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# Effect of interfacial tension on micellization of a polystyrene–poly(ethylene oxide) diblock copolymer in a mixed solvent system

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## Abstract

The micellization of a polystyrene–poly(ethylene oxide) (PS–PEO) diblock copolymer in a mixed solvent of water and tetrahydrofuran (THF) was studied in terms of an aggregation number as measured by laser light scattering. The results show the aggregation number ($f$) of the micelle decreases monotonically as the amount of THF is increased. These experimental results are compared with a theoretical model that includes the variations in the interfacial tension. Experimentally, the interfacial tension is adjusted with the addition of relatively low levels of THF. The theory indicates that the aggregation number decreases as the interfacial tension is decreased. The theoretical prediction is in very good agreement with the experimental results. The main conclusion of this study is that the interfacial tension is the key factor in determining the aggregation number of the diblock copolymer micelle in a water–THF solvent system. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Interfacial tension; Diblock copolymer; Solvent system

## 1. Introduction

The micellization properties of diblock and triblock copolymers have attracted the attention of a large number of research groups. The reason for this interest lies in the unusually large number of structures formed with relatively modest change in polymer molecular weight and composition. These studies [1–6] have focused on solutions, gels and solid-state, as well as interfacial behavior and surface properties. Researchers have exploited these changes in structure and properties for a number of technologically important applications. One of the most widely studied diblocks is the non-ionic poly(ethylene oxide)–polystyrene, PEO–PS diblock copolymer [7–13]. PS–PEO diblock copolymers provide an interesting model system to investigate micellization due to the high incompatibility between the hydrophobic PS and hydrophilic PEO components of the molecule. These materials are characterized by their ability to form uniform suspensions in both organic and aqueous environments. In aqueous solution, these diblock copolymers self-assemble into micelles with the polystyrene (PS) component forming a glassy core surrounded by a solubilized PEO corona.

In fact, the high glass transition temperature ($T_g$) of the PS core can lead to structures that are not in thermodynamic equilibrium [14]. Lowering the $T_g$ of the core by addition of cosolvent should plasticize the core and allow the micelle to approach thermodynamic equilibrium at lower temperatures. Therefore, a cosolvent-plasticized PS–PEO in water can be an excellent model system for probing the characteristics of micelle formation.

In this study, tetrahydrofuran (THF) is added in water to modify the $T_g$ of the glassy PS core of the micelle. THF is miscible with water and is a solvent for PS and PEO [15]. As a result of this common solvation effect, the $T_g$ of the PS core can be systematically controlled. However, there is a limit in the added amounts of THF in water, more than approximately 80% THF in water causes significant PEO aggregation [16].

The aggregation number of the micelle is strongly influenced by the interfacial tension between the micelle core and solvent. For example, the unusually large aggregation number of a poly(ethylene-*co*-propylene)–PEO (PEP–PEO)

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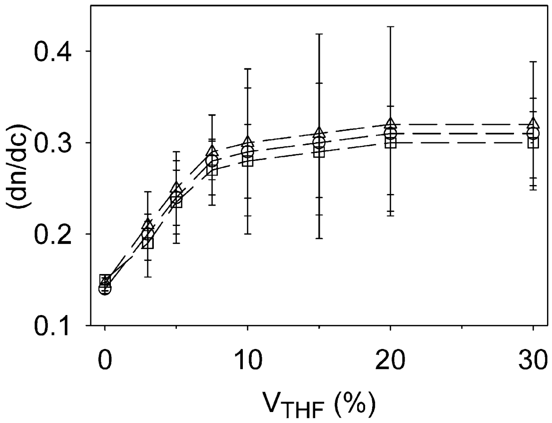

Fig. 1. (d$n$/d$c$) of the PS–PEO diblock copolymer in a mixed water–THF solvent system at 10 °C (circles), 23 °C (squares), 45 °C (triangles). $V_{\mathrm{THF}}$ is the volume fraction of THF.

diblock copolymer in water was attributed to the large interfacial tension between the PEP core and water [17]. In the present work, the effect of interfacial tension on micellization was examined through the modification of solvent composition in a water–THF mixed solvent system. Our results show that THF modifies the interfacial tension between the surface of the micelle core and the surrounding solvent. With increasing THF, the interfacial tension is reduced and a corresponding reduction in the micelle aggregation number is observed. In order to understand the phenomenon, the layer thickness of the corona, the aggregation number, the interfacial tension and hydrodynamic radius of the micelle were examined.

## 2. Experimental section

### 2.1. Materials

Polystyrene/poly(ethylene oxide) (PS–PEO) diblock copolymer ($M_w = 6100/46\,900$) purchased from Polymer Source Inc. was used without further purification. The polydispersity of the PS/PEO diblock copolymer is very small ($M_w/M_n \cong 1.02$). THF (HPLC grade) obtained from Merck Co., and the deionized water, received from Fisher Co., were used without further purification.

### 2.2. Sample preparation

A diblock copolymer solution with the concentration of 10 mg/ml in a mixed solvent of 10% THF and 90% water was prepared and filtered with a 0.45 μm filter paper to remove insoluble aggregates. Furthermore, the solution was lyophilized: freezing the polymer solution in a dry ice/acetone–ethanol (1:1) mixture and drying under high vacuum for 10 h. The lyophilization process was useful for improving the solubility of the copolymer in mixed solvents as well as in pure water. THF may be removed completely during the process. A stock solution of lyophilized PS/PEO in pure water and a THF–water solvent was prepared at a concentration of 1 mg/ml and stirred for 2 weeks at room temperature. These solutions were thermodynamically stable and did not show any time-dependent changes in the scattered light intensity within a period of six months. Each solution was diluted with the same solvent to 0.2–0.6 mg/ml (five samples for each solution). Each sample was filtered through a 0.45 μm filter paper into a light scattering cell. The sample cells were equilibrated thermally at three different temperatures (10, 23, 45 °C) for at least 24 h prior to the light scattering intensity measurements.

