

# Analysis on the Surface Adsorption of PEO/PPO/PEO Triblock Copolymers by Radiolabelling and Fluorescence Techniques

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## SYNOPSIS

We have examined the adsorption of poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide) (PEO/PPO/PEO) triblock copolymers (Pluronics<sup>®</sup>) on dimethyldichlorosilane-treated glass (DDS-glass). The surface concentration of <sup>125</sup>I-labeled Pluronic F-68(76/30/76) reached a maximum of 0.3  $\mu\text{g}/\text{cm}^2$  when the bulk concentration in the adsorption solution was 3.0 mg/mL. Above 5.0 mg/mL, the surface Pluronic F-68 concentration started to decrease and reached 0.17  $\mu\text{g}/\text{cm}^2$  when the bulk concentration for adsorption was 10 mg/mL. The surface concentration of Pluronic F-108 (129/56/129), on the other hand, increased to 4.0  $\mu\text{g}/\text{cm}^2$  at the same bulk concentration. Fluorescence spectroscopic studies using pyrene suggested that the Pluronic F-68 molecules self-associated at the bulk concentration of 5.0 mg/mL and above. Because the aggregates are expected to expose the hydrophilic PEO segments to water, they may have lower affinity to DDS-glass. Aggregation of Pluronic F-68 also decreases the number of individual Pluronic molecules for adsorption. Pyrene fluorescence in Pluronic F-108 solution, however, suggests that Pluronic F-108 molecules do not form aggregates. It appears that the high surface concentrations of Pluronic F-108 may result from the preferential adsorption of individual molecules in multilayers. This explains the high effectiveness of Pluronic F-108 in preventing protein adsorption and platelet adhesion when adsorbed on to the hydrophobic surface.

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## INTRODUCTION

Since their introduction in 1950, poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide) (PEO/PPO/PEO) triblock copolymers (Pluronics<sup>®</sup>, BASF) have become important nonionic polymeric surfactants.<sup>1,2</sup> Pluronic surfactants have found applications in chemical, agricultural, and pharmaceutical industries.<sup>3</sup> Pluronic surfactants play an important role in the stabilization of hydrophobic colloidal particles in water. Pluronic copolymers are known to adsorb on hydrophobic surfaces by the middle PPO segment, while the PEO segments interact with water molecules and extend into the bulk aqueous solution.<sup>4-6</sup> The flexible PEO

segment can also prevent protein adsorption and cell adhesion on biomaterial surfaces by the steric repulsion mechanism.<sup>7-11</sup>

Our previous study showed that Pluronics containing 30 propylene oxide (PO) residues [e.g., Pluronic F-68 (76/30/76)], when adsorbed on dimethyldichlorosilane-treated glass (DDS-glass), could not prevent plasma protein adsorption and platelet adhesion. The adsorption of Pluronics containing 56 PO residues [e.g., F-108 (129/56/129)] on DDS-glass, however, resulted in complete prevention of protein adsorption and platelet adhesion.<sup>12,13</sup> It was thought that Pluronics with 56 PO residues were able to bind tightly to DDS-glass due to the large size of the hydrophobic PPO segment. Pluronic F-68 could prevent platelet adhesion, if the adsorbed copolymer molecules were covalently grafted to the surface by gamma irradiation.<sup>14</sup> The tight binding of Pluronics to the surface by hydrophobic interactions or covalent grafting is important for effective steric repulsion of plasma proteins and cells.

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In addition to tight binding, effective steric repulsion by the adsorbed Pluronics requires complete surface coverage. Previous studies have shown that the surface concentration of adsorbed Pluronics increases dramatically above the critical micelle concentration (CMC).<sup>4</sup> Above the CMC, Pluronic copolymers could adsorb either as micellar aggregates or form surface micelles by self-association after adsorption as suggested by Ligoure.<sup>15</sup> The ability of polymeric surfactant to form micelles in aqueous solution is still a controversial subject. The debate stems from different values of CMC that are reported in the literature. For Pluronic F-68, for instance, the CMC ranges from 0.05 mg/mL to 50 mg/mL.<sup>4,16,17</sup>

In this study we have examined the adsorption of <sup>125</sup>I-labeled Pluronics F-68 and F-108 on DDS-glass. *p*-Methoxyphenyl derivatives of Pluronics F-68 and F-108 were synthesized and labeled with <sup>125</sup>I. The aggregation behavior of Pluronics in bulk aqueous solution was examined using fluorescence spectra of pyrene in bulk Pluronic solutions.

