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SHORT COMMUNICATION

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Effect of copolymer structure on micellar behavior of acrylamide-octylphenylpoly (oxyethylene) acrylate surfactant

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Abstract Acrylamide-octylphenylpoly (oxyethylene) acrylate copolymer (AM-C_8PhEO_nAc) surfactant is the copolymer of acrylamide (AM) and octylphenylpoly (oxyethylene) acrylate macromonomer (C_8PhEO_nAc). The effect of the copolymer structure on the micellar behavior in aqueous solution was studied using dynamic light scattering. It has been found that the length of ethylene oxide (EO) in the branch and the content of C_8PhEO_nAc in the copolymer surfactant have great effects on the size and distribution of the micelles. For AM-C_8PhEO_7Ac copolymer, at the concentration of 5×10^{-4} g/ml, the micellar size increases with the increase of C_8PhEO_7Ac content. However, for AM-$C_8PhEO_{10}Ac$ copolymer, the result is the opposite; the micellar size decreases with the increase of $C_8PhEO_{10}Ac$ content. Larger C_8PhEO_nAc content leads to narrower micellar distribution. For copolymer surfactants with equal C_8PhEO_nAc content, when the concentration of copolymer solution is the same, the copolymer with longer EO length forms smaller micelles.

Key words Surfactant · Micelle · Copolymer

Introduction

The micellar behavior of polymeric surfactants is of great interest and has been extensively studied [1–4]. The study of micelle behavior is of practical interest as the micellar behavior may affect the properties and applications of polymeric surfactants. There are many factors that can influence the micelles such as polymer composition and polymer structure, the property of solvent, salt, etc. One of the most interesting questions is the effect of polymer composition on micelle size, distribution, and morphology. In fact, this question has been studied in many investigations [5–8]. However, most studies have been carried out on block copolymer surfactants, which have relatively simple structures, and most studies are carried out in non-polar solvents. There have been few studies on graft copolymer surfactants and in aqueous solutions.

Graft copolymer surfactants may achieve good performance in areas such as oil recovery. Most graft copolymer surfactants reported have good properties. Their solutions usually have low surface tensions and can decrease interfacial tensions between oil and water [9, 10]. Such good performance is related to their special graft structure. However, their micelle behavior has seldom been studied.

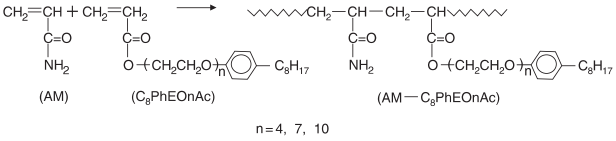
In the previous paper [11], we have synthesized AM-C_8PhEO_7Ac copolymer surfactant and studied the micellar behavior of an aqueous solution over a wide concentration range via UV spectra, surface tension determination, and atomic force microscopy (AFM). In this paper the effect of copolymer structure on polymolecular micelles of AM-C_8PhEO_nAc surfactants is studied by the method of dynamic light scattering. The effects of the length of ethylene oxide (EO) in the branch and the content of C_8PhEO_nAc on micelle size distribution are studied.

Experimental

Synthesis and characterization of AM-C_8PhEO_nAc copolymer

The C_8PhEO_nAc macromonomers were synthesized by the reaction of acrylol chloride and octylphenylpoly (oxyethylene) in benzene [12]. Acrylamide obtained from the Mitsui Toatsu Company (Japan) was recrystallized from chloroform and vacuum dried at room temperature. The copolymer surfactant was prepared from C_8PhEO_nAc macromonomer and acrylamide via free radical polymerization at 70 °C. The copolymer was then isolated and purified.

The reaction process is:



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 of 190–400 nm.

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

Dynamic light-scattering measurements

Dynamic light scattering studies were performed on a Brookhaven Instruments Corp. photon correlation spectrometer with a BI-9000At correlator and Coherent Innova laser resource with a wavelength of 514.5 nm. The scattering angle used was 90° and the temperature was controlled at 25 °C.