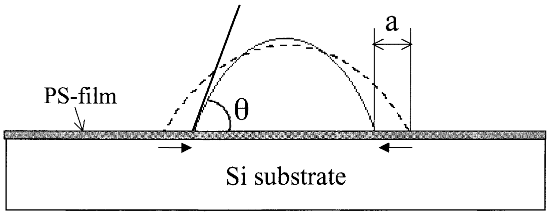

Fig. 2. Schematic view of the droplet of water–THF mixed solvent on the substrate. The droplet shrinks after loaded on the PS film. 'a' indicates the area exposed after shrinkage. The contact angles ($\theta$) are measured after shrinkage.

### 2.3. Specific refractive index measurements

The specific refractive index increments (d$n$/d$c$) (ml/g) for the PS–PEO diblock copolymer in a mixed solvent at three different temperatures were measured at the wavelength of 546 nm by using a C.N. Wood refractometer. The copolymer concentrations used was from 1 to 4 mg/ml. This range was chosen due to the sensitivity of the refractometer. The measured values of (d$n$/d$c$) are summarized in Fig. 1, which also shows that the variation of the values of (d$n$/d$c$) is significant as the volume fraction of THF in the mixed solvent is increased. The average value of (d$n$/d$c$) was used to calculate the molecular weight. The unusually large variation of (d$n$/d$c$) is not due to experimental error, rather it is likely caused by the unusual, but intrinsic, behavior of the water–THF mixtures [18,19]. The liquid–liquid lower critical solution point of the THF–water solvent is 71.85 °C at 22.5 mol% of THF. These concentration fluctuation effects are apparently still active even at lower temperatures over a broad range of concentration. Recently it was observed [20] that a PEO homopolymer at a critical composition of water–THF was collapsed near the critical point.

### 2.4. Contact angle measurement

Contact angles ($\theta$) between PS film ($M_w$ 123k, 105 nm thick film on Si-wafer, made by spin-coating) and water–THF mixed solvent were measured using optical microscopy. Mixed solvent droplet (10 μl each) was formed on the PS film (Fig. 2). To minimize the effect caused by the different evaporation rates of water and THF on the equilibrium of drop formation, a small chamber over the sample with a reservoir containing solution of the same composition with that of the drop. Interfacial tension between PS film and the mixed solvent is calculated by Young's equation

$$\gamma_{\text{PS-mixed}} = \gamma_{\text{PS}} - \gamma_{\text{mixed}} \cos\theta \tag{1}$$

where $\gamma_{\text{PS-mixed}}$ is the interfacial tension between PS and the water–THF mixed solvent, $\gamma_{\text{PS}}$ is the surface tension of PS and $\gamma_{\text{mixed}}$ is the surface tension of the water–THF mixed solvent.

### 2.5. Summary of physical properties

The critical micelle concentration (cmc) of the aqueous solution of the PS–PEO diblock copolymer at 23 °C was measured by the intensity of scattered light and the surface tension was measured using the Wilhelmy plate technique. These values were obtained at low concentrations ($10^{-3}$–$10^{-4}$ mg/ml). In the water–THF solvent, the cmc was marginally higher (with the same order of magnitude) due to an increase in the copolymer solubility, but still much lower than the experimental concentration ranges (0.2–0.6 mg/ml) obtained by laser light scattering measurements. Viscosity of each mixed solvent was measured with capillary viscometer at the three different temperatures. The refractive indices of materials were obtained from the literature; $n_{\text{water}} = 1.332$, $n_{\text{THF}} = 1.406$. Refractive index of water–THF mixed solvent was measured by using a refractometer at room temperature, and values were almost linearly dependent on the volume fraction of THF. We neglected the temperature dependence of refractive index of mixed solvents, which should be very small. The density of the amorphous PS ($\rho_{\text{PS}} = 1.06$ g/cm$^3$) was used to calculate the PS core dimension.

### 2.6. Light scattering measurements

A Brookhaven Instruments BI-200, equipped with a 35 mW He–Ne laser ($\lambda = 632.8$ nm), was used for the light scattering measurements. Dynamic light scattering (DLS) measurements were performed at a fixed angle of 90° to the incident beam at three different temperatures. We used an autocorrelator (BI9000AT) to measure the intensity auto-correlation function of the scattered light. Most of the correlation function was fitted with the accumulant analysis with the average decay rate ($\Gamma$) and the second accumulant ($\Delta\Gamma$). The decay rate gives directly the diffusion coefficient $D = \Gamma/q^2$, where $q = (4\pi n/\lambda)\sin(\theta/2)$, $n$ is the refractive index of a solvent, and $\theta$ is the scattering angle. The hydrodynamic radius ($R_h$) was calculated using the Stokes–Einstein relation

$$R_h = \frac{kT}{6\pi\eta_0 D} \tag{2}$$

where $\eta_0$ is the viscosity of a solvent, $k$ is the Boltzmann's constant and $T$ is the absolute temperature. The value of $\Delta\Gamma$ was about 0.1. This indicates that the micelles are reasonably mono-disperse.

Static light scattering (SLS) was performed at three different temperatures. The scattered light was measured at 10 angles between 30 and 135° as a function of the polymer concentration. The average scattering intensity was used to calculate the radius of gyration $R_g$, the second virial coefficient $A_2$, and the molecular weight of the micelle $M_w$ in the Zimm-plot described in the following equation

$$\frac{KC}{\Delta R_\theta} = \left(\frac{1}{M_w} + 2A_2C\right)\left(1 + \frac{1}{3}q^2\left\langle R_g^2\right\rangle_z\right) \tag{3}$$

with an optical constant

$$K = \frac{4\pi^2}{\lambda_0^4}\frac{n_0^2}{N_A}\left(\frac{dn}{dc}\right)^2,$$

an excess Rayleigh ratio $\Delta R_\theta$ and Avogadro's constant $N_A$, respectively.

## 3. Results and discussion

### 3.1. Solubilization of diblock copolymers

In general, it is difficult to solubilize PS–PEO diblock copolymers in water. This is due in part to the hydrophobic nature of the PS-core. Water cannot easily penetrate into the glassy core ($T_g \sim 100$ °C) at room temperature and therefore, high insolubility of PS core is anticipated. Sonication and heating does improve the rate of solubilization of the diblock copolymer, which results in a stable, and optically clear micellar solution. However, this process must be used with care since degradation of the polymer can occur [20].

