Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Colloid and Interface Science 276 (2004) 290–298

Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

Self-association of water-soluble fluorinated diblock copolymers in solutions

Hiroshi Ito [a], Toyoko Imae [a,b,*], Tetsuya Nakamura [c], Motoyuki Sugiura [c], Yoshihiro Oshibe [c]

[a] *Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan*
[b] *Research Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan*
[c] *NOF Corporation, Chita, Aichi 470-2398, Japan*

Received 2 December 2003; accepted 19 March 2004

Available online 21 April 2004

Abstract

The self-association of the fluorinated diblock copolymer, poly(methacrylic acid)–block–poly(perfluorooctylethyl methacrylate) (PMAA-b-PFMA), in water has been investigated by light scattering, potentiometry, atomic force microscopy, and transmission electron microscopy. The size of the polymer micelles increases, as the degree of dissociation of the PMAA blocks increases. Since the charged PMAA block takes the stretched structure, PMAA-b-PFMA can easily form large micelles due to the low steric hindrance of PMAA blocks. Addition of NaCl shielded electrostatic repulsion in the PMAA chain and induced the formation of smaller micelles than water without NaCl did because of the bulky structure of the PMAA chain in the shell of the micelles. The micelle of PMAA-b-PFMA in ethanol is larger than that of poly(t-butyl methacrylate)–block–poly(perfluorooctylethyl methacrylate) (PtBMA-b-PFMA) in ethanol as a result of the higher steric hindrance of the PtBMA block. The dimensions of the core and shell of the micelles were estimated. The micelle of PMAA-b-PFMA in water possesses a rather thick shell and a large volume per molecule, consistent with the extended PMAA chain. On the other hand, the shell of the micelle in an ethanol solution of PtBMA-b-PFMA is thin but has a large surface area. Facts are consistent with the shrunk structure of the PtBMA block in poor solvent.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Fluorinated diblock copolymer; Core–shell micelle; Self-association; Aggregation number; Transmission electron microscopy; Light scattering

---

1. Introduction

Fluorinated polymers, as well as fluorinated surfactants, are widely applicable because of their hydrophobicity, oleophobicity, heatproof, chemical-proof, nontoxicity, frictionless, low adhesion, and electrically insulating properties [1]. Highly fluorinated polymers are generally less miscible with nonfluorinated compounds and less soluble in most solvents, except fluorinated ones [2]. Therefore, fluorinated polymers combining nonfluorinated [3–6] or ionic moieties [7,8] were synthesized. Alternatively, miscible blends of fluorinated and nonfluorinated polymers were prepared [9–11].

It is well known that copolymers consisting of blocks having different solubilities in solvents possess an amphiphilic character, that is, they have a high surface activity at an interface and self-assembly in solution. It is therefore expected that copolymers consisting of fluorinated blocks have higher surface activity than nonfluorinated block copolymers. Furthermore, a fluorinated block plays a role in the construction of ordered structures as a component different from a hydrophilic or oleophilic block [12]. Copolymers with fluorinated side chains have been synthesized with the expectation of such characteristics [13–30].

Krupers et al. [19,20] have found by transmission electron microscopy (TEM) that fluorinated diblock copolymer forms cylindrical and spherical micelles on the cast films from tetrahydrofuran and toluene solutions, respectively. Matsumoto et al. [27,28] have confirmed by small angle X-ray scattering that the water-soluble fluorinated diblock copolymer aggregates into spherical micelles in water. Busse et al. [30] have recently reported that triblock copolymer including fluorinated block also forms micelles. Imae et al. [29] have revealed that poly(methyl methacrylate)–block–poly(2-perfluorooctylethyl methacrylate) (PMMA-b-PFMA) in acetonitrile and chloroform form micelles in

---

[*] Corresponding author. Fax: +81-52-789-5912.
E-mail address: imae@nano.chem.nagoya-u.ac.jp (T. Imae).

0021-9797/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2004.03.046

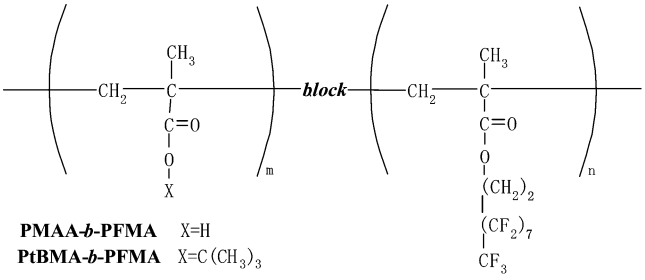

Fig. 1. Chemical structures of diblock copolymers.

which the core and shell (corona) consist of oleophobic fluorinated PFMA blocks and oleophilic PMMA blocks, respectively.

In the present work, we synthesized two diblock copolymers, in which one block is PFMA and the other is hydrophilic poly(methacrylic acid) (PMAA) and oleophilic poly(t-butyl methacrylate) (PtBMA). Their chemical structures are shown in Fig. 1. PMAA-b-PFMA is a water-soluble derivative of PtBMA-b-PFMA obtained by hydrolysis of PtBMA block, so that these diblock copolymers have the same degree of polymerization, polydispersity and block composition. We investigate the self-associative behavior of PMAA-b-PFMA in water and the contribution of solvophilic blocks on the self-association of two diblock copolymers in ethanol. We then discuss the structure of aggregates.

2. Experimental section

2.1. Materials

PtBMA-b-PFMA (Lot 80) was synthesized by anionic block copolymerization, according to the procedure for PMMA-b-PFMA synthesis reported before [29]. PMAA-b-PFMA (Lot 107) was produced by hydrolysis of the *t*-butyl methacrylate unit in PtBMA-b-PFMA. The weigh*t*-average molecular weight and degree of polymerization of each block were determined by gel permeation chromatography (GPC). The calibration of molecular weight was carried out for polystylene. Weight average molecular weight (M_W) and polydispersity (M_W/M_n) of PtBMA-b-PFMA were 106,600 and 1.24, respectively. Those of PMAA-b-PFMA were 82,200 and 1.21, respectively. Compositions were $m = 416$, $n = 87$ for PtBMA-b-PFMA and $m = 412$, $n = 87$ for PMAA-b-PFMA. The values are also listed in Table 1. Other reagents were commercial products.

