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Micellar polymerization of surfactants

Sodium 6-acrylamidocaproate and sodium 11-(*N*-methyl acrylamido)undecanoate

K.W. Yeoh, C.H. Chew, L.M. Gan*, and L.L. Koh

Department of Chemistry, National University of Singapore, Republic of Singapore

Summary

Micelle-forming sodium 6-acrylamidocaproate (Na 6-AAC) and sodium 11-(N-methyl acrylamido)undecanoate (Na 11-MAAU) were synthesized and polymerized in aqueous solutions. The polymerization was very rapid and it followed first-order kinetics with respect to the monomer and one-half order to $K_2S_2O_8$. The activation energy for the polymerization of Na 11-MAAU (62.3 kJ/mol) was much lower than that for Na 6-AAC (98.1 kJ/mol). The $\overline{M}_w$ for the former was around one million and it was only one-third of that for the latter. Their MWD ($\overline{M}_w/\overline{M}_n \simeq 1.5$) are relatively narrow. The relationships between intrinsic viscosity $[\eta]_o$ and $\overline{M}_w$ for these polysurfactants have also been established.

Introduction

Surfactants are widely used in emulsion polymerizations and in microemulsions. There is an increasing interest in polymerization of surface-active monomers which are capable of forming micelles in solutions [1-5]. Polymerization of sodium 9-(and 10)acrylamidostearate [6] adsorbed on the surfaces of a relatively unstable styrene/butadiene copolymer latex resulted in better mechanical stability. This is because the charges are immobilized on the latex surface, and desorption is highly improbable. Emulsion polymerization with a polymerizable surfactant provides no emulsifier migration during film formation, excellent shear stability, and a narrow particle size distribution [7]. The copolymerization of methyl methacarylate with sodium acrylamidostearate in microemulsion has also been reported [8] by us.

Our study on the polymerization of surfactants is based on the monomers derived from the modified unsaturated fatty acid soaps to various acrylamidoalkanoates [8-11]. These surfacatant monomers are free of allylic hydrogens, which are detrimental to free radical polymerization due to degradative chain transfer reactions [12]. In this paper, a comparative study of polymerization between a short chain and a long chain acrylamidoalkanoates will be discussed.

Experimental

Materials

Acryloyl chloride, 6-aminocaproic acid and 11-amino-

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*To whom all correspondence should be addressed undecanoic acid from Aldrich were used as received. Potassium persulfate from Reachim was recrystallized from water. Methylamine from TCI(Japan) was a 40% aqueous solution. Sodium 6-acrylamidocaproate (Na 6-AAC) and sodium 11-(N-methyl acrylamido)undecanoate (Na 11-MAAU) were prepared according to the methods reported for sodium 11-acrylamidoundecanoate [9] and sodium 11-(N-ethyl acrylamido)undecanoate [10] respectively.

Polymerization

The polymerization of the surfactant was conducted in a dilatometer which was placed in a 50 ± 0.1°C water bath. The aqueous monomer solution was purged by nitrogen before it was polymerized using potassium persulfate as an initiator. The volume contraction of the polymer solution in the dilatometer during polymerization was monitored with the help of a cathetometer, and the conversion of monomer to polymer was calculated from the volume change [10].

Measurements

The critical micelle concentration (CMC) of Na 6-AAC and Na 11-MAAU were determined by surface tension measurements using torsion balance tensiometer (White Elect. Inst. Co) at 50°C. The concentration at the break-point of the surface tension versus concentration curve is the CMC.

The viscosities of the polymer solutions were measured with an Ubbelohde dilution viscometer (Kapenekas Laboratory Services, Akron, Ohio) in a water bath at 23 ± 0.1°C. Intrinsic viscosity $[\eta]_0$ was obtained according to both Huggins [13] and Kraemer [14] equations.