In the experiments described in this study, it took at least two months by mild mechanical mixing to obtain an optically clear micellar solution of the PS–PEO diblock copolymer ($M_w = 6100/46\,900$) at room temperature. Even under these conditions, it is questionable that the micelles are in a true thermodynamic equilibrium state. A strong indication that thermodynamic equilibrium was not reached is the large size of micelles. The hydrodynamic radius ($R_h$) of the micelle was approximately 90 nm, which is too large to be considered an individual, spherical micelle [21,22]. However, it is noteworthy that these solutions were stable for over one year at room temperature.[1] Instead of making a solution by mechanical mixing, we prepared and lypophilized PS-PEO diblock copolymer solution in water containing 10% THF. The latter solvent is a good solvent for PS and also for PEO, and occasionally is used as a solvent in the synthesis of PS-PEO diblock copolymers by anionic polymerization [15]. The lyophilized powder enhances the solubility of copolymers in water and in a water–THF

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[1] PEO in water solution is susceptible to bacterial infection. In our case we did not observed any apparent changes in the micellar size and any evidence of bacterial infection.

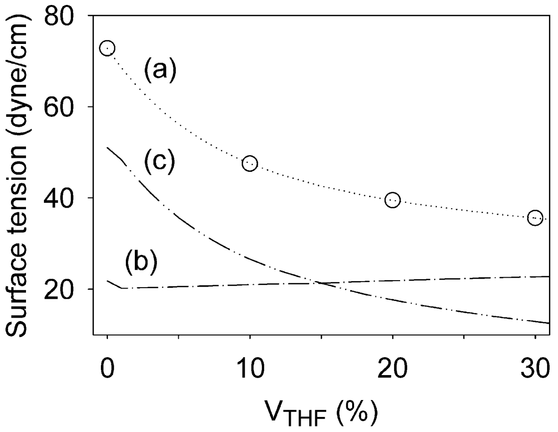

Fig. 3. Surface tension ($\gamma_{\text{mixed}}$) of the mixed water–THF solvent as a function of the volume fraction of THF at room temperature. (a) Experimental data using a Wilhelmy plate, (b) polar contribution $\gamma^{\text{a}}_{\text{mixed}}$ calculated from Eq. (1), and (c) dispersion contribution $\gamma^{\text{d}}_{\text{mixed}}$ calculated from Eq. (4).

mixed solvent. As a result of this procedure the optically clear solution of copolymers were obtained in any composition of a mixed solvent. We used this procedure for preparing micellar solutions in this report.

### *3.2. Determination of the interfacial tension between the PS-core and the mixed solvent system*

#### *3.2.1. From refractive index measurement of the mixed solvent*

Water has relatively large surface tension ($\gamma_{\text{water}} = 72.8$ dyne/cm), which comes from the large polar contribution due to the hydrogen bonding. When small amounts of surface active materials (e.g. surfactants) is added to water, the surface tension of the solution decreases significantly due to the disruption of the hydrogen-bonded network of water. Since THF is miscible with water and disrupts the hydrogen-bonded structure, the surface tension of a water–THF mixed solvent ($\gamma_{\text{mixed}}$) should be reduced. Fig. 3a is the experimentally determined surface tension measurements of the water–THF mixed solvent at room temperature. The results clearly confirm the effect of THF in reducing the surface tension. The reduced surface tension of the mixed solvent is expected to correspondingly reduce the interfacial tension between the PS-core and the mixed solvent, which is an important factor in determining micellar size and its related structure.

The experimentally determined surface tension of the mixed solvent can be decomposed into its individual components. This approach will lead to a better understanding of the underlying molecular interactions responsible for the changes in micellar structure. In general, the experimentally determined surface tension of a solution can be decomposed into two components based on the molecular interactions. One is from the dispersion interaction and the other is from the polar interaction [23]

$$\gamma = \gamma^{\text{d}} + \gamma^{\text{a}} \tag{4}$$

where superscripts 'd' and 'a' are the mean dispersion and polar contributions to the surface tension, respectively. The following equation is an experimentally determined relationship based on the surface tension of an organic solvent without hydrogen bonding from Ref. [24]

$$\gamma^{\text{d}} = 286[(n^2 + 1)/(2n^2 + 1)] - 28.6 \tag{5}$$

The dispersion contribution of water–THF mixed solvent, $\gamma^{\text{d}}_{\text{mixed}}$, can be calculated from the refractive index, $n$, of the mixture by using Eq. (5) because the surface tension reduction of the water–THF mixed solvent system is mainly due to reducing the polar contribution of the mixed solvent (Fig. 3b). As noted previously, the disruption of the hydrogen bonding intermolecular structure of water by THF is responsible for this effect. $\gamma^{\text{a}}_{\text{mixed}}$ is calculated from Eq. (4).

It is known that the micellization process of block copolymers in an aqueous solution is more strongly affected by the interfacial tension between the surface of the core and the solvent than that in an organic solution [17]. We used the surface tension obtained from literature [23] (Table 1) to estimate the interfacial tension between the 'solid' core surface and the surrounding solvent. The following equation [23] is based on immiscible system but still useful to our system to obtain interfacial tension between PS and water–THF mixture because PS is swollen, but not soluble, in relatively low THF concentration (<30%)

$$\gamma_{12} = \gamma_1 + \gamma_2 - \left(\frac{4\gamma_1^{\text{d}}\gamma_2^{\text{d}}}{\gamma_1^{\text{d}} + \gamma_2^{\text{d}}}\right) - \left(\frac{4\gamma_1^{\text{a}}\gamma_2^{\text{a}}}{\gamma_1^{\text{a}} + \gamma_2^{\text{a}}}\right) \tag{6}$$

The results of this calculation, presented in Fig. 4, show that the interfacial tension between the PS core and the mixed solvent decreases strongly with an increase in the volume fraction of THF ($V_{\text{THF}}$).

