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ORIGINAL CONTRIBUTION

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Monolayer films of PS-b-PEO diblock copolymers at the air/water- and an oil/water-interface

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Dedicated to M.J. Schwuger on the occasion of his 60th birthday

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Abstract Amphiphilic diblock copolymers consisting of a hydrophobic polystyrene block (PS) and a hydrophilic poly(ethylene oxide) block (PEO) with block sizes of 1000 or 3000 g/mol for both blocks were studied at the air/water and toluene/water interface. Measurements of the film pressure π of spread monolayers at the water surface reveal two limiting regimes of the $\pi - a_m$ isotherms, in which the mean molecular area a_m is determined either by the size of the hydrophilic or the hydrophobic blocks of the PS-PEO molecules. The interfacial activity of the block copolymers at the toluene/water interface was studied by measuring the interfacial tension σ over a wide range of concentrations. Pronounced differences in the temperature dependence of the interfacial tension were observed, depending mostly on the block length of the hydrophilic PEO block. From the temperature dependence of σ it is inferred that for the block copolymers with the PEO block size of 3000 g/mol the phase inversion temperature (PIT) is well above 60 °C while for those with a PEO block size of 1000 g/mol the PIT is below or near 25 °C in the toluene/water system.

Key words Adsorption at liquid interfaces – block copolymers – film pressure – interfacial tension – polymer surfactants

Introduction

Diblock copolymers composed of a hydrophobic polystyrene block and a hydrophilic poly(ethylene oxide) block represent an important class of amphiphilic compounds, exhibiting many similarities with conventional nonionic surfactants [1–3]. Depending on the chemical nature and chain length of the two blocks, such amphiphilic block copolymers can form highly effective emulsifiers, offering good long-term stability for various types of oil/water systems [4]. Sterically stabilized emulsions based on these materials have been used extensively in emulsion polymerization [3, 5–7] or, in combination with suitable cosurfactants, for the preparation of microemulsions [4]. Block copolymer micelles in water have been studied using light scattering and flourescence probe techniques [8–10]. However, there is still a lack of reliable information about the interfacial performance of amphiphilic block copolymers. This paper presents results on a class of polystyrene-b-poly(ethylene oxide) block copolymers with molar mass below 10 000 g/mol which have been employed previously in several laboratories for various application [3, 5, 11–13].

Experimental

Materials

Polystyrene-b-poly(ethylene oxide) block copolymers, abbreviated as SE *xy* (where *x* and *y* are numbers indicating

Table 1 Properties of the SE *xy* block copolymers [15]

Amphiphile	M [g/mol]	M_w/M_n	N_x	N_y	HLB
SE 1010	2400	1.21	10	25	10
SE 1030	5900	1.06	10	70	15
SE 3010	4800	1.66	30	25	5
SE 3030	8300	1.20	30	70	10

the nominal molar mass of the hydrophobic PS block and the hydrophilic PEO block, respectively) were supplied by the Th. Goldschmidt AG, Germany [14]. Table 1 lists some parameters of the four materials used in this study. The overall mean molar mass M and polydispersity M_w/M_n, and the mean numbers of segments, N_x and N_y, of the PS and PEO block, respectively, of the block copolymers are data supplied by the manufacturer. According to the manufacturer, the samples contain less than 3% of homopolymers and no monomers. The polarity of the materials as characterized by the HLB value is also given in Table 1, using the definition $\mathrm{HLB} = 20M_H/M$, where M_H and M denote the molar mass of the hydrophilic PEO block and the overall molar mass, respectively. On the basis of the HLB concept SE 1010 and SE 3030 have equal affinities for the water and hydrocarbon phase, while SE 1030 should be preferentially soluble in water and SE 3010 preferentially in the hydrocarbon phase. However, according to the data sheets [15], SE 1010 and SE 1030 are well soluble in water but SE 3010 and SE 3030 are insoluble in water. All materials are soluble in toluene up to high concentrations without aggregation.