Molecular Weight Determination

The light scattering measurements were performed with Malvern Instruments - system 4700C submicron particle analyser. The intensities of the scattered light were measured over a range of angles from 10 to 150° using vertically polarized light of wavelength 633 nm and at 21°C. An aqueous NaCl solution was used as solvent. The concentrations of the polymer solutions ranged from 0.1 to 2.4 g/L and they were filtered by 0.22 µm disposable membrane (cellulose acetate) filters. The refractive index increments were determined with an Abbe '60' refractometer at the same wavelength and temperature as for light scattering measurements. The experimental data were analysed by the method of Zimm plot [15].

The gel permeation chromatography (GPC) measurements were performed on a Varian 5500 liquid chromatography system equipped with a RI-3 detector. Two pL-gel 10 µ columns of pore sizes 10^6 and 10^4 Å connected in series were used. The polymers were converted to the acid form (by adding dilute HCl to the aqueous polymer solution) which was dissolved in DMF. The elution solvent DMF flowed at 0.5 mL/min. A calibration curve was obtained by using polystyrene standards supplied by Polysciences Inc.

Results and Discussion

Polymerization

Both surfactants Na 6-AAC and NA 11-MAAU are very soluble in water and their CMC at 50^{o}C were 0.17 mol/L and 7.94 x 10^{-3} mol/L respectively. The polymerizations of these surfactants were carried out at their monomer concentrations much higher than their CMC, i.e. from 0.2 to 0.5 mol/L. The polymer formed was completely soluble in its reaction medium. The polymerization of Na 11-MAAU proceeded rapidly (completion in about 20 min at 50^{o}C) and it was faster than Na 6-AAC (about 60 min) indicating that the former is more reactive than the latter in the micellar state. It is conceivable that the polar heads of the anionic surfactant molecules were distributed over the outer surfaces of the micelles, while their reactive acrylol groups were aggregated in the cores of the micelles. The close proximity of these reactive acrylol groups in the cores of the micelles would thus accelerate the polymerization. There is no significant difference in polymerization kinetics between the two surfactants as shown below:

$$R_p \propto [\mathrm{Na\ 6\text{-}AAC}]^{1.07}[K_2S_2O_8]^{0.6} \qquad (1)$$

$$R_p \propto [\mathrm{Na\ 11\text{-}MAAU}]^{0.93}[K_2S_2O_8]^{0.57} \qquad (2)$$

where R_p is the rate of polymerization. They are in rather good agreement with the general kinetic expression for radical polymerization [16], as given by

$$R_p = k_p[M]\{fk_d[I]/k_t\}^{1/2} \qquad (3)$$

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 activcation energy for polymerization of Na 11-MAAU (62.3 kJ/mol) is lower than most of the radical polymerizations (80-90 kJ/mol), but higher for Na 6-AAC (98.11 kJ/mol). The difference may be due to the higher anionic charge per unit weight of monomer Na 6-AAC as compared to that of monomer Na 11-MAAU. Since the initiator $K_2S_2O_8$ decomposed into anionic-radical species ($2KSO_4^{\cdot-}$), it would require higher energy for these anionic-radicals to diffuse into the higher anionic charged micelles of Na 6-AAC to proceed the polymerization than that of Na 11-MAAU micelles. In addition, it is also highly probable that the anionic-radicals of the decomposed initiator reacted first with Na 6-AAC or Na 11-MAAU in the bulk aqueous phase to form the anionic-radical oligomers. These growing oligomers then diffused into the anionic micelles for further polymerization.