#### *3.2.2. From contact angle measurement*

The measured contact angles are plotted in Fig. 5. When water–THF mixture droplet contacts PS film, THF in the mixed solvent droplet is absorbed into the PS film which causes the droplet shape to change and shrink after 2–3 s (Fig. 2). The area 'a' indicated in the figure renders different

Table 1
Components of the surface tension ($\gamma$, dyne/cm) of the materials used in this study

| Materials | $\gamma$ | $\gamma^{\text{d}}$ | $\gamma^{\text{a}}$ | $-\text{d}\gamma/\text{d}T$ |
|---|---|---|---|---|
| Water | 72.8 | 21.8 | 51.0 | |
| THF | 26.5 | | | |
| PS | 40.48 | 33.64 | 6.84 | 0.072 |
| PEO | 42.67 | 30.49 | 12.18 | 0.076 |

$\gamma = \gamma^{\text{d}} + \gamma^{\text{a}}$. $\gamma^{\text{a}}$ is independent of temperature.

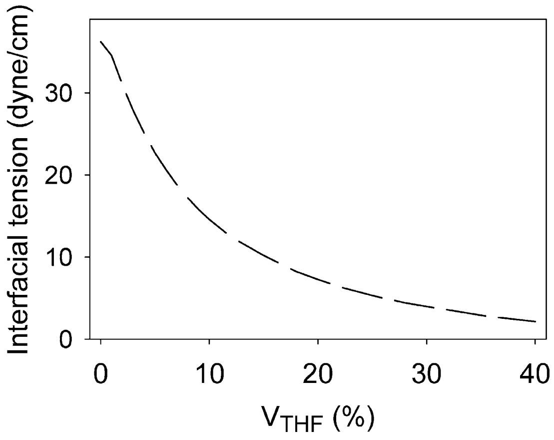

Fig. 4. Interfacial tension ($\gamma_{\text{PS-mixed}}$) between the PS-core and the mixed water–THF solvent calculated from Eq. (6).

color, indicating that PS film thickness increases due to swelling.

A new equilibrium state may be formed between the solvent mixture and the PS film swollen by THF. Therefore, Eq. (1) may be changed into the following equation

$$\gamma_{\text{swollenPS-mixed}} = \gamma_{\text{swollenPS}} - \gamma_{\text{mixed}} \cos\theta \tag{7}$$

where $\gamma_{\text{swollenPS-mixed}}$ is the interfacial tension between PS swollen by THF and the water–THF mixed solvent and $\gamma_{\text{swollenPS}}$ is the surface tension of PS swollen by THF. From Ref. [16] we can calculate the swelling ratio of PS latex (cross-linked, 91 nm in diameter) in the mixed solvent. Below 10% THF, it is shown that PS latex is not swollen but after 10% it is swollen a lot (33 in 50% THF). The crosslinking of PS latex resists swelling by THF but in the case of PS–PEO micelle, or in the uncrosslinked PS film, even below 10% THF, PS can be swollen by THF. Therefore PS swelling ratio is calculated from the data in Ref. [16] except the point at 10% THF. Swelling ratio of PS for different THF% is fitted from the data (Fig. 6).

If we assume that surface tension of non-hydrogen bonding solvent mixture is calculated from the volume fraction and surface tension of each solvent, the $\gamma_{\text{swollenPS}}$ can be calculated from following equation

$$\gamma_{\text{swollenPS}} = V_{\text{PS}}\gamma_{\text{PS}} + V_{\text{THF}}\gamma_{\text{THF}} \tag{8}$$

where $V$s are the volume fractions. In Fig. 7, $\gamma_{\text{PS-mixed}}$ (non-swelling case) is calculated from Eq. (1) and $\gamma_{\text{swollenPS-mixed}}$ (swelling case) is calculated from Eqs. (7) and (8).

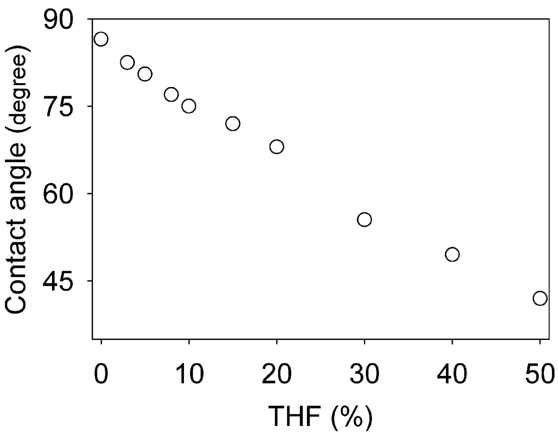

Fig. 5. Contact angles of water–THF mixed solvent droplet (10 μl) on PS film (100 nm film on Si-wafer) using optical microscopy.

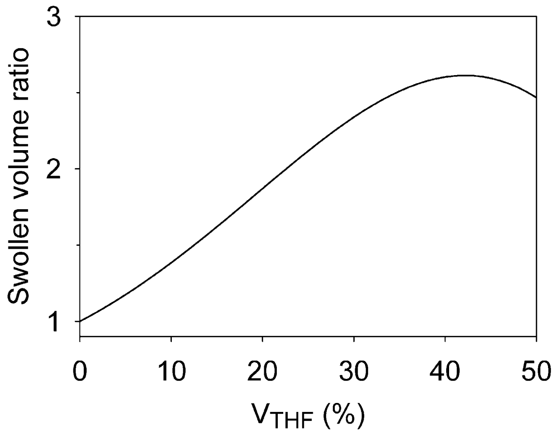

Fig. 6. Swollen volume ratio of PS latex (91 nm) in water–THF mixed solvent. Data are extracted and fitted from Ref. [16].

### 3.3. Structure of the micelle

The static light scattering results show that the aggregation number of a micelle decreased as $V_{\text{THF}}$ is increased (Fig. 8). Error bar of the experimental aggregation number is caused by the variation of (d$n$/d$c$) measurements in Fig. 8. The reduction of the aggregation number can be understood in terms of the reduction of the interfacial tension between a PS and the solvent, as discussed in Section 3.2.

