

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230663530>

# Direct Adsorption of Polystyrene Poly(Ethylene Oxide) Micelles in Water Onto Polystyrene Latex-Particles

ARTICLE *in* LANGMUIR · APRIL 1993

Impact Factor: 4.46 · DOI: 10.1021/la00028a035

---

CITATIONS

18

---

READS

30

9 AUTHORS, INCLUDING:



Gérard Riess

Université de Haute-Alsace

144 PUBLICATIONS 3,182 CITATIONS

SEE PROFILE



José M G Martinho

Technical University of Lisbon

210 PUBLICATIONS 3,305 CITATIONS

SEE PROFILE



## Direct Adsorption of Polystyrene-Poly(ethylene oxide) Micelles in Water onto Polystyrene Latex Particles<sup>1</sup>

J. M. R. d'Oliveira,<sup>2a</sup> Renliang Xu,<sup>2b</sup> Tetje Jensma, and Mitchell A. Winnik\*

*Department of Chemistry and Erindale College, University of Toronto, Ontario, Canada*

Zdenek Hruska,<sup>3</sup> Guy Hurtrez, and Gerard Riess

*Laboratoire de Chimie Macromoléculaire, Ecole Nationale Supérieure de Chimie, Université de Haute-Alsace, Mulhouse Cedex, France*

J. M. G. Martinho

*Centro de Quimica-Fisica Molecular, Complexo 1, I.S.T., Av. Rovisco Pais, Lisboa, Portugal*

Melvin D. Croucher

*Xerox Research Centre of Canada, Mississauga, Ontario, Canada*

Received May 28, 1992. In Final Form: September 4, 1992

The interaction between polystyrene-poly(ethylene oxide) (PS-PEO) diblock copolymers and PS latex particles in water is examined by both dynamic light scattering and size exclusion chromatography (SEC). The two block copolymer samples form micelles with core radii  $r_c = 6$  nm and total (hydrodynamic) radii of 26 and 30 nm, respectively. The SEC experiments establish that while the exchange rate of polymers among micelles is slow, the adsorption and redistribution of block copolymers onto the latex surface occur essentially instantaneously upon mixing. The most unusual observation is a systematic decrease in the adsorbed layer thickness for a series of latices with increased particle diameter. A kinetic model is presented to explain this result.

### Introduction

Poly(ethylene oxide)-polystyrene (PEO-PS) diblock copolymers form spherical micelles<sup>4</sup> in water when the length of the PEO chain exceeds that of the PS.<sup>5,6</sup> These micelles are characterized by a very low critical micelle concentration ( $\text{cmc} \approx 1$  mg/L) whose value depends sensitively on the length of the insoluble PS component.<sup>7</sup> In the presence of PS latex particles, the system rapidly reorganizes leading to adsorption of the block copolymer onto the latex surface.<sup>8</sup> We are interested in the mechanism of this process.

Current theory of block copolymer adsorption kinetics onto surfaces considers only single molecule adsorption processes.<sup>9</sup> For polymers at concentrations above the cmc in a selective solvent, the micelle is seen as a reservoir of material, but the chemical potential which drives adsorption is taken to be that of the free unimer chains in solution.

On the other hand, two recent studies of adsorption kinetics indicate that direct adsorption from the micelle

phase is an important process. Tassin et al.<sup>10</sup> examined adsorption from toluene onto a silver surface for poly(2-vinylpyridine)-polystyrene (P2VP-PS) diblock copolymers using a surface plasmon technique. Here the surface adsorption was selective for the P2VP block. Munch and Gast<sup>11</sup> developed a multiple total internal reflectance technique to study polystyrene-poly(ethylene oxide) (PEO-PS) adsorption from cyclopentane onto a sapphire surface. In these experiments cyclopentane is a selective solvent for PS and the surface is strongly selective toward PEO adsorption. In both sets of experiments an enhanced adsorption rate above the cmc was observed, indicating the existence of a mechanism for transfer of block copolymers to the surface that involves direct adsorption of micelles followed by rearrangement of the polymer onto the surface.

Here we report a set of experiments which also demonstrates the importance of the direct micelle-adsorption mechanism. We use dynamic light scattering (DLS) to follow the interaction of PS-PEO block copolymers in aqueous solution with a series of monodisperse PS latex particles. A drawing depicting this process is shown in Figure 1. For small particles, the radius of curvature can be a significant variable. This is an issue of direct importance to those interested in the stabilization of colloidal particles by block copolymers or in the synthesis of colloidal polymer particles by emulsion or dispersion polymerization in the presence of block copolymers.<sup>12,13</sup> We find the unexpected result that for a given diblock

(1) Paper No. 7 in a series on block copolymers in solution.

(2) (a) Permanent address: Centro de Quimica-Fisica Molecular, Lisboa, Portugal. (b) Permanent address: Coulter Scientific Instruments, Mail Code 195-00, 1950 W. 8th Ave., Hialeah, FL 33010.

(3) Permanent address: Solvay S. A., Rue de Ransbeek 310, 1120 Bruxelles, Belgium.

(4) For a review of block copolymer micelles see Tuzar, Z.; Kratochvil, P. *Colloids Surf.*, in press.

(5) Xu, R.; Winnik, M. A.; Hallett, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* 1991, 24, 87.

(6) Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* 1992, 25, 644.

