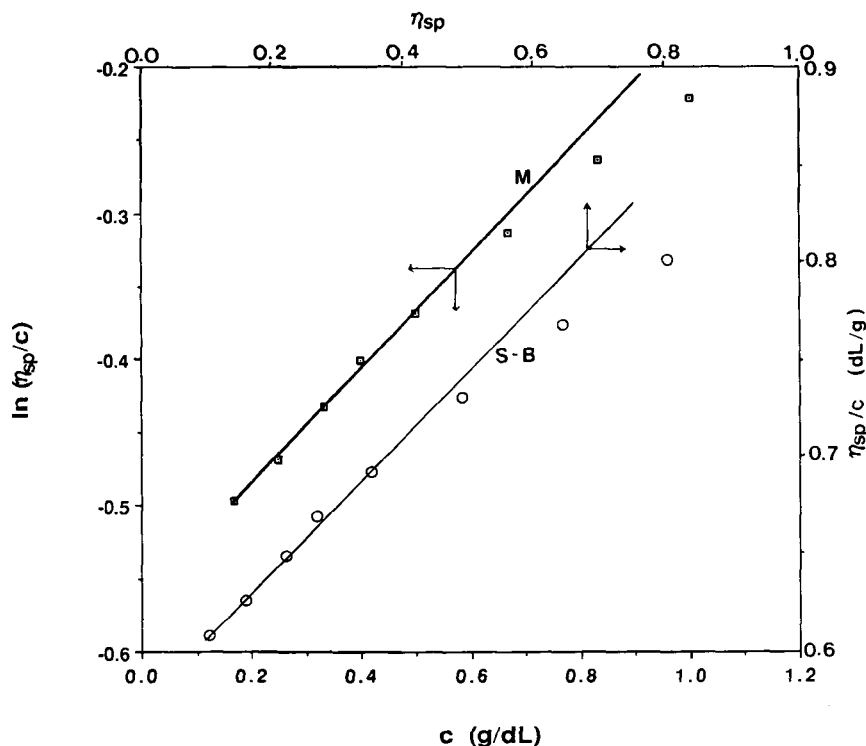


FIG. 12. Schulz-Blaschke and Martin plots of poly(Na 11-EAAU) in 0.5 mol/L NaCl aqueous solution at 23°C.

NaCl. The change of slope can be explained by a conformational transition of the polyelectrolyte molecules [20] in the region of 0.22 mol/L NaCl. At low NaCl concentration, the polymer molecules may be highly ionized, resulting in the expansion of the polymer chains. The dimensions of these expanded polymer chains reduce markedly with increasing NaCl concentration up to about 0.22 mol/L. However, the dependence of the polymer dimensions on salt concentration was less pronounced for NaCl concentrations above 0.22 mol/L. At higher concentrations of NaCl, the poly(Na 11-EAAU) molecules can exist in the form of compact coils due to a reduction of electrostatic repulsion by the screening effect of the counterions.

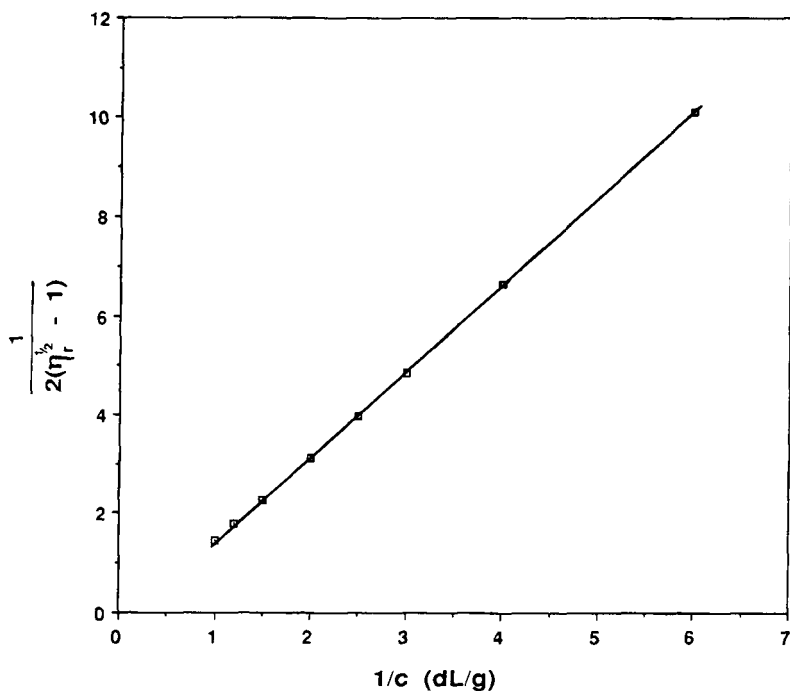


FIG. 13. Fedors plot of poly(Na 11-EAAU) in 0.5 mol/L NaCl aqueous solution at 23°C.