Variations in the aggregation number primarily affects the core dimension of the micelle. If the assumption is made that the core of the micelle is spherical in the entire range of $V_{\text{THF}}$, the radius of the spherical core $R_c$ is

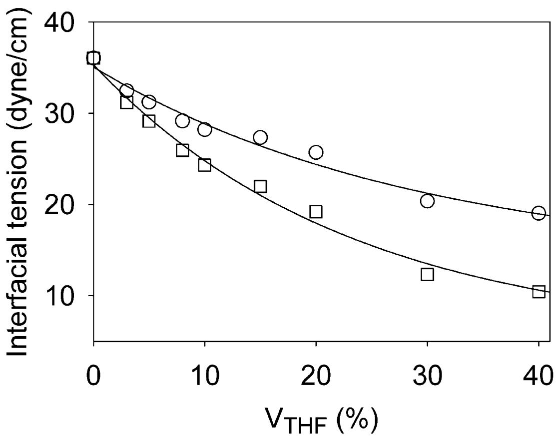

Fig. 7. Interfacial tension calculated from the contact angle measurement. $\gamma_{\text{PS-mixed}}$ (circle) from Eq. (6) and $\gamma_{\text{swollenPS-mixed}}$ (square) from Eqs. (7) and (8) are plotted.

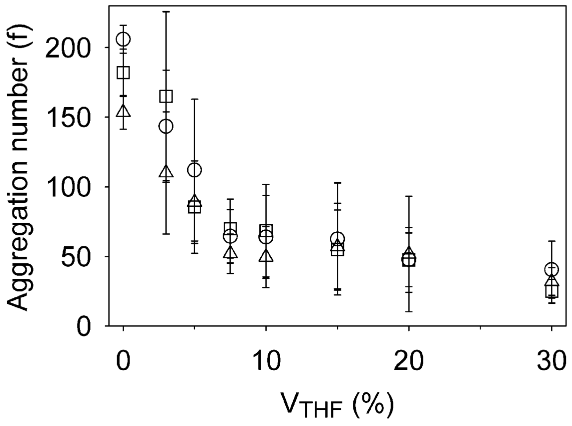

Fig. 8. Variations of the aggregation number ($f$) of PS–PEO diblock copolymer in the mixed water–THF solvent system measured from static light scattering measurement at 10 °C (circles), 23 °C (squares), 45 °C (triangles).

$f^{1/3}(3M_c/4\pi N_A\rho_c)^{1/3}$, where $M_c$ and $\rho_c$ are the molecular weight and the density of the insoluble core block, respectively. In the mixed solvent, the PS core is expected to swell and the core radius is expected to increase due to increasing $V_{THF}$. Previously, Dewalt et al. [16] reported that PS latex particles were swollen by THF in a water–THF solvent system. This was explained by noting that THF is a good solvent for PS. In the case of a mixture of two immiscible solvents, the amount of the solvents absorbed into the micelle core depends on the Flory–Huggins $\chi$-parameter. This parameter can be used to calculate the amount of solvent by SCF calculation [25]. Vagberg et al. [26] reported that a trace amount of water ($\sim$100 ppm) increases the aggregation number and the hydrodynamic radius to a significant amount in the case of a PEO–PS diblock copolymer in cyclopentane, in which case the core is PEO and the corona PS. With the assumption that THF is equally miscible with PS, PEO and water, the core radius swollen by THF in the mixed solvent is given by the expression $R_{c,\text{swollen}} = (1 - V_{THF})^{-1/3}R_c$, where $V_{THF}$ is the volume fraction of THF in water. With the assumption PS core is swollen by THF. The surface coverage ($\sigma = f/4\pi R^2$ where $R$ is a radius of a sphere) on PS core decreases significantly (Fig. 9) mainly due to the decrease in the aggregation number of the micelle and further decreases because PS core is swollen by THF. In other word the corona PEO chains can accommodate a large surface area.

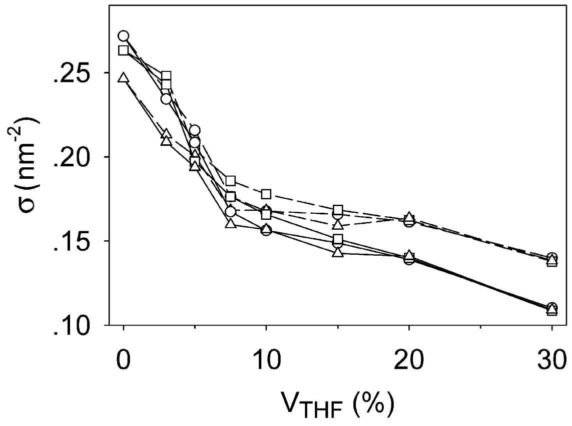

Fig. 9. Variation of the surface coverage (nm$^{-2}$) $\sigma = f/4\pi R_c^2$ (dashed line, for non-swollen core) and $\sigma_{\text{swollen}} = f/4\pi R_{c,\text{swollen}}^2$ (solid line for swollen core) of the micelle in the mixed water–THF solvent system at 10 °C (circles), 23 °C (squares), 45 °C (triangles).

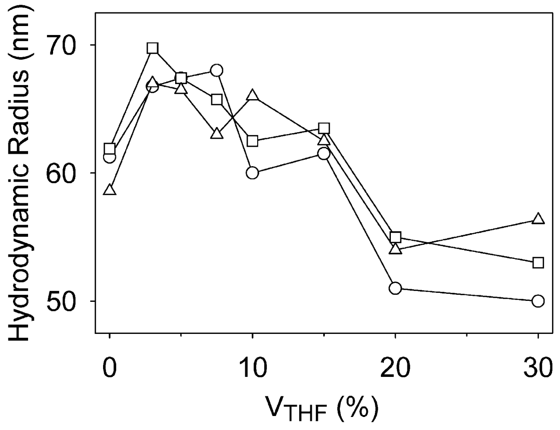

Fig. 10. Hydrodynamic radius of the PS–PEO diblock copolymer micelle in the water–THF mixed solvent system at 10 °C (circles), 23 °C (squares), 45 °C (triangles).

The dynamic light scattering measurements shows that these micelles have a general trend to retain or expand their hydrodynamic radius ($R_h$) in solvents containing up to approximately 15% THF (Fig. 10) even though the aggregation number gradually decreased. This behavior may affect theoretical calculation of the aggregation number, which will be discussed later. The temperature dependence of $R_h$, which deserves further study, is presently unknown.

