Macromolecules **2003,** *36,* 5321−5330

Polymer Micelle Formation without Gibbs Monolayer Formation: Synthesis and Characteristic Behavior of an Amphiphilic Diblock Copolymer Having Strong Acid Groups

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Received September 23, 2002; Revised Manuscript Received March 17, 2003

ABSTRACT: A novel amphiphilic diblock copolymer having sulfonic acid groups in its hydrophilic chain with poly(diethylsilacyclobutane) as a hydrophobic segment was synthesized by living anionic polymerization followed by treatment with 1,3-propane sultone. The polymer backbone with a degree of polymerization of 18 (hydrophobic):37 (hydrophilic) was synthesized, and three kinds of diblock copolymers with different degrees of sulfonation ($\alpha = 0$, 0.50, 0.81) were prepared as sodium salts. The surface tension of aqueous solutions of highly sulfonated polymers as including the $\alpha = 0$ (all carboxylic acid) polymer did not decrease with polymer concentration. The solutions did not show foam formation even after vigorous shaking, and almost no adsorption of polymer molecules was observed at the air/water interface by X-ray reflectivity measurement. However, micelle formation with a radius of 140−200 Å was confirmed by dynamic light scattering and small-angle X-ray scattering experiments. Hence, this polymer showed "micelle formation" without "Gibbs monolayer formation" in water. The surface tension decrease in 0.5 M NaCl aqueous solution was also small, but adsorption of polymer was observed by X-ray reflectivity in addition to formation of foam by shaking. The strong ionic character of this novel class of amphiphilic polymer is thought to be the origin of this curious behavior.

Introduction

Amphiphilic diblock copolymers are attracting keen attention from fundamental and practical points of view.[1] Amphiphilic polymers usually have surface activity and show self-assembling behavior such as a micelle formation in aqueous media and monolayer formation at interfaces. The polymer self-assembly has a great variety in morphologies, and its mechanism and methods of control are novel and important fields in fundamental polymer and surface sciences. Unlike low molecular weight surfactants, amphiphilic polymers have long polymer chains in both the hydrophilic and hydrophobic parts, and this situation makes it possible to design the molecular architecture and introduce functionality in molecules. Needless to say, their specific surface activity and self-assemblization lead to novel and high-performance industrial applications, especially in detergents, cosmetics, electronics, coating, thin films, and medicines such as drug delivery and biocompatibility.

We have been performing a systematic investigation on amphiphilic polymers, from molecular design and synthesis to characterization, including basic properties and the formation of micelles and monolayers. We have clarified the relationship between the molecular structure of polymers and nanostructure of micelles in nonionic amphiphilic diblock copolymer systems. For example, we have found a sphere-to-rod transition with increasing hydrophobic chain length[2] and temperature-dependent sphere−disk transition of micelle morphology for two polymer systems.[3,4] What is interesting and important in these systems is the mechanism of transition: a transition occurs by crystallization of hydrophobic polymer chains in the micelle core, while the commonly studied temperature-sensitive micelle transition is due to dehydration of the hydrophilic headgroup. These might be new temperature-sensitive micellar systems. In addition, we have been studying the specific character of amphiphilic polymers and their micelles in water having silicon and fluorine atoms in polymer chains.[5,6]

Recently, we have been extensively studying amphiphilic diblock copolymer systems having ionic groups in the hydrophilic chain. Needless to say, ionic groups can be divided into two categories by their dissociation behavior: weak acid/base and strong acid/base. For the weak acid systems, we have already succeeded in synthesizing a novel polymer, poly(diethylsilacyclobutane-*b*-methacrylic acid),[7] and investigated its monolayer structure on the water surface in detail by in situ X-ray reflectivity as a function of surface pressure, hydrophobic/hydrophilic chain length, and pH.[8−11] From these studies, we found a very interesting and specific nanostructure of weak polyelectrolyte brush at the air/water interface, i.e., carpet/brush structure.[9] For weak polyelectrolyte block copolymer systems, interesting phenomena such as morphology changes and dynamics have been reported.[12,13]

Although the weak polyelectrolyte block copolymer systems have been studied extensively, strong acid/base block copolymers have hardly been studied. This might be due to difficulty of synthesis because of the large difference between hydrophobicity and hydrophilicity followed by large solubility differences. Szczubialka et al. synthesized a block copolymer of styrene and sulfonated isoprene and investigated its micelle formation in an aqueous solution mainly by utilizing light scattering and fluorescence techniques.[14a] Föster et al. synthesized poly(styrenesulfonate)-*b*-polyisoprene and investigated its micelle structure in aqueous solution by scattering methods.[14b] Helm et al. studied the polyelectrolyte brush structure on water by X-ray reflectivity by utilizing an insoluble polymer monolayer of poly-

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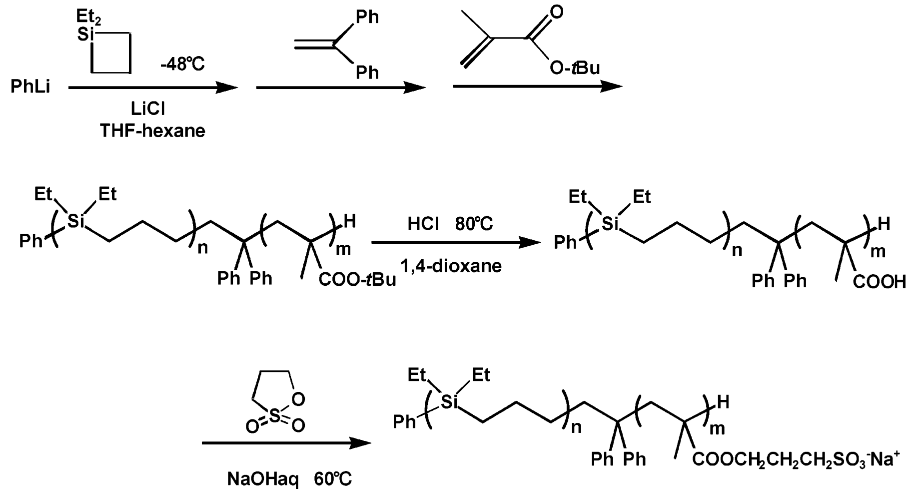
10.1021/ma0215161 CCC: $25.00

Scheme 1



(ethylethylene)-*b*-sulfonated polystyrene.[15] Eisenberg et al. investigated a polystyrene-*b*-quarternized poly(vinylpyridine) micelle and monolayer and found a unique two-dimensional self-assembly named “jelly fish micelles”.[16] In addition, recently, novel methods of synthesizing ionic polymers and ionic block copolymers by utilizing living radical polymerization have been proposed[17] and have increased the interest in ionic polymers. However, these studies focused only on self-assembly; the fundamental properties of amphiphilic block copolymers having a strong acid/base have not yet been clarified enough to discuss the special characteristics of strong polyelectrolyte block copolymers.