(7) Wilhelm, M.; Zhao, C. L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J. L.; Riess, G.; Croucher, M. D. *Macromolecules* 1991, 24, 1033.

(8) Xu, R.; Hu, Y. Z.; Winnik, M. A.; Mohanraj, S.; Riess, G.; Croucher, M. D. *Langmuir* 1991, 7, 831.

(9) Johnner, A.; Joanny, J.-F. *Macromolecules* 1990, 23, 5299.

(10) Tassin, J. F.; Siemens, R. L.; Tang, W. T.; Hadziioannou, G.; Swalen, J. D.; Smith, B. A. *J. Phys. Chem.* 1989, 93, 2106.

(11) (a) Munch, M. R.; Gast, A. *J. Chem. Soc., Faraday Trans.* 1990, 86, 1341. (b) Munch, M. R.; Gast, A. *Macromolecules* 1990, 23, 2313.

(12) Riess, G.; Hurtrez, G.; Badahur, P. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1985; Vol. 2, pp 324-434.



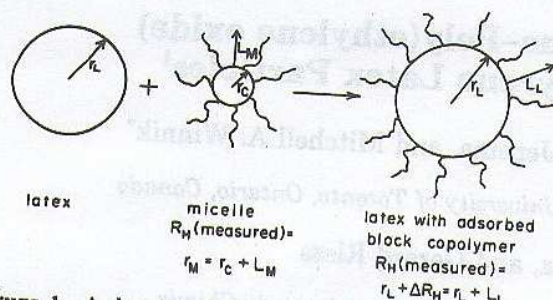


Figure 1. A drawing depicting the interaction of a diblock copolymer micelle with a bare latex in water to give a particle whose surface is covered with adsorbed block copolymers. This figure also defines our notation for core and corona radii.

Table I. Characteristics of the PS-PEO Block Copolymers<sup>a</sup>

sample	$M_{total}$	$M_{PEO}$	PEO wt%	$M_w/M_n$	$R_H(\text{micelle})^b$ nm	$R_G^{PEO}(H_2O)^c$ nm
ZGH4	22 200	18 400	82.8	1.17	$26 \pm 3$	6.6
ZGH5	32 600	28 800	88.3	1.25	$30 \pm 3$	8.6

<sup>a</sup> Both samples were prepared from a common PS block of  $M_{PS} = 3800$  ( $M_w/M_n = 1.2$ ). <sup>b</sup> Micelle radius in water at 22 °C as determined by DLS using the NNLS algorithm. <sup>c</sup> Radius of gyration in water of a PEO chain equal in length to that of the PEO in the block copolymer as calculated from eq 9.

Table II. Characteristics of the Latex Particles with and without Adsorbed Block Copolymer

sample <sup>a</sup>	$d_{EM}^b$	$d_{DLS}^c$	$d_{DLS}^d$	
			+ZGH4	+ZGH5
L69	63	$64 \pm 1$	$110 \pm 2$	$105 \pm 3$
L83	75	$74 \pm 1$	$94 \pm 2$	$101 \pm 4$
L100C	91	$96 \pm 1$	$110 \pm 2$	$110 \pm 3$
L109C	99	$108 \pm 1$	$121 \pm 4$	$127 \pm 1$
L131C	119	$130 \pm 1$	$135 \pm 2$	$137 \pm 4$

<sup>a</sup> Sample name refers to diameters quoted by the manufacturer as determined by DLS. The notation C indicates that the latex contains surface carboxyl groups. <sup>b</sup> Mean diameters (nm) determined by electron microscopy as quoted by the manufacturer. <sup>c</sup> Determined by DLS at a latex concentration of 0.01 mg/mL. <sup>d</sup> Latex mean diameter (nm) in the presence of excess block copolymer as determined by DLS ( $\pm 1$  standard deviation as determined from a minimum of five separate measurements) and analyzed using the NNLS algorithm.

copolymer, the adsorbed layer thickness increases as the substrate diameter decreases.

### Experimental Section

The block copolymers were prepared in Mulhouse by standard anionic polymerization methods using a common living PS block as a precursor. The characteristics of the polymers and their micelles in aqueous solution are presented in Table I. Micelle solutions were prepared by adding the block copolymer directly to water (Milli-Q grade,  $c = 1-2$  mg/mL), warming the mixture to 50 °C for 1 h, and cooling to room temperature. PS latex dispersions were obtained as a gift of D. S. Mohanraj of Seradyne. Three of the samples (cf. Table II) contain surface carboxyl groups; the other two contain only sulfate groups. Previous experiments<sup>8</sup> have suggested that PS-PEO adsorption on these particles is unaffected by this difference in surface functionalization. Here we provide further observations relevant to this issue.

DLS measurements were carried out at 25 °C using a 200-mW Ar-ion laser (Excell 3000) in conjunction with a Brookhaven BI-2030AT autocorrelator. Solutions of block copolymer were added to the latex dispersion (7-13 mg/L) with stirring. Adsorption

occurred as soon as the samples were mixed. To ensure that binding experiments involved a common excess of block copolymer, we calculated how much adsorption would occur if the adsorbed area per block copolymer molecule was equal to the area of onestyrene monomer unit. Analysis of the autocorrelation decay function by Laplace inversion using the nonnegative least-squares (NNLS) algorithms<sup>6</sup> showed either a single sharp peak corresponding to a species with a radius of the order of that of the latex or two peaks with the second, much smaller peak identical to that of the micelle itself.

