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SHORT COMMUNICATION

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Micellar behavior of acrylamide–octylphenylpoly(oxyethylene) acrylate copolymer in aqueous solution

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Abstract The copolymer of acrylamide and octylphenylpoly(oxyethylene) acrylate macromonomer (AM-C_8PhEO_7Ac) was synthesized and characterized by IR and NMR spectroscopy. The molecular weight of the copolymer was determined to be 1.21×10^5 by static light scattering. The weight contents of AM and macromonomer were determined to be 67.8 and 32.2%, respectively, by elemental analysis. The micellar behavior of the copolymer in aqueous solution was studied by UV spectroscopy and atomic force microscopy (AFM). The molecules of AM-C_8PhEO_7Ac copolymer form monomolecular micelles in the concentration range $4 \times 10^{-6} - 3 \times 10^{-5}$ g/ml and polymolecular micelles at concentrations above 3×10^{-5} g/ml according to the UV analysis. The AFM images indicate that the monomolecular micelles are globular with diameters of 70 nm and have a narrow size distribution. The polymolecular micelles can be globular or cylindrical depending on the concentration, and have a wide size distribution.

Key words Micelle · Monomolecular micelle · Polymolecular micelle · Atomic force microscopic · Polymeric surfactant

Introduction

Polymeric surfactants can form micelles in selective solvents like low-molecular-weight surfactants. Merrett [1] was the first to demonstrate the existence of copolymer polymolecular micelles. The micelles may have various shapes, being spherical, cylindrical, lamella or wormlike under different conditions [2–4]. All these studies of micelles were carried out in non-polar solvents. The micellar behavior of polymeric surfactants in aqueous solutions was rarely studied. Piirma [5] considered it difficult to study the micellar behavior of polymeric surfactants in aqueous solutions because of the strong hydrogen-bond interaction between H_2O and the surfactant molecules.

The usual micelles are polymolecular; however, because of their large molecular size, polymeric surfactants are considered to form monomolecular micelles under certain conditions. The term “monomolecular micelle” and the first suggestions regarding the shape were proposed by Sadron [6]. He assumed that in the molecule of a two-block copolymer in very dilute solution in a solvent, microseparation of blocks would occur with the insoluble block forming a gel core and the soluble block providing a swollen shell. Pouchly et al. [7, 8] studied theoretically a “segment cloud” model, and got the same result as Sadron. In investigating poly(methyl methacrylate/styrene) graft copolymers, Gallot et al. [9] found that under certain conditions the polymer can form monomolecular micelles with a small intrinsic viscosity and radius of gyration. Price and Woods [10] found that at a certain temperature a poly(styrene-2-pentene) graft copolymer can form monomolecular micelles. Prasad et al. [11] studied the micellar behavior of polyoxyethylene–polyoxypropylene nonionic copolymers by determining the surface tension of aqueous solutions. They found that the surface tension versus concentration plots show an inflection typical of that shown by conventional surfactants, but the inflection occurs at very low concentrations and it is thought to be the result of monomolecular micelle formation. Despite the extensive study of monomolecular micelles, no convincing demonstration of monomolecular micelles has been achieved.

Micellar behavior may be studied by methods such as light scattering [12], small-angle neutron scattering [13], fluorescence [14] and NMR [15]; however at low concentrations, these methods are insensitive. UV spectroscopy may be used to study micellar behavior in solutions at low concentrations. The shape of micelles is usually studied by transmission electron microscopy; however, the real conformation can hardly ever be obtained because of the difficulty in sample preparation. It may be obtained by atomic force microscopy (AFM). AFM is a highly sensitive technique, and does little destruction to the original micelle conformation [16].

The synthesis of the copolymer of acrylamide and octylphenylpoly(oxyethylene) acrylate (AM-C_8PhEO_7-Ac) is reported in this paper. The micellar behavior of AM-C_8PhEO_7Ac copolymer in aqueous solution was studied. The formations of monomolecular and polymolecular micelles are demonstrated by UV analysis. The micellar conformation was studied by AFM.

