

# Competition Between Micellization and Adsorption of Diblock Copolymers in a Colloidal System

L. E. DEWALT,<sup>1,2</sup> H. D. OU-YANG,<sup>1,2,\*</sup> and V. L. DIMONIE<sup>2</sup>

<sup>1</sup>Department of Physics, Lewis Laboratory, and <sup>2</sup>Polymer Interfaces Center, Lehigh University, Bethlehem, Pennsylvania 18015

## SYNOPSIS

Significant adsorption of polystyrene-poly(ethylene oxide) (PS-PEO) diblock copolymers onto PS latex particles in an aqueous dispersion is accomplished through suppression of micelle formation by adding tetrahydrofuran (THF) as a cosolvent. We add THF, a good solvent for the micelle core, to weaken the micelle and allow free chains for adsorption to the colloidal particles. Choosing a PS colloidal particle as the adsorption substrate (thus the adsorbed PS block can fully wet the subsurface), we eliminate the complications which arise from micelle formation on the colloidal surface. Since the PS particles swell in the mixed solvent, the adsorbed PS block may penetrate into the swollen latex core, which is favored for entropic reasons. A subsequent water quench of the system to a low THF solution shrinks the PS particle to its original size while retaining most of the adsorbed polymers. The adsorbed chains cannot be removed by adding surfactants or raising temperature to 90°C, indicating that the adsorbed layer is tightly attached to the surface due to kinetic hinderance of the chains in a confined environment. Neutron scattering experiments is being carried out to settle whether the PS penetrates the PS particle. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Diblock copolymers are often used to improve colloidal stability or to modify surface properties of other polymeric materials to improve adhesion or interfacial compatibility.<sup>1-3</sup> One of the fundamental and complex issues when diblock copolymers are added in solution with suspended colloidal particles is the competition between polymer adsorption onto colloidal surfaces and micellization.<sup>4-6</sup> The complexity arises from both the kinetics and energetics factors that come into play in such systems. The energies involved here are often large compared with  $k_B T$ , where  $k_B$  is Boltzmann's constant and  $T$  is room temperature. The large energy barrier coupled with slow Brownian of long chains in a confined environment can drastically slow down the kinetics such that the lowest energy state is kinetically hindered. In addition, surface micelles can form when the ad-

sorption block is different from the surface polymer due to noncomplete wetting.<sup>7</sup>

In this report we attempt to address the competitive process by using a system of asymmetric diblock polystyrene-poly(ethylene oxide) (PS-PEO) copolymers in the presence of PS latex particles in an aqueous suspension. We change the competition by tuning the solubility of the PS block through addition of tetrahydrofuran (THF) as a cosolvent. In choosing PS block adsorption on PS surface, we simplify the interfacial energy<sup>4</sup> between the adsorbed layer and colloid surface and avoid the formation of surface micelles.<sup>7</sup> We start the experiment with a aqueous solution, a situation in which micellization is favored over adsorption. By addition of the cosolvent THF, one that is a good solvent for the micelle core, we promote adsorption of the copolymer onto latex spheres. Normally, adding a cosolvent will also reduce the adsorption energy of the polymer. In the case of PS-PEO polymer adsorption on PS latex surface, however, the so-called spreading power,  $S$ , of the adsorbing block is zero and unaffected by the added cosolvent.<sup>8</sup> When the THF co-

\* To whom correspondence should be addressed.

solvent was added, the PS latex particles were found to swell. By water quenching the system back to a solution of low THF, we found that the adsorbed diblock copolymers remain on the surface of the PS latex particles. These polymers can exist on the surface in one of two possibilities: (1) the PS blocks form a thin layer on the latex surface or (2) chain interpenetration occurs during adsorption onto the swollen particle. Either case can be kinetic hinderance. In this study, we use dynamic light scattering to study the competition between micelle formation and adsorption of diblock copolymers onto a swollen latex surface.

The nature of the kinetic hinderance that retained the adsorbed chain on the latex particle surface is also of fundamental interest. Several tests, including raising the temperature and adding surfactants could not remove the adsorbed chains from the surface. Interpenetration of the adsorbing block and the PS substrate is entropically favorable, and it is kinetically allowed during the swollen state. After water quenching, the latex particle reduces to the original size preventing the PS block to leave the surface due to chain interpenetration in the glassy state. Currently, we are investigating the kinetics and the possibility of chain interpenetration using neutron scattering. Results of that study will be reported in a separate work.