2.2. Solutions

PMAA-b-PFMA was dissolved in water (deionized and redistilled by a Millipore Milli-Q Lab) by stirring overnight. The pH of solutions was adjusted by aqueous solutions of hydrochloric acid and sodium hydroxide. Aqueous NaCl solution of PMAA-b-PFMA was prepared by adding an aqueous NaCl solution to an aqueous solution (pH 4.7) of PMAA-b-PFMA. PMAA-b-PFMA, and PtBMA-b-PFMA were also dissolved in ethanol.

2.3. Measurements

Static and dynamic light scattering (SLS and DLS) was measured at 25 °C on Otsuka Electronics DLS-700 and DLS-7000 spectrophotometers equipped with an Ar-laser light source at 488 nm [31] and an ALV-5000E DLS analyzer, where a CONTIN program was used for the analysis of DLS correlation function. The specific refractive index increment was measured at 25 °C by an Otsuka Electronics RM-102 refractometer with an iodine lamp at 488 nm. The values of 0.0738, 0.0854, and 0.0662 cm^3/g for PMAA-b-PFMA in water, 0.1 M NaCl, and ethanol, respectively, and 0.0610 cm^3/g for PtBMA-b-PFMA in ethanol were obtained and used for the calculation of the light scattering intensity. SLS and DLS measurements were carried out at different scattering angles (30°–150°) and concentrations (below 3 mg/cm^3 for PMAA-b-PFMA and 20 mg/cm^3 for PtBMA-b-PFMA). Obtained Zimm plots and CONTIN spectra revealed typical feature and a symmetrical single peak, respectively, for each measurement. Molecular weight, radius of gyration, second virial coefficient, and hydrodynamic radius were evaluated from Zimm plots for SLS and Zimm plot-like plots (extrapolation to zero concentration and zero angle) for DLS except pH dependence. Since aggregation numbers were calculated by dividing molecular weights from SLS by a monomeric molecular weight from GPC, those are apparent values. The pH dependence was examined at a constant polymer concentration of 0.02 mg/cm^3, which is enough dilute to neglect the concentration term in analytical equations.

Aqueous solutions of PMAA-b-PFMA were titrated at room temperature on a potentiometer with addition of an aqueous HCl or NaOH solution. SLS was measured along with the stepwise changing of solution pH. The degree of ionization α was calculated from the difference between the total amount of HCl or NaOH added to a solution and the amount of free HCl or NaOH [32].

Atomic force microscopic (AFM) observation was performed at room temperature on a Digital Instruments NanoScope III. PMAA-b-PFMA in aqueous solution was cast on a freshly cleaved mica substrate, dried in vacuo, and then used for AFM observation. An AFM image was obtained using a tapping mode.

For TEM observation, a Hitachi H-800 TEM instrument was used at an acceleration voltage of 100 kV. The cast film was prepared by a procedure in which the solution of polymer is spread over a copper grid (Nissin EM 300 mesh) covered with carbon film, drained, and dried under a nitrogen atmosphere. For the preparation of a freeze-fracture replica, an aqueous solution of PMAA-b-PFMA was vitrified in icy nitrogen before fracturing at −130 °C. The fractured surface was shadowed with platinum evaporated from 45° and

Table 1
Parameters obtained from light scattering for solutions of diblock copolymers

Diblock copolymer	Solvent	$M_W (10^7)$	Aggregation number	R_G (nm)	R_H (nm)
PMAA-b-PFMA (Lot A107, $M_W \approx 82,200$, $m = 412$, $n = 87$)	Water, pH 10	39.3	4780	148	
	Water, pH 4.7	13.0	1580	78.1	118
	Water, pH 3.0	11.3	1370	61.1	
	0.1 M NaClaq	11.3	1370	69.5	66.6
	Ethanol	11.1	1350	59.2	76.9
PtBMA-b-PFMA (Lot A80, $M_W \approx 106,600$, $m = 416$, $n = 87$)	Ethanol	3.95	373	38.2	46.4

covered with carbon evaporated at 90°. A replica film was separated from an icy solution.

3. Results and discussion

3.1. Self-association of PMAA-b-PFMA in solution

A water-soluble diblock copolymer, PMAA-b-PFMA, in solution is expected to form micelles, since hydrophobic PMMA-b-PFMA molecules are associated into micelles in acetonitrile and chloroform, as previously reported [29]. It was found from SLS measurement that PMAA-b-PFMA in water (pH 4.7) has a weight-average molecular weight M_W of 13.0×10^7 and a radius of gyration R_G of 78.1 nm. The hydrodynamic radius R_H obtained from DLS analysis is 118 nm. Since the molecular weight is much larger than that (82,200) of monomeric diblock copolymer, PMAA-b-PFMA molecules form aggregates with an aggregation number of 1580 in water (pH 4.7). An AFM image and a TEM photograph of PMAA-b-PFMA aggregates in water are shown in Fig. 2. There are spherical particles. We observed an image of dried particles from AFM but an image of micelles in solution from freeze-fracture TEM. Still both images are similar. This means there is no influence from the drying process. Then aggregates can be assumed to be almost spherical core–shell micelles like PMMA-b-PFMA aggregates, although the aggregate molecular weight of PMAA-b-PFMA is larger by one order than that of PMMA-b-PFMA.