Film balance measurements

A Teflon trough, rectangular in shape, with a maximum surface area of 130 cm^2 was used. The subphase was distilled water, purified by a MILLIPORE Milli-Q^{50} water system (pH 5, conductivity 0.4 μS/cm, surface tension 70 ± 3 mN/m at room temperature). All measurements were carried out under clean room conditions. Monolayers of the amphiphiles were spread from a solution in benzene (Fluka, for UV-spectroscopy) at room temperature (22 °C). A constant compression rate of 10 cm^2/min was used in all experiments.

Interfacial tension measurements

The influence of the PS-b-PEO block copolymers on the interfacial tension of the toluene/water interface was measured using a home-built computerized pendant drop apparatus [16]. Data evaluation is based on the selected plane method [17] within an accuracy of 7%. Toluene purum (purity > 99%) was supplied from Fluka. The samples were prepared from a 1 mmol/l stock solution of the surfactant in toluene, with successive volumetric dilution to the desired concentrations. All given concentrations represent the initial concentrations of these toluene solutions. Equal volumes of water and the toluene solution were brought in contact and then the samples were equilibrated at the experimental temperature until phase separation was reached, at least for two days. Additional needed densities of the phases were measured by use of a densimeter (Heraeus Paar DMA 40). As a test of the reliability of the pendant drop results, measurements of the interfacial tension were also made by capillary wave spectroscopy for some samples at high amphiphile concentrations. Details of this technique are given elsewhere [18].

Results and discussion

Film pressure at the air/water interface

Figure 1 shows film pressure isotherms $\pi = \pi(a_m)$ at the first compression of spread monolayers of the four PS-PEO block copolymers at the water/air interface. Two distinct limiting regimes can be identified:

(i) At low surface densities (mean molecular areas > 5 nm^2) the film pressure is dependent almost entirely on the block length of the hydrophilic PEO block, while an increase of the length of the hydrophobic PS block causes only a minor increase of π at a given a_m. Thus, in regime (i) the film pressure of SE 3030 is only a little greater than for SE 1030, but these amphiphiles both exhibit significantly greater values of π than SE 3010 and SE 1010, for which the $\pi(a_m)$ isotherms nearly coincide in this region.

Fig. 1 Film pressure isotherms $\pi - a_m$ of spread monolayers of four PS-PEO diblock copolymers at the air/water interface at 22 °C

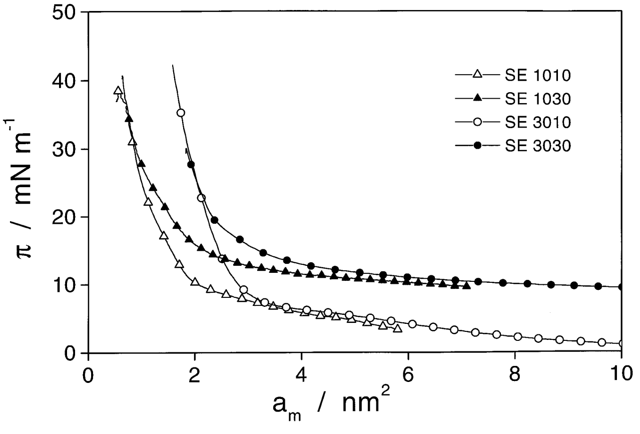

Table 2 Area per molecule in the surface films

Amphiphile	a_m ($\pi = 8\,mN/m$) [nm^2]	a_m ($\pi = 30\,mN/m$) [nm^2]
SE 1010	2.8	0.9
SE 1030	15	0.9
SE 3010	3.1	1.8
SE 3030	16	1.8

(ii) At sufficiently high surface densities of the block copolymer (low mean areas a_m) the film pressure is dependent only on the block length of the hydrophobic PS block, i.e., the isotherms for SE 3010 and SE 3030, as well as those for SE 1010 and SE 1030 coincide within experimental error.