## EXPERIMENTAL

The colloidal surface used in this study is a dispersion of PS latex particles, from Duke Scientific, with a diameter of 91 nm. The diblock copolymer is 40 units of PS and 790 units of PEO. We obtained the polymer sample from Polymers Laboratory (Amherst, MA) and used it without further purification. The total molecular weight is 39,000 g/mol. In water, this copolymer forms micelles with a diameter of about 112 nm with the PS as the core block. The copolymer mixes with water with gentle agitation and forms a clear solution. We added THF in water as a cosolvent, and since THF and water mix completely, we do not expect emulsification by the copolymers to occur. Since THF is not a good solvent for PEO, adding THF to more than about 80% in water causes large PEO aggregation to occur. We limit our investigation to about 50% THF. During sample preparation for subsequent measurements, the micelle solution was added into the prepared PS suspension.

Dynamic light scattering (DLS)<sup>9</sup> was used to measure the size of the micelles and the colloidal

particles with and without adsorbed polymers. When PS latex particles are dispersed in a mixed solvent of water and THF, the particles swell. DLS was used to determine the swollen particle size as a function of added THF in water. Adsorbed polymer layer thicknesses are determined by measuring the size of polymer-coated particles and subtracting the bare particle size. We can distinguish between the particle and micelles because the scattering intensity from the particle dominates over that from the micelles.

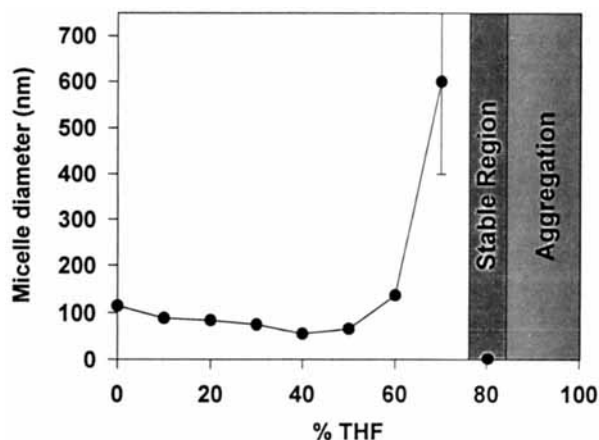
In this experiment, we fix the molar ratio of copolymer to latex sphere to 62,000 : 1 with the number density of PS spheres equal to  $2.5 \times 10^{10}/\text{cm}^3$  (or  $10^{-4}$  volume fraction). The concentration of the copolymer is well above the critical micelle concentration (cmc), and the aggregation number of the chains per micelle is about 2000. The number of micelles dominates over that of the latex spheres. Thermodynamically, the micelles act as an infinite source of copolymers, at the limit when all the latex surfaces are covered with copolymers the micelles still exist.

## RESULTS AND DISCUSSION

Experimentally we found insignificant adsorption of PS-PEO copolymers on PS particles in pure water, even under the condition of gentle sonication at elevated temperatures. However, light scattering found that micelles form readily for these copolymers in water. Calculation by Qiu and Wang<sup>4</sup> also indicated that for a soluble-to-insoluble block molar ratio of 10:1 with a relatively large latex core, micelles dominate.

### Block Copolymer Behavior in the Mixed Solvent

We used the PS-PEO copolymer in pure H<sub>2</sub>O at 0.03%, which is above cmc. The polymers form micelles with a PS core and PEO corona. The behavior of the PS-PEO copolymer in the mixed solvent is shown in Figure 1. Here, we see that, initially, as the percentage of THF in the solvent is increased, the micelle shrinks. This is probably prompted by either a reduction in the solubility of the PEO, causing the PEO corona to contract, or a decrease in the number of chains per micelle. Just above 50% THF, we see a dramatic increase in micelle size and polydispersity. Here, it appears that the micelles is aggregating. Increasing the THF concentration to 80% pushes the system to a point where both the PS and PEO are soluble. Above 80% THF, we see a quickly increasing particle size where the PS-PEO copoly-



**Figure 1** Micelle diameter vs. percent THF in the H<sub>2</sub>O–THF mixed solvent. Around 80% THF there is no evidence for a micelle. We call this the stable region where we have single diblock chains in solution. At high THF concentration the sample aggregates into very large clusters.