From the SCF theory [27], the layer thickness ($H$) defined by the coronal height of the micelle ($R_h - R_c$) can be calculated. Therefore, the layer thickness of the polymeric brush at a spherical interface, i.e. a corona, in a good solvent scales as

$$H = (R_h - R_c) \sim N^{3/5}\sigma^{1/5}R_c^{2/5} \tag{9}$$

where N is a degree of polymerization

Since $\sigma$ and $R_c$ is replaced by terms of aggregation number, Eq. (9) is reduced to the simple scaling relationship $(R_h - R_c) \sim N^{3/5}f^{1/5}$. If this were true, the value of $(R_h - R_c)/f^{1/5}$ should be independent of the aggregation number. However, the value increases linearly with $V_{THF}$ in the concentration range from approximately 5 to 10% THF (Fig. 11). This result implies that the coronal PEO chains have a tendency to resist contraction in the presence of THF even though the PEO chains have gradually taken up a larger volume in the mixed solvent as compared to the pure water. The primary reason for this effect is that THF disrupts the hydrogen-bonding network between PEO and water, and

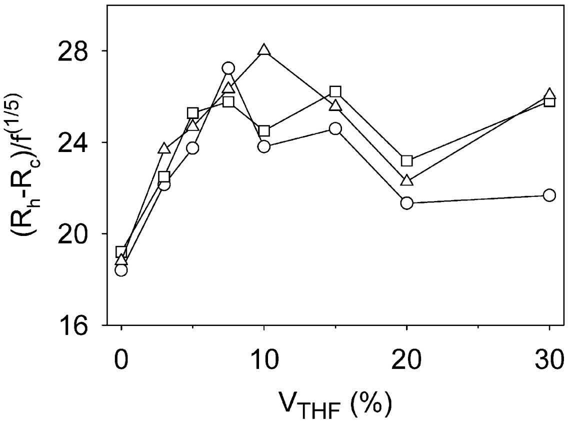

Fig. 11. Comparison of the layer thickness $H \sim N^{3/5}\sigma^{1/5}R^{2/5}$ with the coronal height of the micelle ($R_h - R_c$). The ratio $(R_h - R_c)/f^{1/5}$ shows the stretching of the coronal chain as compared with theory [15] in the mixed water–THF solvent system at 10 °C (circles), 23 °C (squares), 45 °C (triangles). $R_h$ is the hydrodynamic radius from Fig. 10 and $R_c$ is calculated from the equation, $R_c = f^{1/3}(3M_c/4\pi N_A\rho_c)^{1/3}$.

the hydrophobic interaction between THF and the $CH_2CH_2$ units of PEO becomes more energetically favorable.

It is also important to note that the value of $R_g/R_h$ remains invariant (0.9 ± 0.05) up to approximately 15% THF (Fig. 12), which indicates that the shape of the micelle is unchanged. It is quite likely that the shape of the micelle remains spherical in pure water up to about 15% THF and then changes into cylindrical shape above 15% THF. The depolarization ratio ($I_{VH}/I_{VV}$) shown in Fig. 13 was measured to confirm the shape anisotropy of the micelles as the function of polymer concentration.

### 3.4. Comparison with a star-like micelle morphology

The star-like micelle model proposed by Halperin [28] where AB diblock copolymers form a micelle with core–shell structure in a selective solvent can be used to further describe the PS/PEO micelles formed in this study. In the case of $N_{corona} \gg N_{core}$, the radius of a star-like micelle is given by the expression $R \approx a(\gamma_{12}a^2/kT)N_{core}^{4/25}N_{corona}^{3/5}$ where $a$ is a monomer size and $N_{corona}$ and $N_{core}$ are N of corona and core blocks in a diblock copolymer. The radius of a star-like micelle depends only on the interfacial tension between a core and a solvent if the molecular weight and the size of the monomer remain constant. If we compare the ratio for the measured $R_h$ with the theoretical value for $(\gamma_{12}/kT)N_{core}^{4/25}N_{corona}^{3/5}$ as a function of the volume fraction of THF (Fig. 14) we find that the ratio $\varphi$ $(R_h/(\gamma_{12}/kT)N_{core}^{4/25}N_{corona}^{3/5})$ increases gradually from water to a mixed solvent. These results show that the micelles produced in this study are inconsistent with the proposed star-like micelle model.

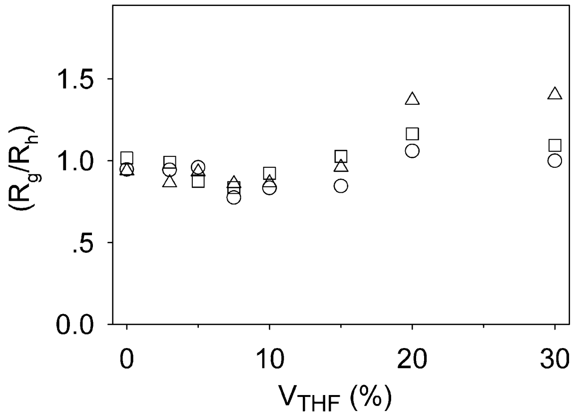

Fig. 12. Ratio of the radius of gyration to hydrodynamic radius ($R_g/R_h$) of the PS–PEO diblock copolymer micelle in the mixed water–THF solvent system at 10 °C (circles), 23 °C (squares), 45 °C (triangles).

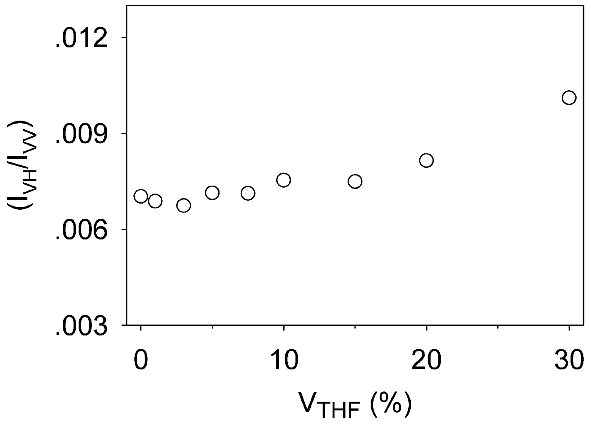

Fig. 13. Depolarization ratio ($I_{VH}/I_{VV}$) of the PS–PEO diblock copolymer micelles measured at 23 °C.