Previous experiments in our laboratory<sup>14</sup> using DLS to follow the hydrodynamic radius increment ( $\Delta R_H$ ) indicated that the concentration dependence of  $\Delta R_H$  followed a simple Langmuir-type binding isotherm. In the presaturation domain,  $\Delta R_H$  underwent a slow relaxation, increasing slightly in magnitude over 10 to 20 h. As a consequence, we allowed all samples reported here to age for 2 days at room temperature prior to DLS measurements. Samples of latex and block copolymer were pipetted into a centrifuge tube and diluted to 10 mL with water, mixed, capped, and set aside. Just prior to the DLS measurements the samples were centrifuged at 11 000 rpm for 2 h to remove dust. These conditions do not sediment either the latex or the micelles.

### Results and Discussion

The PEO-PS diblock copolymer samples examined here rapidly form micelles in hot water with cmc values at 22 °C of the order of 1-2 mg/L.<sup>7</sup> At room temperature they undergo slow equilibration in water.<sup>14</sup> These results are consistent with a rather stiff micellar core. We do not have a direct measure of the glass transition temperature ( $T_g$ ) of the micelle core, expected to be significantly smaller than 100 °C because of the small size of the core and the short PS block length.<sup>15</sup> Dilution experiments from which the cmc values were determined indicate that equilibration occurs on a time scale of a day.<sup>7</sup> On the other hand, size exclusion chromatography experiments in water indicate negligible exchange on a time scale of 10-20 min.<sup>14b</sup> The observation which stimulated the experiments reported here is that within seconds of mixing a micellar solution of PS-PEO with a PS latex dispersion, adsorption of the diblock copolymer takes place.<sup>8</sup> A reasonable explanation for this rapid adsorption is that it involves direct association of the micelles with latex through an attractive interaction between the PEO corona chains and the PS latex surface.

We examine two types of polystyrene latex particles. Samples L69 and L83 contain sulfate groups on the surface. One sees in Table II that the mean diameters determined by transmission electron microscopy (TEM) are nearly identical to those determined by DLS. Samples L100C, L109C, and L131C contain surface carboxylate groups. These particles are slightly swollen in distilled water, as indicated by the ca. 8% increase in particle diameter observed by DLS compared to TEM.

While one might anticipate that these surface characteristics might strongly influence block copolymer adsorption, size exclusion chromatography (SEC) experiments suggest that there is little influence. For both sets of latex, the adsorption is instantaneous on the time scale of seconds. An example is shown in Figure 2 where we compare the SEC profile obtained upon mixing latex and block copolymer in the barrel of the syringe just prior to sample injection with that after the solutions were mixed and allowed to stand 14 h.

(14) (a) Xu, R.; Oliveira, J.; Winnik, M. A.; Riess, G.; Martinho, J.; Croucher, M. D. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 1992, 51, 135. (b) Xu, R.; Hu, Y.; Winnik, M. A.; Riess, G.; Croucher, M. D. *J. Chromatogr.* 1991, 547, 434.

(15) Tucker, P. S.; Barlow, J. W.; Paul, D. R. *Macromolecules* 1988, 21, 2794.

(13) Dawkins, J. V.; Taylor, G. J. *Chem. Soc., Faraday Trans. 1* 1980, 76, 1263.



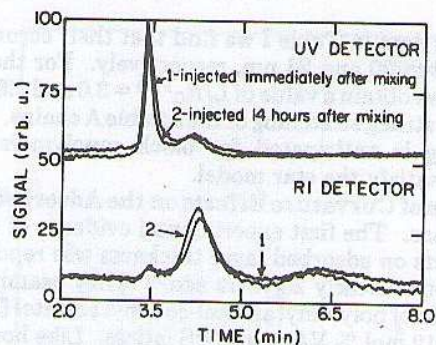


Figure 2. SEC traces of the system ZGH5 + latex L223 (sulfate surface groups,  $d_{\text{DLS}} = 223$  nm,  $d_{\text{EM}} = 202$  nm). The peak at 3.4 min is due to the latex and that at 4.3 min is due to the micelle. For experimental details see ref 8.

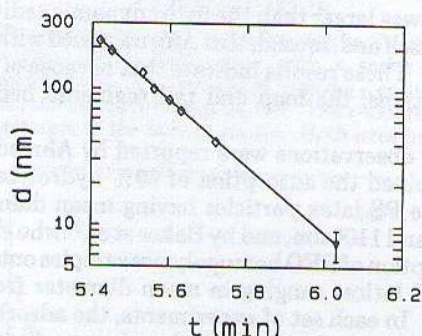


Figure 3. A plot of latex diameter versus the retention time from chromatograms of mixtures of a diblock copolymer. JLM5 ( $M_{\text{PS}} = 1700$ ,  $M_{\text{PEO}} = 6800$ ) and latex particles of different diameters in aqueous media. The diamond symbols represent the copolymer-stabilized latices and the inverted triangle at  $t = 6.03$  min refers to the copolymer micelle. The error bar on the extrapolated value of  $d$  at  $t = 6.03$  min was calculated from  $d_{\text{max}}$  and  $d_{\text{min}}$  values based upon the assumption that  $d = (a \pm \Delta a) \exp[-(b \pm \Delta b)(t \pm \Delta t)]$ , where  $a$  and  $b$  are arbitrary fitting parameters. Flow rate = 0.8 mL/min.

