Adsorption of Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) by Silica from Block-Selective Solvent Mixtures

Jian Tao, Andrew Guo, and Guojun Liu*

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

Received September 5, 1995; Revised Manuscript Received November 21, 1995[⊗]

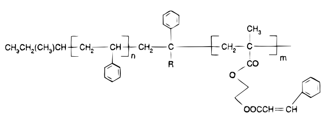
ABSTRACT: Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) of different block lengths have been synthesized. These polymers were adsorbed via the anchoring of the insoluble PCEMA block on silica, in the brush conformation, from cyclohexane/THF or cyclopentane/THF mixtures when cyclohexane or cyclopentane contents were high. The adsorbed amount could be increased or decreased by increasing or decreasing the cyclohexane or cyclopentane content. In a given solvent mixture, number surface coverages ρ_∞ increased as n/m decreased, where n and m are the numbers of repeat units for the PS and PCEMA blocks, respectively. The trend that ρ_∞ increased with decreasing n/m is contradictory to previous experimental observations but can be well explained by the scaling relation derived by Marques et al. for block copolymer adsorption from a micellar solution in the buoy-dominated regime.

I. Introduction

In a block-selective solvent, which is a good solvent for one block but poor for the other, a diblock copolymer may deposit out on a solid substrate which is in contact with the polymer solution. If the interaction between the insoluble block and the solid substrate is favorable, a dense polymeric monolayer called a polymer brush may form. In a polymer brush, the insoluble block spreads on the solid surface like a melt and the soluble block stretches into the solution phase like bristles of a brush (Figure 1).[1−4]

Polymer brush formation has been traditionally used to stabilize latex and pigment particles.[5] We have recently reported the synthesis of poly(isobutyl vinyl ether)-*block*-poly(2-(vinyloxy)ethyl cinnamate), PIBVE-*b*-PVEC, wher PVEC is a photo-cross-linkable block.[6−7] After brush formation, the anchoring PVEC block was cured to produce cross-linked polymer brushes.[8] Due to the stability of cross-linked polymer brushes against organic solvent attacks, we proposed many new applications for them in addition to those already known for un-cross-linked polymer brushes.[9]

To commercialize the polymer brush formation process, it is important to know what factors affect the adsorption rate and the amount of polymer adsorbed upon reaching adsorption equilibrium. It was for this purpose that we investigated the adsorption of the following series of polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) samples onto silica from cyclohexane/THF or cyclopentane/THF binary solvent mixtures:



Polymer I: R = pyrenyl, $n = 302$, $m = 570$.

Polymer II: R = phenyl, $n = 124$, $m = 124$.

Polymer III: R = pyrenyl, $n = 277$, $m = 243$.

Polymer IV: R = phenyl, $n = 265$, $m = 145$.

Polymer V: R = pyrenyl, $n = 276$, $m = 90$.

The series of samples have different n/m ratios so that the effect of changing n/m on polymer adsorption could be examined. Solvent mixtures of different cyclohexane and cyclopentane volume fractions, f_c and f_{cp}, were used to investigate the effect of solvent quality for the PCEMA block on polymer adsorption. Since THF is a commonly good solvent for both blocks and cyclohexane or cyclopentane only solubilizes the PS block, the quality of a solvent mixture for PCEMA was conveniently changed by decreasing or increasing f_c or f_{cp}, respectively.

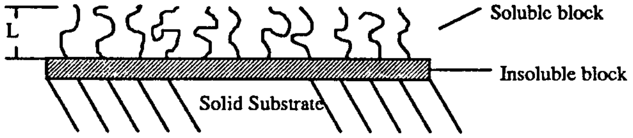


Figure 1. Polymer brush illustrated.