In this study, we synthesized a novel amphiphilic diblock copolymer having strong acid groups PEt$_2$SB-*b*-PSPMNa from poly(diethylsilacyclobutane)-*b*-poly(methyl methacrylate) by utilizing the sulfonation reaction by 1,3-propane sultone. We examined the molecular characteristics of this novel polymer by surface tension and foam formation measurements for its aqueous solution and checked its self-assembling behavior by hydrophobic dye solubilization, dynamic light scattering (DLS), and small-angle X-ray scattering (SAXS) techniques. The common sense of behavior of amphiphiles in aqueous solution with increasing concentration is, needless to say, (1) adsorption at air/water interface to form Gibbs monolayer with equilibrium between a small amount of unimer in solution, which results in a decrease of surface tension, (2) when the water surface is fully covered by a Gibbs monolayer, additional amphiphiles form micelles in solution (the critical micelle concentration, cmc), and (3) an increase in micelle number and/or size with dynamic exchange between unimers and micelles in solution. These are descriptions appearing commonly in textbooks for surface and interface science, but our polymer does not follow this well-established criterion.

Experimental Section

Materials. 1,1-Dichlorosilacyclobutane was a product from Aldrich. *tert*-Butyl methacrylate was purchased from Wako Pure Chemical Co. (Osaka, Japan) and distilled twice under vacuum (3.9×10^3 Pa) at 40 °C with calcium hydride after removal of inhibitor by extraction and humidity by sodium sulfate. 1,1-Diphenylethylene was a product of Tokyo Kasei (Tokyo, Japan) and also purified by distillation before use. Sodium chloride, hydrochloric acid, sodium hydroxide, methanol, toluene, and chloroform were purchased from Wako. *trans*-Stilbene, tetrahydrofuran, dimethyl sulfoxide, and sodium sulfonate were obtained from Nacalai Tesque (Kyoto, Japan). Tetrahydrofuran was also distilled over sodium benzophenone ketyl radical. Phenyllithium was purchased from Kanto Chemicals Co. (Tokyo, Japan). Water used for polymer sample preparation, and solution preparation was ultrapure water obtained by a Milli-Q system (Millipore, Pittsburgh, PA) whose resistance was more than 18 MΩ•cm. Deuterated reagents for NMR measurements, *d*-methylene chloride, *d*-tetrahydrofuran, and deuterium oxide, were all products of Aldrich.

Synthesis. Synthesis of PEt$_2$SB-*b*-P*t*BuMA Block Copolymer. As described in the Introduction, a difficulty in strong polyelectrolyte block copolymer studies lies in the synthesis procedure. Our strategy to overcome this hurdle is the “stepwise” procedure. First, a nonionic diblock copolymer was synthesized; this was converted to a weak polyelectrolyte block copolymer, and then the weak acid groups were changed to a strong acid group, i.e., sulfonic acid.

The procedure of synthesizing PEt$_2$SB-*b*-PSPMNa is shown in Scheme 1. The details are as follows. 1,1-Diethylsilacyclobutane was synthesized from 1,1-dichlorosilacyclobutane by the Grinard reaction as previously described.[18] Lithium chloride (60 mg) was put into a double-necked flask and dried at 130 °C under 10.5 mmHg for 3 h followed by Ar gas flow. The solvent (9 mL of tetrahydrofuran and hexane) and 1,1-diethylsilacyclobutane monomer (2.28 mL) were added. By titration of lithium naphthalene, impurities were removed. The temperature was changed to −48 °C, and then the living anionic polymerization reaction was started by addition of phenyllithium as an initiator. After 30 min of reaction, diphenylethylene (DPE, 0.53 mL) was added to end-cap the living end. Thirty minutes later, the second monomer, *tert*-butyl methacrylate (4.85 mL), was added. The polymerization reaction was stopped by addition of methanol after 1.5 h. The diblock copolymer was extracted in toluene/water. Sodium sulfonate was added to remove any trace of water in the toluene phase, and then the resultant polymer was precipitated by addition of methanol. The degree of polymerization of each block was estimated by ^{1}H NMR with benzene rings in the initiator and DPE as a standard. n:m = 18:37 was obtained, which means that both of the Et$_2$SB and *t*-BuMA segments have almost the same chain length. The polydispersity was found to be $M_w/M_n = 1.09$ by GPC relative to a polystyrene standard.

Hydrolysis. Five grams of PEt$_2$SB-*b*-P*t*BuMA obtained above was dissolved into 90 mL of dioxane. For the hydrolysis reaction, we added 16.2 mL of hydrochloric acid at 80 °C and left the solution overnight. PEt$_2$SB-*b*-PMA thus obtained was purified as follows. The resulting mixture was poured into water to precipitate the polymer. After being washed with water, the polymer was redissolved in 1,4-dioxiane and then lyophilized. The completion of reaction was confirmed by the absence of the *tert*-butyl unit signal of the polymer in *d*-THF solution in ^{1}H NMR spectra.

Table 1. Solubility before (PEt$_2$SB-*b*-PMA) and after Sulfonation (PEt$_2$SB-*b*-PSPMNa)[a]

solvent	before	after
chloroform	×	×
tetrahydrofuran	O	×
methanol	O	×
dimethyl sulfoxide	O	O
0.1 M NaOH(aq)	O	O
water	×	O

[a] O = soluble; × = insoluble.

Sulfonation by 1,3-Propane Sultone. PEt$_2$SB-*b*-PMA (1.5 g) was dissolved in 5 equiv of sodium hydroxide aqueous solution (20 mL) and then treated with a large excess of 1,3-propane sultone (18 mL). Since the reaction mixture becomes acidic by the proceeding reaction, the solution pH was kept under an alkaline condition by addition of sodium hydroxide during the reaction. Since PEt$_2$SB-*b*-PMA is already amphiphilic, the polymer in solution is thought to already have formed micelles in solution, but the details could not be elucidated. The polymers obtained in sodium salt form were purified by dialysis against ultrapure water. As shown in Table 1, the marked change of the solubility against solvents was confirmed, which guarantees the successful completion of the sulfonation reaction. The degree of sulfonation was determined by ^{1}H NMR and conductometric titration using an aqueous solution of sodium hydroxide after treatment of polymers with ion-exchange resin to make both sulfonic and carboxylic groups in acid form. Two kinds of PEt$_2$SB-*b*-PSPMNa with a degree of sulfonation of 0.50 and 0.81 in addition to the $\alpha = 0$ sample were prepared. An α value of 0.50 means that 50% in hydrophilic segment has a sulfonic group and the other 50% has a weak acid, carboxylic group.

Gel Permeation Chromatography (GPC). GPC experiments were carried out by a Jasco 880-PU with a Jasco 830-RI refractive index detector with four kinds of polystyrene-gel columns (Shodex K-802, K-803, K-804, K805). The eluent was chloroform.

Nuclear Magnetic Resonance (NMR). ^{1}H NMR measurements were performed by JEOL GSX270 (JEOL Ltd., Tokyo, Japan). Solvents were *d*-methylene chloride for the parent block copolymer and D$_2$O for the homopolymer of hydrophilic segments after sulfonation.

Surface Tension. Surface tension measurements were performed by an automatic surface tensiometer CBVP-Z (Kyowa Interface Science, Co. Ltd., Tokyo, Japan) at room temperature in fully automatic mode.

Solubilization of Hydrophobic Dye. Solubilization of hydrophobic dye into a polymer solution was measured in a rectangular quartz cell with a U-3310 spectrophotometer (Hitachi, Tokyo, Japan). The large excess of hydrophobic dye was put into the polymer solution. After waiting one night to make excess dye sediment to the bottom, the UV adsorption spectrum was measured. The pure polymer solution without dye was used as a reference sample. The hydrophobic dye used was *trans*-stilbene, which has a specific adsorption peak at 300 nm.