Since PMAA-b-PFMA contains carboxylic acid groups in the PMAA block, the dissociation degree of PMAA block is changeable by changing pH. The pH dependence of M_W and R_G of PMAA-b-PFMA micelles in water is shown in Fig. 3, which includes the pH -dependent dissociation degree α of PMAA-b-PFMA. As pH rises, both M_W and R_G of the micelles increase cooperatively. The midpoint of the transition is close to the pK_a of carboxylic acid. Since the profiles of M_W and R_G curves are similar to that of the α curve, the dissociation degree of PMAA block causes the change of association behavior of diblock copolymer. That is, with increasing pH, PMAA block suffers the dissociation of carboxylic acid groups and changes its structure from globular

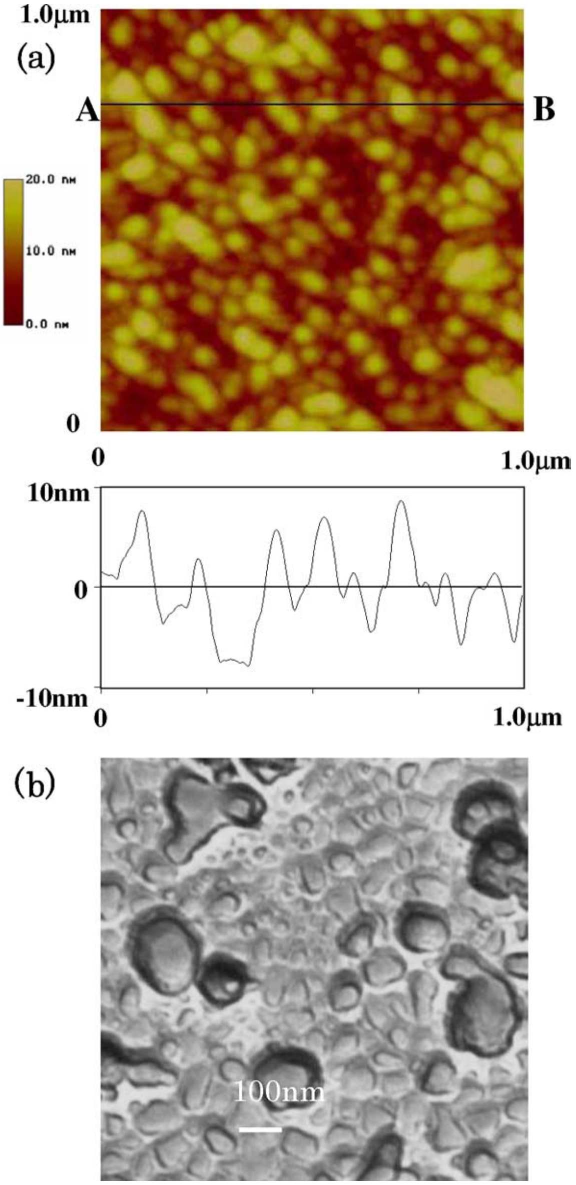

Fig. 2. (a) An AFM image of cast film on mica and (b) a TEM photograph of freeze-fracture replica film from an aqueous solution (pH 4.7) of PMAA-b-PFMA. Solution concentration: (a) 0.50 mg/cm^3, (b) 1.0 mg/cm^3.

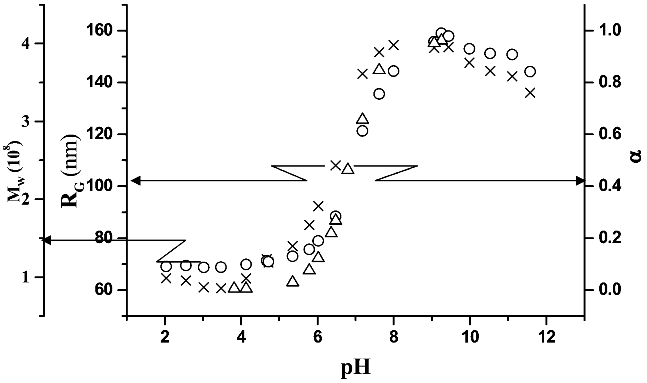

Fig. 3. The pH dependence of M_W, R_G, and dissociation degree α in aqueous solutions of PMAA-b-PFMA. (○) M_W; (×) R_G; (△) α.

random-coil to the extended chain, resulting from the electrostatic repulsion of carboxylate ions in a chain. It is well known that linear polymer expands when it is electrically charged [33]. Moreover, the stretching of PMAA blocks leads to the decrease of steric hindrance between polymers in micelles so that PMAA-b-PFMA molecules are likely to associate. The electrostatic repulsion between charged PMAA-b-PFMA molecules expands the volume of the micellar size. Consequently, M_W and R_G increase with pH, although they decrease slightly at a pH higher than 8. This decrease can be explained by the reason that, in addition of excess NaOH, sodium ion acts as the ionic strength screening the electrostatic repulsion. It should be noted from the large aggregation numbers that, in the case of this diblock copolymer, the solvophobicity of fluorinated block is more dominant in micelle formation than other factors.

Micellar aggregation numbers depending on the conformational change of PMAA block in water were compared with that in aqueous NaCl solution. The size of the PMAA-b-PFMA micelle in an aqueous 0.1 M NaCl solution (see Table 1) is consistent with these of PMAA-b-PFMA micelles in water below pH 4 (see Fig. 3). Addition of NaCl to an aqueous solution of PMAA-b-PFMA increases the ionic strength and screens the electrostatic repulsive interactions between carboxylate in PMAA block. Then, PMAA blocks take the bulky random-coil conformation, which is entropically preferable, so that large micelles are not formed because of the steric hindrance, as a case of aggregation of nonionic PMAA-b-PFMA in water below pH 4.

