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ORIGINAL CONTRIBUTION

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Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene)oxide triblock copolymers at the water/air interface and in foam films

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Abstract The behavior of commercial poly(ethylene oxide)(PEO)–poly(propylene oxide)(PPO)–PEO triblock copolymers at the water/air interface and in microscopic foam films is studied. In aqueous solution these amphiphilic nonionic substances exhibit a surfactant-like aggregation and adsorption behavior. Even below the critical micelle concentration (cmc) the surface concentration is so high that the PEO chains are squeezed and protrude into the solution in order to accommodate to the situation at the interface. As evidenced by measurements of the ellipticity of light reflected from the free surface of the solution a PEO brush is created at the fluid interface. The microscopic foam film is used as a tool for investigating the normal interaction between two PEO brushes facing each other. Stable foam films are obtained at concentrations below the cmc and steric repulsion predominates (in 0.1 M NaCl). A brush-to-brush contact is established only at higher capillary pressures and the disjoining pressure isotherm follows de Gennes' scaling prediction. At lower pressure a softer steric repulsion occurs. It is governed by the bulk copolymer concentration and hence is fundamentally different from the brush-to-brush repellency. On the whole PEO–PPO–PEO copolymers behave as nonionic surfactants, but the large size of their molecules exemplifies the excluded-volume features.

Key words Amphiphilic block copolymer · Polymeric surfactant · Brush · Ellipticity · Foam film

Introduction

Poly(ethylene oxide)(PEO)–poly(propylene oxide) (PPO)–PEO triblock copolymers are produced in a large variety of sizes of the PEO and PPO blocks. They form a two-dimensional homologous series (referred to as a "Pluronic grid" [1]) whose different members are used in a very wide range of applications: emulsification, cleaning, rinsing, solubilization, antifoaming, water treatment, lubrication, fermentation, drug delivery, etc. The low toxicity and price also contribute to the usefulness of these polymeric surfactants. Their solution behavior combines surfactant-like features with the polymeric behavior of the relatively long chains. The academic interest toward their association properties has steadily grown in recent years [2–5].

Copolymer adsorption at fluid interfaces and particularly at the water/air interface has received less attention in comparison to solid/liquid interfaces [6], but the situation has greatly improved in the last few years [7–10]. Information on adsorbed polymer layers is obtained with scattering and reflection methods [6]. The structures of adsorbed polymers, surfactants, and their mixtures at fluid interfaces have been probed with spectroscopic techniques [11, 12], but neutron reflectometry is especially useful [7–10, 13–15]. Less demanding techniques, however, can also give useful, if not direct, information [16, 17].

In this paper we investigate the behavior of a few PEO–PPO–PEO triblock copolymers at the water/air interface and in foam films. Surface tension measurements showed that these copolymers strongly adsorb at the surface of the aqueous solution. Measurements of the ellipticity of light reflected from the solution/air interface indicate the formation of a PEO brush. The repulsion between two adsorption layers, as manifested in foam films, reveals that brush-to-brush repellency follows the theoretical expectations beyond a certain threshold. Prior to this, a softer repulsion is detected and this is attributed to coiled molecules trapped in the core of the film.

Materials and methods

Commercial *ABA* triblock copolymers were used as received. These are water-soluble polymeric surfactants. PPO represents the middle hydrophobic block, *B*, and hydrophilic PEO forms the two terminal chains, *A*. The average molecular mass and EO content are known from the manufacturer, and approximate chemical formulae are derived (Table 1). These nonionic surfactants are rather pure though not monodisperse ($M_w/M_n \approx 1.2$ [18]).

The surface tension, σ, of aqueous copolymer solutions was measured by the Wilhelmy-plate method (Krüss K10T tensiometer). All experiments were carried out in 0.1 M NaCl solutions.

The ellipticity, $\bar{\rho}$, of light reflected from the free surface of the copolymer solutions was measured with a home built ellipsometer [19, 20] employing the phase-modulation technique [21]. With this technique a high frequency (50 kHz) photoelastic modulation (Hinds, model FS5, Serie I) is applied to the light beam before reflection from the sample. Phase-sensitive detection is performed on the detected signal (photomultiplier tube) with a lock-in amplifier (EG&G PARC, model 5210 two-phase, Princeton Applied Research) at 50 and 100 kHz. The output signals, R_1 and R_2, are related to the ellipsometric parameters ψ and Δ by [19, 20]

$$S = \sin 2\psi \sin \Delta = R_1/R_1^*$$
$$C = \sin 2\psi \cos \Delta = R_2/R_2^* \ ,$$