TABLE 2. Intrinsic Viscosity Obtained by the Methods of Huggins-Kraemer (H-K), Martin (M), Schulz-Blaschke (S-B), and Fedors (F) for Different Molecular Weights of Poly(Na 11-EAAU) in 0.5 mol/L NaCl Aqueous Solution at 23°C

$\bar{M}_w \times 10^6$	$[\eta]_{\text{H-K}}$ dL/g	$[\eta]_{\text{M}}$ dL/g	$[\eta]_{\text{S-B}}$ dL/g	$[\eta]_{\text{F}}$ dL/g
1.26	0.810	0.815	0.820	0.819
1.20	0.765	0.766	0.767	0.758
0.97	0.579	0.580	0.600	0.578
0.84	0.538	0.538	0.539	0.535
0.71	0.471	0.472	0.472	0.472

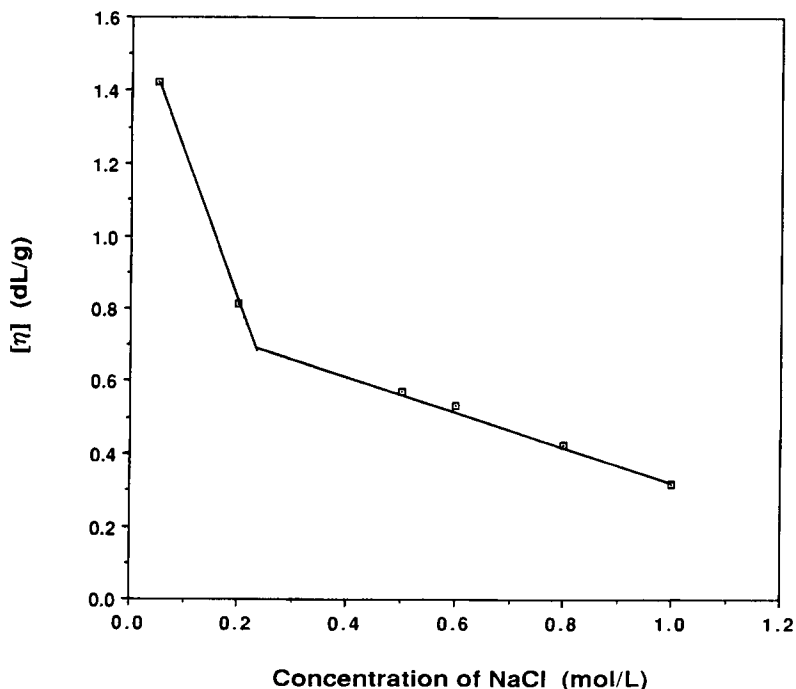


FIG. 14. Dependence of the intrinsic viscosity $[\eta]$ of poly(Na 11-EAAU) on NaCl concentration at 23°C.

The intrinsic viscosity of poly(Na 11-EAAU) in 0.5 mol/L NaCl was found to decrease with increasing temperature (Fig. 15). This suggests that the hydrodynamic volume of the polymer molecules decreases with increasing temperature due to increasing hydrophobic interactions among the polymer chains at higher temperatures.

Aging Effects

The viscosities of many polyelectrolyte solutions show a gradual decrease with time. Such an aging effect has been observed for aqueous solutions of polyacrylamide [21] and its copolymers [22–25] as well as for the ampholytic copolymers [26]. Figure 16 shows the aging effect on