## MATERIALS AND METHODS

### Preparation and Characterization of Surfaces

Dimethyldichlorosilane-treated glass (DDS-glass) tubing was prepared by the method described previously.<sup>18</sup> Glass tubing (i.d. 2.50 mm, Kimble, Vineland, NJ) was cleaned with 2% (v/v) Isoclean (Isolab, Akron, OH) for 3 h at 60°C. The tubing was then rinsed with deionized distilled water and dried. Clean glass tubing was treated with 5% (v/v) DDS (Sigma Chemical Co., St. Louis, MO) in chloroform for 2 h at room temperature. The reaction introduces methyl groups on the glass surface through a silane-ether bridge. DDS-glass tubing was washed with chloroform and ethanol in sequence twice, followed by deionized distilled water. DDS-glass tubing was dried overnight at 60°C. DDS-glass tubing was used to measure the surface concentration of <sup>125</sup>I-labeled Pluronics.

For contact angle studies, glass coverslip (25 × 75 mm, #1, Bellco, Vineland, NJ) was used instead of glass tubing. Glass coverslip was cleaned and modified with DDS as described above. Underwater contact angles were measured using a contact angle goniometer (Rame-Hart, Mountain Lakes, NJ) equipped with an immersion chamber.<sup>19,20</sup> Air-water-surface and octane-water-surface static bubble contact angles were measured. Contact angles were measured on ten different regions of each surface.

The surface free energies at the solid-liquid interface were calculated from contact angle measurements using the harmonic mean approximation method described by Andrade et al.<sup>21</sup> The method utilizes the following harmonic mean equation:

$$\gamma_{sw} = \gamma_{sv} + \gamma_{wv} - 4[\gamma_{sv}^d \gamma_{wv}^d / (\gamma_{sv}^d + \gamma_{wv}^d)] - 4[\gamma_{sv}^p \gamma_{wv}^p / (\gamma_{sv}^p + \gamma_{wv}^p)]$$

where the subscripts *S*, *V*, and *W* refer to the solid, vapor, and water phases, respectively. The superscripts *p* and *d* refer to the polar and dispersive components of the surface free energies.

### Preparation of <sup>125</sup>I-Labeled Pluronics

Pluronics F-68 and F-108 were obtained from the Performance Chemical Division of BASF Corporation (Parsippany, NJ). The physical properties of Pluronics are listed in Table I. Pluronic F-68 and F-108 were dissolved in phosphate-buffered saline solution (PBS, pH 7.4) and labeled with <sup>125</sup>I, as previously described.<sup>14</sup> For <sup>125</sup>I-labeling, the terminal hydroxyl groups of PEO chains in Pluronic copolymers were modified by reaction with *p*-methoxyphenyl chloroformate (Sigma). The *p*-methoxyphenyl derivatives of Pluronic F-68 and Pluronic F-108 were labeled with <sup>125</sup>I using IODO-GEN (Pierce, Rockford, IL). The bulk concentration of radiolabeled Pluronic was calculated from a standard curve.

### Quantitation of the Surface Pluronic Concentration

The final solutions of Pluronic F-68 and Pluronic F-108 for adsorption on DDS-glass tubing were made by mixing radiolabeled Pluronics with unlabeled Pluronics in a weight ratio of 1 : 10. The radioactivity of a known Pluronic concentration was measured

**Table I** Properties of Pluronic Copolymers<sup>a</sup>

Pluronic Copolymer	Mol. Wt.	EO/PO/EO	Thickness of Adsorbed Layer <sup>b</sup> (Å)
Pluronic F-68	8,350	76/30/76	60 ± 6
Pluronic F-108	14,000	129/56/129	118 ± 15

<sup>a</sup> From ref. 2.

