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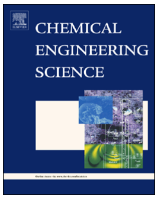

Block length determines the adsorption dynamics mode of triblock copolymers to a hydrophobic surface

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HIGHLIGHTS

- Polymer block length determines the adsorption dynamics to liquid/solid interface.
- Above CMC P100 polymers present three-stage adsorption and form two-layer structure.
- P500 polymers display monotonous adsorption and form uniform adsorbed structure.
- The adsorption mechanism is explored with DPD simulation from molecular interaction.

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ABSTRACT

Many material processes including surface modification and material fabrication depend on the mechanism by which polymers are adsorbed onto solid/liquid interfaces. Although the morphologies of block copolymers near the interface have been extensively investigated, the understanding of the adsorption dynamics is still limited. Here, we show that the block length determines the dynamic adsorption mode under conditions beyond the critical micelle concentration (CMC). The adsorption kinetics are investigated using in situ experimental characterization combined with Dissipative Particle Dynamics simulations. Two types of symmetrical triblock copolymers, i.e., PEO–PPO–PEO, with different hydrophilic PEO block lengths are studied. While both types of copolymers present similar adsorption dynamics at concentrations below the CMC, their dynamic adsorption modes are distinct at concentrations above the CMC. The present experimental–numerical study provides a mechanistic interpretation of this difference, which casts helpful insight for the dynamic control process of surface modification and material fabrication.

1. Introduction

The adsorption of polymers at solid/liquid interfaces has received increasing attentions due to their importance in the stabilization of colloids, development of materials, surface modification, and advancements in life science (Napper, 1983; Chakraborty and Golumbfskie, 2001; Frisch et al., 1953; Silberberg, 1962; Scheutjens and Fleer, 1979; Watts et al., 1984; Munch and Gast, 1988; Zhu and Gu, 1991; Wang and Mattice, 1994; Zhan and Mattice, 1994; Amiel et al., 1995; Misra, 1996; Huang et al., 2002). In comparison with homopolymers, block copolymers usually exhibit specific adsorption behavior, forming a variety of structures such as micelles or lamellae in appropriate solvents (Frisch et al., 1953; Munch and Gast, 1988; Wang and Mattice, 1994; Amiel et al., 1995). For instance, Brandani and Stroeve (2003) investigated the adsorption from water of a family of triblock poly (ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymers, i.e., $(PEO)_n$–$(PPO)_m$–$(PEO)_n$ (the subscripts n and m represent the number of repeat units), on a hydrophobic surface and observed that the morphology adopted by the triblock copolymers on the surface was closely associated with the composition of the blocks. Li et al. (2011) studied the adsorption of $(PEO)_{19}$–$(PPO)_{29}$–$(PEO)_{19}$ on three different substrates using Atomic Force Microscopy, and significant morphological differences were found. In addition to the chemical composition and surface properties, the effects of concentration and temperature on the adsorption of block copolymers in equilibrium have also been investigated (Brandani and Stroeve, 2003; Kamerlin et al., 2011; Marques et al.,

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1988; Johner and Joanny, 1990; Munch and Gast, 1990; Tiberg et al., 1991; Alexandridis et al., 1994; Eskilsson and Tiberg, 1997; Green et al., 1997; Emoto et al., 1999).

However, the majority of work previously reported focuses on the equilibrium properties of adsorbed polymers, including the morphology of the polymer on different substrates, the physicochemical and thermodynamic properties of the adsorbed polymers (Chen et al., 2003, 2001; Guo et al., 2003) or tethered polymer brushes (Tong, 2014; Lian et al., 2014a, 2014b), and investigations concerning the adsorption dynamics of polymers from a solvent onto a substrate are still limited (Munch and Gast, 1988; Johner and Joanny, 1990; Munch and Gast, 1990; Eskilsson and Tiberg, 1997). Generally, polymeric micelles are not expected to be adsorbed directly onto a solid surface. Instead, they act as reservoirs for chains to be adsorbed (Munch and Gast, 1988; Johner and Joanny, 1990). The adsorption process is believed to consist of several stages. First, free chains cover the unoccupied surface through diffusion. Second, due to the aggregation and disaggregation equilibrium between micelles and free polymer chains in solution, some polymer chains are released from the micelles and are then adsorbed onto the surface. In this stage, the adsorption dynamics are dominated by the chain expulsion from the micelles. Third, due to the exclusion of the pre-adsorbed chains to incoming chains, the adsorption process slows down. Finally, the surface is saturated with polymer chains and the adsorption terminates (Munch and Gast, 1988; Johner and Joanny, 1990). Empirically it has been observed that poly(ethylene oxide)-b-poly(tetrahydrofuran)-b-poly(ethylene oxide) exhibits a three-regime adsorption onto a water/hydrophobic silica interface, involving a diffusion-controlled regime, substitution-limited regime, and brush-dominated regime (Eskilsson and Tiberg, 1997). On the other hand, Munch and Gast (1990) demonstrated that polystyrene-b-poly(ethylene oxide) exhibited a much faster adsorption at concentrations above the critical micelle concentration (CMC) than below the CMC. It has also been shown that the amount of PEO–PPO–PEO adsorbed onto a hydrophobic surface significantly increases at concentrations above the CMC due to the formation of a multilayer structure (Tiberg et al., 1991). Nevertheless, the adsorption mechanism of block copolymers is not well understood, particularly the adsorption dynamics.