For the determination of size distribution, the program CONTIN was used.

Results and Discussion

Composition and molecular weight of AM-C_8PhEO_nAc copolymer surfactants

The composition and molecular weight of AMC_8-$PhEO_nAc$ copolymer surfactants are listed in Table 1. As to the sequence of the monomer units in the copolymers, Xu has reported in detail [13]. The monomers in the copolymer are randomly distributed. In molecular weight determination, the existence of micelles can greatly affect the result. To diminish the effect of micelles, the copolymers are hydrolyzed in NaOH solution to achieve polyelectrolytes. The degree of hydrolysis was determined. The molecular weights of polyelectrolytes were determined in dilute aqueous solutions. The molecular weights of the copolymer surfactants were then calculated. The theory base is that the chain length cannot be changed when the copolymer surfactants are hydrolyzed. This method can cause some error, but it is the best way for AM-C_8PhEO_nAc copolymer surfactants.

Table 1 Constituents and molecular weights of copolymers

Copolymer	Copolymer composition (w%)		Molecular weight ($\times 10^4$)
	AM	C_8PhEO_nAc	
AM-C_8PhEO_7Ac (I)	67.8	32.2	12.1
AM-C_8PhEO_7Ac (II)	83.85	16.15	–
AM-C_8PhEO_7Ac (III)	92.15	7.85	52.8
AM-$C_8PhEO_{10}Ac$ (I)	78.75	21.25	14.8
AM-$C_8PhEO_{10}Ac$ (II)	69.1	30.9	28.6

Effect of C_8PhEO_nAc content on micellar behavior

For AM-C_8PhEO_nAc surfactant, the effect of C_8PhEO_nAc content on micellar behavior is first demonstrated from the change of CMC (critical micelle concentration) with the change of C_8PhEO_nAc content. CMC was obtained from the surface tension vs concentration line. The CMC decreases with the increase of C_8PhEO_nAc content, as seen from Table 2. As the molecules are more hydrophobic with the increase of C_8PhEO_nAc content, this trend is the same as that of low molecular weight surfactants. The more hydrophobic surfactants can form micelles at lower concentrations.

In order to study the effect of C_8PhEO_nAc content on the micellar behavior of copolymer surfactant, the micellar behaviors of AM-C_8PhEO_7Ac and AM-$C_8PhEO_{10}Ac$ in aqueous solution were studied respectively. In each group, the branch chain length is the same, so the effect of the branch chain can be neglected in each group. As the molecular weight of polymeric surfactant affects the micellar behavior very little [14], this effect can also be ignored. Thus the effect of C_8PhEO_nAc content can be studied.

AM-C_8PhEO_7Ac copolymer surfactant

Figure 1 compares the micelle size and distribution of AM-C_8PhEO_7Ac copolymer surfactants with different

Table 2 CMC of AM-C_8PhEO_nAc copolymer surfactants

AM-C_8PhEO_7Ac copolymer		AM-$C_8PhEO_{10}Ac$ copolymer	
C_8PhEO_7Ac content (%)	CMC (g/ml)	$C_8PhEO_{10}Ac$ content (%)	CMC (g/ml)
7.85	6×10^{-4}	21.25	4×10^{-4}
16.15	4×10^{-4}	30.9	3.2×10^{-4}
32.2	1×10^{-4}	47.7	9×10^{-5}

C_8PhEO_7Ac content at the concentration of 5×10^{-4} g/ml in aqueous solutions. Table 3 shows the average micelle size and the relative variance POLY. The average micelle size increases with the increase of C_8PhEO_7Ac content. This is because that, with the increase of C_8PhEO_7Ac content, the polymeric surfactant becomes more hydrophobic, which increases the ability of polymeric surfactant to form micelles. As the copolymer becomes more hydrophobic with the increase of C_8PhEO_7Ac, the micelle size will become smaller when the aggregation number of micelles remains the same because of the hydrophobic effect. Thus it can be deduced that the increase of micellar size is then due to the increase in aggregation number. It can also be seen from Fig. 1 and Table 3 that the micelles of copolymer surfactant with lower C_8PhEO_7Ac content show wider distribution.