None of the latex samples elute from the SEC column in the absence of surfactant. Sharp peaks are obtained with PS particles exposed to excess surfactant such as sodium dodecyl sulfate (SDS) or to block copolymers. For a given PS-PEO block copolymer and a series of latex particles, the retention time varies systematically with latex diameter, Figure 3. This variation is independent of the surface characteristics of the latex itself. We rationalize this finding by suggesting that the interaction energy between the PS anchor block and the PS latex is sufficient to dominate over other interactions, including functional groups at the latex surface, in the binding process.

When block copolymer adsorbs to the latex surface, the hydrodynamic radius of the particle increases. If micelles adsorbed to the surface underwent no further rearrangement, the increase in radius,  $\Delta R_{\text{H}}$ , would be on the order of twice the micelle radius,  $2r_{\text{M}}$ . The particle radii we determine by DLS (Table II) are always larger than that  $r_{\text{L}}$  of the bare latex but smaller than  $(r_{\text{L}} + 2r_{\text{M}})$ . These observations indicate that the block copolymer distributes itself along the latex surface with the PS block in contact with the latex and also that the surface density of chains adsorbed to the latex surface is smaller than that in the micelle.

A similar slow relaxation is also observed in DLS experiments. In Figure 4 we show our best data for changes in the adsorbed layer thickness,  $\Delta R_{\text{H}}$ , as a function of the weight ratio of block copolymer to latex. Here we show a PEO-PS-PEO triblock copolymer and see that the

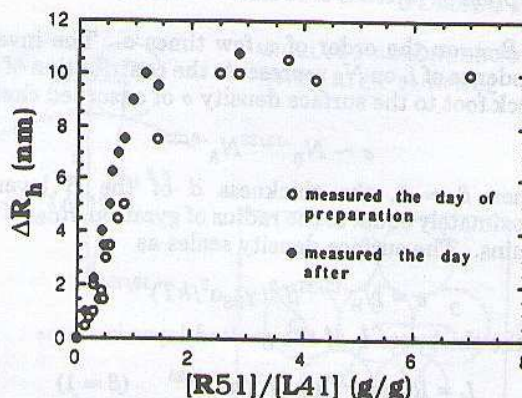


Figure 4. A plot of the adsorbed layer thickness as a function of the block copolymer to latex ratio. R51 refers to a PEO-PS-PEO triblock copolymer ( $M_{\text{PS}} = 1800$ ,  $M_{\text{PEO}} = 2 \times 9000$ ,  $M_{\text{w}}/M_{\text{n}} = 1.4$ ), and L41 to a latex with surface carboxyl groups,  $d_{\text{EM}} = 38$  nm,  $d_{\text{DLS}} = 41$  nm. Reproduced with permission from ref 14a. Copyright 1992 Wiley.

increase in  $\Delta R_{\text{H}}$  that occurs over 24 h is confined to the steeply growing preplateau region of the plot.

**Theory of Block Copolymer Adsorption.** Current descriptions of chains attached at one end to a surface follow ideas originally presented by Alexander.<sup>16</sup> These have been applied to the case of block copolymer adsorption by Marques et al.<sup>17</sup> They consider the adsorption of an A-B diblock copolymer from solution onto a surface selective for B. The A block is considered to be repelled by the surface, and in the case most appropriate for our experiments, the solvent is strongly selective for the A chains.

For typical situations where the asymmetry ratio  $\beta = N_{\text{A}}^{3/5}/N_{\text{B}}^{1/2}$  is larger than unity, the surface is flat and solid, and the surface density of chains ( $\sigma$ ) is high enough that the soluble chains are stretched, the equilibrium layer thickness  $L$  is given by the expression

$$L = N_{\text{A}} a \sigma^{1/3} \quad (1)$$

If the chain spacing is determined by chemical grafting onto the surface, then the polymer brush thickness  $L$  increases linearly with  $N_{\text{A}}$ . When block copolymers adsorb to the surface, repulsions between adjacent chains affect the magnitude of  $\sigma$ , leading to decreased dependence of  $L$  on  $N_{\text{A}}$ . When adsorption takes place from solution, two regimes dominate the adsorption process at equilibrium.<sup>17</sup> When  $\beta \approx 1$ , the adsorption is governed by the elastic energy of the swollen buoys of A chains. When  $\beta \gg 1$ , the geometry of the adsorbed copolymer results from a balance between the van der Waals forces and the buoy layer elastic energy.

In the theory of Marques et al.,<sup>17</sup> micelles are treated only as a reservoir of block copolymers. The chemical potential of the block copolymer driving adsorption is only that of the free chains in solution. Its magnitude is determined by the critical micelle concentration of the system, which is normally very small for polymers in which the B-blocks are immiscible with the solvent. For  $\beta \gg 1$ , strong interaction between adjacent A chains induces substantial stretching and

$$L = a N_{\text{A}}^{21/23} N_{\text{B}}^{-4/23} \quad (\beta \gg 1) \quad (2)$$

$L$  is almost linear in  $N_{\text{A}}$ . In this regime,  $d$  is much smaller

(16) For a review, see Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* 1991, 100, 1.