Foam Formation Experiments. A foam formation at the air/water interface of aqueous polymer solutions was directly observed by the naked eye after 1 min vigorous shaking and recorded with a digital camera.

Small-Angle X-ray Scattering (SAXS) Measurement. A Kratly U-slit type SAXS apparatus with a Rotaflex RU-200 X-ray generator and 1D-PSPC detector (Rigaku Corp., Tokyo) was used for SAXS experiments. The details of the instrument were fully described elsewhere.[19] A glass capillary of 2 mm diameter (Mark, Darmstatt, Germany) was used as a solution cell. The typical accumulation time was 6000 s. The data from solution were treated by solvent background subtraction and sensitivity correction and then desmeared. The details of the instrument and data treatment have been also fully described elsewhere.[19]

Dynamic Light Scattering (DLS) Measurement. DLS experiments were carried out with an ELS-800 (Otsuka Electric, Osaka, Japan). The decay rate Γ was evaluated by single- or double-exponential fitting of the time correlation function of scattered field $g^{(1)}(q,\tau)$ evaluated by application of the Siegert relation to the experimentally obtained time correlation function of scattered intensity $g^{(2)}(q,\tau)$.[20] q is the scattering vector [$q = 4n\pi \sin \theta/\lambda$, where n is the refractive index, 2θ is the scattering angle, and λ is the wavelength of the laser light (6328 Å of He−Ne laser)]. After the translational nature of the Γ evaluated was confirmed by angular dependence, the translational diffusion coefficient D was calculated from Γ by $\Gamma = Dq^2$, and then the hydrodynamic radius R_h was calculated by using the Stokes−Einstein equation.

X-ray Reflectivity (XR) Measurement. XR experiments were performed by RINT-TTR-MA (Rigaku Corp., Tokyo, Japan) in our laboratory. The 1.5406 Å radiation from the Cu target was used as an incident beam with 50 kV−300 mA power. This XR apparatus has an LB trough (specially designed and constructed by USI System, Fukuoka, Japan) at the sample position, which enables measurement of water surface. The details of the instrument, data treatment, and data analysis have been fully described elsewhere.[21,22]

Results and Discussion

Synthesis and Characterization of PEt$_2$SB-*b*-PSPMNa. Figure 1a shows the ^{1}H NMR spectra of PEt$_2$SB-*b*-P*t*-BuMA in *d*-methylene chloride solution. As alphabetically indicated in the figure, the peaks in the spectra can be successfully assigned to the hydrogen atoms in PEt$_2$SB-*b*-P*t*-BuMA and the block ratio was calculated to be m:n = 18:37. Figure 1b shows an example of ^{1}H NMR spectra after sulfonation, i.e., PEt$_2$SB-*b*-PSPMNa in D$_2$O. The broadness of peaks of polysilacyclobutane segment compared to Figure 1a insinuates a micelle formation in water. Observation of peaks *k*, *l*, and *m* certainly guarantees that the sulfonation reaction was successful. The degree of sulfonation was determined by a conductometric titration of aqueous solution of H-form polymer by sodium hydroxide standard solution. The conductometric titration curves are shown in Figure 2. The existence of a weak acid (carboxylic acid) and strong acid (sulfonic acid) can be clearly confirmed: the rapid decrease of conductivity at the initial stage of NaOH(aq) addition corresponds to a strong acid, and the middle almost flat region is for the weak acid. From the amount of titrated NaOH(aq) to neutralize these functional groups as shown by arrows in Figure 2, the degree of sulfonation was calculated to be $\alpha = 0.50$ and 0.81 for these samples. The solubility of the polymer in Table 1 (H-form before sulfonation, Na-form after sulfonation) also shows that sulfonation was successful. The polymer became insoluble in THF and methanol and become soluble in pure water, indicating the increase of the ionic character of the polymer by sulfonation. The characteristics of polymers synthesized are summarized in Table 2.

Surface Tension: Apparent Lack of Surface Activity. The concentration dependence of surface tension of the PEt$_2$SB-*b*-PSPMNa solution in pure water and in 0.5 M NaCl(aq) for three α values is shown in Figure 3. For all samples, the surface tension of the solution is almost perfectly constant in the concentration range studied, and its absolute value is close to that of pure water (72.1 mN/m at 25 °C). A similar tendency was observed for other amphiphilic diblock copolymers having carboxylic acid in the hydrophilic chain.[23] From these surface tension measurements, for the behavior of PEt$_2$SB-*b*-PSPMNa near the air/water interface, two possibilities can be pointed out: (1) these polymers do not adsorb at the air/water interface, and (2) some