The size of a PMAA-b-PFMA micelle in an ethanol solution, listed in Table 1, is also comparable to those of PMAA-b-PFMA micelles in water below pH 4 and in an aqueous NaCl solution. In ethanol where PMAA blocks are protonated, PMAA blocks take the bulky random-coil conformation, and the low aggregation number of the micelles is a result of the high steric hindrance. When ionization degree, ionic strength, and solvent were changed, the sizes of the PMAA-b-PFMA micelles controlled by the extended or bulky conformation of PMAA blocks are schematically presented in Fig. 4 with drawing of the chemical species of protonated and nonprotonated PMAA-b-PFMA. Groenewegen et al. [34] have mentioned that the dimension of the micelles is regulated by the balance of the elastic, conformational, stretching forces and the osmotic pressure exerted by the counterions trapped within the corona. Ravi et al. [35] have recently reported association behavior of poly(methacrylic acid)–block–poly(methyl methacrylate) in

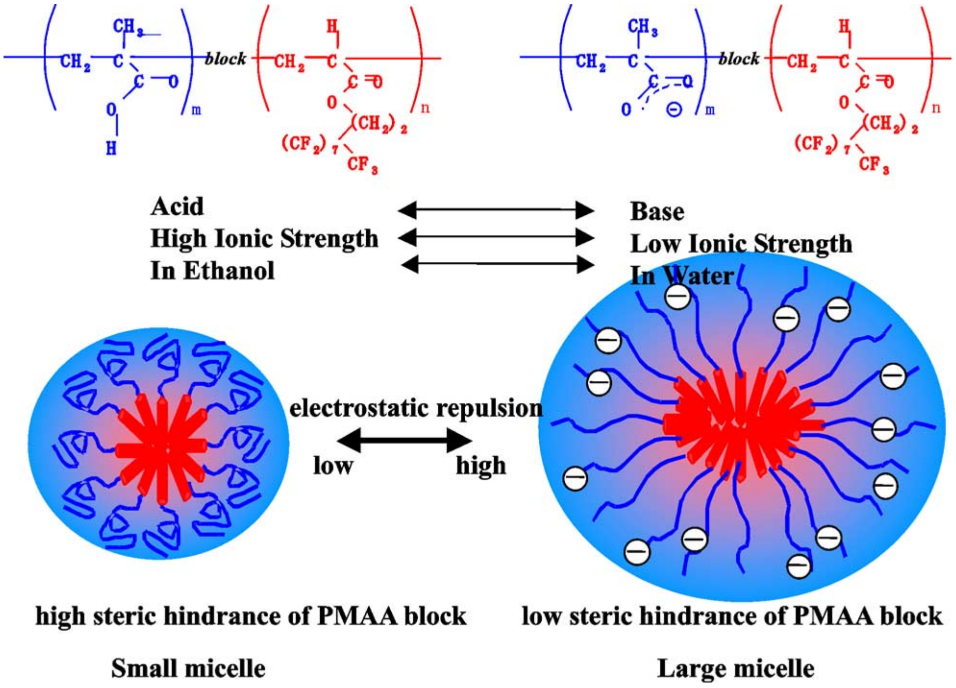

Fig. 4. Schematic presentation of size and structure of small and large PMAA-b-PFMA micelles depending on ionization degree, ionic strength, and solvent. Chemical species of protonated and nonprotonated PMAA-b-PFMA are also included.

an aqueous medium. The molar mass of the micelle increased with the degree of ionization, characterizing the expansion of the shell layer upon ionization, as well as a case of PMAA-b-PFMA micelles in the present work.

3.2. *Effect of solvophilic blocks on association*

Two block copolymers, PMAA-b-PFMA and PtBMA-b-PFMA, have similar degrees of polymerization. However, the former contains hydrophilic PMAA block and latter consists of hydrophobic (oleophilic) PtBMA block. The parameters obtained from light scattering for PtBMA-b-PFMA micelles in ethanol are listed in Table 1. The M_W and aggregation number of PtBMA-b-PFMA micelles in ethanol are about one-fourth of those of PMAA-b-PFMA micelles in ethanol. The values of R_G and R_H of PtBMA-b-PFMA micelles in ethanol are also smaller than those of PMAA-b-PFMA micelles in ethanol. Thus, it can be assumed that the conformation of solvophilic blocks contributes to the size of the micelle. Ethanol is a better solvent for PMAA block than for PtBMA block, as the second virial coefficient points out: The second virial coefficients of PtBMA-b-PFMA and PMAA-b-PFMA micelles were 0.22×10^{-6} and 2.2×10^{-6} mol cm^{3}g^{-2}, respectively. Then, PtBMA chains are likely to take the conformation as minimizing the penetration of ethanol. Therefore, PtBMA-b-PFMA molecules form small micelles owing to the disadvantage of steric hindrance of PtBMA block.

As well as PMAA-b-PFMA micelles, PtBMA-b-PFMA micelles are formed by the solvophobic interaction of PFMA blocks. The difference of aggregation number between micelles of these two block copolymers arises from the solubility of solvophilic blocks, PtBMA block and PMAA block, in the solvent, which changes the conformation of these blocks accompanied with different steric hindrances.

3.3. *Structure of fluorinated block copolymer micelles*

PMAA-b-PFMA micelles in water and ethanol and PtBMA-b-PFMA micelle in ethanol were cast on copper grid coated by carbon film. The TEM photographs of specimens prepared are shown in Figs. 5–7 with their size distribution, which was prepared by measuring particle sizes in each photograph. As seen in Fig. 5, on a cast film prepared from an aqueous solution of PMAA-b-PFMA, there were ellipsoidal particles regarded as micelles. Their sizes, where average long hemiaxis is 41 nm and short hemiaxis is 24 nm, are smaller than the radius ($R = 101$ nm) calculated from the radius of gyration. On the TEM observation, since the fluorine atom has large electron density, only a fluorinated block; i.e., the PFMA core of the micelle is contrasted as a dark region and the PMAA micelle shell displays less contrast. Thus, the image obtained from the TEM photograph is only a micelle core. Fig. 6 is a TEM photograph from an ethanol solution of PMAA-b-PFMA. PMAA-b-PFMA micelle in ethanol possesses an ellipsoidal core with long and short hemiaxes of similar sizes as to a micelle in water. Since aggregation numbers of PMAA-b-PFMA micelles in water and ethanol are large, both micelles can form an ellipsoidal micelle core. In Fig. 7, which was obtained from an ethanol solution of PtBMA-b-PFMA, a micelle core consisting of PFMA, whose size is 24 nm for long hemiaxis and 17 nm for short hemiaxis, is rather spherical.