Experimental

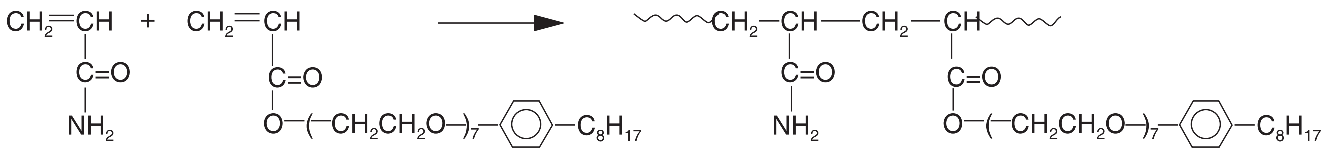
Materials

Potassium persulfate (Beijing Reagent Factory) was used as received. AM monomer from the Mitsui Toatsu Company (Japan) was recrystallized from chloroform and vacuum dried at room temperature prior to use. The surfactant macromonomers were synthesized by the reaction of acrylol chloride and C_8PhEO_7Ac [17].

Polymerization

Distilled water (235 ml) and *N*,*N*-dimethylformamide (15 ml) were added to a 500-ml flask equipped with a water condenser, thermometer, mechanical stirrer, and a nitrogen inlet and outlet. The solvent was purged by N_2 for 30 min. AM (11 g) and macromonomer (5 g) were then added and the solution was further purged for 30 min. The temperature was adjusted to 70 °C. The potassium persulfate initiator (0.16 g) was then charged. The polymerization lasted 10 h. The copolymer was isolated and purified by repeated precipitation with ketone and was then vacuum dried.

The reaction process was as follows:



(AM) (C_8PhEO_7Ac) (AM–C_8PhEO_7Ac)

Characterization of AM-C_8PhEO_7Ac copolymer

The IR spectrum was recorded on a Nicolet-560 Fourier transition IR spectrometer.

The ^1H NMR spectrum of a D_2O solution was obtained using an Innova 400 spectrometer (Varian, USA).

The copolymer composition was obtained by determining C, H, and N content using a Perkin Elmer series II element analyzer.

The molecular weight was obtained by static light scattering (DLS-700, Japan).

Characterization of micelles

UV spectra of micelles in aqueous solutions at 25 °C were obtained on a Shimadzu 240 spectrometer in the wavelength range 190–400 nm. The repeatability accuracy of the wavelength was ±0.1 nm.

AFM images were observed with an atomic force microscope (Nanoscope IIIa, Digital Instruments Co., Santa Barbara, USA) at room temperature. The cantilevers used were microfabricated from Si_3N_4 and had spring constants of $0.06\ Nm^{-1}$. The AM-C_8PhEO_7Ac copolymer thin films were dip-coated on the silicon wafer substrate from their aqueous solution.

The surface tension was determined using a Kruss SITE04 tensionmeter, using a plate method, at 25 °C.

The micellar weight of the monomolecular micelle was determined by static laser light scattering (DLS-700, Japan) in the concentration range 5×10^{-6}–2.0×10^{-5} g/ml.

Results and discussion

Copolymer characterization

The copolymer structure was characterized by IR and ^1H NMR spectroscopies. As seen from Fig. 1, the IR spectrum shows the bands of AM 3353 cm^{-1} ($Vas_{N\text{-}H}$), 3200 cm^{-1} ($Vs_{N\text{-}H}$), and 1662 cm^{-1}($Vc{=}o$), ethylene oxide, 1108 cm^{-1} (Vc-o-c), and the phenyl group, 1600 and 1520 cm^{-1}($Vc{=}c$). The NMR spectrum is shown in Fig. 2. It displays all the resonance structures corresponding to the amide protons (4.5 ppm), the aromatic protons (7.75 ppm), the protons of the ethylene oxide moiety (3.5 ppm) and the -CH_3, -CH_2-, and -CH units (1.0 ~ 3.0 ppm). The NMR spectrum corresponds well with the IR spectrum. The IR and NMR spectrum correspond to a copolymer of AM and C_8PhEO_7Ac copolymer. The copolymer contains 32.2 wt% C_8PhEO_7 and 67.8 wt% AM, as determined by elemental analysis. The molecular weight is 1.21×10^5, as determined by static light scattering.