Values of a_m for fixed values of π in these two regions are collected in Table 2. A film pressure of 30 mN/m is close to the breakdown limit of the films. These findings suggest that at low surface densities (regime i) the PEO chains of the amphiphilic molecules adopt a highly extended configuration at the water surface, forming a single monolayer as in the case of spread poly(ethylene oxide) monolayers at the air/water interface [19–21]. Moreover, the observation that even at such low surface densities the film pressure is almost unaffected by the chain length of the hydrophobic PS block implies that the latter is not in an expanded state but collapsed and forming a blob. As the surface density of the polymer is increased beyond the regime (i), the isotherms exhibit a pronounced increase of the film pressure. For the polymers with the greater PS block length this increase of π commences at a distinctly greater mean molecular area a_m than for those with shorter PS blocks. This result clearly indicates that the repulsion between the PS blocks becomes the dominating interaction. Such a behaviour is expected if the concentration of oxyethylene segments in the surface layer decreases, implying that the hydrophilic PEO chains progressively penetrate the aqueous subphase as a_m decreases in that transition region between the regimes (i) and (ii). This picture of a gradual penetration of the PEO chains deeper into the subphase is consistent with the results of a neutron reflectivity study of the organization of poly(ethylene oxide) monolayers at the air water interface [20]. In that study it was concluded that for PEO the borderline between spreading as a single layer on water and penetration into the subphase is at a surface concentration of 0.4 mg/m^2. This figure cannot be immediately compared with the situation of the PS-PEO block copolymers of the present study. If one considers the PEO blocks alone (i.e. not counting the contributions of the PS blocks to the molar mass, and neglecting their contribution to the mean molar area at low surface coverage) the values of a_m at $\pi = 8\,mN/m$ of Table 2 correspond to a surface concentration of PEO of 0.6–0.65 mg/m^2 for the polymers with short PEO blocks (SE 1010 and SE 3010), but only 0.32–0.34 mg/m^2 for the polymers with long PEO chains (SE 1030 and SE 3030). This crude estimate seems to indicate that for the polymers with longer PEO chains a given film pressure (say 8 mN/m) corresponds to a significantly higher surface concentration of PEO chains for polymers with short PEO chains. In the limiting regime (ii) the mean areas a_m of the polymers are affected solely by the length of the PS block, which implies that the hydrophilic chains are detached from the surface and penetrate deep into the aqueous subphase. Assuming that the PS blocks form spherical blobs of a density equal to that of polystyrene in its bulk state ($\rho = 1\,g/cm^3$), then for a regular dense packing of the blobs in the surface we expect an area per molecule $a_m = 2\sqrt{3}R_{PS}^2$ with $R_{PS} = (3M_{PS}/4\pi\rho N_A)^{1/3}$ the radius of the PS sphere and N_A the Avogadro constant. With the nominal values of M_{PS} from Table 1 we obtain $a_m = 1.9$ and 4.0 nm^2, respectively, for the polymers with the short and long PS chains. These estimated values are about a factor 2 greater than the experimental values at $\pi = 30\,mN/m$ (Table 2), indicating that in this highly compressed state the PS blocks are assuming a ellipsoidal shape, with the long axis of the ellipsoid pointing away from the surface. With the ellipticity ε defined as the ratio of the long and the short axis of the ellipsoid and assuming a regular dense packing of ellipsoids we have

$$\varepsilon = (2\sqrt{3}/a_m)^{1.5}R_{PS}^3 , \tag{1}$$

where a_m is now the experimental mean molar area of the polymer and R_{PS} is derived from M_{PS} and ρ as above. In this way one derives for the highly compressed state ($\pi = 30\,mN/m$) $\varepsilon = 3.1$ for the copolymers with the short PS chain (SE 1010 and SE 1030), and $\varepsilon = 3.3$ for those with the long PS chains (SE 3010 and SE 3030). This crude analysis indicates that the hydrophobic blocks become strongly compressed and stretch out in the direction vertical to the surface at the highest experimental film pressures.