### 3.5. Aggregation number determination by free energy minimization

A–B diblock copolymer micelles in a selective solvent consist of three distinct structural regions. A core consisting of an insoluble A block, a corona of B block swollen by the solvent and the interfacial region located between the surface of the core and the solvent. The micellization

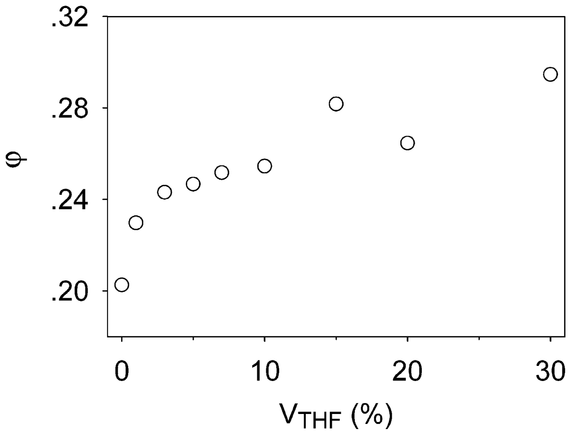

Fig. 14. Ratio of the hydrodynamic radius of the PS–PEO diblock measured at 23 °C compared with a star-like micelle, $\varphi = R_h/(\gamma_{12}a^2/kT)N_{core}^{4/25}N_{corona}^{3/5}$, $(a^2/kT = 1)$.

process can be analyzed by minimization of total free energy [29,30]. This analysis is based on the assumption that $F_{\mathrm{Tot}}$ of a copolymer chain situated in a micelle can be divided into three parts

$$F_{\mathrm{Tot}} = F_{\mathrm{corona}} + F_{\mathrm{core}} + F_{\mathrm{int}} \tag{10}$$

where $F_{\mathrm{corona}}$ is the conformation free energy of an outer chain, $F_{\mathrm{core}}$ is the conformation free energy of the A-chain in the core and $F_{\mathrm{int}}$ is the free energy cost due to the interfacial contact between the A chain and the solvent. A polymer attached to a spherical particle can be accurately described as a core–shell type morphology. From the result of Halperin [28], $F_{\mathrm{corona}}$ is expressed by the following expression

$$F_{\mathrm{corona}}/kT = f^{1/2}\ln(R_{\mathrm{m}}/R_{\mathrm{c}}) \tag{11}$$

where $R_{\mathrm{m}}$ is the radius of the micelle and $f$ is the number of attached polymers. In the case of a micelle composed of block copolymers, $R_{\mathrm{m}}$ and $R_{\mathrm{c}}$ are dependent on $f$. The total number of skeletal bonds of the coronal part of the micelle is obtained by integration of radial density profile $\rho(r) \sim f^{(3\nu-1)/2\nu} r^{(1-3\nu)/\nu}$ (exponent, $\nu = 3/5$ for good solvent) of an outer corona

$$\int_{R_{\mathrm{c}}}^{R_{\mathrm{m}}} \rho(r)\,\mathrm{d}V = nNf \tag{12}$$

where $n$ is the number of the skeletal bonds per monomer unit of the corona. By using the appropriate boundary condition, $R_{\mathrm{m}}$ [26] is expressed in the following expression

$$R_{\mathrm{m}} = \left[\frac{n\cdot 8Nf^{1/3}}{3\cdot 4^{(5/3)}\cdot(3/5)} l^{5/3} + R_{\mathrm{c}}^{5/3}\right]^{3/5} \tag{13}$$

where $l$ is described [30] as follows: $l^2 = C_\infty l_{\mathrm{b}}^2$, $l_{\mathrm{b}}^2$ denotes the mean-square bond length and $C_\infty$ is the characteristic ratio of the coronal polymer.

The elastic free energy $F_{\mathrm{core}}$ term derived by Semennov [32] using the SCF theory is given by the expression

$$F_{\mathrm{core}}/kT = \frac{\pi^2}{160}\frac{R_{\mathrm{c}}^2}{R_0^2} \tag{14}$$

where $R_0 = n_\lambda^{1/2}\lambda$ is the radius of the unperturbed radius of the core block, $n_\lambda$ the number of statistical segments and $\lambda$ the statistical segment length. $F_{\mathrm{int}}$ is simply expressed by the surface area of the insoluble core and interfacial tension, $\gamma_{12}$, between the surface of the core and solvents:

$$F_{\mathrm{int}}/kT = \left(\frac{4\pi\gamma_{12}}{kT}\right)\left(\frac{R_{\mathrm{c}}^2}{f}\right) \tag{15}$$

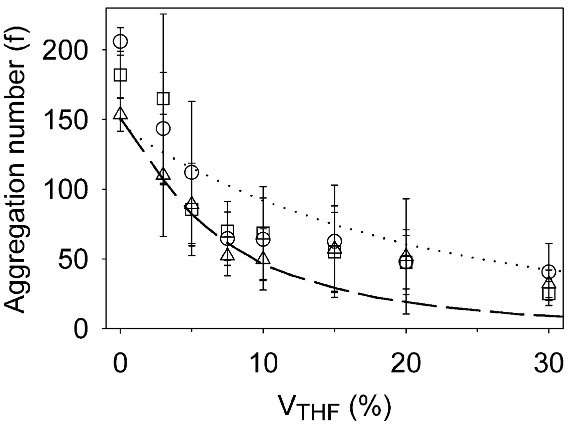

Fig. 15. The theoretical prediction of the aggregation numbers (calculated from Eqs. (16) and (6) (dashed line) and Eq. (7) (dotted line)) as a function of the THF content of the PS–PEO diblock copolymer in water–THF mixed solvent system. These values can be compared with the experimental aggregation numbers at 10 °C (circles), 23 °C (squares), and 45 °C (triangles) as shown in Fig. 8.