<sup>b</sup> The thickness of adsorbed Pluronic copolymers on polystyrene latices (diameter 0.305 μm) measured by photon correlation spectroscopy (from ref. 7).

**Table II Contact Angles ( $\theta$ ) and Surface Free Energies ( $\gamma$ ) on Pluronic-Adsorbed DDS-Glass**

Surface Treatment	$\theta_{\text{air}}$ (degree)	$\theta_{\text{octane}}$ (degree)	$\gamma_{\text{sv}}^{\text{p}}$ (dynes/cm)	$\gamma_{\text{sv}}^{\text{d}}$ (dynes/cm)	$\gamma_{\text{sv}}$ (dynes/cm)	$\gamma_{\text{sw}}$ (dynes/cm)
Control DDS-glass	75.6 $\pm$ 3.4 <sup>a</sup>	98.3 $\pm$ 2.1	13.9	24.3	38.1	21.0
F-68-adsorbed DDS-glass <sup>b</sup>	60.8 $\pm$ 2.9	78.3 $\pm$ 3.7	21.9	21.4	43.2	11.4
F-108-adsorbed DDS-glass <sup>b</sup>	59.8 $\pm$ 2.7	76.8 $\pm$ 4.9	22.3	21.4	43.7	10.9

<sup>a</sup> Average  $\pm$  SD ( $n = 10$ ).

<sup>b</sup> Pluronics were adsorbed at the bulk concentration of 10 mg/mL for 1 h at room temperature. Nonadsorbed Pluronics were removed by washing with PBS prior to contact angle measurements.

using a gamma counter (Gamma 5500B, Beckman, Arlington Heights, IL). Pluronic F-68 or F-108 at the bulk concentration ranging from 0.001 mg/mL to 10 mg/mL was allowed to adsorb on DDS-glass tubing for 1 h at room temperature. Nonadsorbed Pluronics were removed by rinsing the tubing with PBS. The surface Pluronic concentrations were determined from the surface radioactivities and the known relationship between the radioactivity and Pluronic concentration. The data represents mean  $\pm$  SD from four separate experiments.

### Pyrene Fluorescence Studies

Pyrene (Sigma) was added to Pluronic solutions from a 1.0 mM stock solution in ethanol to give the final concentration of 2.0  $\mu\text{M}$ . No excimer emission was observed at such a pyrene concentration. Pyrene emission spectra were obtained with SLM 8000C (SLM-Aminco, Urbana, IL) fluorescence spectrophotometer. Pyrene was excited at 343 nm and the emission spectra were obtained with slit opening of 0.5 mm at an integration time of 1 s per 1 nm. The emission spectrum of pyrene showed five distinct peaks. The ratio of the third to the first peaks (III/I ratio) was calculated from the emission intensities at 384 nm and 372 nm. The data represent mean  $\pm$  SD from four separate experiments.

## RESULTS AND DISCUSSION

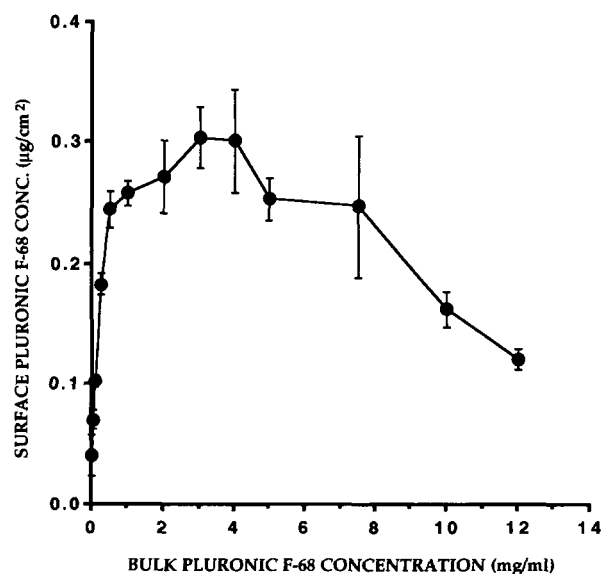
### Characterization of Pluronic-Adsorbed DDS-Glass