There have been a few studies of diblock adsorption equilibrium in block-selective solvents.[10−13] Polymers studied included polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-PVP),[10,11] polyisoprene-*block*-poly(2-vinylpyridine),[12] and polystyrene-*block*-poly(propylene sulfide).[13] In all previous studies except one,[10] the polymer coating solutions used have been very less than 1 mg/mL. The use of dilute solutions ensured, on one hand, that micelles did not form in any significant amount in the solution phase, and on the other, that the osmotic force acting on a brush layer from the solution phase was small. Because of the low concentrations used, the number surface coverages ρ_∞, chains adsorbed per unit substrate surface area, have all been explained by the scaling relation derived by Marques et al.[14] for unimer adsorption in the van der Waals−buoy regime. That is, ρ_∞ increased with the asymmetric ratio of a diblock copolymer defined by

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

where n and m represent the degree of polymerization for the soluble and insoluble block, respectively.

It is surprising to note that the results of Bossé et al.[10] could also be explained by the theory of Marques et al.[14] for unimer adsorption in the van der Waals−buoy regime, despite the fact that the concentration used was as high as 25 mg/mL of PS-*b*-PVP in toluene. This was probably due to the fact that toluene-d_8 was not a sufficiently poor solvent for PVP to cause significant micelle formation.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

To prepare polymer brushes on a commercial scale, it is more economical to use concentrated polymer coating solutions. Then, one would prefer to use mixed solvents instead of single solvents traditionally adopted as the medium for brush preparation. The use of single solvents would facilitate data comparison with theoretical predictions. The use of a binary solvent mixture is, however, much more convenient, as changing the solvent composition may offer a convenient way for tuning surface coverages. Preparing a diblock coating solution in a binary solvent mixture can also be much quicker, as one can dissolve a diblock first in the solvent which is good for both blocks and then add the block-selective solvent. This avoids the direct dissolution of a diblock in a block-selective solvent, which can be very slow.

Our study focused on polymer brush formation on a silica substrate from more concentrated polymer coating solutions. Our study was new, not only because of the new polymer used but also because it was directed to the use of relatively concentrated polymer solutions prepared in binary solvents as coating solutions. In a concentrated solution, micelle formation was possible and polymer adsorption behavior turned out to be very different from that observed previously.

The kinetic studies of diblock copolymer adsorption from block-selective solvents have also been traditionally restricted to dilute solutions prepared from single solvents. These studies have involved the use of techniques such as scintillation counting,[11,13,15] X-ray photoemission spectroscopy,[13,15] surface plasmon spectroscopy,[16] and internal reflection interferometry.[13,17] In our study, we followed the kinetics of PS-*b*-PCEMA adsorption on silica by analyzing the decrease in the polymer concentration in a supernatant with time using UV spectrophotometry.

II. Experimental Section

Polymer Synthesis. The synthesis of the precursor, polystyrene-*block*-poly(2-hydroxyethyl methacrylate) (PS-*b*-PHEMA), has been described in detail elsewhere.[18] To esterify the PHEMA block, 1.5 equiv of cinnamoyl chloride was mixed with PS-*b*-PHEMA and stirred in dry pyridine at room temperature for 24 h. The resultant mixture was then filtered and the polymer in the filtrate was purified by precipitation twice either from methanol or pentane.

Polymer Characterization. GPC analysis was done on a Varian Model 5000 HPLC instrument using a Styragel HR 4 (Waters) column calibrated by monodisperse polystyrene standards (Polymer Laboratories). The ratio in the number of styrene to CEMA units, n/m, was determined using ^{1}H NMR. The absolute weight-average molar masses were measured using a Brookhaven model 9025 light scattering instrument. The specific refractive index increment dn_r/dc, where n_r and c represent the refractive index and concentration of a polymer solution, was determined using a differential refractometer (Precision Instruments Co.).

Adsorption Isotherms. To prepare a coating solution, PS-*b*-PCEMA was first dissolved in THF. A given amount of cyclohexane or cyclopentane was then added to prepare a coating solution with a designated f_c or f_{cp}.