In the present study, we investigate the adsorption of PEO–PPO–PEO triblock copolymers with different hydrophilic PEO block lengths from an aqueous solution to a hydrophobic surface in situ using a quartz crystal microbalance with dissipation (QCM-D) and Surface Plasmon Resonance (SPR). Further theoretical investigations are performed using Dissipative Particle Dynamics (DPD) simulations, which provide a more detailed and tangible depiction of the adsorption dynamics. The effect of the PEO block length on the adsorption dynamics, in particular, is addressed.

2. Experimental section

2.1. Materials

Two kinds of PEO–PPO–PEO samples, i.e., $(PEO)_4$–$(PPO)_{56}$–$(PEO)_4$ and $(PEO)_{37}$–$(PPO)_{56}$–$(PEO)_{37}$, are considered. These triblock copolymers have the same PPO block length but different PEO block lengths, are hereafter referred as P100 (with short PEO block length) and P500 (with long PEO block length). BASF® (BASF, China) donated these samples, and for P100, M_w=3610 g/mol, 10 wt% PEO, and for P500, M_w=6500 g/mol, 50 wt% PEO. Undecanethiol and ethanol (SINOPHARM® SINOPHARM, China) were used as received.

2.2. Preparation of the hydrophobic surface

The representative hydrophobic surface used in this study is an undecanethiol-modified gold surface (Creager and Clarke, 1994). QCM-D and SPR gold sensor chips were first cleaned using Piranha solution (H_2SO_4/H_2O_2, V/V=3:1), rinsed with deionized water, and then dried under a nitrogen flow. The self-assembly of each hydrophobic monolayer was achieved by immersing the freshly cleaned chips in a 5.0 mM undecanethiol solution in ethanol for 20 h (Creager and Clarke, 1994). The QCM-D crystal was mounted in a protective casing made of Teflon to shield the other side from the undecanethiol solution. The SPR sensor chip was immersed directly into the undecanethiol solution. The modified chips were rinsed with adequate alcohol and water to remove residual undecanethiol before being dried under a nitrogen flow.

2.3. Laser Light Scattering (LLS)

Laser Light Scattering (LLS) measurements were conducted on an ALV/DLS/SLS-5022F spectrometer equipped with a multi τ digital time correlation (ALV5000, ALV® Langen (Germany)) and a cylindrical 22 mW UNIPHASE He–Ne laser (λ_0=632 nm) light source. The CMC of each PEO–PPO–PEO solution was determined by dynamic LLS because the scattered light intensity was sensitive to polymer aggregation. The solution was filtered using a 0.45-μm Millipore filter to remove dust before the measurements. All LLS measurements were performed at 25 °C and at a scattering angle of 90°. The CMC for P100 and P500 were determined as 0.1 and 0.59 mg/mL, respectively.

2.4. QCM-D measurements

The QCM-D and the AT-cut quartz crystal with a fundamental resonant frequency of 5 MHz were from Q-sense AB (Rodahl et al., 1995). The measurable frequency shift is within ±1 Hz in aqueous media. The effects of surface roughness are neglected because the crystal is highly polished with a root-mean-square roughness less than 3 nm (Chen et al., 2001).

When a quartz crystal is excited to oscillate in the thickness shear mode at its fundamental resonant frequency by applying a RF voltage across the electrodes, a small change in the mass added on the electrodes results in a decrease in the resonant frequency (Δf). In vacuum or air, if the added layer is rigid, evenly distributed, and much thinner than the crystal, Δf is related to Δm (the mass change of the added layer per area) and the overtone number (n=1, 3, 5....) through the Sauerbrey equation (Sauerbrey, 1959):

$$\Delta m = -\frac{\rho_q l_q}{f_0}\frac{\Delta f}{n} = -K\frac{\Delta f}{n} \tag{1}$$

where f_0 is the fundamental frequency, and ρ_q and l_q are the specific density and thickness of the quartz crystal, respectively. The constant (K) of the AT-cut quartz crystal is 17.7 ng/cm^2 Hz (Rodahl et al., 1995; Zheng et al., 2014) The dissipation factor (ΔD) is defined by $\Delta D = E_d/2\pi E_s$, where E_d is the energy dissipated during one oscillation and E_s is the energy stored in the oscillating system. The measurement of ΔD is based on the fact that the voltage over the crystal decays exponentially as a damped sinusoidal when the driving power of a piezoelectric oscillator is switched off (Rodahl et al., 1995). By switching the driving voltage on and off periodically, we can simultaneously obtain a series of changes in the resonant frequency and the dissipation factor.

The solvent effect on the frequency and dissipation responses could be removed by using the corresponding solvent as the reference (Stockbridge, 1966; Kanazawa and Gordon, 1985; Rodahl and Kasemo, 1996). Both Δf and ΔD values were recorded in the