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

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 by the ellipticity of light reflected from the solution/air interface and in foam films, reveals that brush-to-brush repellency is convex.

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 ($M_w/M_n = 1.2$ [18]).

The surface tension, $\sigma$, 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, $\hat{\rho}$, 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 via the locked 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 $\psi$ and $\Delta$ 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 $\hat{\rho}$ becomes

$$\hat{\rho} = S/2$$

The dependence of the disjoining pressure, $\Pi$, 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 counter-balances 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.

**Results and discussion**

The equilibrium surface tension, $\sigma$, 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 [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 absorbs at the water/air interface. Thus, each PPO block anchors two PEO brushes. It is assumed that the situation with one

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

<table>
<thead>
<tr>
<th>Name</th>
<th>$M$</th>
<th>PEO (%)</th>
<th>$N_{EO} - N_{PEO} - N_{EO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F68a</td>
<td>8 400</td>
<td>80</td>
<td>76–30–76</td>
</tr>
<tr>
<td>F88b</td>
<td>10 800</td>
<td>80</td>
<td>97–39–97</td>
</tr>
<tr>
<td>F108b</td>
<td>14 000</td>
<td>80</td>
<td>122–56–122</td>
</tr>
</tbody>
</table>

$a$ Pluronic from BASF

$b$ Synerponic from ICI

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