Monolayers of PS-b-PEO materials of similar molar mass as in this work have been studied by Sauer et al. [22]. These authors deduced viscoelatic properties of the film in different states of compression. Compression isotherms of copolymers of higher molar mass were studied by Yoshikawa et al. [23]. However, a direct comparison of these data with those of the present work is not possible.

Film pressures at the toluene/water interface

Time dependence

The interfacial tension between portions of the two equilibrated phases (drawn from the bulk of the toluene and

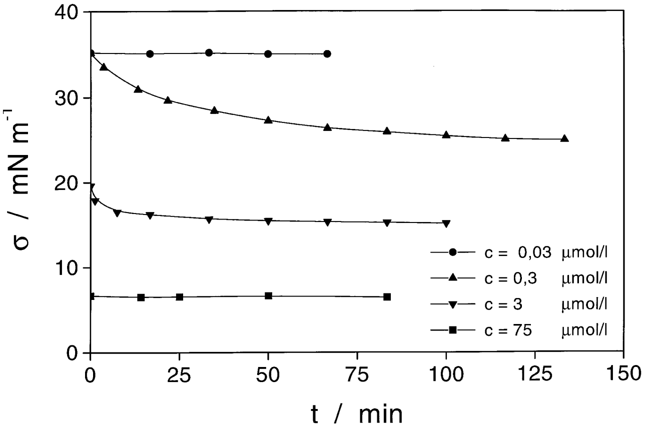

Fig. 2 Time dependence of the interfacial tension σ for freshly prepared interfaces between preequilibrated toluene and water phases as a function of the nominal concentration c of SE 1010 in the oil phase (25 °C)

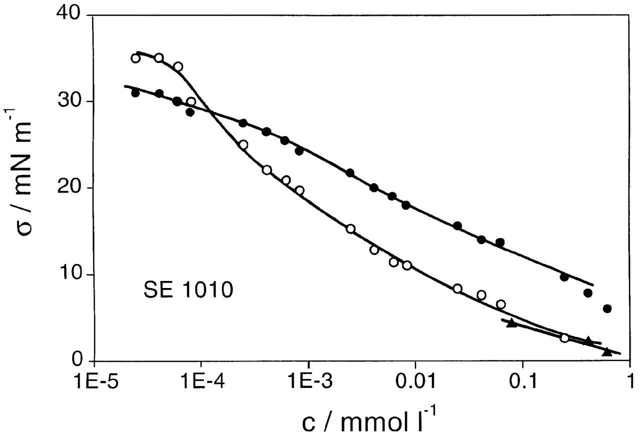

Fig. 3 Interfacial tension σ of the toluene/water interface as a function of the concentration c of SE 1010 in the oil phase. Results obtained by the pendant-drop method (○, 25 °C; ●, 60 °C) and by capillary wave spectroscopy (○, 25 °C)

aqueous phase) initially exhibits a time dependence with time constants up to several hours. This time dependence becomes more pronounced as the concentration of the block copolymers decreases, as to be expected for diffusion-controlled adsorption at the oil/water interface [24]. As an example, Fig. 2 shows the time dependence of the interfacial tension for different initial concentrations of SE 1010 in the toluene phase. For the lowest polymer concentration (0.03 μmol/l) the measured time dependence of the tension σ was < 0.1 mN/(m h), i.e. of the order of experimental uncertainty of the measurement. For nominal concentrations (i.e. initial concentrations in toluene) up to 0.3 μmol/l it is estimated that the equilibrium values of σ were not reached in the experimental time window of the measurements of σ (ca. 2 h for a given pendant drop).

Equilibrium tensions and film pressures

Isotherms of the interfacial tension σ vs. concentration of the block copolymer were measured at 25 and 60 °C for a wide range of nominal concentrations c (initial concentration in the oil phase), from 2×10^{-5} up to 0.04 mmol/l (SE 3030), and up to concentrations greater than 0.2 mmol/l for the other materials. Figure 3 shows the results for SE 1010. The toluene/water interface without added block copolymer has an interfacial tension $\sigma^* = 36$ mN/m at 25 °C and 31 mN/m at 60 °C. As seen in Fig. 3, the surface tension isotherm for 25 °C falls off more steeply with increasing concentration c than at 60 °C, and the two isotherms intersect at a nominal concentration $c \approx 0.1$ μmol/l SE 1010 in the oil phase. A more direct measure of the efficiency and effectiveness for reducing the interfacial tension at different temperatures is the film pressure.

$$\pi = \sigma^* - \sigma \ . \qquad (2)$$

Film pressure isotherms for the toluene/water interface of the four block copolymers are shown in Fig. 4. Here again c represents the nominal concentration in the oil phase before equilibration of the oil/water system.