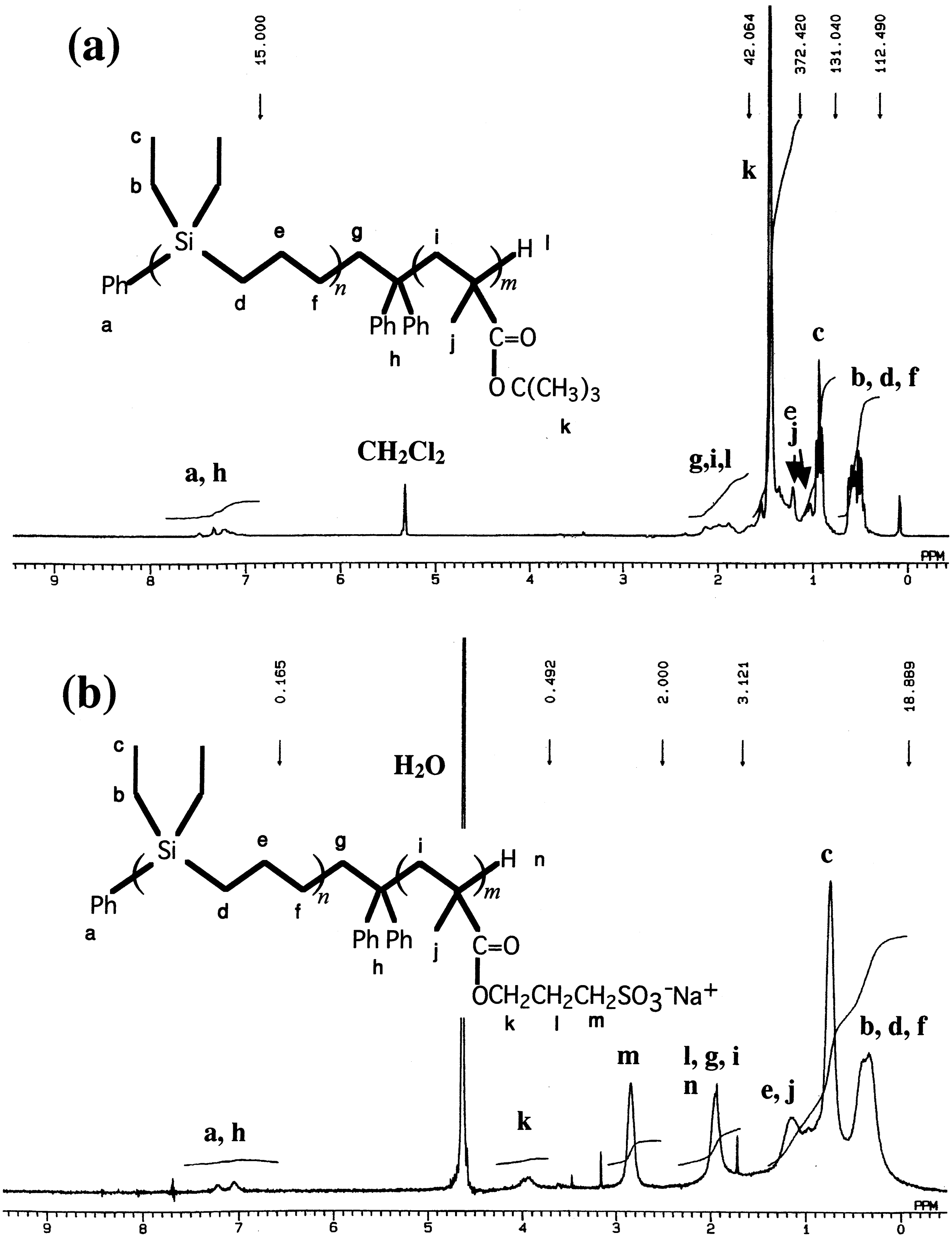


Figure 1. (a) ^{1}H NMR spectra of PEt$_2$SB-*b*-P*t*-BuMA in CD$_2$Cl$_2$. (b) ^{1}H NMR spectra of PEt$_2$SB-*b*-PSPMNa ($\alpha = 0.50$) in D$_2$O.

polymers are adsorbed at the water surface but the local concentration is the same as bulk concentration of polymers; in other words, adsorption occurs but “surface excess” is zero.

Note that there is a small “fluctuation” of surface tension value in the middle polymer concentration range: slightly smaller surface tension values were observed at about $C = 10^{-6}$ mol/L for $\alpha = 0$ and $C = 3$

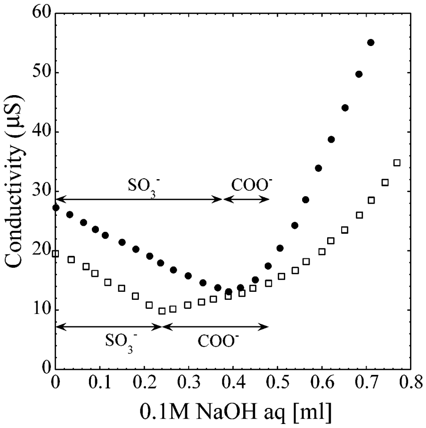


Figure 2. Titration curves of PEt$_2$SB-*b*-PSPMH (α = 0.50 and 0.81) aqueous solution by 0.1 M NaOH(aq). The arrows indicated the amount of NaOH(aq) to fully neutralize sulfonic acid and calboxylic acid groups on polymer chain.

Table 2. Characteristics of Poly(Et$_2$SB)$_n$-*b*-poly(SPMNa)$_m$

n:m^a	M_w/M_n^b	degree of sulfonation^c
18:37	1.09	0
18:37	1.09	0.50
18:37	1.09	0.81

[a] Determined by ^{1}H NMR for the parent copolymer before hydrolysis in *d*-methylene chloride. [b] Determined by GPC for the parent copolymer before hydrolysis with chloroform as an eluent and polystyrene standards. [c] Determined by conductometric titration by 0.1 M NaOH(aq).

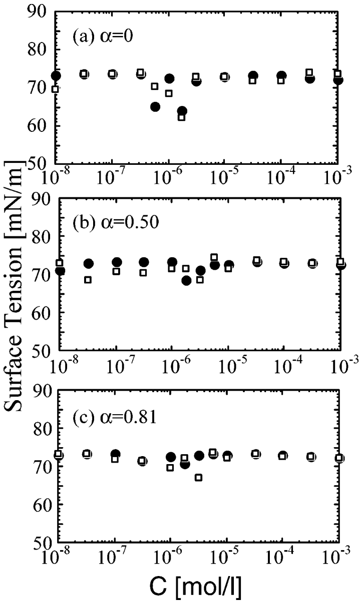
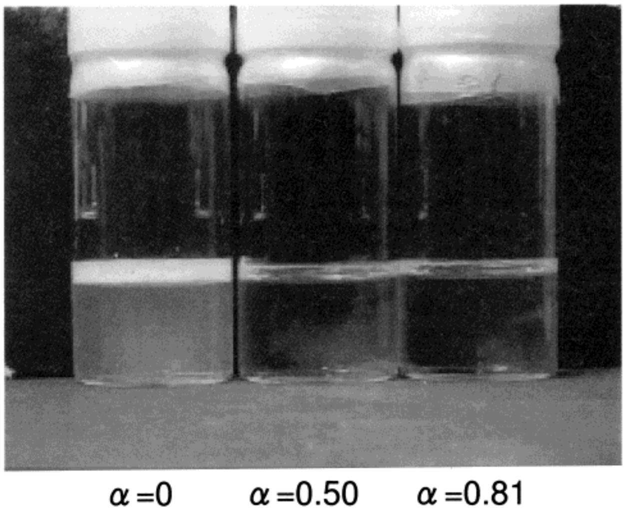
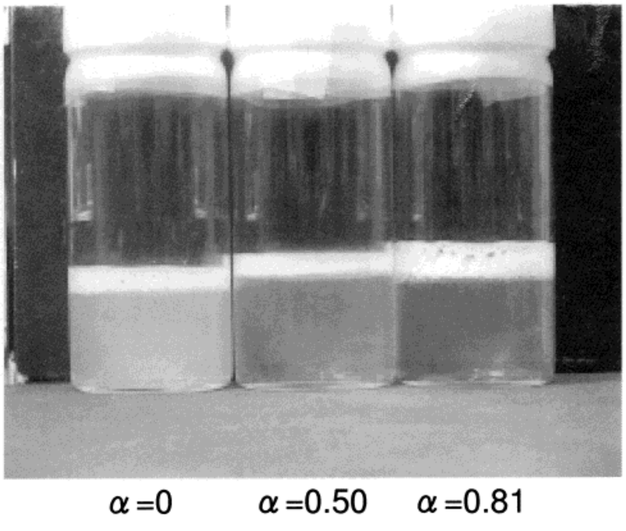


Figure 3. Polymer concentration dependence of surface tension for aqueous solutions of PEt$_2$SB-*b*-PSPMNa. (a) α = 0, (b) α = 0.50, (c) α = 0.81. Filled circle: in water, open square: in 0.5 M NaCl(aq). Concentration is in polymer moles.



(a) in water



(b) in 0.5M NaClaq

Figure 4. Foam formation for aqueous solutions of PEt$_2$SB-*b*-PSPMNa after vigorous shaking for 1 min: (a) in water, (b) in 0.5 M NaCl(aq). Polymer concentration = 10^{-3} M.