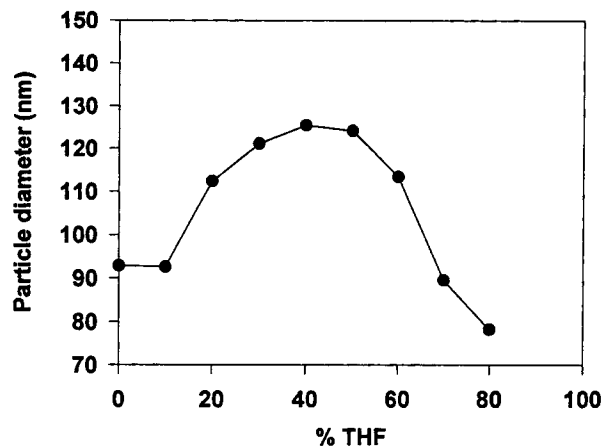
mer no longer seems soluble in the mixed solvent, indicating that we are seeing significant aggregation due to the poor solubility of PEO in THF.

### Polystyrene Particles in the H<sub>2</sub>O–THF Mixture

In order to study the diblock adsorption from a mixed solvent onto a colloidal particle, we need to know the effects of this solvent on the particle. In Figure 2, we see that, below 10% THF, there is little effect on the hydrodynamic size of the particles. However, increasing the concentration above 10%, we see significant swelling. This swelling increases to a maximum at 50% THF where there is a 33% increase in the particle diameter. The particles still appear to be stable in this solvent mixture. However, further increases in the concentration cause a decrease in the particle size, which we interpret as the beginning of chain removal from the noncrosslinked PS particle. Above 80% THF, there is no longer a measurable particle size; therefore, the particle has been completely dissolved. This THF concentration also corresponds to the point at which the PS–PEO micelles are no longer seen.

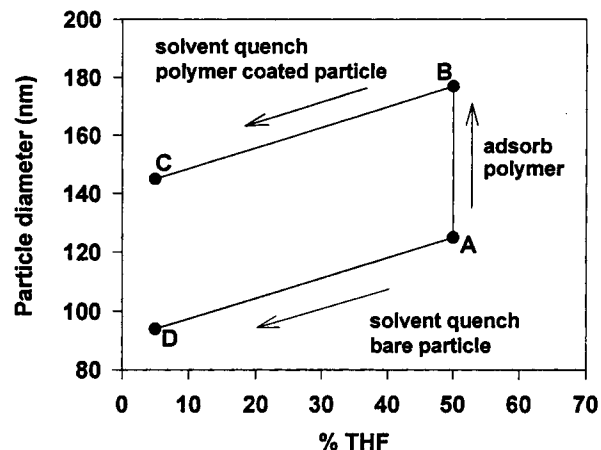
### Adsorption of PS–PEO Block Copolymer onto PS Particles

In pure water, the micelle is the more favorable conformation for the PS–PEO copolymer than adsorption. When the copolymer solution is mixed with the particles in pure water, we see a negligible increase in the apparent particle size. Increasing the amount of THF in the system has two effects. First,



**Figure 2** PS particle swelling vs. percent THF in the H<sub>2</sub>O–THF mixed solvent. Above 80% THF the particles have become completely soluble and have broken up.

the equilibrium condition between the micelle formation and adsorption is changed in favor of adsorption, causing the polymer adsorbed particle size to increase while the micelle size decreases. Second, it causes PS particles to swell. At 50% THF, we maximize this difference in sizes, thus enhancing the discrimination between the particle and micelle. Here, the swollen particle diameter is about 125 nm, while the micelle diameter reduces to about 50 nm. At this THF concentration, any increase in the apparent particle size will be caused by polymer adsorption. In Figure 3, we illustrate the scheme for adsorbing the PS–PEO diblock onto PS particles. Starting at the 50% THF concentration (point A in



**Figure 3** Grafting procedure: Polymer adsorbs to the swollen PS particle at high THF concentration (A to B). Subsequently quenching the samples with H<sub>2</sub>O down to 5% THF we see the PS particle shrinks to near its initial size (A to D) while polymer-coated particles retain the adsorbed layer (B to C).