(17) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* 1988, 21, 1051.



than  $R_{GB}$ , on the order of a few times  $a$ . The inverse dependence of  $L$  on  $N_B$  represents the contribution of the B-block foot to the surface density  $\sigma$  of adsorbed chains.

$$\sigma \sim N_B^{-12/23} N_A^{-6/23} \quad (3)$$

When  $\beta \approx 1$ , the thickness  $d$  of the B layer is approximately equal to the radius of gyration,  $R_{GB}$ , of the B chains. The surface density scales as

$$\sigma = N_B^{-13/25} \beta^{-2} (\gamma_{BS} a^2 / kT)^{18/25} \quad (4)$$

and the thickness  $L$  of the grafted layer is

$$L = R_{FA} N_B^{4/25} (\gamma_{BS} a^2 / kT)^{6/25} \quad (\beta \approx 1) \quad (5)$$

where  $a$  is the size of a monomer,  $\gamma_{BS}$  is the B/solvent interfacial energy, and  $R_{FA}$  is the root-mean-square end-to-end distance of the A chains in the presence of solvent.

These chains have the same dependence on  $N_A$  as the Flory radius, but  $L$  is much larger than  $R_{FA}$  because of the dependence on  $N_B$ .  $L$  in eq 5 has the same dependence on polymer properties as does the micelle corona radius  $L_M$

$$L_M = R_{FA} N_B^{4/25} (\gamma_{BS} a^2 / kT)^{6/25} \quad (6)$$

even though for this range of  $\beta$  values the density of chains at the surface of the micelle core is slightly larger than that described in eq 4 for surface-bound chains.

$$\sigma_M = N_B^{-2/5} (\gamma_{BS} a^2 / kT)^{2/5} \quad (7)$$

We are primarily interested in block copolymers in which the soluble chains are significantly longer than the insoluble chains: i.e.  $\beta \gg 1$ . In this regime (cf. eq 2),  $L$  is predicted to be larger than the micelle corona thickness,  $L_M$ . We find experimentally that  $\Delta R_H$ , which we can identify with  $L$  for the adsorbed chains, is smaller than  $L_M$ .

For adsorption onto curved surfaces  $L$  depends upon  $\sigma$  and, for small spheres, the radius of curvature  $r_L$ : in fact, the equations reduce to those describing either the corona thickness of a star micelle (eq 8a) or the brush thickness for adsorption onto a flat surface (eq 8b).

$$L = R_{FA} (\sigma r_L^2)^{1/5} \quad \text{if } L \gg r_L \quad (8a)$$

$$L = N_A \sigma^{1/3} \quad \text{if } L \ll r_L \quad (8b)$$

**Chain Stretching in the Micelle.** PS-PEO diblock and triblock copolymers containing in excess of 60 wt % PEO form micelles in water that satisfy the star model<sup>18</sup> of the micelle structure.<sup>5,6</sup> In this model, coil repulsions between the soluble A chains should lead to significant coil extension. To assess the magnitude of chain stretching, one needs to compare the corona thickness of the micelle with the coil dimensions of isolated PEO chains. These values for PEO in water have only recently become available, thanks to the extremely careful light scattering experiments reported by Devanand and Sesler.<sup>19</sup> At 30 °C in water they obtained the result

$$R_G = 0.215 M_w^{0.583} \text{ (Å)} \quad (9)$$

Our samples fall outside the range of samples used to obtain eq 9. By extrapolation to molecular weights comparable to the PEO components of samples ZGH4 ( $M_{PEO} = 18\,400$ ) and ZGH5 ( $M_{PEO} = 28\,800$ ) we calculate radii of gyration of 6.6 and 8.6 nm, respectively. Micelles from both samples in water have core radii of 6 nm.

From the data in Table I we find that their corona radii are equal to 20 and 24 nm, respectively. For these two samples we obtain a value of  $L/R_G^{PEO} = 3.0$  and 2.8, which indicates strong stretching of the soluble A chains. Strong stretching is anticipated for block copolymers whose micelles satisfy the star model.

**Radius of Curvature Effects on the Adsorbed Layer Thickness.** The first experimental evidence of particle size effects on adsorbed layer thickness was reported by Garvey et al. nearly 20 years ago.<sup>20</sup> They examined the adsorption of poly(vinyl alcohol-co-vinyl acetate) (PVOH-PVAc, 0.12 mol % VAc) onto PS latices. Like homopolymers, one expects PVOH-PVAc to adsorb onto the PS surface, with the more hydrophobic VAc groups adsorbed preferentially. Two important observations emerged from this work. First, they found that the adsorbed layer thickness was larger than the hydrodynamic radius of the polymer itself and, second, that  $\Delta R_H$  increased with particle diameter. These results indicate that because of packing considerations, the loop and tail segments become extended.

Similar observations were reported by Ahmed et al.,<sup>21</sup> who examined the adsorption of 99% hydrolyzed PVAc onto three PS latex particles having mean diameters of 190, 400, and 1100 nm, and by Baker et al.<sup>22</sup> who examined the adsorption of PEO homopolymer samples onto a series of five PS latices ranging in mean diameter from 58 to 1100 nm. In each set of experiments, the adsorbed layer thickness increased with  $r_L$ , but there is some disagreement about the factors which affect the magnitude of change in  $\Delta R_H$  with increasing  $r_L$ . Baker et al.,<sup>22</sup> for example, point to slow relaxation processes which occur in PEO adsorption. They suggest that closer packing of chains occurs on surfaces with larger  $r_L$ , and this in turn precludes access of extended PEO tail segments to surface regions of the latex.