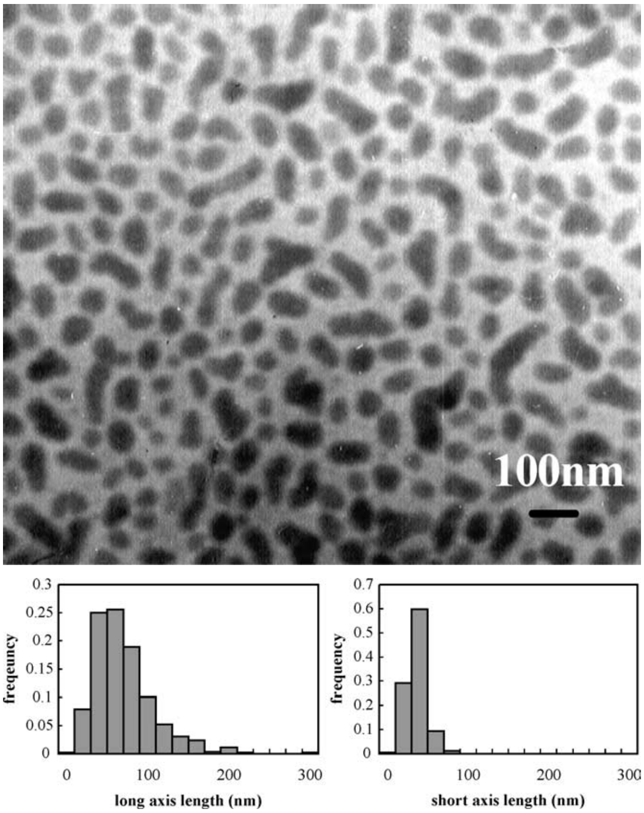

Fig. 5. A TEM photograph of cast film on carbon grid from an aqueous solution (pH 4.7) of PMAA-b-PFMA at a concentration of 2.0 mg/cm^3. Figures in bottom display size distribution.

The radius of gyration of AB-type block copolymers follows an equation [36]

$$R^2_{\mathrm{G,app}} = f'_{\mathrm{A}} R^2_{\mathrm{G,A}} + f'_{\mathrm{B}} R^2_{\mathrm{G,B}} + f'_{\mathrm{A}} f'_{\mathrm{B}} R^2_{\mathrm{G,AB}}, \tag{1}$$

$$f'_{\mathrm{A}} = f_{\mathrm{A}} (\partial n/\partial c)_{\mathrm{A}} / (\partial n/\partial c),$$

$$f'_{\mathrm{B}} = f_{\mathrm{B}} (\partial n/\partial c)_{\mathrm{B}} / (\partial n/\partial c), \tag{2}$$

$$(\partial n/\partial c) = f_{\mathrm{A}} (\partial n/\partial c)_{\mathrm{A}} + f_{\mathrm{B}} (\partial n/\partial c)_{\mathrm{B}}, \tag{3}$$

where $R^2_{\mathrm{G,app}}$ is an apparent radius of gyration, $R^2_{\mathrm{G,A}}$, $R^2_{\mathrm{G,B}}$, and $R^2_{\mathrm{G,AB}}$ are radii of gyration of core (A), shell (B), and micelle (AB), respectively, and f_{A} and f_{B} are weight fractions of core (A) and shell (B), respectively. $(\partial n/\partial c)_{\mathrm{A}}$, $(\partial n/\partial c)_{\mathrm{B}}$, and $(\partial n/\partial c)$ are specific reflective index increments of core (A), shell (B), and micelle (AB), respectively. If the specific reflective index increment of core (A) is close to zero,

$$R_{\mathrm{G,app}} \approx R_{\mathrm{G,B}}. \tag{4}$$

Assuming that the micelle of a diblock copolymer is a prolate ellipsoid of a core (A) of PFMA block and a shell (B) of

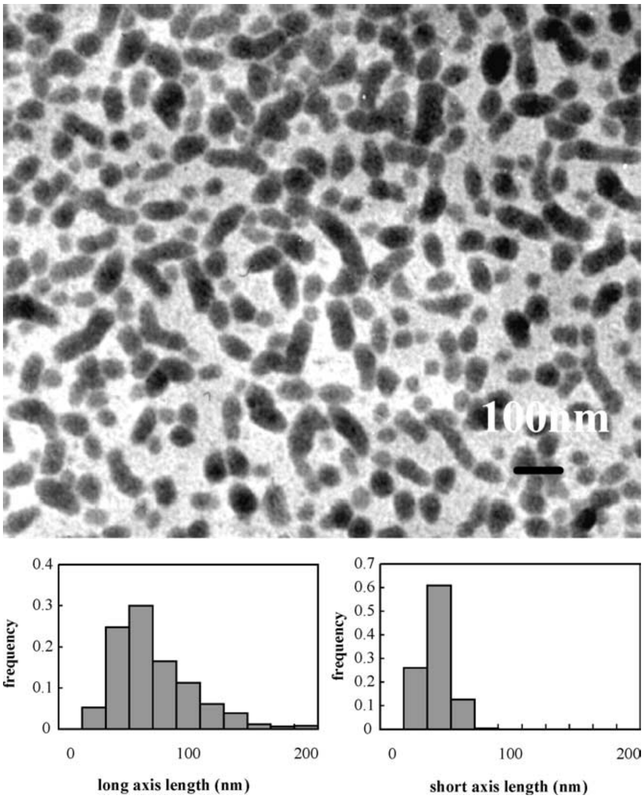

Fig. 6. A TEM photograph of cast film on carbon grid from an ethanol solution of PMAA-b-PFMA at a concentration of 1.0 mg/cm^3. Figures in bottom display size distribution.

solvophilic block, in which the shell thickness is x, as shown in Fig. 8, long and short hemiaxes, a and b, respectively, are

$$a = s + x,$$
$$b = t + x, \tag{5}$$

where s and t are long and short hemiaxis lengths, respectively, of the PFMA core of a micelle.