AM-$C_8PhEO_{10}Ac$ copolymer surfactant

Figure 2 and Table 4 illustrate the micelle size and distribution of AM-$C_8PhEO_{10}Ac$ copolymers. The copolymer with higher $C_8PhEO_{10}Ac$ content forms smaller micelles than that with lower $C_8PhEO_{10}Ac$ content does. This result is different from that of AM-C_8PhEO_7Ac copolymers. The reason for this difference may be that the size of micelles formed by AM-$C_8PhEO_{10}Ac$ copolymer in aqueous solution is mainly determined by the extension degree of hydrophilic chains. Hydrophilic chains form the outer layer of the micelles; their extension degree is the main determination of micelle size. The micelles of AM-$C_8PhEO_{10}Ac$ copolymer with lower $C_8PhEO_{10}Ac$ content are less compact than the micelles of copolymer with higher $C_8PhEO_{10}Ac$ content due to the extension of the hydrophilic chains that makes the outer layer. It can also be seen from Fig. 2 and Table 4 that micelles of copolymer with higher $C_8PhEO_{10}Ac$ content have smaller POLY. This result is the same as that of AM-C_8PhEO_7Ac copolymer.

There are two main factors that influence micelle size: the aggregation number and the extension of hydrophilic chains. The larger the aggregation number, the larger the micelle size. In aqueous solutions the hydrophilic chains form the outer layer. The more they extend the larger the micelle size. For different copolymers the influences of the two factors are different. For AM-C_8PhEO_7Ac copolymer the increase of micelle size with the increase of C_8PhEO_7Ac content is due to the increase of aggregation number. For AM-$C_8PhEO_{10}Ac$ copolymer the main effect is the extension degree of hydrophilic chains; the decrease of $C_8PhEO_{10}Ac$ content makes the copolymer more hydrophilic and thus leads to greater extension extent of hydrophilic chains, which in turn makes larger micelles.

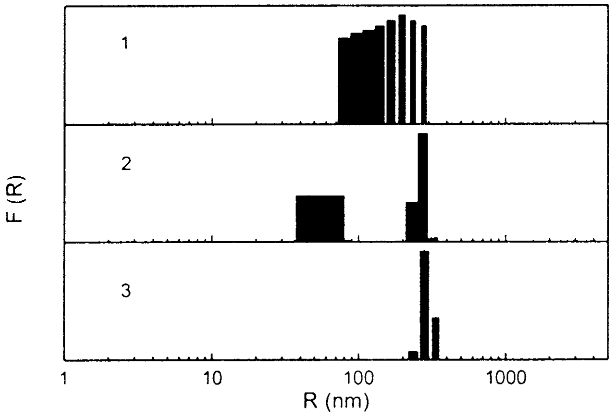


Fig. 1 The intensity-averaged distribution curves, F(R), for 5×10^{-4} g/ml AM-C_8PhEO_7Ac copolymers in aqueous solutions as functions of macromonomer content of C_8PhEO_7Ac in weight: 1: 7.85%, 2: 16.15%, 3: 32.2%

Table 3 Photo correlation spectrum characterization results of copolymer micelles in aqueous solution determined by CONTIN method

Content of C_8PhEO_7Ac	Radius (nm)	POLY
7.85	169	0.148
16.15	212.5	0.183
32.2	292	0.009

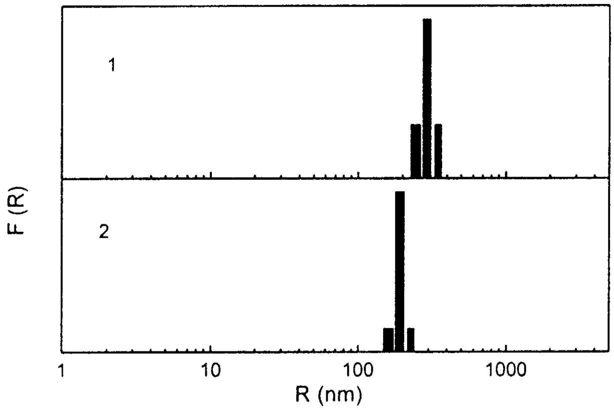


Fig. 2 The intensity-averaged distribution curves, F(R), for 5×10^{-4} g/ml AM-$C_8PhEO_{10}Ac$ copolymers in aqueous solutions as functions of macromonomer content macromonomer content: 1: 021.25, 2: 030.9