Figure 3), we see the bare swollen particle diameter is 125 nm. Adding PS-PEO diblock in the ratio of 6000 chains per particle (point *B*), we see a dramatic increase of the particle diameter in marked contrast to what is observed in pure water. This jump indicates that a significant layer of polymer has adsorbed onto the swollen particle. We know that micelles cannot form on the surface because complete wetting must be achieved between the PS block and PS latex surface.

### Water-Quench the Swollen PS Particles with Adsorbed Chains

At 50% THF concentration, the PS particle is swollen. This raises the question of where the PS block of the copolymer resides: Does this block stay on the surface of the swollen particle? Or, given time, can this block diffuse into the swollen PS core? Due to lack of other direct methods on hand, we investigate this question by diluting (water-quenching) a sample of swollen PS particles with an adsorbed polymer layer (*B* to *C* in Fig. 3). Independently, we dilute (water-quench) a sample of swollen PS particles without adsorbed polymers (*A* to *D* in Fig. 3). Note that the final solvent composition of both samples is 5% THF. At 5% THF, before the particles are swollen, we measure negligible adsorption. A water quench, such as this, induces a bare swollen PS particle to shrink to approximately its original particle size, as shown in Figure 3 by point *D*. Thus, a water quench can have different effects on the adsorbed copolymer layer, depending on the position of the PS block. If the block has diffused into the particle, the solvent quench will trap the block in a now glassy PS core, effectively grafting the polymer to the surface. In another case, simple adsorption to the swollen particle would be washed off by the water quench, assuming the desorption is not kinetically hindered. Considering this assumption, we should see a significant decrease in the polymer layer. Looking at points *C* and *D*, in Figure 3, we see that, after the water quench, the particle retains a significant polymer layer. Thus, the adsorbed polymers have not left the surface either due to the kinetic hinderance in the adsorbed layer or due to a kinetic hinderance of PS chain interpenetration.

The question whether the PS block has penetrated into the PS latex core remains a key interest for future study. Nevertheless, we want to test further the stability of the adsorbed chains. Several approaches are taken to address this kinetic hinderance issue, namely, washing by surfactants and raising system temperature. We know that end-ad-

sorbing short chains will displace preadsorbed long chains.<sup>10</sup> Adding Triton X-100 surfactant into the quenched solution, we observe no significant change in the layer thickness, suggesting that the block copolymer chains are tightly attached to the particle surface. Preliminary results on the temperature effect show that raising the temperature to 90°C shrinks the layer thickness from 30 to 10 nm; but when the temperature is subsequently returned to room temperature, the layer thickness returns to about 25 nm. The reduction in layer thickness at high temperature could be related to the fact that the system is above the  $\Theta$  temperature of PEO where water becomes a poorer solvent.<sup>1</sup> We are currently studying the adsorption of the same PS-PEO copolymer onto highly crosslinked PS particles to limit the effect due to swelling of the latex. We are also carrying out neutron scattering experiments on the deuterated PS particles to investigate the interpenetration of the adsorbed blocks.

### CONCLUSIONS

Significant adsorption of PS-PEO diblock copolymers onto PS latex particles in an aqueous dispersion is accomplished through suppression of micelle formation by the use of a mixed solvent and a subsequent water quench. Our experiments indicate that the adsorbed layer is tightly attached to the surface since neither washing with surfactant nor raising the temperature can remove the chains from the surface. Besides the solvency effect studied here, the competition between micellization and adsorption can also be altered by changing the curvature of the latex particles as well as the molar ratio between the blocks of the copolymers. Different approaches along these lines are currently under investigation.

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8. Note that the spreading power  $S$  is defined as  $S = \gamma_{AS} + \gamma_{AC} - \gamma_{CS}$  as given in Ref 4; in the case here we have  $S = \gamma_{PS-S} + \gamma_{PS-PS} - \gamma_{PS-S}$  and it is always zero.
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