where R_1^*, R_2^* are calibration constants. At the Brewster angle the second signal vanishes ($C = 0$) and the ellipticity $\bar{\rho}$ becomes

$$\bar{\rho} = S/2 \ .$$

The dependence of the disjoining pressure, Π, in foam films on film thickness, h, was monitored using the thin liquid film–pressure balance technique [22]. A horizontal liquid bridge is formed in a small hole (radius about 1 mm) drilled into a porous plate soaked with the solution and enclosed in a vapor-saturated environment. When the liquid is sucked out the two liquid/gas interfaces approach each other and ultimately a foam film is created. The pressure inside the gas-tight glass chamber holding the porous plate is varied and measured. At equilibrium the gas pressure counterbalances the disjoining pressure inside the film. An optical film thickness is obtained via Fabry-Perot interferometry. Assuming that the film has a constant refractive index equal to that of the bulk solution an equivalent film thickness is calculated.

All experiments were carried out at 23 °C.

Table 1 Characteristics of the poly(ethylene oxide) (*PEO*)–poly (propylene oxide) (*PPO*)–PEO triblock copolymers

Name	*M*	PEO (%)	N_{EO}–N_{PO}–N_{EO}
F68[a]	8 400	80	76–30–76
F88[b]	10 800	80	97–39–97
F108[b]	14 000	80	122–56–122

[a] Pluronic from BASF
[b] Synperonic from ICI

Results and discussion

The equilibrium surface tension, σ, of F88 solutions is plotted as a function of the logarithm of the bulk concentration, *c*, in Fig. 1. The shape of the isotherm is typically surfactant-like. There is a well-defined critical micelle concentration (cmc) beyond which the surface tension remains constant. The dependence is fairly linear between c_0 and the cmc, and the area per molecule, *A*, can be estimated via the Gibbs equation ($A = k_B T / |\partial\sigma/\partial \ln c|$). At concentrations lower than c_0 the isotherm is convex.

It is now acknowledged that the solution behavior of PEO–PPO–PEO copolymers is essentially surfactant-like [2–5]; however, the reported values of the cmc and *A* vary greatly between authors. While arguments have been drawn that such discrepancy is inherent to these polymeric surfactants [2], our experience is that reproducibility is good as long as the same sample is used. Thus, many differences are probably due to sample-to-sample variations and this inhibits comparison between miscellaneous results.

Characteristic parameters pertaining to the samples used in this study are collected in Table 2.

The area per molecule is rather small and therefore the PEO chains are expected to adopt a brush configuration at the interface in order to accommodate to the situation there [17, 23, 24]. Our model of the adsorption layer is sketched in Fig. 2.

Water is a good solvent for the PEO tails, while the PPO block is a hydrophobic moiety and adsorbs at the water/air interface. Thus, each PPO block anchors two PEO brushes. It is assumed that the situation with one

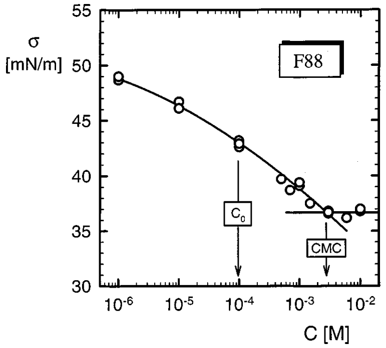

Fig. 1 Equilibrium surface tension, σ, versus concentration, *c*, of F88 (aqueous solution in 0.1 M NaCl, Wilhelmy plate, 23 °C)

Table 2 Critical micelle concentration (cmc) and area per molecule, (A), at the water/air surface of the PEO–PPO–PEO triblock copolymers (from surface tension measurements)

Name	cmc (M)	A (nm^2)
F68^a	2×10^{-5}	1.8
F88	3×10^{-3}	2.2
F108^a	3×10^{-5}	1.9

[a] From Ref. [17]

$EO_xPO_yEO_x$ molecule is identical to that with two $PO_{y/2}EO_x$ molecules. This simplification is plausible since the PPO blocks are not too short (Table 1).

According to the theory of the simple polymer brush [25, 26] its thickness, L_0, is

$$L_0 = a^{5/3}NA^{-1/3} \ , \tag{1}$$

where a is the monomer size and N is the degree of polymerization of the chain forming the brush.