Nonporous Aerosil Ox 50 from Degussa has been used as the adsorbent. This type of silica has been claimed to consist essentially of primary spherical particles, 400 Å in diameter, with a small amount of chain-shaped aggregates. The specific surface area is 50 m^2/g. The silica particles were evacuated just before use and stored in a desiccator when not in use.

For isothermal curve construction, we equilibrated ~0.040 g of silica with 2.00−4.00 mL of a coating solution for 24−48 h. The silica was then separated from the supernatant by centrifuging. The supernatant was diluted and analyzed for cinnamate content by UV spectrophotometry at 274 nm. The amount of polymer adsorbed by silica was calculated from the initial and final cinnamate absorbances, A_0 and A_t, by

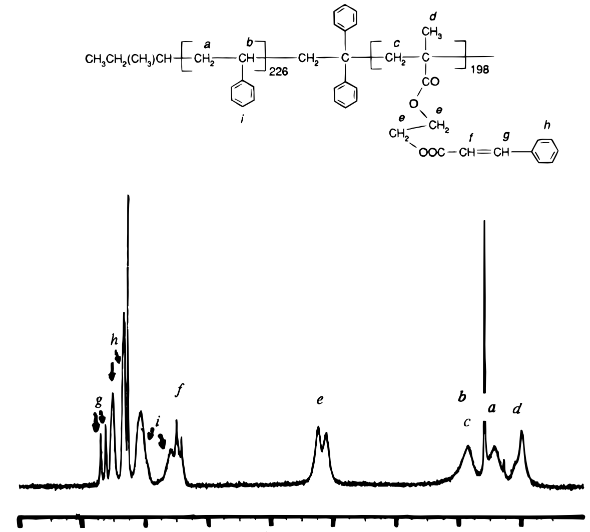


Figure 2. ^{1}H NMR spectrum of polymer III.

$$w_a = \frac{A_0 - A_t}{A_0} c_0 V_0 \qquad (2)$$

where c_0 and V_0 are the initial concentration and volume of the coating solution to which silica is added, respectively. The equilibrium coverage was calculated using

$$\sigma_{eq} = \frac{w_a}{50 \times 10^4\ \mathrm{cm}^2/\mathrm{g} \times w_s} \qquad (3)$$

where w_s is the amount of silica used.

Adsorption Kinetic Data. For kinetic studies, silica in a coating solution at a given time was filtered off with a 0.50 μm filter (Lida Corp.). The filtrate was then diluted to an appropriate concentration and analzyed by UV absorption at 274 nm for cinnamate content. The amount of polymer adsorbed was also calculated using eq 2.

III. Results and Discussion

NMR Characterization of the Polymer Samples. Five samples were used in this study. Except for polymer II, all other samples had similar numbers of styrene units but varying numbers of CEMA units.

Illustrated in Figure 2 is an ^{1}H NMR spectrum of polymer III. From ratioing the proton peak intensity of PCEMA at δ 7.66 (d, 1H, 15.9 Hz) or δ 4.17 (d, 4H, 24.5 Hz) to that of PS at δ 7.15 (b, 3H), we have obtained a styrene to CEMA ratio, i.e. n/m, of 1.14. Similarly, we determined the n/m ratios for polymers I, II, IV, and V to be 0.53, 1.00, 1.82, and 3.07, respectively.

Polymers I−V were synthesized by esterifying their corresponding PS-*b*-PHEMA using cinnamoyl chloride. NMR results clearly indicated that the conversion of PHEMA to PCEMA approached 100%. This high conversion may have arisen from the easy accessibility of the hydroxyl groups of PHEMA, as they are relatively far from the backbone.

GPC Characterization of the Polymer Samples. Since the GPC column was calibrated using PS standards, the molar masses determined for diblocks were not meaningful. We only report the polydispersity indices of the diblocks in Table 1. These values suggest that our samples have narrow molar mass distributions.