Polymer Solution

The polysurfactants of poly(Na 6-AAC) and poly(Na 11-MAAU) are, in fact, anionic polyelectrolytes which are readily soluble

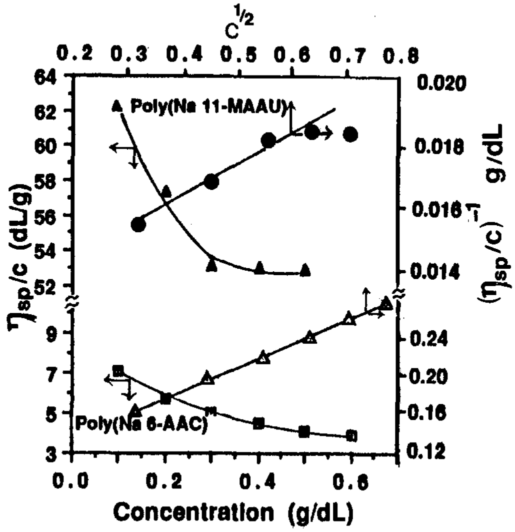

Figure 1. Dependence of reduced viscosity on the concentration of polysurfactants in water at 23°C.

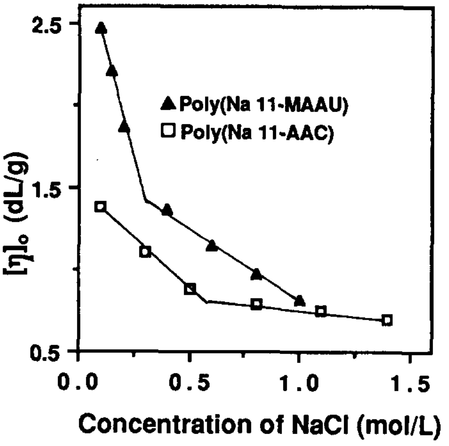

Figure 2. Effect of NaCl concentration on the intrinsic viscosities $[\eta]_o$ of the polysurfactants at 23°C.

in water. At low concentrations of the polymers, their reduced viscosities η_{sp}/c underwent a marked increase with dilution as shown in Fig 1. However, when $(\eta_{sp}/c)^{-1}$ is plotted against $c^{1/2}$ based on Fuoss equation [17], a nearly straight line is obtained as often observed for a typical polyelectrolyte solution. The intrinsic viscosities $[\eta]_o$ of these polysurfactants were drastically reduced by the addition of NaCl. Figure 2 shows the effect of NaCl on $[\eta]_o$ for both polysurfactants. The transition of $[\eta]_o$ seems to occur at 0.25 mol/L NaCl for poly(Na 11-MAAU) solution and 0.55 mol/L NaCl for poly(Na 6-AAC). The $\overline{M}_w$ for poly(Na 6-AAC) was 3.6×10^5 which is only one-third of poly(Na 11-MAAU). At a very low NaCl concentration, the highly ionized anionic polymer chains were expanded due to charge repulsion and resulted in high $[\eta]_o$. The dimensions of these expanded polymer chains reduced markedly with increasing NaCl concentration up to the transition point. Beyond which, the effect of NaCl concentration on the polymer dimensions was less pronounced, especially for poly(Na 6-AAC). At higher concentration of NaCl, the polysurfactant molecule could be in a form of compact coils resulting in minimum $[\eta]_o$

Molecular weights of polysurfactants

The molecular weights of poly(Na 6-AAC) and poly(Na 11-MAAU) could not be determined directly from the GPC measurements owing to the adsorption of the anionic polymers onto the columns. However, the polymers having converted into the acid form and dissolved in DMF were successfully determined by GPC. Table 1 shows that $\overline{M}_w$ for the acid form of poly(Na 11-MAAU) was around

Table 1. Molecular weights and polydispersity ($\overline{M}_w/\overline{M}_n$) of poly(Na 6-AAC) and poly(Na 11-MAAU) in acid forms as determined by GPC.

Polymer	Polymerization* Temperature (^oC)	$\overline{M}_w$ (10^5)	$\overline{M}_w/\overline{M}_n$
Poly(Na 6-AAC)	50	3.67	1.52
	60	3.56	2.18
Poly(Na 11-MAAU)	50	10.49	1.46
	60	9.52	1.75

*[Na 6-AAC] = [Na 11-MAAU] = 0.2 mol/L
$[K_2S_2O_8] = 5 \times 10^{-4}$ mol/L

Table 2. The effect of ionic strength on second virial coefficients and gyration radii of the polysurfactants.