Micellar behavior of copolymer in aqueous solution

Formation of mono- and polymolecular micelles

For phenyl groups, the UV absorption band of the maximum absorbance is the π-π^* transition band. It shifts with the environmental polarity. As the environmental polarity increases, the band shifts to the red. In micellar solutions, the band of maximum absorbance is also related to the micellar size; the band shifts to the red as the micellar size increases [18].

As there are phenyl groups in the copolymer molecules, the AM-C_8PhEO_7Ac copolymer solution absorbs in the UV. The UV spectrum can reflect the polarity of the environment in which the phenyl groups are located and it thus reflects changes in the structure of the micelles. The UV spectra of copolymer solutions of different concentrations are shown in Fig. 3. The (λ_{max})s and related absorbances are plotted versus concentrations in Figs. 4 and 5.

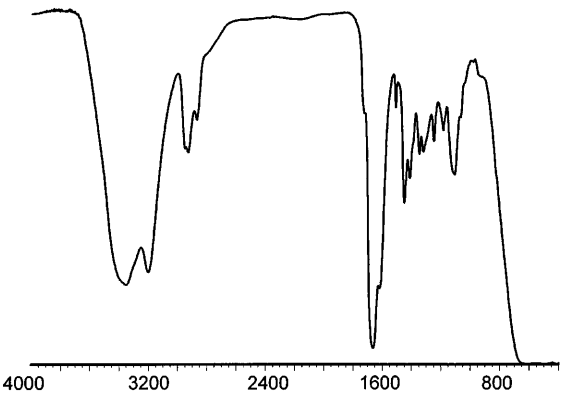
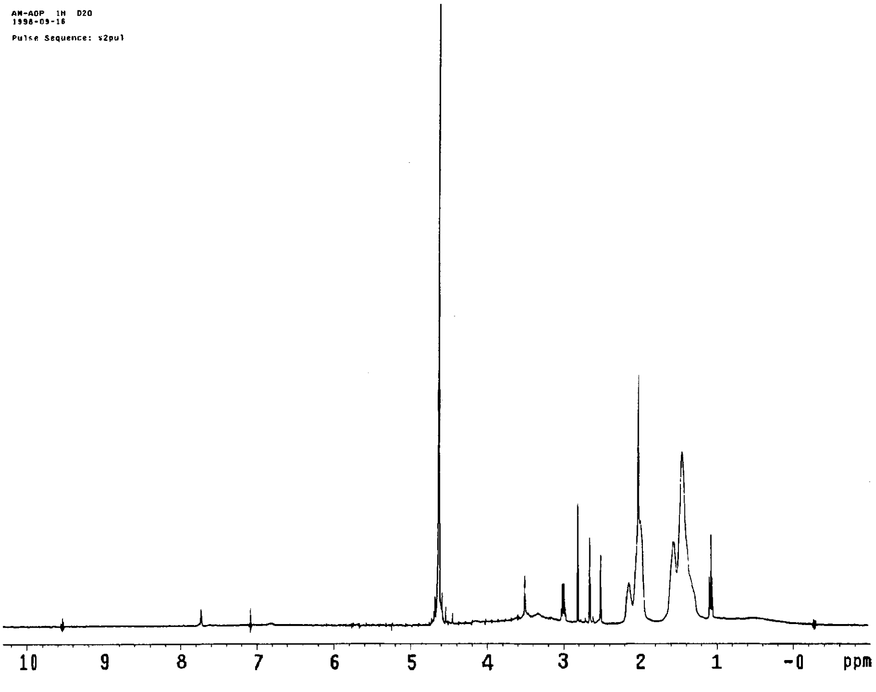


Fig. 1 IR spectrum of acrylamide–octylphenylpoly(oxyethylene) acrylate (AM-C_8PhEO_7Ac) copolymer