Therefore, the total free energy per copolymer chain is

$$F_{\mathrm{Tot}}/kT = f^{1/2}\ln\left[\frac{\left(\frac{n\cdot 8Nf^{1/3}}{3\cdot 4^{(5/3)}\cdot(3/5)} l^{5/3} + f^{5/9}A^{5/3}\right)^{3/5}}{f^{1/3}A}\right] + \left(\frac{\pi^2}{160}\right)\left(\frac{f^{2/3}A^2}{n_\lambda\lambda^2}\right) + \left(\frac{4\pi\gamma_{12}}{kT}\right)f^{-1/3}A^2 \tag{16}$$

where $A = (3M_{\mathrm{c}}/4\pi N_A\rho_{\mathrm{c}})^{1/3}$.

In the PS–PEO (6100/46 900) micelle system, the relevant parameters are as follows: $n = 3$, $C_\infty = 4.2$ (simulation of a quantum chain of PEO) for the coronal PEO [31], $l_{\mathrm{b}}^2 = 2.1426$ Å$^2$ and $\lambda = 15.5$ Å and $n_\lambda = 12$ for the PS-core [26]. We calculate the equilibrium aggregation number at 23 °C from the minimization of Eq. (16) with respect to $f$. The theoretical values can now be compared with the experimental aggregation number obtained by static light scattering (Fig. 15). The experimental results below 10% THF in water are in a good agreement with the predictions based on the calculation using Eq. (16).

As mentioned before, the micelles in water–THF mixed solvent retain their $R_{\mathrm{h}}$ even though $f$ decreases. Calculated $R_{\mathrm{m}}$ from Eq. (13) with experimental $f$(Fig. 8) is generally ~10% smaller than the experimental values of $R_{\mathrm{h}}$ (Fig. 10) in water–THF mixed solvent, while in water $R_{\mathrm{h}}$ is slightly larger than $R_{\mathrm{m}}$. This discrepancy will be compensated if we use slightly larger value of $\nu = (3.05/5)$ instead of (3/5). In Eq. (16) the value $\nu = (3.05/5)$ shifts the free energy minima to give generally ~7% lower $f$ than $\nu = (3/5)$ below 10% THF in water. This value is within the experimental error and does not change the general trends of the aggregation behavior caused by the interfacial tension. Therefore we conclude that the interfacial tension is the primary contribution in determining the aggregation number of the micelles in the water–THF solvent system. We also observed the temperature dependence of the aggregation number, which may arise from the temperature dependence of the interactions between PEO and mixed solvent and/or from the change in the equilibrium aggregation number.

As shown in Fig. 15, above 10% THF, the experimental results no longer fit with theory. We propose several possibilities to explain this discrepancy in the high $V_{\mathrm{THF}}$ regime. One possibility is that the solvent quality may change significantly with the addition of THF. Although PEO is soluble in both THF and water, the intermolecular interactions between the molecules and their subunits (ethylene oxide units, water and THF) may vary with solvent composition. In this case, the core–shell model may no longer be valid in the presence of a high volume fraction of THF in water. Alternately, the shape of the micelle may change with higher $V_{\mathrm{THF}}$ as shown in the depolarization measurements. In addition, the effect of critical phenomena in the water–THF system, which is mentioned previously with regard to the uncertainty of $(\mathrm{d}n/\mathrm{d}c)$ at high $V_{\mathrm{THF}}$ needs to be considered.

The apparent molecular weight $M^*$ of homopolymers in a mixed solvent obtained by static light scattering is somewhat different from the real value because the volume fraction of each component of the mixed solvent is not equally distributed from the bulk solvent to the inside of polymer network. The difference becomes more important when the composition of the mixed solvent is good and a non-solvent for the polymers. For mixed solvents (solvents 1 and 2) the apparent molecular weight $M^*$ of a dilute polymer can be expressed as follows [33]

$$M^* = M\left(1 + \alpha_{\mathrm{a}}\frac{(\mathrm{d}n_0/\mathrm{d}\phi_1)}{(\mathrm{d}n/\mathrm{d}c)_{\phi_1}}\right)^2 \tag{17}$$

where $\alpha_{\mathrm{a}}$ is the selective adsorption coefficient and relative to the selective adsorption of solvent 1 and $n_0$ and $n$ are the refractive index of the mixed solvent and the solution, respectively. $(\mathrm{d}n/\mathrm{d}c)_{\phi_1}$ is the refractive index increment at constant solvent composition and usually solvent 1 is considered as the main or good solvent. A negative value of $\alpha_{\mathrm{a}}$ indicates a preferential adsorption of solvent 2. Especially in the case of a hydrogen bonding solvent, the difference is more significant due to the breaking of a hydrogen-bonded network with the addition of another solvent. For polyethyleneglycol monomethacrylate ($M_{\mathrm{w}} = 225\,000$ and solvent composition with propanol/water $= 0.95{:}0.05$), the apparent molecular weight is 210 000 where $\alpha_{\mathrm{a}} = -0.15$ and $(\mathrm{d}n/\mathrm{d}c)_{\phi_1}/(\mathrm{d}n_0/\mathrm{d}\phi_1) = 2.79$. In the PS–PEO diblock system it is possible that $M^*$ is different from $M$ due to the preferential adsorption of THF and water in the micelle corona. Moreover, we need to consider the effect of the temperature dependence of the preferential adsorption. It is known that THF becomes a better solvent as the temperature increases, while water becomes a poorer solvent for PEO [20]. As a result the temperature dependence of the solvent quality may markedly change the preferential adsorption characteristics as well. The temperature dependence of the PS–PEO micelle system remains to be investigated.

## 4. Conclusion

PS–PEO diblock copolymers form micelles in a mixed solvent of water and THF. The added THF changes significantly the interfacial tension between the micellar core and the solvent due to changes in the polar contribution of the surface tension of water. When THF is added to an aqueous solution, the reduction of interfacial tension between a core-block and the solvent causes a reduction in the aggregation number of the micelle. In low volume fractions of THF ($<10\%$) in water, the overall size of the micelle has a tendency to resist contraction due to stronger interactions between THF and the coronal PEO chains. This occurs even though the aggregation number of the micelle decreases.

Finally, the experimental results are compared with a theoretical model that includes the variation of the interfacial tension at an interface. The theoretical prediction is very consistent with the experimental results for THF $< 10\%$, which indicates that the interfacial tension may be one of the key factors in determining the aggregation number of the PS–PEO diblock copolymer micelle in a water–THF solvent system.

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