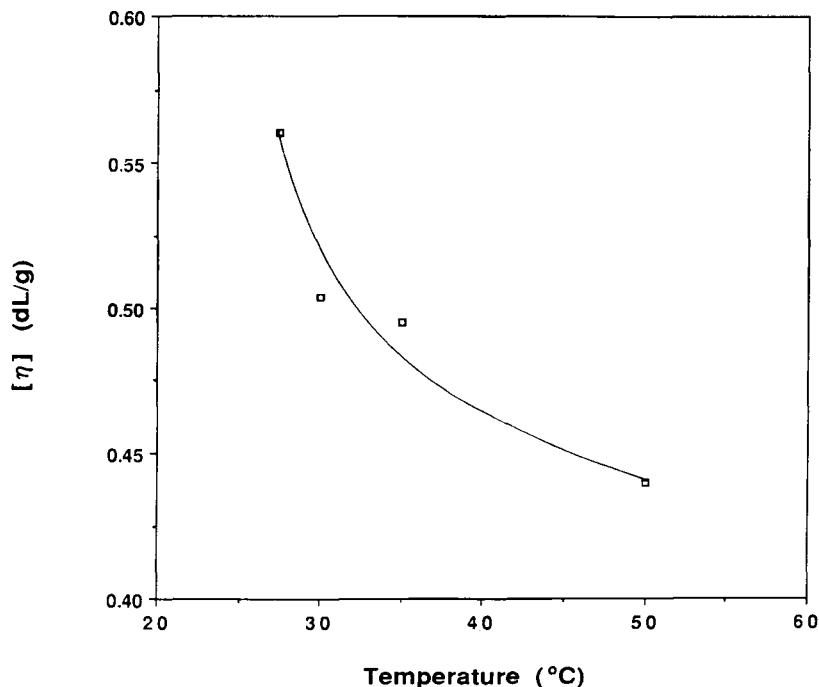


FIG. 15. Effect of temperature on intrinsic viscosity $[\eta]$ of poly(Na 11-EAAU) in 0.5 mol/L NaCl.

poly(Na 11-EAAU) in water and in aqueous NaCl. The initial reduced viscosity in water (27 dL/g) sharply decreased during the first 3 weeks of aging and gradually diminished to an almost constant low value (0.6 dL/g) in 40 days. This represents a drastic drop of about 98% in viscosity. However, the reduced viscosity of the same concentration of poly(Na 11-EAAU) in 0.3 mol/L NaCl decreased only slightly, from 0.62 to 0.45 dL/g, during the same period. It indicates that electrolyte (0.3 mol/L NaCl) exerts a similar effect in reducing the viscosity as simple aging. Thus the aging of poly(Na 11-EAAU) in water is attributed to conformational changes leading to a diminished hydrodynamic volume as a function of time. Such changes will eventually lead to the most thermodynamically stable polymer conformation.

Additional aging data are presented in Table 3. The molecular weights of the polymer in three concentrations of aqueous NaCl varied only

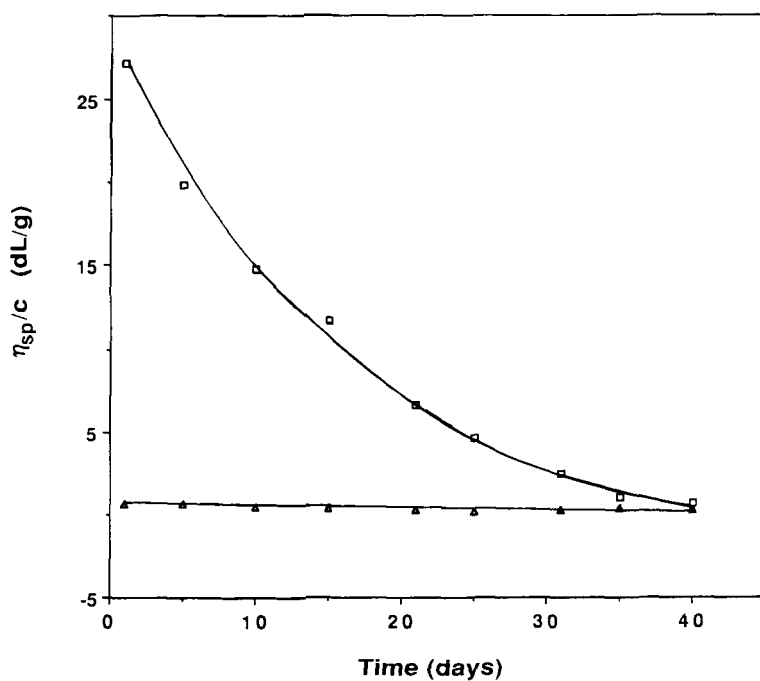


FIG. 16. Aging of poly(Na 11-EAAU) in water (□) and in 0.3 mol/l NaCl solution (Δ) at 23°C. Polymer concentration: 0.05 g/dL.

TABLE 3. Aging of Poly(Na 11-EAAU) in Different NaCl Concentrations

NaCl, mol/L	Time, days	$\bar{M}_w \times 10^{-6}$	η_{sp}/c , ^a dL/g	$[\eta]$, dL/g	$\langle \bar{s}^2 \rangle^{1/2}$, nm
0.1	0	1.34	1.364	1.072	53.1
	10	1.18	1.178	0.900	47.5
	22	1.01	0.960	0.750	31.4
0.5	0	1.16	0.680	0.639	37.0
	10	0.99	0.625	0.522	39.5
	22	1.03	0.513	0.505	27.8
0.7	0	1.01	0.597	0.464	31.2
	10	0.99	0.543	0.456	38.9
	22	0.87	0.465	0.425	21.1

^aConcentration of poly(Na 11-EAAU): 0.2 g/dL.

slightly compared to the substantial changes in the viscosities of the aqueous polymer solutions before and after aging. This further confirms the view that the viscosity reduction during aging is due to polymer conformational changes rather than degradation.

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