On general grounds one expects that the area per molecule, A, will depend on the size of the anchor and brush blocks. While larger anchor blocks will increase the tendency of the molecule to adsorb, longer brush blocks will strongly resist it as their stretching energy increases [27]. For the present block copolymers, however, A only changes within 20% (Table 2) and since its influence on L_0 is rather weak on the basis of Eq. (1), this variation may be ignored. If A is constant it follows from Eq. (1) that the thickness of the brush should scale linearly with the length of the PEO block, i.e. $L_0 \propto N_{EO}$.

On the basis of indirect evidence it has been speculated previously that this is indeed the case [17]. Ellipsometric measurements were performed to obtain more direct information about the thickness of the adsorbed polymer layer.

The ellipticity, $\bar{\rho}$, of light reflected from the free surface of a copolymer solution is interpreted via the Drude equation [28]. If the adsorption layer is assumed to be uniform, with a refractive index $n = n_1$ at $0 \le z \le L_0$, Drude's equation becomes

$$\bar{\rho} = \frac{\pi}{\lambda}\frac{\sqrt{n_B^2+1}}{n_B^2-1}\frac{(n_B^2-n_1^2)(n_1^2-1)}{n_1^2}L_0 \ , \tag{2}$$

where λ (632.8 nm) is the wavelength of the light incident through the gas phase and n_B is the refractive index of the bulk solution ($z \rightarrow +\infty$).

It follows from Eqs. (1) and (2) that the relationship between ellipticity and the number of EO monomers is linear:

$$\bar{\rho} = \frac{\pi}{\lambda}\frac{\sqrt{n_B^2+1}}{n_B^2-1}\frac{(n_B^2-n_1^2)(n_1^2-1)}{n_1^2}\frac{a^{5/3}}{A^{1/3}}N_{EO} \propto N_{EO} \ . \tag{3}$$

We have found that ellipticity decreases with bulk copolymer concentration and reaches a plateau value at about the cmc. These plateau values are plotted in Fig. 3 for the three copolymers investigated.

A linear decrease of ellipticity with the PEO chain length is observed for the present block copolymers in accord with Eq. (3). Thus, ellipsometric measurements explicitly prove the formation of a PEO brush at the free surface of solutions of PEO–PPO–PEO polymeric surfactants.

From the slope of the line drawn in Fig. 3, the refractive index of the brush can be estimated via Eq. (3). Assuming $a = 0.2$ nm [23] one obtains $n_1 = 1.36$. If this value is written as a volume fraction average of the value for solid PEO ($n_{PEO} = 1.4563$ [29]) and the value for pure water, n_W,

$$n_1 = n_{PEO}\phi_{PEO} + n_W(1 - \phi_{PEO})$$

it implies $\phi_{PEO} = 25\%$. This roughly corresponds to three water molecules per EO segment in agreement with published data [30, 31].

The intercept in Fig. 3 may be attributed to the contribution of the PPO anchor block. As a matter of fact Eq. (2) splits into two similar terms if PPO and PEO

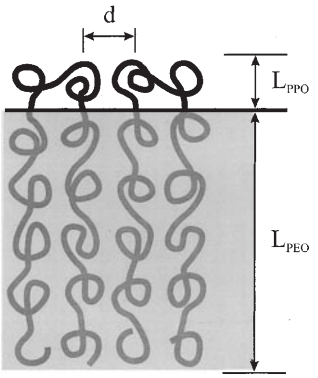

Fig. 2 Conformation of poly(ethylene oxide)(*PEO*)–poly(propylene oxide)(*PPO*)–PEO triblock copolymer at the water/air surface. Every PPO block anchors two PEO brushes. The area per brush is $A \cong d^2$

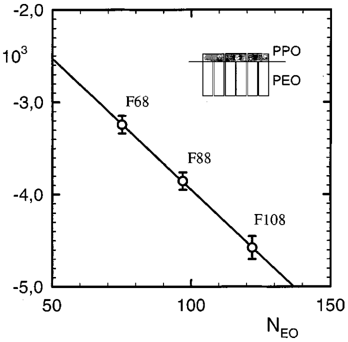

Fig. 3 Ellipticity of PEO–PPO–PEO copolymers solutions (in aqueous 0.1 M NaCl) versus the number of EO segments in the PEO chain (23 °C)

layers are considered separately. By inserting the refractive index of solid PPO ($n_{\mathrm{PPO}} = 1.45$ [29]) into Eq. (2) one obtains an estimate for the thickness of the PPO layer. The value ($L_{\mathrm{PPO}} = 0.6$ nm) appears to be of a reasonable order of magnitude.