Figures 3 and 4 show that λ_{max} changes with concentration. As the concentration increases from 5×10^{-7} to 4×10^{-6} g/ml λ_{max} decreases, which means that the polarity of the environment in which the phenyl groups are located decreases with the increase in concentration in this range. The reason for the decrease in λ_{max} is that the copolymer molecules collapse with the increase in concentration and the hydrophobic chains tend to aggregate. λ_{max} tends to remain constant at concentrations from 4×10^{-6} to 3×10^{-5} g/ml, which indicates that the polarity of the environment in which the phenyl groups are located does not change. This is because monomolecular micelles are formed in this range, with the hydrophobic chains forming the micelle cores and the hydrophilic chains forming the outer shells. With the increase in concentration in this range, the number of monomolecular micelles increases. The micellar weight in this concentration range is 1.66×10^5, as determined by static light scattering; the aggregation number of the micelle is then 1.37, close to that of separate molecules. This further demonstrates that monomolecular micelles are formed. λ_{max} increases at a concentration of 3×10^{-5} g/ml. The increase in λ_{max} in this region is considered to be the result of an increase in micellar size as stated in Ref. [18]. With the increase in the copolymer concentration, larger aggregates of hydrophobic groups are formed and thus lead to a red shift

Fig. 2 400 MHz H NMR spectrum of AM-C_8PhEO_7Ac copolymer in D_2O



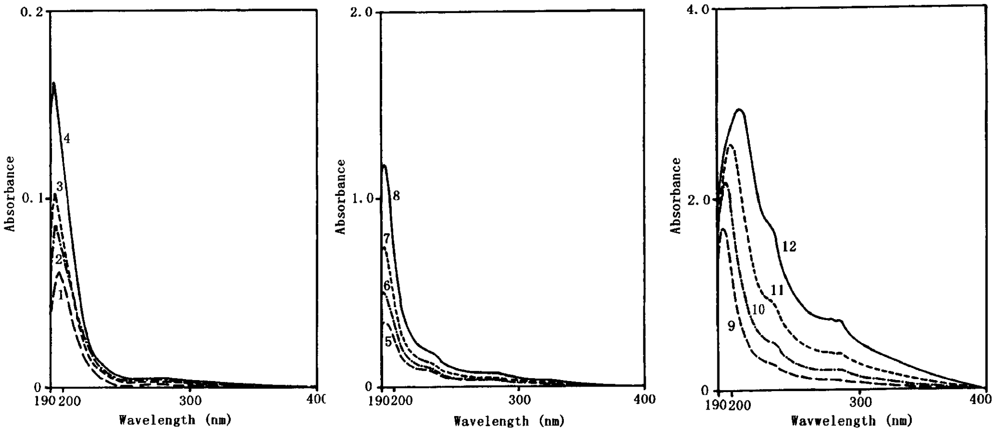


Fig. 3 UV spectra of AM-C_8PhEO_7Ac copolymer in aqueous solutions with different concentrations. Concentration from curve *1* to curve *12*: 2.5×10^{-7}, 5×10^{-7}, 1×10^{-6}, 2×10^{-6}, 4×10^{-6}, 8×10^{-6}, 1.6×10^{-5}, 3.1×10^{-5}, 6.25×10^{-5}, 1.25×10^{-4}, 2.5×10^{-4}, 5×10^{-4}

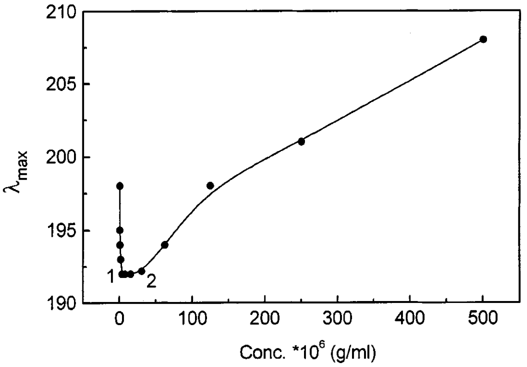


Fig. 4 Plot of λ_{max} versus AM-C_8PhEO_7Ac copolymer concentration in aqueous solution. Concentration at each transition: *1*: 4×10^{-6} g/ml; *2*: 3×10^{-5} g/ml

