Polymer Bulletin 25, 467–474 (1991)

Polymer Bulletin

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Water-soluble and amphiphilic polymers

7. Synthesis and characterization of a novel comb-type amphiphilic polymer PAMC$_{16}$S

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SUMMARY

A novel comb-like amphiphilic polymer, poly(2-acrylamidohexadecylsulfonic acid)(PAMC$_{16}$S), was synthesized by free radical polymerization of the corresponding amphiphilic monomer in 1,4-dioxane-water mixed solvents. Depending on the ratio of water/dioxane in the solvent, the reaction proceeded by either precipitation polymerization or micellar polymerization. The molecular weight of the polymer obtained under similar conditions decreased and subsequently increased with the increase of water content in the mixed solvent. The polyion nature of PAMC$_{16}$S was confirmed by viscosity data of ethanolic solutions. In addition, the polymer was characterized by solubility, IR, TG and wide angle X-ray diffraction methods.

INTRODUCTION

Langmuir-Blodgett film formation utilizes the tendency of an amphiphilic molecule, such as a fatty acid, to form a monolayer at an air-water interface. A major drawback in the application of LB films made of low molecular amphiphiles is the inability to form stable mono- and multilayers. In order for these thin films to exhibit good mechanical and thermal properties, they must be in a polymeric form. It can be expected that the synthesis of tailored amphiphilic monomers and polymers will become more and more important.

As to amphiphilic polymers, we would like to classify them into four categories: block-type (1-11), graft-type (12-18), comb-type (19), and random copolymer-type(20, 21) . The representative amphiphilic polymers are illustrated in Figure 1.

The comb-type amphiphilic polymers are homopolymers of amphiphilic monomers. Due to the great structural similarity between fatty acids and comb-type amphiphilic polymers, the latter

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*To whom offprint requests should be sent will be of particular importance for the formation of well-organized polymeric LB films, although three other types of amphiphilic polymers have also been studied (11,18,20,21).

In this work, a new comb-type amphiphilic polymer,poly(2-acrylamidohexadecylsulfonic acid), was synthesized in 1,4-dioxane-water mixed solvents by free radical polymerization and characterized by solubility, viscometry, IR, thermogravimetry (TG) and wide angle X-ray diffraction methods.

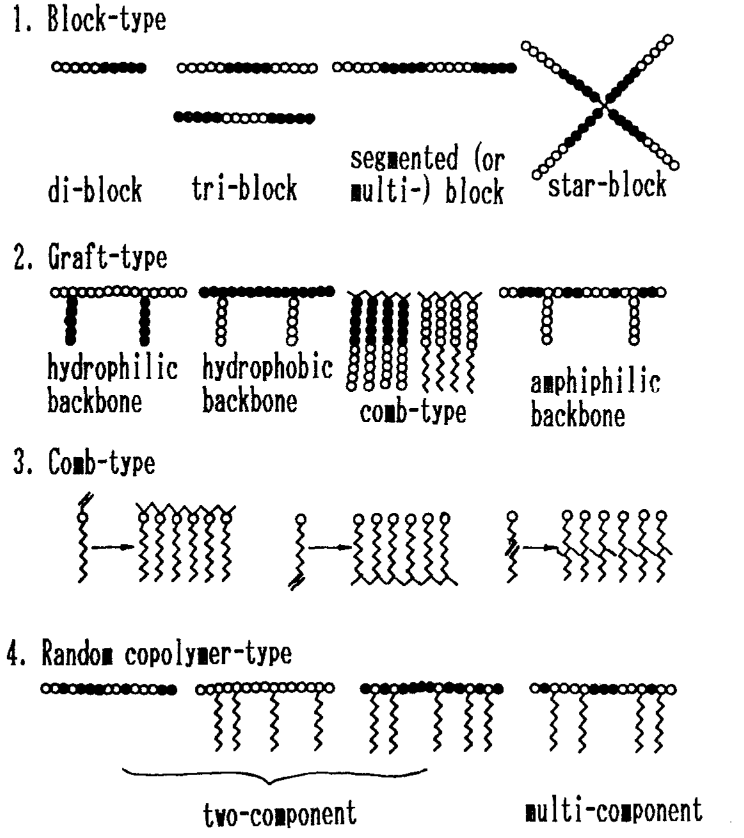

Figure 1. An illustration of classification of amphiphilic polymers
○○○○○ hydrophilic segment; ●●●●● hydrophobic segment;
〰 aliphatic chain; ○ hydrophilic unit;
● hydrophobic unit

EXPERIMENTAL

Materials --- Synthesis and characterization of the amphiphilic monomer, 2-acrylamidohexadecylsulfonic acid (AMC$_{16}$S) was described in a previous paper (22). THF and 1,4-dioxane were dried with CaH_2 (refluxed under N_2 for more than 24 hours) and distilled before use. Water was twice-distilled. Ethanol and DMF were standard A. R. grade solvents and used as received.

