Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) Adsorption in the Buoy-Dominated Regime

Jian Tao, Andrew Guo, Sean Stewart, Viola I. Birss, and Guojun Liu*

Department of Chemistry, The University of Calgary, 2500 University Drive, NW, Calgary,
Alberta, Canada T2N 1N4

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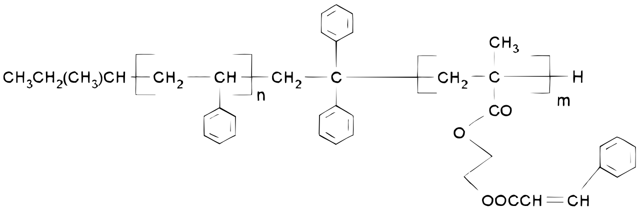
ABSTRACT: Eleven polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) samples with molar masses varying over 30-fold were prepared and characterized. Each of the samples had approximately equal styrene and CEMA lengths. Ten of the samples formed stable micelles in THF/cyclopentane (CP) with 82% of CP by volume. The micelles deposited from the THF/CP mixture to form brushes on silica surfaces. The adsorption data of the seven samples having relatively high molar masses followed the theoretical scaling relation derived by Marques et al. for diblock adsorption from micellar solution in the buoy-dominated regime.

I. Introduction

In a block-selective solvent, which is good for one block but poor for the other, a diblock copolymer may deposit out on a solid substrate that contacts the polymer solution. If the interaction between the insoluble block and the solid substrate is favorable, a dense polymeric monolayer, a polymer brush, may form. In a polymer brush, the insoluble block spreads on the solid substrate like a melt and the soluble block stretches into the solution phase like bristles of a brush (Figure 1).[1−3]

Several groups have studied diblock adsorption in block-selective solvents.[4−10] Work before ours was mainly concerned with diblock adsorption in dilute solutions in which polymer chains existed as unimolecular micelles or unimers.[4−7] Diblock adsorption on silica surfaces occurred in our study in relatively concentrated polymer solutions in which diblocks existed as micelles. The diblock copolymers we used were polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA), and the solvents were THF/cyclohexane or THF/cyclopentane (CP) mixtures in which PS existed as the corona of the micelles.[8−10]



PS-*b*-PCEMA

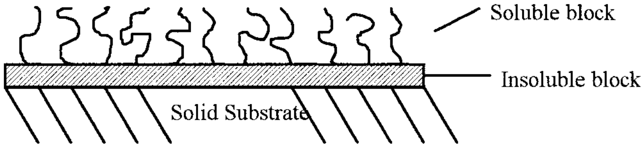


Figure 1. Polymer brush illustrated.

Due to the use of micellar solutions, our adsorption data[8−9] followed scaling relations different from that established previously.[4−7] The scaling relations followed by our data depended on the asymmetric ratios, β, of the samples defined by

$$\beta = n^{3/5}/m^{1/2} \tag{1}$$

where n and m are the number of styrene and CEMA units in a diblock, respectively. For β larger than 4,[8] the number of chains adsorbed on unit silica surface area, ρ_∞, for 14 PS-*b*-PCEMA samples covering a 30-fold variation in m, followed a scaling relation derived by Marques et al.[11] for block copolymer adsorption from a micellar solution in the van der Waals−buoy regime with

$$\rho_\infty \propto m^{-(17/23)}\beta^{-(10/23)} \tag{2}$$

For samples with $\beta \approx 1$, Marques et al.[11] predicted that ρ_∞ should fall in the buoy-dominated regime with

$$\rho_\infty \propto m^{-(13/25)}\beta^{-2} \tag{3}$$

Since the adsorption data, ρ_∞, of only three of a series of four samples with $\beta \approx 1$ that we examined previously fell on a straight line when plotted versus $m^{-13/25}\beta^{-2}$, we could conclude only qualitatively that the ρ_∞ values followed eq 3.[9] The present study was aimed at a more rigorous testing of eq 3 with the use of a total of 11 samples. The fact that the adsorption data of the new series spanning a much wider range of $m^{-13/25}\beta^{-2}$ values could be described by eq 3 demonstrates unambiguously the validity of eq 3.