Polysurfactant	[NaCl] mol/L	$\overline{M}_w$ (10^5)	A_2 (10^{-3} mol cm^3 g^{-2})	$<\bar{s}^2>^{1/2}$ nm
Poly(Na 6-AAC)	0.05	3.41	0.737	79.6
	0.20	2.40	0.353	53.1
	0.70	2.71	0.147	48.2
Poly(Na 11-MAAU)	0.10	22.3	0.324	83.8
	0.30	17.6	0.171	58.2
	0.50	19.4	0.176	36.4

one million and it was only one-third of a million for that of poly(Na 6-AAC), though both monomers were polymerized under the same conditions. The feature of these polysurfactants is their relatively narrow MWD ($\overline{M}_w/\overline{M}_n \simeq 1.5$) when both the surfactants were polymerized at 50^{o}C. At higher polymerization temperature, the $\overline{M}_w$ of the polysurfactants decreased and their MWD broadened as would be expected for general radical polymerizations.

The $\overline{M}_w$ for the polysurfactants were also determined by light scattering measurements. The effect of NaCl concentration on the second virial coefficients (A_2) and the radius of gyration $<\bar{s}^2>^{1/2}$ for these polysurfactants are shown in Table 2. Both A_2 and $<\bar{s}^2>^{1/2}$ decreased with the

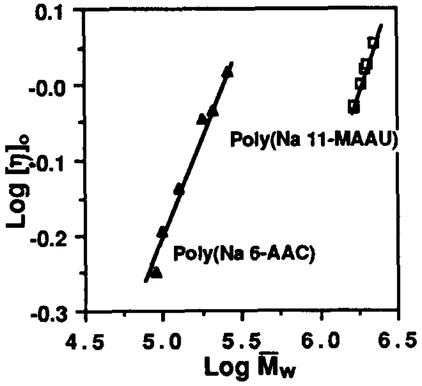

Figure 3. Double logarithmic plot of intrinsic viscosity versus $\overline{M}_w$.

increase of ionic strength for the polysurfactant solutions. Though $\overline{M}_w$ for poly(Na 11-MAAU) was about three-fold higher than poly(Na 6-AAC), their radii of gyration were about the same at low NaCl concentration. However, the decrease of $<\overline{s}^2>^{1/2}$ was more pronounced for poly(Na 11-MAAU) than poly(Na 6-AAC) by the effect of NaCl concentration on compressing the electrical double layers of the polysurfactants. This is in consistent with the view that the charge density of poly(Na 6-AAC) is higher than poly(Na 11-MAAU).

The intrinsic viscosities $[\eta]_o$ for different MW of the polysurfactants dissolved in 0.7 mol/L NaCl solution at 23°C were also determined. A linear relationship is obtained by plotting $\log[\eta]_o$ against $\log \overline{M}_w$ as shown in Fig 3. The linear relationship can be described by the general form of Mark-Houwink empirical equation, $[\eta]_o = KM^a$, as follow:

$$[\eta]_o = 6.25 \times 10^{-4}\ \overline{M}_w^{0.60}, \qquad \text{poly(Na 6-AAC)} \qquad (4)$$

$$[\eta]_o = 8.40 \times 10^{-5}\ \overline{M}_w^{0.65}, \qquad \text{poly(Na 11-MAAU)} \qquad (5)$$

where $[\eta]_o$ is expressed in dL/g and $\overline{M}_w$ was obtained from light scattering measurements. The value of the exponent ($a = 0.60$ or 0.65) lies between the theoretical values of 0.5 and 0.80 for the randomly coiled linear polymers [17]. The lower limit applies to the tightly coiled chains in the poor solvents and the upper limit to the highly swollen polymers in very good solvents.

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