Table II shows the results of contact angle measurements and the calculated surface-free energies on control DDS-glass and DDS-glass modified by preadsorption of Pluronic F-68 or Pluronic F-108. Contact angle measurements on DDS-glass clearly show that it is a very hydrophobic substrate. Pluronic F-68-treated DDS-glass had a 37% increase in

the polar component of the surface free energy ( $\gamma_{\text{sv}}^{\text{p}}$ ) and 12% decrease in the dispersive component ( $\gamma_{\text{sv}}^{\text{d}}$ ) compared to the control DDS-glass. The same results were observed on Pluronic F-108-treated DDS-glass. The results clearly indicate that the hydrophilicity of DDS-glass is increased by Pluronic coating. Although the difference in contact angle between Pluronic F-68- and F-108-modified DDS-glass was not significant, the adsorption behavior of these two copolymers on DDS-glass was significantly different (see below).

### Surface Pluronic Concentration on DDS-Glass

The surface Pluronic F-68 concentration on DDS-glass increases as the bulk Pluronic concentration used for adsorption increases as shown in Figure 1. The surface concentration was 0.10  $\mu\text{g}/\text{cm}^2$ , even

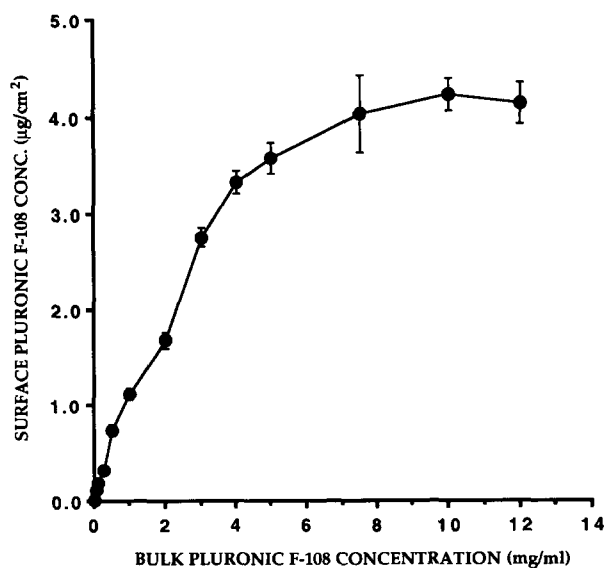


**Figure 1** The adsorption isotherm of Pluronic F-68 on DDS-glass. Radiolabeled Pluronic F-68 was adsorbed for 1 h at room temperature.

at the bulk Pluronic F-68 concentration of 0.10 mg/mL. The surface Pluronic F-68 concentration reached a maximum of  $0.30 \mu\text{g}/\text{cm}^2$  when the bulk concentration was 3.0 mg/mL. At the surface Pluronic F-68 concentration of  $0.3 \mu\text{g}/\text{cm}^2$ , the area occupied by each Pluronic F-68 molecule on DDS-glass is calculated to be  $4.6 \text{ nm}^2$ . At bulk concentrations higher than 4.0 mg/mL, the surface Pluronic F-68 concentration decreased. At the bulk Pluronic F-68 concentrations of 5 mg/mL and 10 mg/mL, the surface concentrations decreased to  $0.25 \mu\text{g}/\text{cm}^2$  and  $0.17 \mu\text{g}/\text{cm}^2$ , respectively.