II. Experimental Section

Polymer Synthesis and Characterization. The procedures for PS-*b*-PCEMA synthesis and characterization have been described many times previously[8,12] and will thus not be repeated here. The precursors to PS-*b*-PCEMA were synthesized by anionic polymerization. GPC, calibrated using polystyrene standards, was used to obtain the polydispersity of the samples. The styrene to CEMA repeat unit ratio, n/m, was determined using ^{1}H NMR. The specific refractive index increment, dn_r/dc, of a diblock with a PS weight fraction of w_{PS} in toluene, at 633 nm, was calculated using the following

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Table 1. Characteristics of PS-*b*-PCEMA Polymers[a]

sample *n*-*m*	(*n*/*m*) by NMR	$\bar{M}_w/\bar{M}_n$ by GPC	$10^{-4}\,\bar{M}_w$ by GPC	$10^{-4}\,\bar{M}_w$ by LS
44-33	1.32	1.20	0.88	1.31
75-43	1.73	1.14	1.3	1.90
90-51	1.76	1.14	1.3	2.26
110-60	1.80	1.13	1.78	2.72
179-153	1.17	1.14	4.2	5.8
237-125	1.90	1.11	3.4	5.7
278-154	1.82	1.08	5.2	6.9
4.3×10^2-191	2.24	1.11	6.1	9.4
7.7×10^2-8.5×10^2	0.91	1.06	17.9	30.3
1.08×10^3-1.16×10^3	0.93	1.10	31.7	41
12.9×10^2-6.2×10^2	2.07	1.10	24.4	29.6

[a] Symbols *n* and *m* denote the number of styrene and CEMA units in a polymer, respectively.

empirical relationship[9]

$$\mathrm{d}n_r/\mathrm{d}c = 0.0938 + 0.0299w_{\mathrm{PS}} - 0.0115{w_{\mathrm{PS}}}^2\ \mathrm{mL/g} \tag{4}$$

The absolute weight-average molar masses were measured in toluene using a Brookhaven model 9025 light-scattering instrument. Due to the close match between the specific refractive index increments of PCEMA and PS relative to toluene, the apparent diblock molar masses obtained following the Zimm method were not corrected further.[13]

Adsorption Data. The method for preparing PS-*b*-PCEMA coating solutions has been described previously.[8,9] All coating studies were carried out in THF/CP mixtures with 82% CP by volume. The amount of polymer adsorbed was determined by monitoring the decrease in PS-*b*-PCEMA concentration after a PS-*b*-PCEMA solution was stirred with a known weight, w_s, of silica. UV absorption at 274 nm was used to follow the PS-*b*-PCEMA concentration change. The silica used was nonporous Aerosil Ox 50 from Degussa with a specific surface area of 50 m^2/g. The initial PS-*b*-PCEMA concentration used was typically ~15 mg/mL, and the equilibrium polymer concentration was always higher than 3 mg/mL.

The silica surface coverage, i.e., the polymer weight adsorbed per unit area, was calculated with:

$$\sigma = \frac{w_{\mathrm{a}}}{50 \times 10^4\ \mathrm{cm}^2/\mathrm{g} \times w_{\mathrm{s}}} \tag{5}$$

where w_a is the weight of PS-*b*-PCEMA adsorbed, established from UV spectrophotometry. For equilibrium surface coverage, σ_{eq}, determination, silica was stirred with a polymer solution for 1 week before the amount of polymer adsorbed was determined.

III. Results and Discussion

Polymer Characterization Results. The molar mass determined from light scattering and the *n*/*m* value determined from NMR were used to calculate the number of styrene and CEMA units, *n* and *m*, for a polymer. A specific polymer is denoted by *n* and *m* separated by a hyphen in this paper (Table 1). All of our samples had narrow molecular weight distributions, as indicated by their low polydispersity indices determined by GPC. Since the GPC column was calibrated using monodisperse PS standards, the weight-average molar masses of the diblocks determined from this technique are included in Table 1 only to provide a check against the light scattering data.

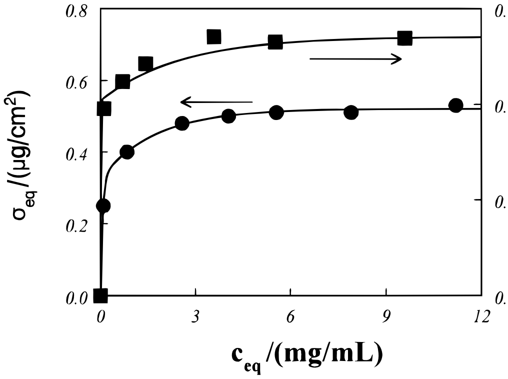

Figure 2. Isotherms of 109-61 (■) and 4.3×10^2-191 (●) adsorption by silica.