Concentration dependence

The pronounced decrease of the o/w-interfacial tension with increasing concentration is due to the adsorption of the block copolymers. For adsorption from ideal solutions the surface concentration Γ is given by the Gibbs equation

$$\Gamma = \frac{1}{RT}\frac{\mathrm{d}\pi}{\mathrm{d}\ln c^{i}_{\mathrm{eq}}} \ , \qquad (3)$$

where c^{i}_{eq} is the equilibrium concentration in the respective phase i (i = o, w for the oil and water phase, resp.). In the present work it was not possible to determine these equilibrium concentrations. One expects that $c^{\mathrm{o}}_{\mathrm{eq}}$, the equilibrium concentration in the oil phase, will be lower than the nominal concentration c due to equilibration with the water phase, or due to artifacts of the sample preparation as discussed below. However, in the absence of such artifacts, Eq. (3) will hold with c^{i}_{eq} replaced by c if the distribution coefficient of the amphiphile between the two phases, $K = c^{\mathrm{w}}_{\mathrm{eq}}/c^{\mathrm{o}}_{\mathrm{eq}}$, is constant in the experimental concentration range. Accordingly, Eq. (3) with c^{i}_{eq} replaced by c is likely to yield an overestimate of the true surface concentrations.

Since Γ is an increasing function of the concentration one expects that the film pressure isotherms exhibit a positive and gradually increasing curvature in graphs of π vs. $\ln c$. Only two of the experimental isotherms conform to this expectation and may be used to estimate the maximum adsorption $\Gamma_{\max}$. Specifically, for SE 1010 at 25 °C and SE 3030 at 60 °C the isotherms exhibit a nearly constant limiting slope $(\mathrm{d}\pi/\mathrm{d}\ln c)_{\max}$ over an extended concentration range, corresponding to a plateau value of the adsorption $\Gamma_{\max} = 1/(N_A a_m)$ with $a_m \approx 1.8\,\mathrm{nm}^2$ (SE 1010 at 25 °C) and $a_m \approx 0.60\,\mathrm{nm}^2$ (SE 3030 at 60 °C). The latter value is similar to the respective values of conventional nonionic surfactants at the alkane/water interface near the cmc [25]. Note, however, that these estimated values may be influenced by artifacts as explained below. Most of the isotherms in Fig. 4 exhibit positive curvature of π vs. $\ln c$ only at low concentrations, but a negative curvature at higher concentrations. This behavior indicates that at these higher concentrations the equilibrium concentration c°_{eq} is no longer proportional to the nominal concentration c. This deviation is believed to be due mostly to artifacts of sample preparation: When polymer-rich toluene solutions were contacted with water, spontaneous emulsification occured in the oil phase, and the resulting emulsion layer extended deep into the oil phase. This emulsification caused a depletion of the supernatant oil phase used in the subsequent measurements of the interfacial tensions. The tendency for spontaneous emulsification and thus the depletion of the oil phase became more pronounced as the initial concentration c was increased, but it differed significantly with the nature of the amphiphile and also with temperature. Estimates of the amount of amphiphile absorbed in the emulsion layer lead to the conclusion that the observed levelling off of the film pressure isotherms in Fig. 4 at higher nominal concentrations can be attributed to this artifact.