Polymerization --- The polymerization of AMC$_{16}$S was carried out in dioxane-water mixed solvents by the use of azobisisobutyronitrile (AIBN) as initiator in a degassed sealed vial. After 6 hours reaction at 70 ℃, the polymerization was stopped by introducing 2 ml of a hydroquinone solution in dioxane (C=10mg/ml). The resulting polymer was isolated by treating the reaction mixture three times with dioxane and dried in vacuum at about 50 ℃.

Characterization --- Viscosity measurements were performed at 30±0.05℃, using an Ubbelohde viscometer. The constants K′ and β were calculated as usual from the plots of η_{sp}/C and $\ln\eta_r/C$ against concentration C, respectively. The thermogravimetric (TG) curves were recorded on a Thermoflex thermal analyzer. Samples of about 4~4.5 mg were degraded in dynamic air or nitrogen atmosphere (50 ml/min) at a heating rate of 10℃/min. Wide angle X-ray diffraction was carried out on a D/max-ⅡB X-ray diffractometer (Rigaku) with a Cu target by running at 40 kV, 20 mA, and a scan speed of 2 deg./min.

RESULTS AND DISCUSSION

AMC$_{16}$S is soluble in water, ethanol, THF, DMF, and 1,4-dioxane-water mixed solvents containing more than about 5 vol % water, and can be polymerized via free radical polymerization mechanism by using AIBN, H_2O_2, or (Ce^{+4}+ROH), etc. as initiator.

In this work, the polymerization was carried out in dioxane-water mixed solvents by using AIBN as initiator. The polymerization recipes are given in Table 1. AMC$_{16}$S was polymerized almost completely under the conditions used. One of the interesting features of AMC$_{16}$S polymerization in dioxane-water mixed solvents was the change in polymerization behavior with the increase of water content in the solvent. In the cases of dioxane-rich solvents (sample NP1~3), the resulting polymer precipitated out from the solutions as a transparent sticky mass because PAMC$_{16}$S was insoluble in the mixed solvents. When polymerization was effected in water-rich solvents (NP4 and 5), the reaction mixture became a white gel-like mass soon after polymerization had started. Taking into account that $AMC_{16}S$ is a micelle-forming surfactant in water (22), we can visualize that the architecture and conformation of $AMC_{16}S$ change with the ratio of water/dioxane. In a water-rich solvent $AMC_{16}S$ exists in the form of an emulsion with the double bond located at the outer layer of the micelles, and gel-like products are obtained due to intra- and inter-micelle polymerization and insolubility of the resulting polymer in the mixed solvents. The gel-like mixture became sticky and transparent after being treated with dioxane to remove the water.

The resulting polymer was found to be soluble in THF, DMF, and ethanol. Contrary to the monomer, $PAMC_{16}S$ is insoluble in water and dioxane-water mixed solvents.

Viscosity measurements of the resulting polymer in ethanol reveal the polyion nature of $PAMC_{16}S$. As shown in Figure 2, the η_{sp}/C rises without an intercept with the decrease of concentration because of the progressive loss of the shielding counterions from the domain of the polyion. A normal type of viscosity behavior was observed when the viscosity measurements were performed in THF solutions. The data obtained from viscosity measurements are tabulated in Table 1. Interestingly, the molecular weight of $PAMC_{16}S$, expressed in terms of intrinsic viscosity $[\eta]$, was found to decrease and subsequently increase with the increase of water content in the mixed solvent. The minimum value of $[\eta]$ was obtained when water/dioxane (v/v) was about 40/60. It seems likely that the increase of molecular weight with the increase of the water content (in the region water/dioxane> 40/60) is connected with the micellar polymerization occured in this mixed solvent region.