× 10^{-6} for α = 0.50 and α = 0.81 samples. These are not experimental errors because these are experimentally reproducible, and also because a similar point has been observed for other ionic amphiphilic diblock copolymer aqueous solutions.[23] The importance of this point will be discussed later, but here we would like to call this point “M-point”.[24]

Foam Formation: No Foam Formation with Highly Sulfonated Block Copolymer. To investigate the polymer adsorption at the air/water interface in more detail, we carried out foam formation experiments. Figure 4 shows digital photos of (a) pure water solution and (b) 0.5 M NaCl(aq) solution with 10^{-3} M polymer concentration after 1 min of vigorous shaking. The α = 0 sample solution in water, which shows slight turbidity due to nonperfect solubility, showed clear foam at the air/water interface. On the other hand, α = 0.50 and 0.81 sample solutions in water, which are perfectly clear, showed no foam formation. Foam is destabilized by the water drain effect through a Plateau Boarder, but it is stabilized by amphiphilic molecules adsorbed at both sides of the foam thin film.[25] Hence, foam formation means that polymer molecules are adsorbed at the water surface, and no foam formation indicates no adsorption of polymer molecule at the air/water interface. If we apply this logic, it can be said that α = 0 polymers are certainly adsorbed at the water surface but there is no surface excess and that α = 0.50 and 0.81 polymers are not adsorbed at all since none of these three polymers reduce the surface tension of the solution.

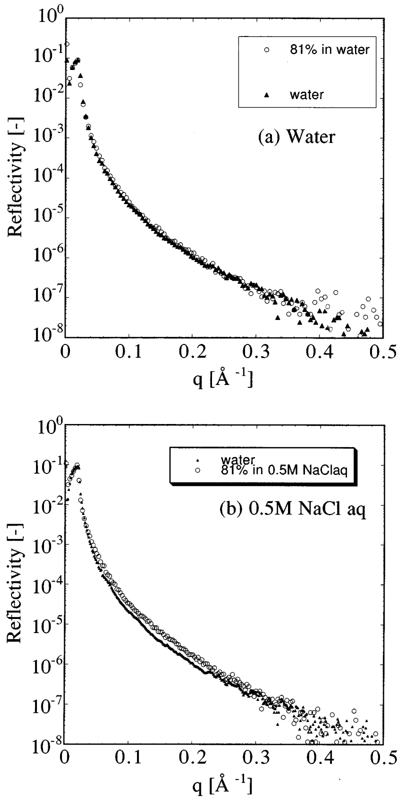
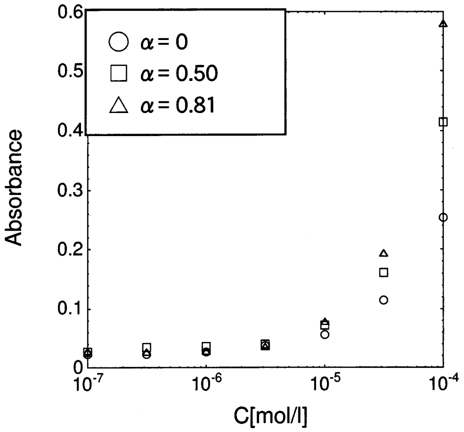


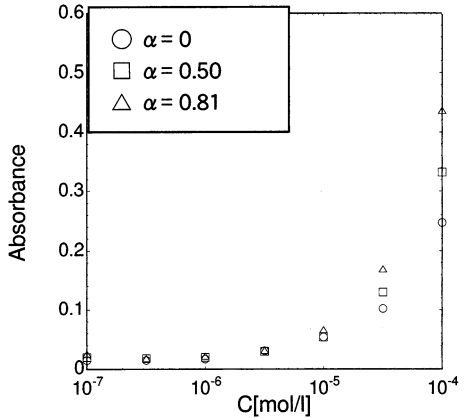
Figure 5. XR profiles for PEt$_2$SB-*b*-PSPMNa (α = 0.81) aqueous solutions. Circles: polymer solution, triangle: solvent only (a) in pure water, (b) in 0.5 M NaCl. Polymer concentration = 10^{-4} M.

In the 0.5 M NaCl solution, foam formation was observed for all three polymers. This means that α = 0.50 and 0.81 samples are also adsorbed at the water surface, but there is no surface excess because of no reduction of surface tension even in 0.5 M NaCl(aq). Addition of a simple salt induces no change of hydrophobicity but induces a screening effect of Coulomb interaction. Hence, it can be concluded that the absence of water surface adsorption for α = 0.50 and 0.81 samples in pure water is due to the strong ionic nature of these polymers.

X-ray Reflectivity: Examination of Adsorbed Layer at the Air/Water Interface. To directly observe the existence of adsorbed polymer at the water surface, we carried out XR experiments. Figure 5 shows XR profiles for the α = 0.81 sample solution in water (a) and in 0.5 M NaCl(aq) (b). XR profiles for pure solvents, i.e., pure water and 0.5 M NaCl, are also shown for comparison. As shown in Figure 5a, the pure water solution of this polymer showed almost exactly the same XR profile as that of pure water itself. On the other hand, a slight difference in profile for solution and solvent was observed in 0.5 M NaCl in Figure 5b. This means that in 0.5 M NaCl solution, which shows foam formation, polymer molecules are adsorbed at the water surface although the amount may be small. In principle, XR measurement is a highly precise technique with 1 Å accuracy,[8-10] and it always gives exactly the same profile for pure water surface as shown in Figure 5a. Hence, the small difference in the 0.5 M NaCl case is certainly meaningful. Furthermore, an excess reflection between q = 0.05−0.26 means a layer formation, which means polymer adsorption. By the polymer molecules adsorbed, the foam was stabilized, which results in foam formation phenomena. On the other hand, in pure water, the absence of polymer adsorption is strongly supported by XR results although XR might not be sensitive to an extremely small amount of adsorbed polymer.



(a) in water solution



(b) in 0.5M NaClaq

Figure 6. Solubilization of *trans*-stilbene by PEt$_2$SB-*b*-PSPMNa in aqueous solution detected by UV absorbance at 300 nm: (a) in pure water, (b) in 0.5 M NaCl(aq). Open circle: α = 0, open square: α = 0.50, open triangle: α = 0.81. Concentration is in polymer moles.

Hydrophobic Dye Solubilization: Evidence for Micelle Formation. So far, the absence of polymer adsorption for α = 0.50 and 0.81 polymers in pure water solution was confirmed, and also no surface excess condition was suggested in a 0.5 M NaCl condition and for the α = 0 polymer. A hydrophobic dye solubilization experiment with UV−vis adsorption detection is a common conventional technique to confirm micelle formation in solution and for determining the critical micelle concentration (cmc). We applied this method with *trans*-stilbene as a hydrophobic dye. Surprisingly, for all the samples and under all conditions studied here, an increase of absorbance at λ = 300 nm, which is a specific absorption band of *trans*-stilbene, at a certain concentration was observed (Figure 6). Up to a polymer concentration of about (2−3) × 10^{-6} mol/L, no absorption was observed, but it increased rapidly over this concentration. The final absorption at 10^{-4} mol/L is in the order of $\alpha = 0.81 > \alpha = 0.50 > \alpha = 0$. This means that for all conditions micelles are formed in solution and cmc is located at about 10^{-6} mol/L.