Since the specific reflective index increment of poly(2-perfluorooctylethyl methacrylate) was almost null, the approximate equation (4) can be applied for PMAA-b-PFMA micelles. Then the radius of gyration $R_{\mathrm{G,B}}$ for a prolate ellipsoid shell is described [37,38] as

$$R_{\mathrm{G,B}} = \left(\frac{(a^5 - s^5)}{5(a^3 - s^3)} + \frac{2(b^5 - t^5)}{5(b^3 - t^3)}\right)^{1/2}. \tag{6}$$

From the substitution of Eq. (5) into Eq. (6), shell thickness x can be calculated by using the R_{G} value from SLS measurement and the s and t values from TEM photographs. The evaluated x values are listed in Table 2. It is inferred from the calculated shell thickness x that PMAA blocks are extended in water and shrunk in ethanol. Moreover, PtBMA blocks in ethanol are in more compact random-coil conformation than PMAA block in ethanol. Those coincide with the discussion that the aggregation of micelle is ruled by the conformation of solvophilic block, as stated above.

In Table 2, ratios of s to t in a micelle core and a to b in the whole micelle are also listed. While the s/t values

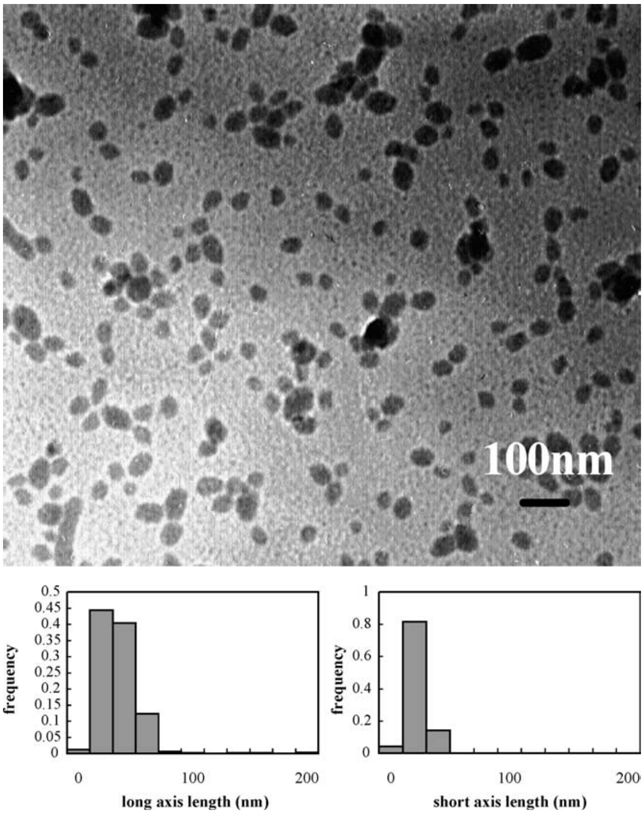

Fig. 7. A TEM photograph of cast film on carbon grid from an ethanol solution of PtBMA-b-PFMA at a concentration of 2.0 mg/cm^3. Figures in bottom display size distribution.

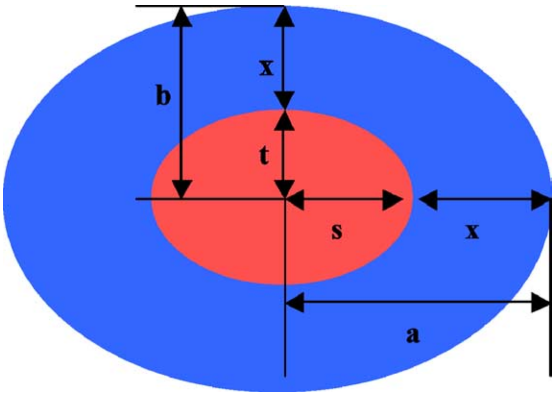

Fig. 8. A core–shell model of an ellipsoidal micelle.

Table 2
Calculated shell thickness and $R_{\mathrm{H,cal}}$ of micelles

Diblock copolymer	Solvent	s (nm)	t (nm)	x (nm)	s/t	a/b	$R_{\mathrm{H,cal}}$ (nm)
PMAA-b-PFMA	Water, pH 4.7	41	24	70	1.7	1.2	100
	Ethanol	41	25	43	1.7	1.2	73
PtBMA-b-PFMA	Ethanol	23	17	29	1.4	1.1	48

Table 3
Volume and surface area per molecule for core and shell in micelles

Diblock copolymer	Solvent	Volume per molecule (nm^3)		Surface area per molecule (nm^2)	
		Core	Shell	Core	Shell
PMAA-b-PFMA	Water, pH 4.7	62	2500	7.7	83
	Ethanol	75	1100	9.2	53
PtBMA-b-PFMA	Ethanol	72	1200	13	81

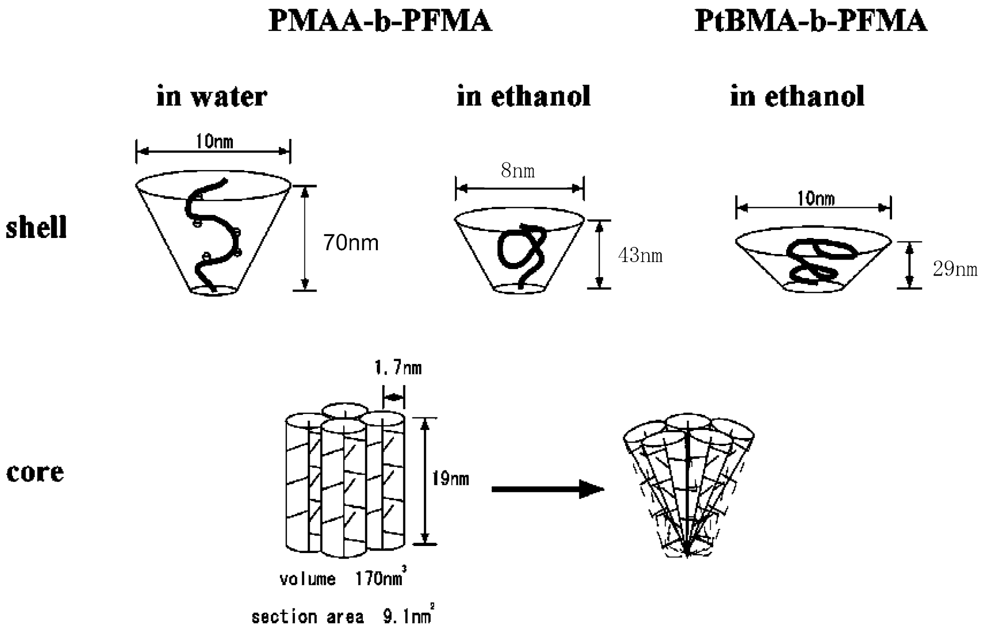

Fig. 9. Schematic structures of shell and core in micelles.