Figure 2 shows the surface Pluronic F-108 concentration as a function of the bulk Pluronic concentration used for adsorption. At lower concentrations of 0.1 mg/mL and 1.0 mg/mL, the surface Pluronic F-108 concentration was  $0.20 \mu\text{g}/\text{cm}^2$  and  $1.13 \mu\text{g}/\text{cm}^2$ , respectively. These values are much higher than those in Figure 1. The surface Pluronic F-108 concentration continued to rise as the bulk concentration for adsorption increases. At the bulk Pluronic F-108 concentration of 3.0 mg/mL, for instance, the surface concentration was  $2.75 \mu\text{g}/\text{cm}^2$ . The surface Pluronic F-108 concentration reached a plateau value of about  $4.0 \mu\text{g}/\text{cm}^2$ , when the bulk Pluronic concentration was increased to 10 mg/mL. At the surface concentration of  $4.0 \mu\text{g}/\text{cm}^2$ , the area occupied by each Pluronic F-108 molecule is  $0.58 \text{ nm}^2$ .

Pluronic F-68 showed two salient features in its adsorption behavior. First, the surface concentration reached a transient maximum at the bulk concen-



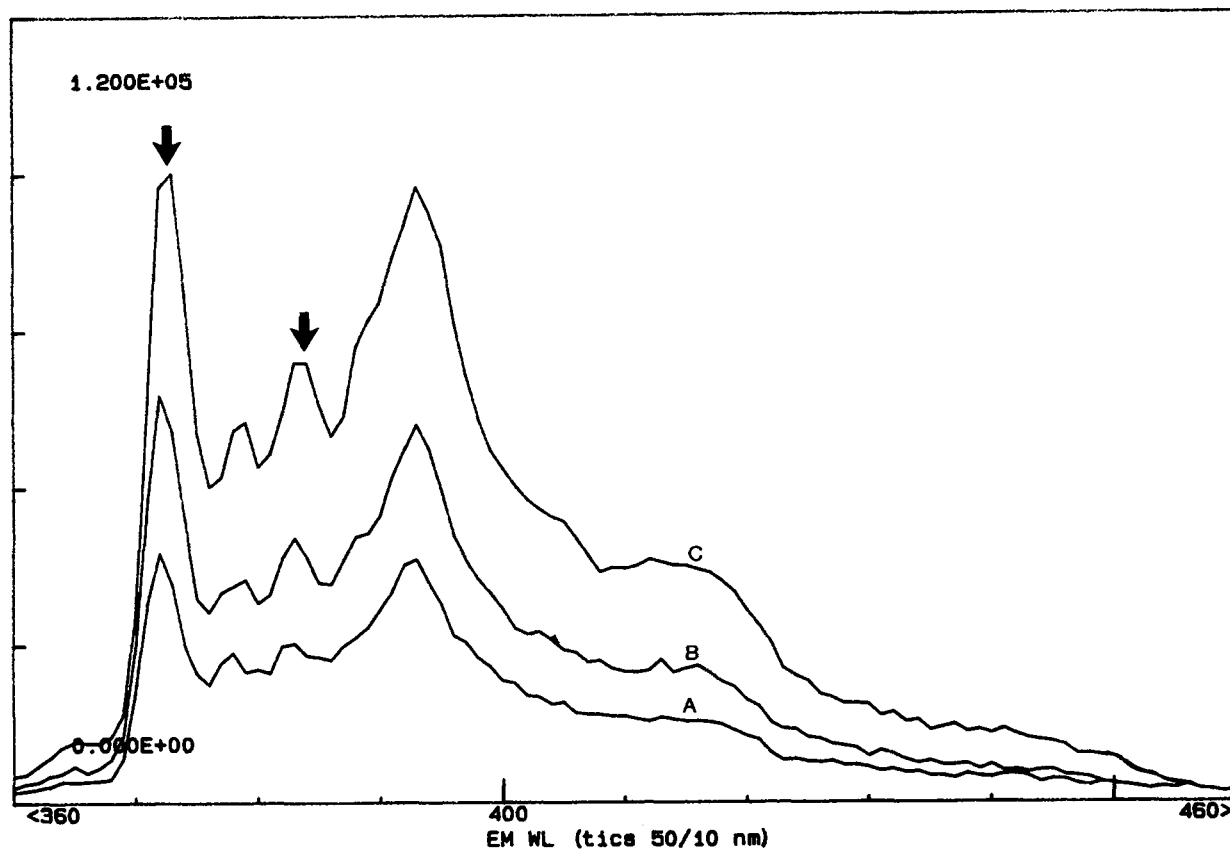
**Figure 2** The adsorption isotherm of Pluronic F-108 on DDS-glass. Radiolabeled Pluronic F-108 was adsorbed for 1 h at room temperature.