Baker et al.<sup>22</sup> also examined the adsorption of a series of Pluronic ABA triblock copolymers onto the same set of PS latex particles. The Pluronics are relatively low molecular weight commercial materials manufactured by BASF Wyandotte Corp. and contain a poly(propylene oxide) (PPO) center block with PEO ends. At room temperature and at low concentrations, these materials are largely present as unimers rather than as micelles. They adsorb readily onto hydrophobic surfaces. In the experiments reported by Baker,  $\Delta R_H$  seemed to decrease as  $r_L$  increased. The differences were so close to experimental error that they preferred not to insist too strongly on this result.

There is a curious contradiction between the Baker result<sup>22</sup> and similar experiments with similar samples of Pluronics reported by Tan's group at Kodak.<sup>23</sup> They found larger values of  $\Delta R_H$  for the polymers on the PS latex of 85 nm diameter than on the sample of 305-nm diameter. Their explanation for the radius of curvature effect is that on the larger particle, the PEO chains may have more easy access to the PS surface, where the chain ends could loop back to the surface, decreasing the tail extension.

Our experiments differ from the Baker<sup>22</sup> and Tan<sup>23</sup> experiments in that PS-PEO adsorption occurs directly

(20) Garvey, M. J.; Tadros, Th. F.; Vincent, B. J. *Colloid Interface Sci.* 1974, 41, 57; 1976, 55, 440.

(21) Ahmed, M. S.; El-Aasser, M. S.; Vanderhoff, J. W. In *Polymer Adsorption and Dispersion Stability*; Goddard, E. D., Vincent, B., Eds.; ACS Symposium Series 240; American Chemical Society: Washington, DC, 1984; p 77.

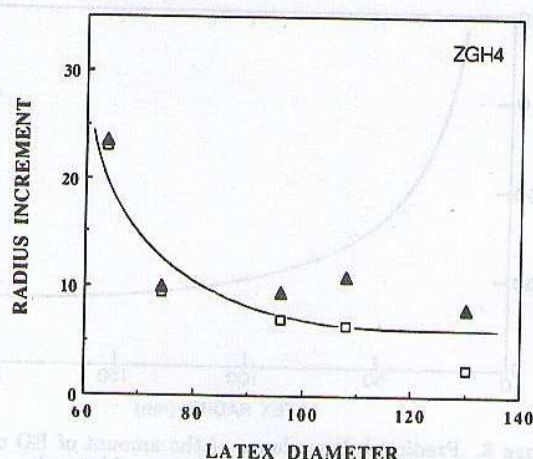
(22) Baker, J. A.; Pearson, R. A.; Berg, J. C. *Langmuir* 1989, 5, 339.

(23) (a) Lee, J.; Martic, P. A.; Tan, J. S. *J. Colloid Interface Sci.* 1989, 131, 252. (b) Tan, J. S.; Martic, P. A. *J. Colloid Interface Sci.* 1990, 136, 415.

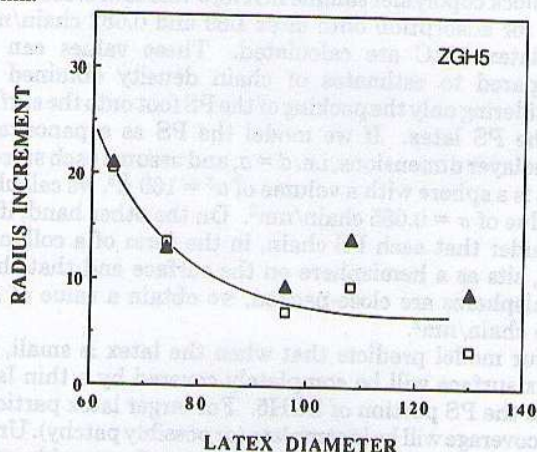
(18) Halperin, A. *Macromolecules* 1987, 20, 2943.

(19) Devanand, K.; Sesler, J. C. *Macromolecules* 1991, 24, 5943.





**Figure 5.** Plot of the measured hydrodynamic radius increment  $\Delta R_H$  for polymer ZGH4 interacting with a series of latex particles: open squares,  $\Delta R_H$  calculated from  $d_{DLS}$ , eq 10a; closed triangles,  $\Delta R_H$  calculated from  $d_{EM}$ , eq 10b. The x-axis represents the DLS diameters of the bare particles. Both axes have units of nm.

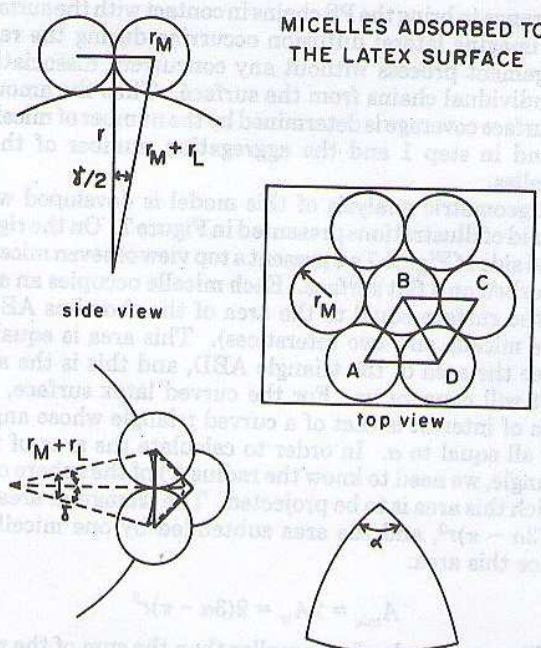


**Figure 6.** Plot of  $\Delta R_H$  vs particle diameter for experiments identical to those shown in Figure 4 except that here the polymer is ZGH5.