For the 0.5 M NaCl solution and α = 0 sample, this situation is reasonable since the foam formation was observed although the surface tension was not reduced. However, for α = 0.50 and 0.81 samples in a pure aqueous solution, this result is quite paradoxical since no adsorption of polymer molecules at the water surface has been confirmed by surface tension, foam formation, and XR experiments. According to general textbooks for surface science, below cmc, the amphiphilic molecules are adsorbed at air/water interface with the hydrophilic part in water and hydrophobic part in the air, which is the most hydrophobic material. With increasing concentration, the amount of adsorbed molecules increased to form a Gibbs monolayer. Adsorbed molecules are in equilibrium to the small amount of unimer in the solution. When the water surface is saturated by molecules, the additional molecules are entering the water phase and start to form micelles (cmc). However, the observed behavior for α = 0.50 and 0.81 polymer in pure water is perfectly inconsistent with this *common sense* of surface science.

It is interesting to note here the relation between dye experiment and surface tension experiment. We have pointed out the existence of “M-point” in the surface tension vs concentration relationship (Figure 3). The concentration at M-point is similar to the “cmc” value estimated by the dye solubilization experiment. Hence, we can speculate that something, probably micelle formation, happens at the M-point.

Dynamic Light Scattering: Confirmation of Multimolecular Micelle Formation. Since the induction of micelle formation by addition of hydrophobic molecules cannot be perfectly denied, DLS experiments were performed to confirm micelle formation. Figure 7 shows the time correlation functions of scattered field $g^{(1)}(q,\tau)$ for 1 wt % solutions. For all the experimental conditions, a slow decay can be observed in $g^{(1)}(q,\tau)$, which means the existence of large particles. DLS data for 0.5 M NaCl solution were well fitted by a single-exponential function, which results in the hydrodynamic radius R_h of 205 Å for α = 0, 160 Å for α = 0.50, and 140 Å for α = 0.81 polymers. Needless to say, these R_h values are too big for a unimer and means micelle formation. For pure water solution, α = 0 polymer data could be well fitted by a single-exponential function and R_h = 165 Å was evaluated. The time correlation function of α = 0.50 and 0.81 polymers cannot be described by a single-exponential function. The profile for α = 0.50 polymer could be fitted by double-exponential function, but that for α = 0.81 polymer has a function largely deviated from a simple exponential type decay. This is due to the interparticle Coulomb interaction.[26] Hence, it is difficult to evaluate the particle size for pure water systems, but it is certain that there are large size particles, probably micelles, existing in the solution even in pure water solution since the decay with a similar time constant can be observed. The R_h values are summarized in Table 3.

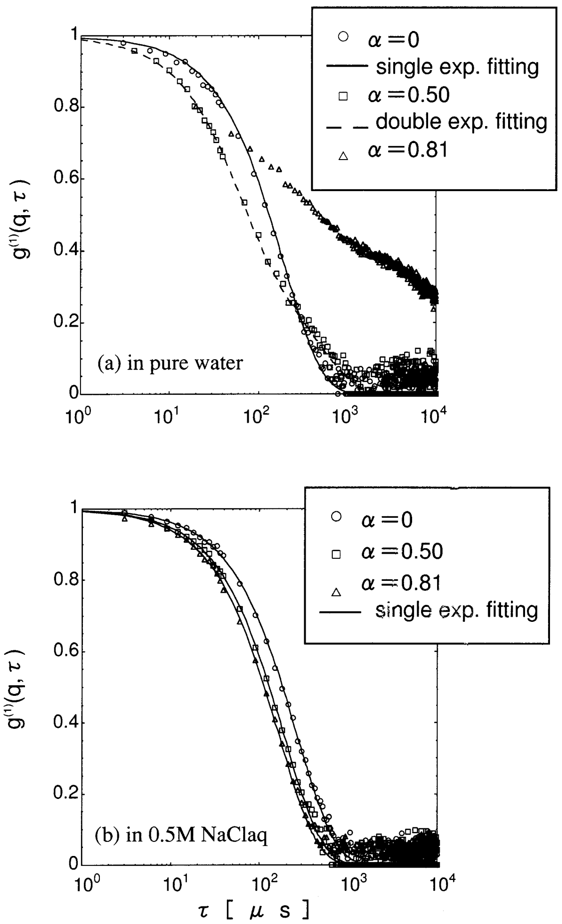


Figure 7. Time correlation function obtained for PEt$_2$SB-*b*-PSPMNa solution by DLS at 25 °C at scattering angle 90°: (a) in pure water, (b) 0.5 M NaCl. Open circle: α = 0, open square: α = 0.50, open triangle: α = 0.81. Polymer concentration = 1 wt %.

Small-Angle X-ray Scattering: Evidence for Core−Shell Micelle Formation. To evaluate the size of micelles of these polymers, we performed SAXS experiments. Figure 8 shows the SAXS profiles for α = 0, 0.50, and 0.81 polymers in aqueous solutions and in 0.5 M NaCl(aq). In Figure 8, strong scattering at smaller angle regions can be observed, which means micelle formation in water. Pure water solutions for α = 0.50 and 0.81 polymers did not show surface activity in surface tension measurements and also did not show any foam formation, but now micelle formation in these systems has further been confirmed. In every SAXS profile, a clear peak was observed at around q = 0.04−0.05 Å^{-1}. This peak, which is typical for micelles, is due to the intraparticle interference peak.[27] The interference is from shell−shell correlation in the same particle, and its position roughly reflects the diameter of the micelles. This peak position shifts toward higher q regions with increasing α value, which means the size of the micelle is in the order of α = 0 > α = 0.50 > α = 0.81. This is in good agreement with the DLS results. The scattering intensity is proportional to the square of volume of the scatter. The intensity is also in the order of α = 0 > α = 0.50 > α = 0.81, which is consistent with the size estimation above and by DLS. To evaluate the size and shape of micelles more in detail, a model fitting analysis of SAXS profiles was performed. We used a simple core−shell model, and the fitted curves are shown by solid lines for pure water system and dashed lines for salt systems in Figure 8. The agreement is satisfactory. The excess scattering due to a contribution of a blob scattering is observed in experimental profiles at higher q region (q > 0.5 Å): In this q region, a scattering from each polymer chain in the shell part contributes to scattering profile, which is not taken into account in a simple core−shell model. Nevertheless, the slight undulation in experimental SAXS profiles at higher q regions are well reproduced by fitted model calculation. The core radius (R_c) and the whole radius (R_s) thus estimated are summarized in Table 3 together with

Table 3. Summary of the Characteristic Behavior of PEt$_2$SB-*b*-PSPMNa and PαMeSt-*b*-PSPMNa

PEt$_2$SB-*b*-PSPMNa	$\alpha = 0$		$\alpha = 0.50$		$\alpha = 0.81$	
[NaCl]	0	0.5	0	0.5	0	0.5
surface tension	as water	as salt solution	as water	as salt solution	as water	as salt solution
	small drop near 1 μmol/L		small drop near 2 μmol/L		small drop near 2 μmol/L	
solution appearance	turbid	turbid	clear	turbid	clear	turbid
foam	yes	yes	no	yes	no	yes
adsorption (XR)					no	yes
cmc (mol/L) (dye solubilization)	$\sim 5 \times 10^{-6}$	$\sim 5 \times 10^{-6}$	$\sim 5 \times 10^{-6}$	$\sim 5 \times 10^{-6}$	$\sim 5 \times 10^{-6}$	$\sim 5 \times 10^{-6}$
R_h (DLS) (Å)	165	205	N. A.	160	N. A.	140
core radius (SAXS) (Å)	55	58	57	53	56	54
whole radius (Å)	197	215	160	161	154	153
aggregation no.	180	211	200	161	190	170