tration for adsorption of 3.0 mg/mL. Somehow, the affinity of Pluronics decreased as the bulk concentration increased. This suggests that they form aggregates that expose hydrophilic PEO segments to water, and the aggregates have lower affinity to the hydrophobic surface. In addition, there will be fewer individual Pluronic F-68 molecules for adsorption. Second, at the maximum surface concentration, the area occupied by each molecule is  $4.6 \text{ nm}^2$ . This indicates that Pluronic F-68 molecules adsorb as a monolayer on the surface. The adsorption profile of Pluronic F-108 molecules was quite different from that of Pluronic F-68. The surface concentration of Pluronic F-108 increased monotonically without transient maximum, and the area occupied by an individual Pluronic F-108 molecule was only  $0.58 \text{ nm}^2$ , which is unusually small. This suggests that Pluronic F-108 molecules adsorb as individual molecules to form multilayers.

### Fluorescence Spectra of Pyrene in Pluronic Solutions

Pyrene fluorescence studies were carried out in Pluronic solutions to examine whether Pluronic F-68 and F-108, indeed, form aggregates in solution at concentration range used in the above study. Due to the hydrophobic nature of the probe, pyrene concentrates in the hydrophobic regions of amphipathic molecules.<sup>22</sup> In Pluronics, pyrene is expected to localize in the hydrophobic PPO segment of the copolymer. Fluorescence spectrum of pyrene monomer is characterized by five peaks whose intensities depend strongly on the dielectric constant and other polarity scales of the medium.<sup>23,24</sup> Pyrene, a weak base, interacts with polar solvents through dipole-dipole interactions, leading to an enhancement in the intensity of peak I at 372 nm.<sup>23</sup> The intensity enhancement is due to the reduction in pyrene symmetry by complexation with solvent molecules.<sup>24</sup> In polar solvents, the intensity of peak I at 372 nm increases, whereas little effect is observed on peak III at 384 nm. The III/I ratio of pyrene fluorescence, therefore, has been used to study the change in environmental polarity. In polar and nonpolar solvents such as water and benzene, the values of III/I ratio are about 0.57 and 0.88, respectively.<sup>25</sup> Kalyanasundaram and Thomas<sup>26</sup> have used the III/I ratio to determine the CMC values of various surfactants.

Figure 3 shows pyrene spectra in Pluronic F-68 solutions at the bulk Pluronic concentrations of 0.1 mg/mL (A), 1.0 mg/mL (B), and 10 mg/mL (C). The III/I ratio increased with increase in the bulk Pluronic F-68 concentration. In Pluronic F-68 solution at the bulk concentration of 0.01 mg/mL, the



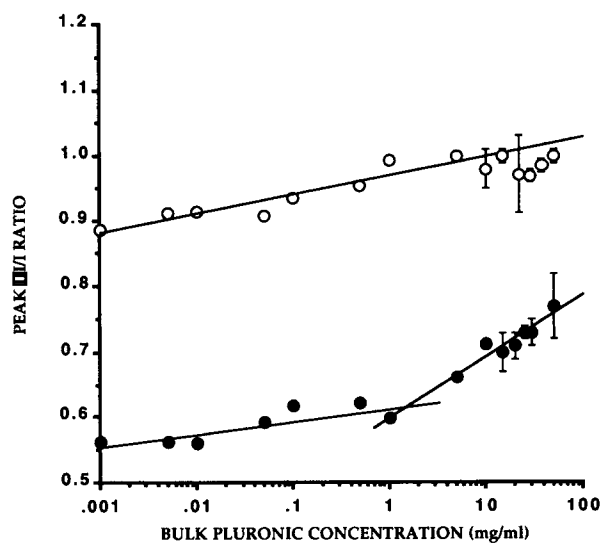
**Figure 3** Fluorescence spectra of pyrene in Pluronic F-68 solutions. Peaks at 372 nm (peak I) and 384 nm (peak III) are indicated by the arrows. Pyrene was dissolved in Pluronic F-68 solution at the final concentration of  $2.0 \mu\text{M}$ . The bulk concentration of Pluronic F-68 was 0.1 mg/mL (A), 1.0 mg/mL (B), and 10 mg/mL (C).