Table 2. Data of PS-*b*-PCEMA Adsorption by Silica (f_{cp} = 0.82)

sample *n*-*m*	β	σ_∞ (μg/cm^2)	$10^{-12}\,\rho_\infty$ (chains/cm^2)	(ρ_∞/ρ^*)	*e*/Å
75-43	2.03	0.36	11.4	2.11	21
90-51	2.08	0.32	8.5	1.95	19
110-60	2.14	0.48	10.6	3.1	26
179-153	1.82	1.27	13.1	6.8	86
237-125	2.38	0.60	6.3	4.3	34
278-154	2.36	0.66	5.7	5.0	45
4.3×10^2-191	2.74	0.70	4.5	6.0	38
7.7×10^2-8.5×10^2	1.86	1.86	3.7	12.0	135
1.08×10^3-1.16×10^3	1.94	2.67	3.9	15.0	195
12.9×10^2-6.2×10^2	2.94	1.10	2.3	11.5	60

Polymer Adsorption Data. Illustrated in Figure 2 are the adsorption isotherms of 109-61 and 4.3×10^2-191, in which the equilibrium surface coverages, σ_{eq}, are plotted against c_{eq}, the concentration of the polymer solution in contact with silica at adsorption equilibrium. As is obvious from Figure 2, σ_{eq} initially increases sharply with c_{eq} and levels off for c_{eq} larger than ~3 mg/mL. This trend is in agreement with those observed for other samples we have studied.[8,9]

To compare the surface coverages of different polymers, we determined the maximum σ_{eq} of each sample, i.e., σ_∞. Since all isotherms are expected to level off, the isotherms of the other PS-*b*-PCEMA samples were not measured. Instead, σ_{eq} was determined at a sufficiently high c_{eq}, e.g., greater than 3 mg/mL, to approximate σ_∞.

Polymer Brush Formation from PS-*b*-PCEMA on Silica. The brush conformation of PS-*b*-PCEMA, as illustrated in Figure 1, requires that PCEMA anchors on the silica and that the PS chains stretch into the solution phase. The adsorption of PS-*b*-PCEMA, under our conditions, mainly via the PCEMA block has been established previously by our transmission electron microscopy and surface-enhanced Raman scattering studies.[10] Unfortunately, we could not determine the magnitude of PS chain stretching, although it can be shown that the PS chains in the buoy layer are crowded. In a crowded PS layer, the chains should be extended, as the neighboring chains repel one another.

To show that the PS chains are crowded, the surface coverage, ρ_∞, in terms of the number of chains adsorbed on unit silica surface area for a sample was evaluated. Then calculated was the critical surface coverage, ρ^*, at which the chains of the PS buoy layer begin to overlap. If ρ_∞/ρ^* is considerably larger than 1, the PS chains are crowded. ρ_∞ can be calculated from the σ_∞ values listed in Table 2 with

$$\rho_\infty = \frac{\sigma_\infty}{\bar{M}_{\mathrm{w}}} N_{\mathrm{A}} \tag{6}$$

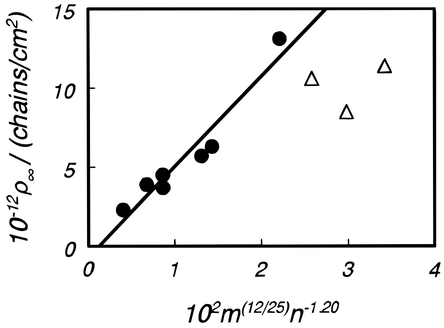

Figure 3. Plot of ρ_∞ vs $m^{-(13/25)}n^{-1.20}$ for a range of PS-*b*-PCEMA samples. The solid line represents the best fit to the ρ_∞ data except those (△) of 75-43, 90-51, and 109-61.

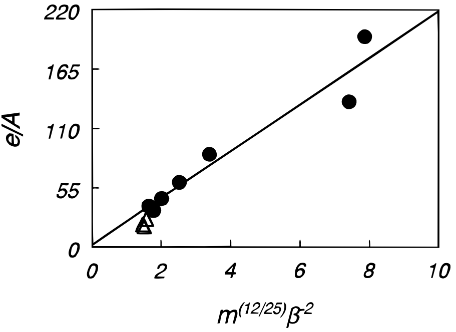

Figure 4. Plot of PCEMA layer thickness, *e*, vs $m^{(12/25)}\beta^{-2}$. The solid line represents the best fit to the ρ_∞ data, except those (△) of 75-43, 90-51, and 109-61.