Table 1. Polymerization recipe and results of viscosity measurements of $PAMC_{16}S$ in THF

Sample code	Recipe				Viscosity measurement			
	dioxane (ml)	water (ml)	$AMC_{16}S$ (g)	AIBN (g)	$[\eta]$ (ml/g)	K'	β	$K'+\beta$
NP1	46	4	4.5	0.02	39.2	0.222	0.256	0.478
NP2	40	10	4.5	0,02	17.7	0.332	0.168	0.500
NP3	30	20	4.5	0.02	14.6	0.316	0.181	0.497
NP4	20	30	4.5	0.02	20.3	0.328	0.167	0.495
NP5	10	40	4.5	0.02	32.6	0.357	0.148	0.505

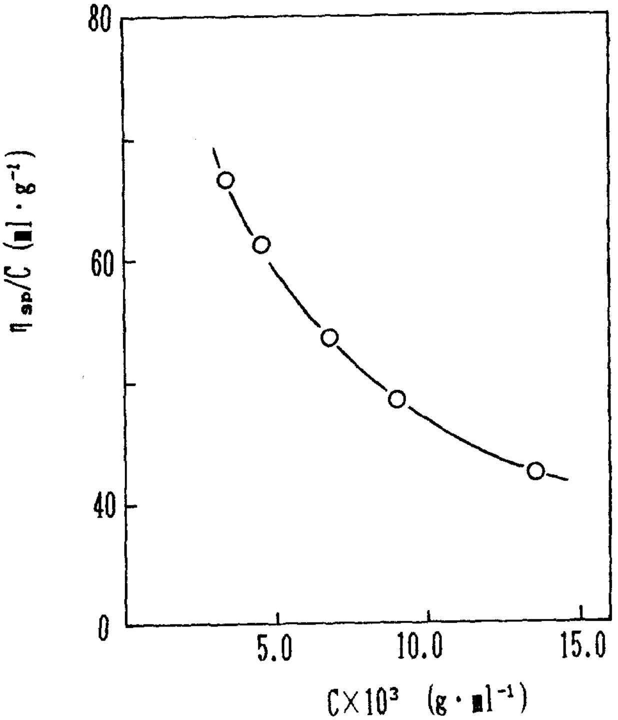

Figure 2. Variation of η_{sp}/C with C of NP4 in ethanolic solutions

Figure 3 shows the IR spectrum of PAMC$_{16}$S. Compared with that of AMC$_{16}$S (22), the apparent difference is the disappearance of the characteristic peak of the C=C double bond at 1620 cm^{-1}.

The wide angle X-ray diffraction curve of PAMC$_{16}$S is depicted in Figure 4. It is of interest to note that a strong diffraction peak appears at low angle (about 3.2°) for sample NP1.

Figure 5 shows dynamic TG curves of PAMC$_{16}$S in both air and nitrogen. As it can be seen, the pyrolysis of PAMC$_{16}$S takes place in three steps in air. The temperature range and weight loss for each stage are listed in Table 2. It seems that these results are consistent with the structure of the polymer. Three stages appear in the TG curve: they correspond approximately to the decomposition of CH_3-$(CH_2)_{13}$- aliphatic tail, polyacrylamido-backbone, and $>$CH-CH_2-SO_3H residue, respectively. In nitrogen , however, only two steps exist in the TG curve and this polymer exhibits a much faster rate of pyrolysis.

Compared with low molecular weight amphiphiles, PAMC$_{16}$S has a much better thermal stability.

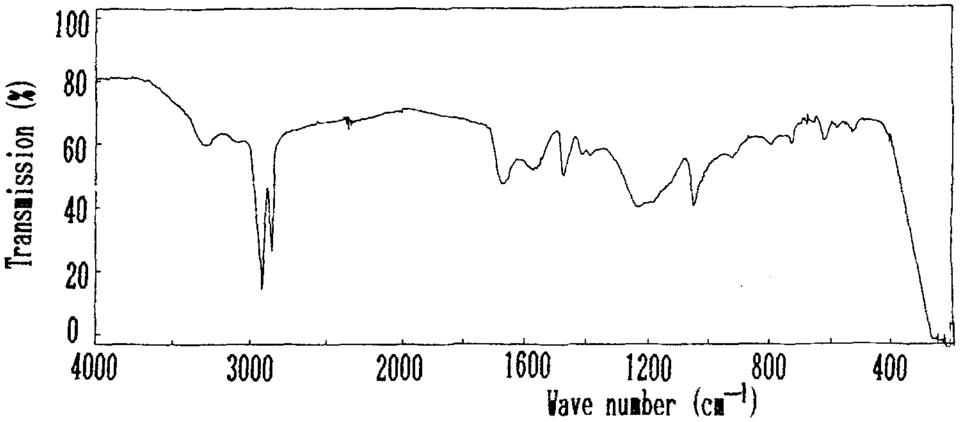

Figure 3. IR spectrum of PAMC$_{16}$ S (NP1, cast from THF solution)