III/I ratio was 0.56 as shown in Figure 4 (closed circles). This value is the same as the value of pyrene in water. As the bulk Pluronic F-68 concentration increases to 1.0 mg/mL, the III/I ratio increases to 0.60. The transition in III/I ratio occurs at the bulk concentration of 2.0 mg/mL. Above this bulk concentration, the III/I ratio increases sharply. The III/I ratio was 0.71 at the bulk Pluronic concentration of 20 mg/mL. The value of 0.71 indicates that pyrene molecules are in an environment similar to methylene chloride rather than water.

The surface Pluronic F-68 concentration decreased as the bulk concentration for adsorption increased more than 4.0 mg/mL (Fig. 1). Figure 4 shows that the hydrophobicity of pyrene's environment increases as the bulk concentration increases above 2.0 mg/mL. In aqueous solution, Pluronic copolymers are known to self-associate above a certain critical bulk concentration.<sup>27</sup> The increase in the III/I ratio is consistent with the aggregation of Pluronic F-68. The aggregate is expected to have a hydrophobic core of PPO segments and hydrophilic surface of PEO segments. Because the adsorption of

Pluronic to the DDS-glass is due to the hydrophobic interactions, the aggregates may not have the same affinity to the surface as individual Pluronic molecules. Aggregation of Pluronic F-68 also decreases the number of individual Pluronic molecules for adsorption. This may result in a decrease in the surface Pluronic F-68 concentration when the bulk concentration was above 5.0 mg/mL, as observed in Figure 1.

For Pluronic F-108 (open circles in Fig. 4), the III/I ratio was 0.90 even at the bulk concentration of 0.01 mg/mL. This value of III/I ratio at low Pluronic F-108 concentration suggests individual Pluronic F-108 molecules have hydrophobic PPO core wrapped around by the hydrophilic PEO chains. In Pluronic F-108 molecules, the pyrene microenvironment is similar to that in benzene. With increasing bulk Pluronic concentrations, the III/I ratio in Pluronic F-108 solution did not change as much as in Pluronic F-68 solution. At the bulk Pluronic F-108 concentration of 20 mg/mL, the III/I ratio increased to only 0.95. The III/I ratio in Pluronic F-108 remained in a range from 0.90 to 1.0, regardless



**Figure 4** The III/I ratios of pyrene monomer fluorescence in Pluronic F-68 (1) and F-108 (m) solutions as a function of bulk Pluronic concentration.

of the bulk Pluronic concentration. This suggests that pyrene's microenvironment does not change significantly with increasing Pluronic F-108 concentration. Thus, it is reasonable to assume that the individual Pluronic F-108 molecules remain unassociated with each other. This may have resulted in a big difference in the adsorption behavior between Pluronic F-108 and Pluronic F-68.

In summary, our fluorescence study showed that Pluronic F-68 molecules form aggregates in solution when the bulk concentration was increased above 2.0 mg/mL and the adsorption of aggregates is not as favorable as that of individual molecules. This may have resulted in a decrease in surface concentration as the bulk concentration increased above 3.0 mg/mL. In contrast to Pluronic F-68, Pluronic F-108 molecules do not form aggregates. In any case, the high surface concentration appears to result from the adsorption of individual molecules in multilayers. Our previous study showed that Pluronic F-108 was highly effective in preventing protein adsorption and platelet adhesion.<sup>13</sup> This may be due to its preferential adsorption to the hydrophobic surface.

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