Temperature dependence

Figure 4 shows that the block copolymers with short PEO block and those with long PEO block are causing an opposite temperature dependence of the film pressure: At concentrations $c > 10^{-4}$ mmol/l the former (SE 1010 and SE 3010) exhibit a negative temperature coefficient, $(\Delta\pi/\Delta T)_c < 0$, while the latter (SE 1030 and SE 3030) are causing a positive coefficient, $(\Delta\pi/\Delta T)_c > 0$. Related differences between these two types of block copolymers are also seen in the temperature dependence of the interfacial tension σ in the respective concentration range, as shown in Fig. 5 (upper graph). At the chosen nominal concentration ($c = 5 \times 10^{-3}$ mmol/l) the temperature coefficient $\Delta\sigma/\Delta T$ amounts to $+0.23$ mN/(m K) for SE 1010 and -0.03 mN/(m K) for SE 3010, but -0.20 and -0.29 mN/(m K) for SE 1030 and SE 3030, respectively. These trends can be discussed in terms of the concept of the phase inversion temperature (PIT), at which emulsion systems transform from o/w to w/o emulsion [26]. In microemulsion systems the oil/water interfacial tension exhibits a pronounced minimum near the PIT [27, 28],

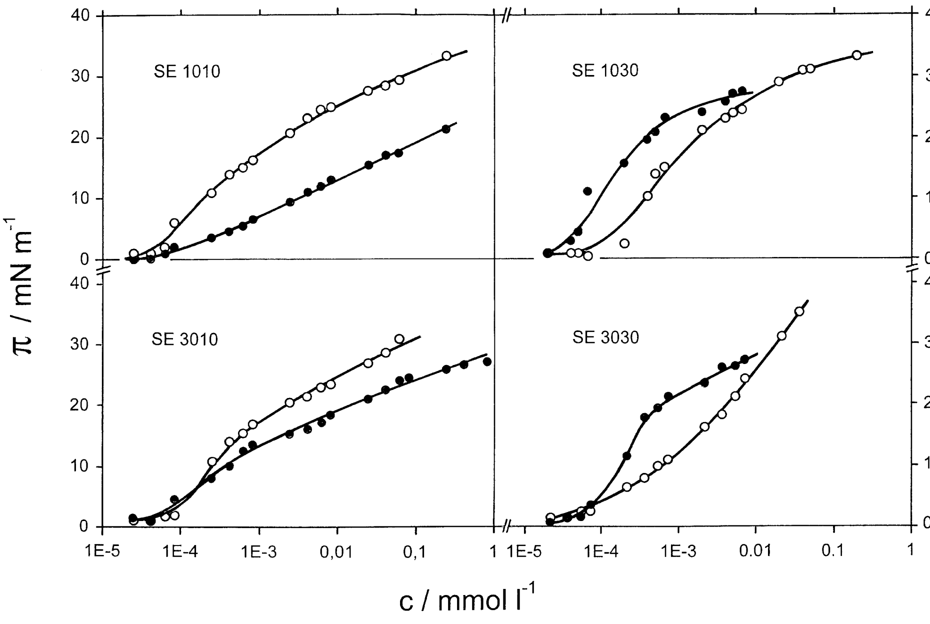

Fig. 4 Semilogarithmic plots of the film pressure isotherms $\pi - c$ of the four PS-PEO diblock copolymers at the toluene/water interface (○, 25 °C; ●, 60 °C)