If two adsorption layers are brought together a foam film is created. Since our experiments are conducted in 0.1 M NaCl electrostatic interaction is totally screened and steric forces stabilize the liquid film [23, 24]. The interaction between two brushes has been analyzed by de Gennes [32, 33]. According to his perception the two brushes do not interdigitate upon compression ($h \leq 2L_0$, where is h film thickness). The brush-to-brush repulsion derived from scaling arguments is

$$\Pi_{\mathrm{B}} \cong \frac{k_{\mathrm{B}}T}{A^{2/3}}\left(H^{-9/4} - H^{3/4}\right) , \qquad (4)$$

where $H = h/2L_0$. The first term is the osmotic pressure arising from the increased monomer concentration in the film and this always prevails at constant A. The second term accounts for an elastic restoring force (polymer molecules always coil and hence the negative sign).

A disjoining pressure isotherm for F108 is shown in Fig. 4. As can be seen, de Gennes' theory gives a satisfactory fit of the experimental data below a certain threshold where allegedly brush-to-brush contact first occurs [23, 24].

Essentially similar behavior for polymer brushes grafted at a solid/liquid surface (mica) has been observed with the surface forces apparatus [34–36]. Such a similarity between polymer brushes symmetrically compressed by different phases is not unexpected.

The repulsion found prior to the brush-to-brush contact (at $h > 2L_0 \approx 30$ nm) is attributed to freely coiled polymer molecules trapped between the two brushes [24, 37] as sketched in the right inset in Fig. 4. The initial softer resistance to compression of these coils is shown qualitatively by a dotted line in Fig. 4. In this region the softer coils are gradually squeezed down to the blob size of the brush d ($\cong A^{-1/2}$). Below this threshold brush-to-brush repulsion occurs and the isotherm follows Eq. (4) (the solid line in Fig. 4).

Further evidence of this core resistance is shown in Fig. 5, where the thickness of the film core, h_{C} [$= h - 2(L_{\mathrm{PPO}} - L_{\mathrm{PEO}})$], is plotted as a function of the bulk copolymer concentration, c.

Stable foam films are obtained firstly at c_0 and their thickness grows with further increase in the concentration up to about the cmc. Within this concentration range the thickness of the film core increases from zero to a few times the radius of gyration of a single molecule in the bulk solution [24, 37] as sketched in the right inset of Fig. 4. A simple calculation of the free energy of coils trapped in the film core [37] yields

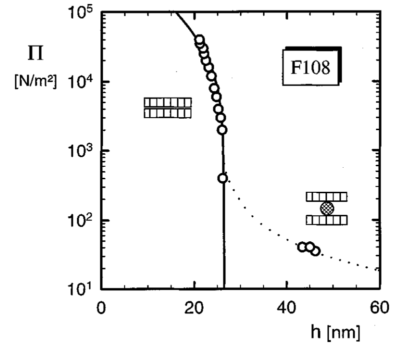

Fig. 4 Disjoining pressure, Π, versus film thickness, h, (1.43×10^{-5} M F108 in aqueous 0.05 M NaCl, 23 °C). Brush repulsion, Π_{B}, is shown by a *solid line*; core repulsion, Π_{C}, is qualitatively shown by a *dotted line*

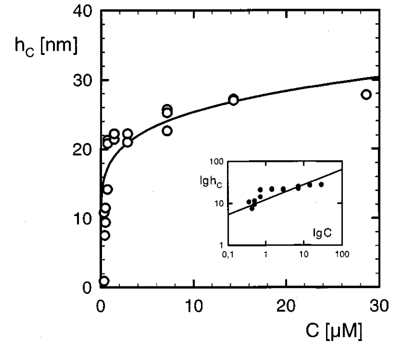

Fig. 5 Thickness of the film core, h_{C}, versus bulk copolymer concentration, c (F108 in aqueous 0.1 M NaCl, 23 °C)

$$h_{\mathrm{C}} \cong c^{1/4} ,$$

The least-squares fit shown in Fig. 5 yields an exponent of 0.21(4) which is in fairly good accord with the above prediction.

Concluding remarks

Amphiphilic PEO–PPO–PEO triblock copolymers behave as surfactants at the water/air interface. Measurements of the ellipticity of light reflected from the free surface of the copolymer solutions prove that a PEO brush is built at the fluid interface at $c_0 \leq c \leq$ cmc. Stable foam films are obtained in this concentration range. At lower capillary pressures softer steric repulsion occurs due to coiled polymer molecules trapped in the film core. At higher pressures brush-to-brush contact is established. The disjoining pressure isotherm becomes steeper and follows de Gennes' equation.

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