from the micelles. This is a consequence of the much lower cmc values for PS-PEO block copolymers in water than for PEO-PPO-PEO. We find that addition of micellar PS-PEO block copolymer solutions in water to PS latex dispersions leads to a rapid increase in hydrodynamic radius of the latex. These values of  $\Delta R_H$  vary from 20 nm for our smallest latex sample to ca. 5 nm for the largest latex sample. In Figure 5 we plot  $\Delta R_H$  vs  $r_L$  for the interaction of ZGH4 with the various latex samples listed in Table II, and in Figure 6 we plot the corresponding data for ZGH5. In every case  $\Delta R_H$  is much smaller than  $R_H$  (micelle), indicating that the block copolymers spread onto the latex surface. Our most significant observation is that  $\Delta R_H$  decreases as the latex diameter increases.

One of the ambiguities in interpreting these results is the role of the surface carboxyl functions present in samples L100C, L109C, and L131C. Without quantitative binding isotherms,<sup>24</sup> we cannot determine if these functional groups affect the amount of block copolymer adsorbed. We suspect from our SEC results (Figure 3) that this effect is minor. Of great concern to us is the appropriate value of  $r_L$  to employ in calculating  $\Delta R_H$ . In samples L69 and L83, the values of  $d_{EM}$  and  $d_{DLS}$  are essentially identical

(24) Traditional centrifugation experiments to separate latex from supernate are rendered much more difficult because of the tendency of the micelles to sediment under conditions appropriate for sedimenting the latex.



**Figure 7.** Side view and top view of micelles adsorbed in a close-packed configuration on a spherical surface showing the angle  $\gamma$  subtended by adjacent micelles and the effective area occupied by one micelle.

so that either value could be used to compute  $\Delta R_H$ . For the other three samples,  $d_{DLS}$  is about 8% larger than  $d_{EM}$ . If the block copolymer adsorbs onto the bare PS latex surface, possibly accompanied by collapse of the swollen carboxylated polymer, then we should use  $d_{EM}$  to calculate  $\Delta R_H$ . In Figures 5 and 6 we denote with open squares values of  $\Delta R_H$  calculated as

$$\Delta R_H = \frac{1}{2}(d_{DLS}(\text{latex} + \text{block}) - d_{DLS}(\text{latex})) \quad (10a)$$

and closed triangles to denote values

$$\Delta R_H = \frac{1}{2}(d_{DLS}(\text{latex} + \text{block}) - d_{EM}(\text{latex})) \quad (10b)$$

In both instances,  $\Delta R_H$  values decrease with increasing latex diameter. This result is also found for the two samples lacking carboxyl groups at the surface. Thus, in spite of the ambiguities caused by surface functionalization, the radius-of-curvature effect is real and needs to be explained. It is important to recognize that equilibrium theories of chain adsorption cannot account for this result. If the surface area per chain  $\sigma$  were constant, eqs 8a and 8b would predict that  $L$  would decrease as  $r_L$  decreases since the greater curvature reduces the interactions between adjacent coils that lead to chain extension. Enhanced buoy interactions on surfaces of low curvature will lead to an increase in the spacing between chains, so that at equilibrium one expects a smaller dependence of  $L$  on  $r_L$ . These theories cannot accommodate the result that  $L$  increases as  $r_L$  decreases.

**A Kinetic Micelle Adsorption Model.** We imagine a kinetic adsorption model along the lines of that depicted at the left-hand side of Figure 7. Because of a weak but attractive interaction between the bare latex surface and the PEO corona chains,<sup>22</sup> micelles rapidly adsorb onto the latex surface. Subsequent to adsorption, individual micelles might rearrange to generate surface-bound hemimicelles similar to that described in the recent theoretical treatment of Ligoure.<sup>25</sup> Alternatively, the micelles might self-adjust on the surface, and then, in a much slower step,

(25) Ligoure, C. *Macromolecules* 1991, 24, 2968.



rearrange to bring the PS chains in contact with the surface. We imagine lateral diffusion occurring during the rearrangement process without any concurrent dissociation of individual chains from the surface. Thus the amount of surface coverage is determined by the number of micelles bound in step 1 and the aggregation number of these micelles.