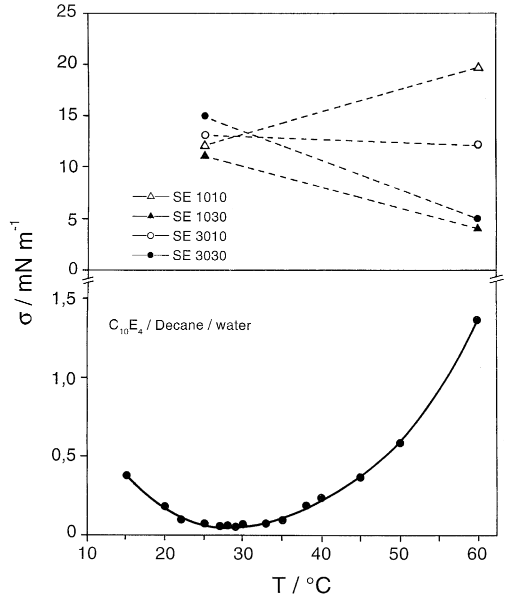

Fig. 5 Temperature dependence of the oil/water interfacial tension σ at fixed concentration c of the amphiphile. Upper graph: Four PS-PEO diblock copolymers at the toluene/water interface, $c = 5 \times 10^{-3}$ mmol/l. Lower graph: Nonionic surfactant $C_{10}E_4$ at the decane/water interface (5 wt% surfactant), illustrating the minimum of $\sigma(T)$ near the phase inversion temperature (PIT = 28 °C [28])

illustrated in Fig. 5 for decane/water with the surfactant $C_{10}E_4$ [28]. On the assumption that such a correlation between the interfacial tension and phase inversion applies also to the present block copolymer systems, we conclude that for the polymers with short-chain PEO blocks, the PIT is either well below 25 °C (SE 1010) or somewhere in the experimental temperature range (SE 3010), but for the polymers with large hydrophilic PEO blocks the PIT appears to be well above 60 °C. Such an increase in PIT with increasing chain length of the hydrophilic block is consistent with the trends observed with C_nE_m and other conventional nonionic surfactants. However, in microemulsion systems with conventional nonionic surfactants the PIT depends equally on the chain length of the hydrophobic chain, and generally there is a close relation between the hydrophile-lipophile balance (HLB) and the PIT [26]. Such a correlation does not exist for the present PS-PEO block copolymer systems, as seen from the grossly different behaviour of the systems with SE 1010 and SE 3030, which have the same HLB value. In fact it appears that for the present systems the block length of the PS block has only a weak influence on the PIT. (The present results even indicate an increase of the PIT with increasing block length of the PS block, which is opposite to the behaviour of microemulsion systems with C_nE_m surfactants.) This weak influence of the PS block on the PIT may be due to the fact that aromatic oils like toluene are good solvents for both the hydrophobic and the hydrophilic block of PS-PEO block copolymers. In such a case one may expect that the phase inversion temperature is controlled mainly by the decreasing hydration and/or change of the conformation of the PEO block as the temperature is increased, but not by changes in the solvation of either block in the oil phase. Further experiments are needed to verify this conjecture.

Conclusions

The present study shows that short-chain PS-b-PEO copolymers exhibit an interfacial behaviour which in several respects bears great resemblance to conventional nonionic surfactants such as alkylphenolethoxylates (C_nPhE_m) or alkylpolyglycolethers (C_nE_m). Film pressure measurements on monolayers of PS-b-PEO spread at the air/water interface indicate that at sufficiently large mean areas per molecule the PEO chains are entirely confined to the surface, but they are penetrating the aqueous subphase as the surface density is increased, and ultimately the molecular area is determined solely by the size of the hydrophobic PS block which appears to be compressed to an ellipsoid at the highest film pressures.

At the toluene/water interface the PEO-b-PS block copolymers are causing a pronounced decrease of the interfacial tension. Estimates of the minimum area per molecule a_m based on the Gibbs adsorption equation yield values down to ca. 0.60 nm^2, i.e. close to those for conventional nonionic surfactants at concentrations near the cmc. It is found that the temperature dependence of the interfacial tension σ depends mostly on the block length of the PEO chain rather than the HLB of the block copolymers: From the fact that in the experimental temperature range the coefficient $(\Delta\sigma/\Delta T)_c$ is positive for SE 1010 but negative for SE 1030 and SE 3030 it is inferred that the former has a phase inversion temperature (PIT) below 25 °C while for the latter it is above 60 °C. The remarkable observation that an increase of the size of the hydrophobic PS block does not cause a decrease of the PIT is attributed tentatively to the hydrophilicity of the chosen oil (toluene) which represents a good solvent for both the hydrophobic and hydrophilic block of the PEO-b-PS copolymers.

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