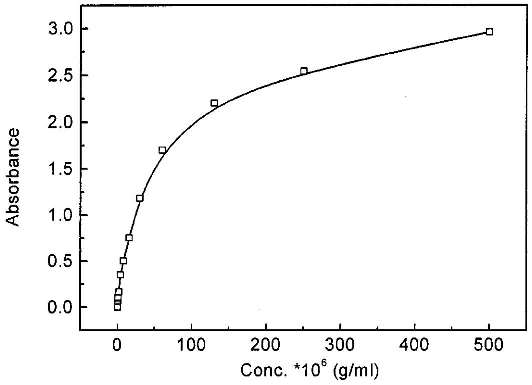


Fig. 5 Absorbance at λ_{max} of AM-C_8PhEO_7Ac copolymer solution versus concentration

of the absorption band. The increase in micellar size means that polymolecular micelles are formed.

The isothermal curve of the surface tension versus the concentration which gives the critical micelle concentration (cmc) of 1×10^{-4} g/ml is shown in Fig. 6. Comparison of Figs. 4 and 6 shows that the concentrations at which micelles begin to form are much lower than the cmc. The cmc is usually considered to be the concentration above which micelles are formed, but for the AM-C_8PhEO_7Ac copolymer the formation of micelles (monomolecular micelles and polymolecular micelles) begins at concentrations much lower than the cmc.

According to Beer's law, the absorbance increases linearly with concentration; however Fig. 5 shows that the absorbance at λ_{max} of the copolymer solution does not increase linearly with concentration and the increase in absorbance with concentration becomes slower. This is because micelles are formed in the copolymer solution, with the hydrophobic groups forming the core and the hydrophilic groups forming the outer shell. The shielding effect of the hydrophilic groups constrains the movement of the phenyl groups. As the copolymer concentration increases, the micelles become more compact, so the shielding effect becomes stronger. It can be concluded further from Fig. 5 that polymolecular micelles are more compact than monomolecular micelles.

Micellar conformations

The formation of the micelles over the whole concentration range reflected by the UV spectra can be further

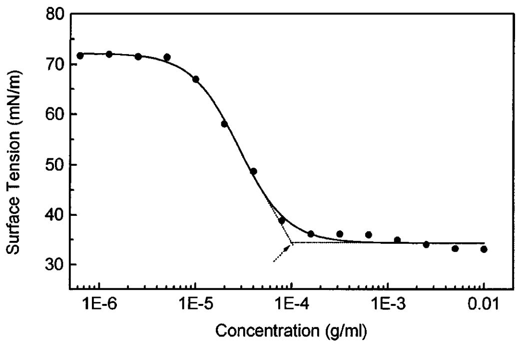


Fig. 6 Surface tension of copolymer solution versus concentration (determined at 25 °C)