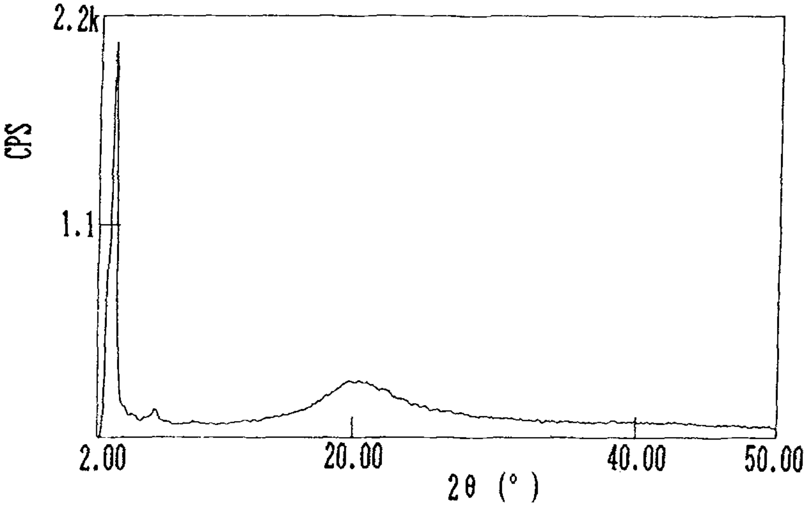

Figure 4. X-ray diffraction pattern of PAMC$_{16}$ S (NP1)

Table 2. Thermal analysis data of PAMC$_{16}$ S

Atmosphere	First stage		Second stage		Third stage	
	temp. range(° C)	weight loss(%)	temp. range(° C)	weight loss(%)	temp. range(° C)	weight loss(%)
air	215-340	52.0	340-439	18.8	439-592	29.2
nitrogen	215-352	70.0	352-484	27.5		

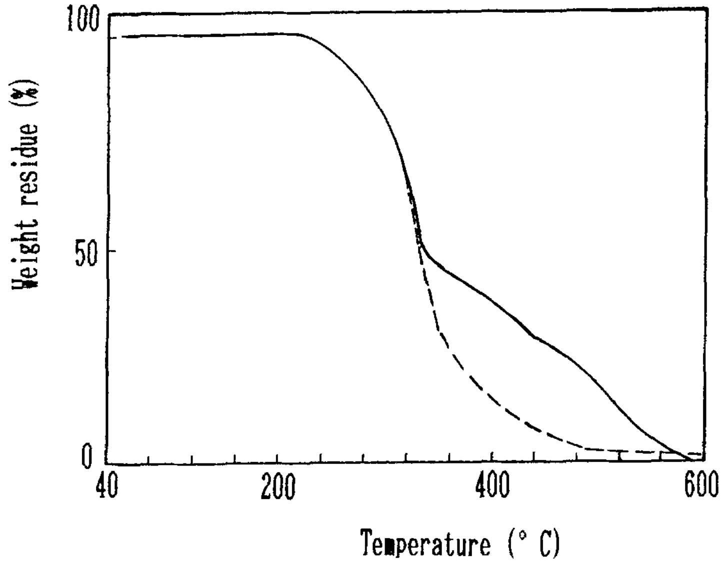

Figure 5. TG curves of NP4 in air (solid line) and nitrogen (dotted line)

$\mathrm{PAMC}_{18}\mathrm{S}$ is a novel comb-type amphiphilic polymer, each repeat unit of which contains a hydrophilic sulfonic acid and an amido group, and a hydrophobic long aliphatic hydrocarbon chain. It has been found that $\mathrm{PAMC}_{18}\mathrm{S}$ is a good candidate for LB films and exhibits excellent adsorption stability of hydrophilic substrates. The formation and properties of LB films of $\mathrm{PAMC}_{18}\mathrm{S}$ will be reported in the future.

ACKNOWLEDGEMENT

The financial supports of this work by the Chinese Academia Sinica and National Natural Science Foundation of China are gratefully acknowledged. The authers wish to thank Dr. J. P. Kennedy for his helpful discussions.

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Accepted December 11, 1990 K