where N_A is Avogadro's constant and $\bar{M}_w$ are the weight-average molar masses of the diblocks. The formula for ρ^* evaluation is

$$\rho^* = \frac{1}{\pi R_{\mathrm{GPS}}{}^2} \tag{7}$$

where R_{GPS} is the radius of gyration of the PS block in a dilute solution. We did not determine R_{GPS} for our samples in THF/CP with $f_{\mathrm{CP}} = 0.82$. Instead, we used

$$R_{\mathrm{GPS}} = 1.86n^{0.595}\ (\text{Å}) \tag{8}$$

which is valid for PS in toluene,[14] to estimate the ρ^* values. Since the ρ_∞/ρ^* values for the majority of our samples, except those with low molar masses, are all considerably larger than 1 (Table 2), we deduce that the PS chains are stretched. Thus, the PS-*b*-PCEMA polymers are adsorbed in the brush conformation in the present work.

Verification of the Theory of Marques et al. for the Buoy-Dominated Regime. Of the 11 samples studied, 44-33 did not form stable micelles in THF/CP with 82% CP. The formation of micelles for the other samples was demonstrated by the bluish tinge of the solutions. Since our polymers were designed to have β values close to 1 (Table 2), ρ_∞ should follow eq 3, the scaling relation derived by Marques et al.[11] for polymer adsorption from a micellar solution in the buoy-dominated regime. A plot of ρ_∞ versus $m^{12/25}n^{-1.20}$ for our samples is illustrated in Figure 3. Other than three polymers with low molar masses and low ρ_∞/ρ^* values, the ρ_∞ data of the other seven polymers can be fitted with

$$10^{-12}\rho_\infty = 5.7 \times 10^2 m^{-(13/25)}\beta^{-2} - 0.69 \tag{9}$$

with a correlation coefficient of 0.964. As a 6-fold variation is seen in $m^{-(13/25)}\beta^{-2}$ in Figure 4, the linear relation over the whole $m^{-(13/25)}\beta^{-2}$ range suggests the validity of the scaling relation of Marques et al. The fact that the ρ_∞ values of the low molar mass samples do not fit eq 9 may be due to the failure of chain statistics for these low molar masses.

Scaling Behavior of the PCEMA Thickness. Assuming a density, *d*, of 1.00 g/cm^3 for the anchoring layer and that it is essentially free of solvent, as is assumed in most theoretical models, the thickness, *e*, of the anchoring layer can be calculated with:

$$e = \frac{w_{\mathrm{PCEMA}}\sigma_\infty}{d} \tag{10}$$

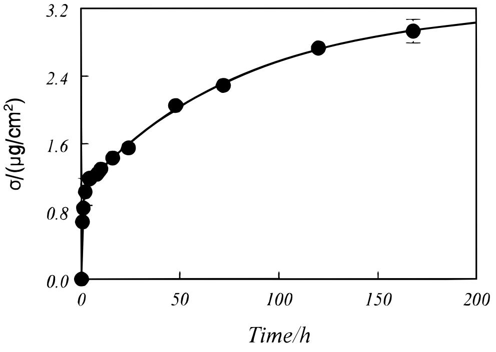

Figure 5. Increase in the surface coverage of silica by 1.08 × 10^3-1.16 × 10^3 as a function of adsorption time. The initial polymer coating solution concentration used is 14.4 mg/mL.

where w_{PCEMA} is the mass fraction of the PCEMA block of a diblock. Using eq 10, we calculated *e* for all of our samples (Table 2).

The PCEMA thickness, *e*, should scale according to[11]

$$e \propto m^{12/25}\beta^{-2} \tag{11}$$

Plotting the *e* values of the seven samples with higher molar masses vs $m^{12/25}\beta^{-2}$ yielded

$$e = 22m^{12/25}\beta^{-2} + 2.3\ (\text{Å}) \tag{12}$$

with a correlation coefficient of 0.966.

Kinetics of 1.08 × 10^3−1.16 × 10^3 Adsorption. To check if 1 week was sufficient for the establishment of adsorption equilibrium of PS-*b*-PCEMA, we carried out adsorption kinetic studies of 1.08 × 10^3-1.16 × 10^3. This polymer was studied as it had the highest molar mass of the series and should be the slowest to achieve adsorption equilibrium.[15] It is obvious from Figure 5 that adsorption equilibrium is approximately established in 1 week for this sample and therefore that of all of the data shown in this work are equilibrium data.

IV. Conclusion

Eleven PS-*b*-PCEMA samples with β values close to 1 were synthesized and characterized. This adsorption study again demonstrates that the theoretical scaling relations derived by Marques et al. for diblock adsorption from a micellar solution in the buoy-dominated regime is valid under our experimental conditions.

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