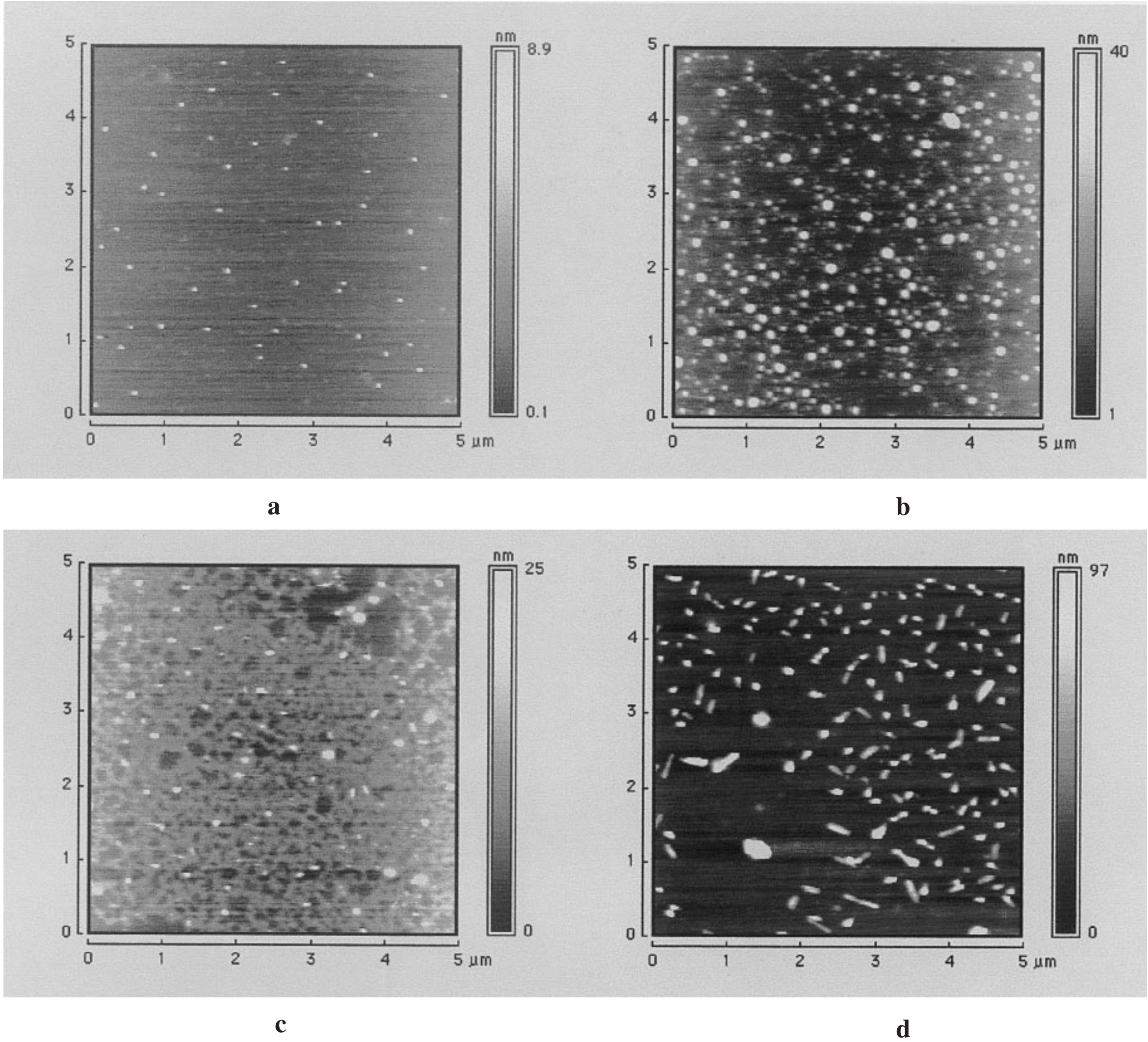


Fig. 7a–d Atomic force microscopy images of micelles in aqueous solutions of AM-C_8PhEO_7Ac copolymer. Concentrations of copolymer solutions (g/ml): **a**: 1×10^{-5}; **b**: 3×10^{-5}; **c**: 5×10^{-5}; **d**: 5×10^{-4}

demonstrated by AFM images (Fig. 7). At a concentration of 1×10^{-5} g/ml, the micelles are globular, with a size of 70 nm, and a very narrow size distribution. This concentration is just in the concentration range (4×10^{-6}–3×10^{-5} g/ml) for the formation of monomolecular micelles, shown in Fig. 4: so the micelles observed are monomolecular micelles.

At a concentration of 3×10^{-5} g/ml, which corresponds to the second transition in Fig. 4, the micelles are still globular, but the micellar size distribution is wide, with the micellar size varying from 70 to 200 nm. This means that some polymolecular micelles have been formed and coexist with monomolecular micelles. This result corresponds well with that of the analysis of the UV spectra. At a concentration of 5×10^{-5} g/ml, most micelles are globular, but some cylinders appear. At a concentration of 5×10^{-4} g/ml, the micelles are cylindrical. These results mean that polymolecular micelles may be globular or cylindrical depending on copolymer concentration.

Conclusion

The formation of micelles in aqueous solutions of AM-C_8PhEO_7Ac copolymer occurs at concentrations much lower than the cmc (1×10^{-4} g/ml). Monomolecular micelles are formed at concentrations between 4×10^{-6} and 3×10^{-5} g/ml. They are globular, with a diameter of 70 nm and a narrow size distribution. Polymolecular micelles are formed at concentrations above 3×10^{-5} g/ml. They may be globular or cylindrical depending on copolymer concentration.

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