(1.4–1.7) for a micelle core suggest ellipsoidal morphology for three micelles, the shape of micelles as a whole is almost spherical, as the a/b values suggest. The difference is apparent from the comparison of a freeze-fracture TEM photograph from a solution in Fig. 2b with a TEM photograph from a cast film in Fig. 5. The former, presenting the whole structure of micelles, displays a rather spherical shape, and the latter gives a view of the texture of an ellipsoidal micelle core.

Hydrodynamic radius R_H is described using geometrical parameters, a and b, of a prolate ellipsoid, as follows [39]:

$$R_H = \frac{(a^2 - b^2)^{1/2}}{\ln(a + (a^2 - b^2)^{1/2})/b}. \qquad (7)$$

The hydrodynamic radii $R_{H,cal}$ for micelles of diblock copolymers calculated from Eqs. (5) and (7) with the values s, t, and x in Table 2 are also listed in Table 2. The $R_{H,cal}$ values for three micelles are comparable to R_H obtained from DLS (see Table 1). This consistency proves the accuracy of the estimated values a and b.

Based on the radii of a whole micelle and a micelle core, the volume and surface area per diblock copolymer molecule were calculated for the core and shell of each micelle, as listed in Table 3. Comparison of the three micelles of diblock copolymers shows that the shell of the PMAA-b-PFMA micelle in water has the largest volume and the larger surface area per molecule, since contains a large amount of a good solvent, water. While PMAA-b-PFMA and PtBMA-b-PFMA micelles in ethanol have the same shell volume per molecule, the surface area per molecule of a PtBMA-b-PFMA micelle shell in ethanol is larger than that of PMAA-b-PFMA micelle shell in ethanol. The reason for this is related to the small aggregation number of the PtBMA-b-PFMA micelle and the thinness of its shell. The structure of the shell of each micelle is illustrated in Fig. 9.

For the micelle core, both volume and surface area per diblock copolymer molecule are nearly the same in the three systems. If a PFMA block is regarded as rigid cylinder, as given in Fig. 9 (bottom, left), its volume and surface area are 170 nm^3 and 9.1 nm^2, respectively. The calculated surface area is close to the observed value, but the volume is larger than the observed volume, so that the PFMA blocks are tightly packed in the micelle center, as shown in Fig. 9 (bottom, right). The averaged shorter radii 24–25 nm for PMAA-b-PFMA micelles (see Table 2) are larger than a calculated maximum extension of the PFMA block. This causes from the steric hindrance of PFMA blocks at the center of the core and results in the roughness in the core–shell interface.

The self-association of fluorinated polymers has been studied by some investigators. Xu et al. [40] have synthesized and characterized polyethylene glycols end-capped with fluorocarbon hydrophobes. They interpreted the rheological behavior of these polymers in terms of an association structure of flowerlike micelles connected by bridging fluorocarbon chains. Loppinet and Gebel [7] have investigated the colloidal structure of short pendant chain perfluorinated ionomer in polar solvents and confirmed the existence of rodlike aggregates with a diameter of 1.7 nm in aqueous solution.

The aggregation behavior of a series of 2-(N-ethylperfluorooctanesulfonamido)ethyl acrylate copolymerized with polyacrylamide in water has been investigated by Zhang et al. [16]. Each aggregate consisted of 5–9 individual polymer chains on average. Krupers et al. [19,20] have discussed the micellar morphology of a semifluorinated diblock copolymer of methyl methacrylate and 1H,1H,2H,2H-perfluorooctyl methacrylate. While the pure block copolymer formed cylindrical micelles, the addition of poly(methyl methacrylate) shifted the association equilibrium to the side of spherical aggregates. Busse et al. [30] have determined the dimension and inner structure of micelles consisting of copolymers of *tert*-butyl methacrylate and 2-(N-methylperfluorobutanesulfonamido)ethyl methacrylate.

Matsumoto et al. [27] have reported that fluorine-containing amphiphilic block copolymers consisting of poly(2-hydroxyethyl vinyl ether) and poly(2-(2,2,2-trifluoroethoxy)ethyl vinyl ether) formed core–shell spherical micelles at a concentration of 1.0 wt%. Similar core–shell (core-corona) micelles were reported by Imae et al. [29,41] for a block copolymer of methyl methacrylate and 2-perfluorooctylethylmethacrylate (PMMA-b-PFMA). The micellar shape of PMMA-b-PFMA in acetonitrile and butyl acetate is similar to that of PtBMA-b-PFMA in ethanol in the present work, while the micelle of PMMA-b-PFMA in chloroform is of the crewcut type. This indicates that the association structure of fluorinated copolymers with oleophilic block depends on the solvents. On the other hand, the present investigation reveals that the size and structure of the core–shell micelles of fluorinated copolymers with hydrophilic block are highly sensitive not only to the solvent but also to the degree of ionization and ionic strength. Moreover, the aggregation number of the PMAA-b-PFMA micelle is larger than that (∼20) of poly(methacrylic acid)–block–poly(methyl methacrylate) in water reported by Ravi et al. [35]. This reveals the strong contribution of the solvophobic fluorinated segment.