A geometric analysis of this model is developed with the aid of illustrations presented in Figure 7. On the right-hand side of Figure 7 we present a top view of seven micelles adsorbed on a flat surface. Each micelle occupies an area on the surface equal to the area of the rhombus ABCD (one micelle and two interstices). This area is equal to twice the area of the triangle ABD, and this is the area that will concern us. For the curved latex surface, the area of interest is that of a curved triangle whose angles are all equal to  $\alpha$ . In order to calculate the area of this triangle, we need to know the radius ( $r$ ) of the sphere onto which this area is to be projected. The triangular area  $A_{tr} = (3\alpha - \pi)r^2$ , and the area subtended by one micelle is twice this area.

$$A_{mic} = 2A_{tr} = 2(3\alpha - \pi)r^2 \quad (11)$$

The magnitude of  $r$  is smaller than the sum of the radii  $r_L + r_M$  but related to those radii by

$$r = [(r_M + r_L)^2 - r_M^2]^{1/2} \quad (12)$$

From trigonometry we find<sup>26</sup>

$$\cos \alpha = \frac{\cos \gamma - \cos^2 \gamma}{\sin^2 \gamma} \quad (13)$$

where

$$\gamma = 2 \sin^{-1} \left( \frac{r_M}{r_M + r_L} \right) \quad (14)$$

The number of micelles which can adsorb onto a latex of radius  $r_L$  is

$$N_s = \frac{A_{sphere}}{A_{micelle}} = \frac{2\pi}{3\alpha - \pi} \quad (15)$$

The number of block copolymers per unit area is related to  $\alpha$  by

$$\sigma = \frac{f}{2(3\alpha - \pi)r_L^2} \quad (16)$$

where  $f$  is the aggregation number of the micelle. In fact,  $\sigma$  increases as  $r_L$  decreases, but this is not immediately apparent in eq 16, since  $\alpha$  itself is a function of  $(r_L/r_M)$  and decreases as  $r_L$  increases. This model provides an explanation for the type of results observed here: for a micelle of fixed  $r_M$  exposed to a series of latex particles varying in  $r_L$ , a decrease in  $r_L$  will lead to an increase in  $\sigma$ , and from eq 6, will lead in turn to an increase in  $L$ .

Our model allows us to calculate the number of polymer chains per unit surface area ( $\sigma$ ) adsorbed onto latex

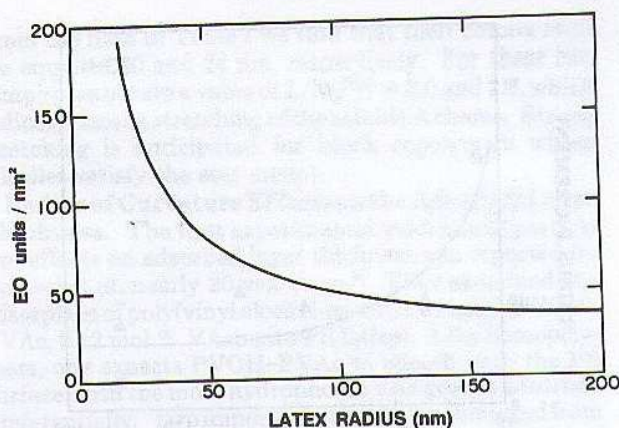


Figure 8. Predicted dependence of the amount of EO units adsorbed for a given micelle, as a function of latex diameter, based upon the model presented in the text. In this example, we chose  $r_M = 30$  nm,  $N_{PS} = 40$ ,  $N_{PEO} = 700$ , and an aggregation number of 130.

particles of various diameters, as shown in Figure 8. For the block copolymer sample ZGH5,  $\sigma$  values of 0.125 chain/nm<sup>2</sup> for adsorption onto latex L69 and 0.082 chain/nm<sup>2</sup> for latex 131C are calculated. These values can be compared to estimates of chain density obtained by considering only the packing of the PS foot onto the surface of the PS latex. If we model the PS as a pancake of monolayer dimensions, i.e.  $d = a$ , and assume each styrene unit is a sphere with a volume of  $a^3 = 160$  Å<sup>3</sup>, we calculate a value of  $\sigma = 0.085$  chain/nm<sup>2</sup>. On the other hand, if we consider that each PS chain, in the form of a collapsed ball, sits as a hemisphere on the surface and that these hemispheres are close-packed, we obtain a value of  $\sigma = 0.15$  chain/nm<sup>2</sup>.

Our model predicts that when the latex is small, the latex surface will be completely covered by a thin layer from the PS portion of ZGH5. For larger latex particles, the coverage will be incomplete (or possibly patchy). Under these conditions, portions of the latex surface would remain exposed to the solvent and allow some of the PEO chains to loop back onto the surface. Lee et al.<sup>23a</sup> suggested the possibility of PEO chains looping back to adsorb onto exposed patches of the surface in the binding of PEO-PPO-PEO triblock copolymers to PS latex particles in water.

To test our model, it will be important to measure the amount of block copolymers adsorbed. We have not yet been able to measure binding isotherms with sufficient accuracy to comment on this prediction of the model, but experiments in this direction are in progress.<sup>24</sup> Equations 13–15 break down as the micelle radius approaches that of the latex. As  $r_M \rightarrow r_L$ , the number of interstices excluded by each micelle decreases as the interstices increase in size. Equation 14 is correct to within 5% for  $r_L \geq r_M$ , and hence a reasonable approximation for systems examined here. Nevertheless, it may be interesting in the future to examine the situation where the micelle radius actually exceeds that of the latex.

**Acknowledgment.** The Toronto authors thank NSERC Canada and the Province of Ontario for their support of this research.

(26) A Chinese handbook of mathematics gives the expression  $\tan(\alpha/4) = [(\tan(3\gamma/2))(\tan^2(\gamma/2))]^{1/2}$ , which gives a numerical relationship between  $\alpha$  and  $\gamma$  very close to that of eq 13, except in the vicinity of  $\gamma = 2\pi$  and  $2\pi/3$ , where the  $\tan(\alpha/4)$  equation is singular.