PαMeSt-*b*-PSPMNa	$\alpha = 0.49$		$\alpha = 0.73$	
[NaCl]	0	0.5	0	0.5
surface tension	as water	as salt solution	as water	as salt solution
	small drop near 0.3 μmol/L		small drop near 2 μmol/L	
solution appearance	slightly turbid	turbid	slightly turbid	turbid
foam	no	yes	no	yes
R_h (DLS) (Å)	NA	190	NA	245

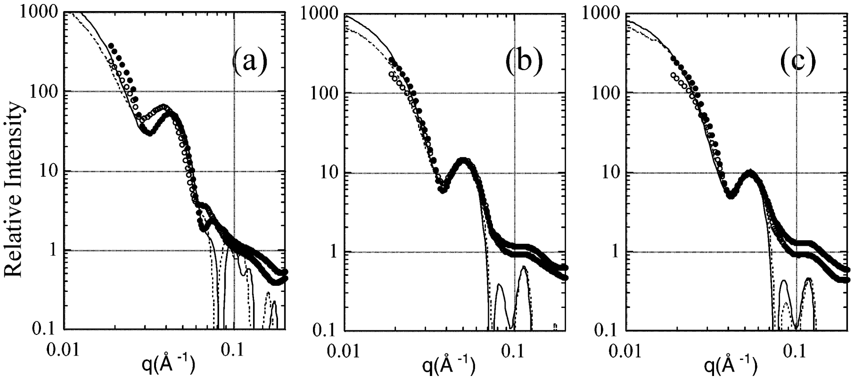


Figure 8. SAXS profiles for Et$_2$SB-*b*-PSPMNa solutions in pure water and 0.5 M NaCl(aq). (a) $\alpha = 0$ polymer, (b) $\alpha = 0.50$, (c) $\alpha = 0.81$. Polymer concentration = 1 wt %. Closed symbols: in water, open symbols: in 0.5 M NaCl. Solid and dashed lines are fitting curves by core–shell model for in pure water and 0.5 M NaCl(aq), respectively. Fitted parameters are listed in Table 3.

other information. The micelle size estimated by SAXS is also smaller for larger α samples. This size order is also reasonable from the concept of "packing parameter" proposed by Israelachvili.[28] The higher sulfonated polymer should have a larger "head group" due to the electrostatic repulsion between many strong ions, which results in smaller micelles. In this SAXS fitting, we assumed density values of 0.9857 for the hydrophobic chain and 1.069, 1.055, and 1.073 for hydrophilic chains with $\alpha = 0$, 0.50, and 0.81, respectively. However, exact density values will be obtained by small-angle neutron scattering (SANS) experiments, which will be reported separately. A small discrepancy for initial slope observed especially for salt systems might be due to the nonperfectly spherical nature of micelle geometry. More information about the shape of micelles will also be obtained by SANS, which covers smaller scattering angle regions than our SAXS system.

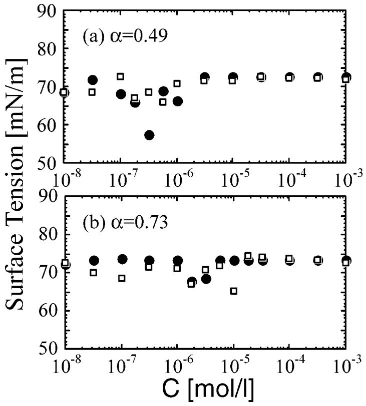
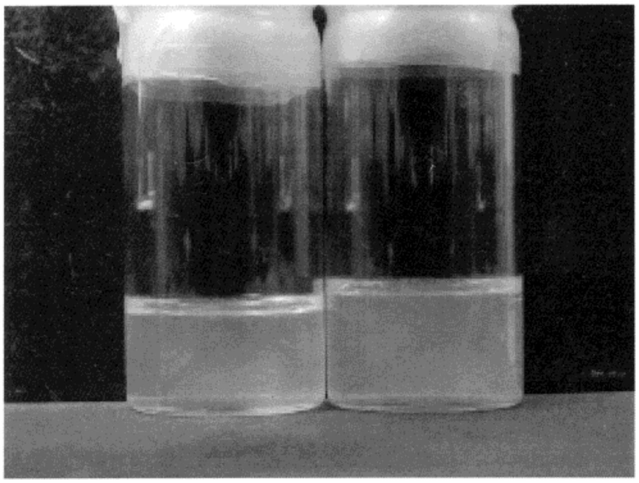


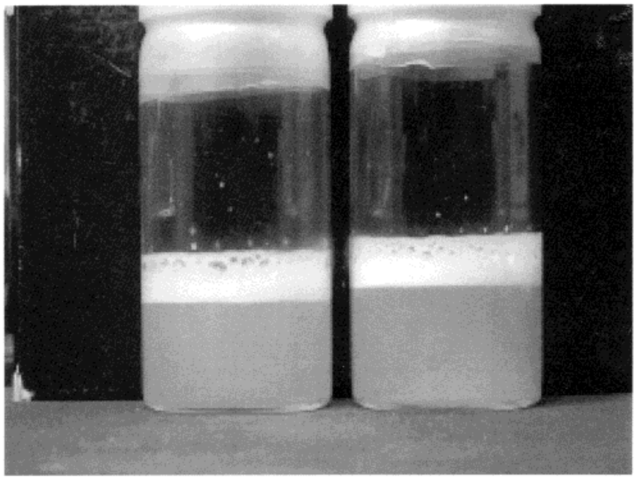
Figure 9. Surface tension of aqueous solutions of PαMeSt-*b*-PSPMNa. (a) $\alpha = 0.49$, (b) $\alpha = 0.73$. filled circles: in pure water, open square: in 0.5 M NaCl. Concentration is in polymer moles.

Figure 8 shows an interesting character for added salt effect of micelles of these polymers. The peak position of the $\alpha = 0$ polymer shifted toward smaller angles by addition of 0.5 M NaCl, which means an increase in size. This is reasonable because the reduction of electrostatic repulsion by added small ions results in a decrease of headgroup size. On the other hand, neither the peak position nor the whole profile of $\alpha = 0.50$ and 0.81 polymers is affected by addition of 0.5 M NaCl. This is a quite unexpected result since it is well-known that the micelle and the size, shape, and morphology of common ionic surfactants are largely affected by ionic strength. The origin can be thought to be located in the strong ionic nature and polymeric nature of the hydrophilic segments. One possibility might be an extremely high ionic strength in the shell. The shell is fulfilled by polyelectrolyte with strong ions so the ionic strength in the shell should be so high. Hence, even when salt ions are added in the bulk solution, small ions cannot go into the inside of the shell, which results in no change of