4. Conclusions

It was confirmed that the fluorinated diblock copolymers, PMAA-b-PFMA and PtBMA-b-PFMA, form micelles. The size of the micelles of water-soluble PMAA-b-PFMA is controlled by pH, ionic strength or the solvent. PtBMA-b-PFMA molecule is associated into micelles different in size from PMAA-b-PFMA micelles. Such variation of micellar size is due to the conformational variation of the solvophilic blocks, which is induced mainly by electrostatic repulsion interaction and an affinity for the solvent. The difference of conformation affects the permeability and the void for small guest molecules. This may be advantageous for applications.

References

[1] J.G. Drobny, Macromol. Symp. 170 (2001) 149.
[2] B. Fuchs, U. Lappan, K. Lunkwitz, U. Scheler, Macromolecules 35 (2002) 9079.
[3] S.C. Yoon, B.D. Ratner, Macromolecules 19 (1986) 1068.
[4] S.C. Yoon, B.D. Ratner, Macromolecules 21 (1988) 2392.
[5] S.C. Yoon, B.D. Ratner, Macromolecules 21 (1988) 2401.
[6] K. Tadano, Y. Tanaka, T. Shimizu, S. Yano, Macromolecules 32 (1999) 1651.
[7] B. Loppinet, G. Gebel, Langmuir 14 (1998) 1977.
[8] P. Liu, J. Bandara, Y. Lin, D. Elgin, L.F. Allard, Y.-P. Sun, Langmuir 18 (2002) 10,398.
[9] J.P. Penning, R.S.J. Manley, Macromolecules 29 (1996) 77.
[10] J.P. Penning, R.S.J. Manley, Macromolecules 29 (1996) 84.
[11] L. Liu, B. Chu, J.P. Penning, R.S.J. Manley, Macromolecules 30 (1997) 4398.
[12] M.A. Hillmyer, T.P. Lodge, J. Polym. Sci. Part A Polym. Chem. 40 (2002) 1.
[13] M. Miyamoto, K. Aoi, T. Saegusa, Macromolecules 22 (1989) 3540.
[14] D.L. Schmidt, B.M. DeKoven, C.E. Coburn, G.E. Potter, G.F. Meyers, D.A. Fischer, Langmuir 12 (1996) 518.
[15] D.R. Iyengar, S.M. Perutz, C.-A. Dai, C.K. Ober, E.J. Kramer, Macromolecules 29 (1996) 1229.
[16] Y. Zhang, C. Wu, Q. Fang, Y.-X. Zhang, Macromolecules 29 (1996) 2494.
[17] C.M. Kassis, J.K. Steehler, D.E. Betts, Z. Guan, T.J. Romack, J.M. DeSimone, R. Linton, Macromolecules 29 (1996) 3247.
[18] F. Petit, I. Iliopoulos, R. Audebert, S. Szönyi, Langmuir 13 (1997) 4229.
[19] M.J. Krupers, M. Möller, Macromol. Chem. Phys. 198 (1997) 2163.
[20] M.J. Krupers, S.S. Sheiko, M. Möller, Polym. Bull. 40 (1998) 211.
[21] R.R. Thomas, D.R. Anton, W.F. Graham, M.J. Darmon, B.B. Sauer, K.M. Stika, D.G. Swartzfager, Macromolecules 30 (1997) 2883.
[22] R.R. Thomas, D.R. Anton, W.F. Graham, M.J. Darmon, K.M. Stika, Macromolecules 31 (1998) 4595.
[23] I.J. Park, S.-B. Lee, C.K. Choi, Macromolecules 31 (1998) 7555.
[24] B.B. Akhremitchev, B.K. Mohney, K.G. Marra, T.M. Chapman, G.C. Walker, Langmuir 14 (1998) 3976.
[25] T. Ishizone, K. Sugiyama, Y. Sakano, H. Mori, A. Hirao, S. Nakahama, Polym. J. 31 (1999) 983.
[26] Y. Tanaka, H. Hasegawa, T. Hashimoto, A. Ribbe, K. Sugiyama, A. Hirao, S. Nakahama, Polym. J. 31 (1999) 989.
[27] K. Matsumoto, M. Kubota, H. Matsuoka, H. Yamaoka, Macromolecules 32 (1999) 7122.
[28] K. Matsumoto, H. Mazaki, R. Nishimura, H. Matsuoka, H. Yamaoka, Macromolecules 33 (2000) 8295.
[29] T. Imae, H. Tabuchi, K. Funayama, A. Sato, T. Nakamura, N. Amaya, Colloids Surf. A Phys. Eng. Aspects 167 (2000) 73.
[30] K. Busse, J. Kressler, D. van Eck, S. Höring, Macromolecules 35 (2002) 178.
[31] T. Imae, T. Kohsaka, J. Phys. Chem. 96 (1992) 10,030.
[32] T. Imae, S. Suzuki, A. Abe, S. Ikeda, Y. Fukui, M. Senoh, S. Tsujii, Colloids Surf. 33 (1988) 75.
[33] C. Tanford, Physical Chemistry of Macromolecules, Wiley, New York/London, 1961, p. 489–491.
[34] W. Groenewgen, S.U. Egelhaap, A. Lapp, R.C. van der Maarel, Macromolecules 33 (2000) 3283.

[35] P. Ravi, C. Wang, K.C. Tam, L.H. Gan, Macromolecules 36 (2003) 173.

[36] R.H. Ewart, C.P. Roe, P. Debye, J.R. McCartney, J. Chem. Phys. 14 (1946) 687.

[37] W. Burchard, G.D. Patterson, Light Scattering from Polymers, Springer-Verlag, Berlin, 1983.

[38] T. Imae, Colloids Surf. 109 (1996) 291.

[39] B.J. Berne, R. Pecora, Dynamic Light Scattering, Willey, New York, 1976.

[40] B. Xu, L. Li, A. Yekta, Z. Masoumi, S. Kanagalingam, M.A. Winnik, K. Zhang, P.M. Macdonald, Langmuir 13 (1997) 2447.

[41] T. Imae, Kobunshi Ronbunshu 58 (2001) 178, (In Japanese).