Table 4 Photo correlation spectrum results of copolymer micelles in 5×10^{-4} g/ml aqueous solution determined by CONTIN method

Content of $C_8PhEO_{10}Ac$	Radius (nm)	POLY
21.25	293.5	0.012
30.9	192	0.007

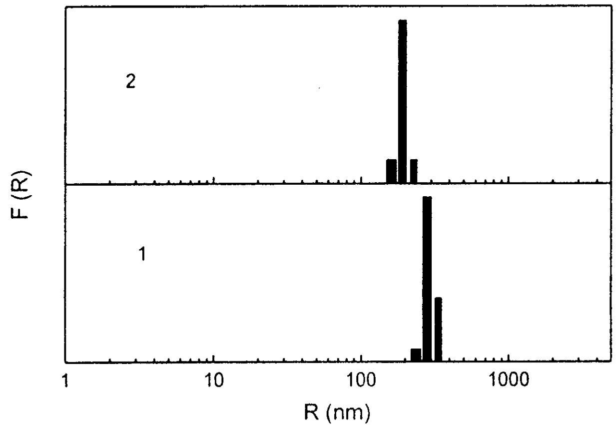


Fig. 3 The intensity-averaged distribution curves, F(R), for 5×10^{-4} g/ml AM-C_8PhEO_nAc copolymers in aqueous solutions as functions of EO length: 1: 7, 2: 10. Content of C_8PhEO_7Ac and $C_8PhEO_{10}Ac$ in copolymers: 32.2 wt%, 30.9 wt%

Table 5 Photo correlation spectrum characterization results of copolymer micelles in aqueous solution determined by the CONTIN method

EO length of branch	Diameter (nm)	POLY
7	292	0.009
10	192	0.007

Copolymer concentration: 5×10^{-4} g/ml
Content of C_8PhEO_7Ac and $C_8PhEO_{10}Ac$: 32.2 wt%, 30.9 wt%

Effect of branched chain length

For AM-C_8PhEO_nAc copolymer, the branched chain length affects the hydrophilicity and thus affect the micellar behavior. Here we refer to the EO chain length (n) other than the branched chain length because only the EO length determines the branch length. The micellar behaviors of AM-C_8PhEO_nAc copolymers with the EO length of 7 and10 respectively were compared in Fig. 3 and Table 5. The copolymers compared are of nearly equal macromonomer content. The micelles formed by AM-$C_8PhEO_{10}Ac$ copolymer have smaller size than that formed by AM-C_8PhEO_7Ac copolymer. At the same concentrations, because AM-$C_8PhEO_{10}Ac$ copolymer is more hydrophilic, its molecular chains extend more than that of AM-C_8PhEO_7Ac, so if the micelles of the two copolymers have the same aggregation number, the micelles of AM-$C_8PhEO_{10}Ac$ will have a larger size. So it can be deduced that a smaller aggregation number causes smaller micelles of AM-$C_8PhEO_{10}Ac$. From Fig. 3 and Table 5 it can also be seen that micelles of the two copolymers all have a narrow distribution.

Conclusions

For AM-C_8PhEO_7Ac copolymer, the average micelle size increases with the increase of C_8PhEO_7Ac content. However, for AM-$C_8PhEO_{10}Ac$ copolymer, the micelle size decreases with the increase of $C_8PhEO_{10}Ac$ content. For both copolymer systems, the micelles size shows narrower distribution when the content of macro monomer increases.

For copolymers with the same macro monomer content, at the same concentration, copolymer with larger EO length forms smaller micelles.

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