$\alpha = 0.49$ $\alpha = 0.73$

(a) in water



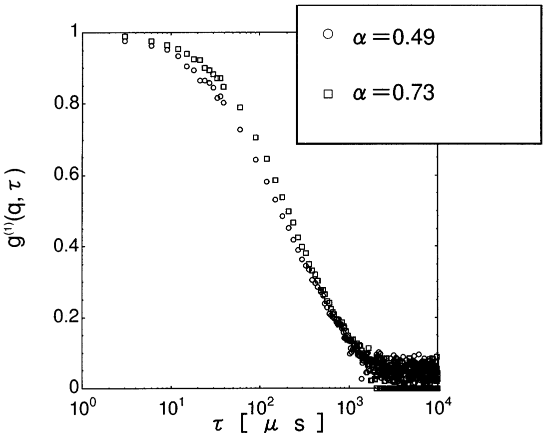
$\alpha = 0.49$ $\alpha = 0.73$

(b) in 0.5M NaClaq

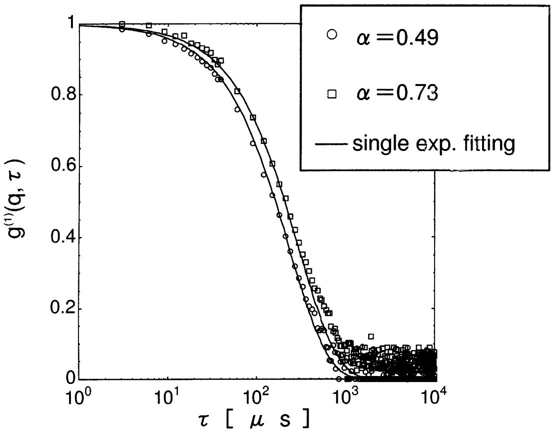
Figure 10. Foam formation for aqueous solutions of PαMeSt-*b*-PSPMNa after vigorous shaking for 1 min: (a) in water, (b) in 0.5 M NaCl(aq). Polymer concentration = 10^{-3} M.

micelle structure. However, this is a speculation at this stage, and the details will be studied in the future.

Polymers with Poly(α-methylstyrene) as a Hydrophobic Segment. Finally, we would like to show briefly tentative results on polymers with poly(α-methylstyrene) (PαMeSt) as a hydrophobic segment. The synthetic procedure is almost the same but with α-methylstyrene as the first monomer instead of silacyclobutane. $n{:}m = 35{:}32$ polymer could be synthesized, and two kinds of polymers with $\alpha = 0.49$ and $\alpha = 0.73$ were prepared. The surface tension, foam formation, and DLS results are shown in Figures 9, 10, and 11, respectively. The surface tension did not decrease with increasing polymer concentration and equaled the value of pure water at any condition. The "M-point" is also observable around 10^{-6} mol/L. These highly sulfonated polymers did not show foam formation in the pure water system as shown in the photos in Figure 10, but micelle formation was confirmed by DLS (Figure 11). $R_h = 190$ and 245 Å was calculated for the $\alpha = 0.49$ and 0.73 polymer, respectively, in 0.5 M NaCl solution (Table 3).



(a) in water solution



(b) in 0.5M NaClaq

Figure 11. Time correlation function obtained for PαMeSt-*b*-PSPMNa solution by DLS at 25 °C at a scattering angle of 90°: (a) in pure water, (b) 0.5 M NaCl. Polymer concentration = 1 wt %. circle: $\alpha = 0.49$; square: $\alpha = 0.73$.

All the observations here are the same as those for the polymers with polysilacyclobutane as a hydrophobic chain. Hence, "polymer micelle formation without Gibbs monolayer formation" is not a specific phenomenon for silacyclobutane polymer but a common nature for amphiphilic diblock copolymers having many strong acid groups in hydrophilic chains.

Comments on Unimer–Micelle Equilibrium and Absence of Gibbs Monolayer Formation. We clarified that our novel diblock copolymer having a large number of strong acid groups forms micelles in aqueous solution without Gibbs monolayer formation at the water surface. One possibility to explain this paradox might be the high stability of micelles formed. Since a sulfonation reaction by 1,3-propane sultone would proceed with polymers in a micelle state, there is a possibility that all the polymers are fixed in micelles and stabilized by sulfonation, which results in the absence of monolayer formation on the water surface. However, this feasibility may be denied for the following reasons: (1) hydrophobic dyes were adsorbed in micelles, which means an existence of micelle–unimer dynamics; (2) foam formation and polymer adsorption were observed by addition of salt. Hence, this specialty should come from the strong acid nature of the hydrophilic polymer chain. However, the dynamics of this system, such as micelle–unimer exchange rate and corona dynamics,[29,30] especially its similarity and difference with other conventional polymer micelle systems, are of great interest, and those should be our further targets.

One possibility for no Gibbs monolayer formation might be the strong electrostatic repulsion between hydrophilic segments in the monolayer. The polymer like to form monolayer at water surface, but the strong repulsion between many strong acid ions located at the interface destabilizes the monolayer. This interpretation is one possibility, but one question arises; in the corona region in the micelle in solution, the hydrophilic segments are more densely packed, so the more strong electrostatic repulsion should destabilize the micelle aggregate. However, this is not the case. The hydrophobic interaction to form micelles or monolayer should also stronger at water surface since the air is the most hydrophobic. Hence, the origin of “no Gibbs monolayer” should be electrostatics, but it should be also some specific one at interface.[31]

Conclusion

A novel amphiphilic diblock copolymer having strong acid groups in the hydrophilic segment, PEt$_2$SB-*b*-PSPMNa, was synthesized, and its interfacial properties and association behavior in aqueous media have been duly investigated. Results of a series of experiments are summarized in Table 3. PEt$_2$SB-*b*-PSPMNa with a degree of sulfonation of more than 50% showed no surface activity; i.e., no decrease of surface tension of their solutions was observed. They showed no foam formation and no adsorption at the air/water interface. These observations could be interpreted by solubilization of polymers as a unimer into water due to the high hydrophilicity by the action of strong acid groups on its hydrophilic backbone. However, unexpectedly, a micelle formation, with a radius of 150−200 Å, has been confirmed by hydrophobic dye absorption, DLS, and SAXS. The micelle structure was not affected by the presence of salt, but foam formation activity was induced. In the polymer without sulfonation, i.e., all weak acid groups in its hydrophilic backbone, foam formation was observed even without salt in addition to micelle formation. From these observations, the strange behavior observed here, i.e., “*micelle formation without Gibbs monolayer formation*”, is a special characteristic for the amphiphilic diblock copolymer with strong acid groups at a low salt condition. This observation cannot be explained in terms of common surface science, and its origin and mechanism should be duly investigated in the future. This polymer might be classified into a new class of amphiphiles, which forms micelles in solution without foam formation at the interface. This special characteristic is also useful for industrial application such as in detergent soap without foam or bubbles, in addition to the fundamental scientific interests.

Acknowledgment. The authors express their sincere thanks to Prof. Hitoshi Yamaoka (University of Shiga Prefecture) for his useful comments, suggestions, and encouragement. Highly valuable comments were received from Prof. Hiroshi Maeda (Kyushu University, Japan). This work was supported by the grants-in-aid for Scientific Research by the Ministry of Education, Culture, Sports and Technology (B12555266 and A13031051) to whom our sincere gratitude is due.

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(24) We would like to propose a term “M-point” since the γ (surface tension) vs C (concentration) plot has the shape of a character “M” by this fluctuation and also because the last names of all four authors begin with “M”.

(25) For example: Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley: New York, 1997.

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(31) In this sense, a high possibility as an origin might be something like a mirror charge effect,[32] which should be carefully and quantitatively considered in the future.

(32) Maeda, H., private communication.

MA0215161