Specific Refractive Index Increment ν of the Polymer Samples. For determining the weight-aver-

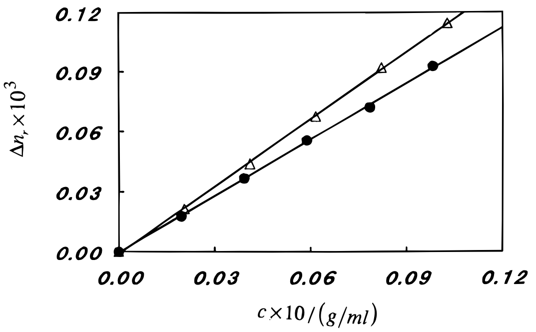


Figure 3. Increase in the differences Δn_r between refractive indices of PS (△) and PCEMA (●) solutions and that of pure toluene as a function of their concentrations c.

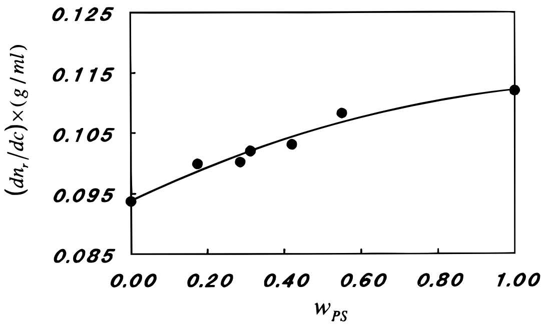


Figure 4. Change in the specific refractive index increment of diblocks as a function of PS weight fraction.

Table 1. Characterization of the Diblocks

	n/m		$\bar{M}_w/\bar{M}_n$	$10^{-4}\bar{M}_w$ (g/mol)
sample	feed ratios	NMR	GPC	LS
I	0.50	0.53	1.07	18.0
II	1.00	1.00	1.08	4.6
III	1.00	1.14	1.11	9.2
IV	2.00	1.82	1.08	6.9
V	4.00	3.07	1.10	5.0

Table 2. Differential Refractometry and Light Scattering Results

polymer	ν (mL/g)	R_G* (Å)	$10^{-4}\bar{M}_w$* (g/mol)	$10^{-4}\bar{M}_w$ (g/mol)
PCEMA	0.094			
I	0.100	120	16.9	18.0
II	0.100	69	4.5	4.6
III	0.102	79	8.8	9.2
IV	0.103	104	6.7	6.9
V	0.108	51	4.6	5.0
PS	0.112	56	2.9	2.9

age molar masses $\bar{M}_w$ of the diblocks by light scattering, we measured the specific refractive index increment ν or dn_r/dc of each diblock plus those of PS and PCEMA homopolymers. Figure 3 shows the increase in the differences Δn_r between refractive indices of PS (Polysciences: $\bar{M}_w = 3.0 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.05$) and PCEMA (synthesized by us) solutions and that of pure toluene as a function of polymer concentration c. Similar data were obtained for all the diblocks. Best fit to the data using

$$\Delta n_r = a_0 + \nu c \qquad (4)$$

yielded ν values for all our samples (Table 2). In all cases, the intercept a_0 approached zero, as expected.

The ν values of our samples are plotted in Figure 4, as a function of w_{PS}, where w_{PS} is the weight fraction of PS in the polymer as calculated from the n/m ratios determined from NMR. The data could not be fitted by a straight line[19] but could be fitted by the following polynomial:

$$\nu = 0.0938 + 0.0299 w_{PS} - 0.0115 w_{PS}^2 \text{ (mL/g)} \qquad (5)$$

Since our ν data precision was not superior, we will not speculate on the reasons for the experimentally observed deviation of the ν vs w_{PS} plot from a straight line.

Polymer Characterization by Static Light Scattering. Plotting light scattering data following the Zimm method, we obtained the apparent weight-average molar masses $\bar{M}_w$* of polymers I–V. The values are shown in Table 2. Since the specific refractive index increments of the two blocks relative to toluene are different, the apparent molar masses should be corrected to obtain the true molar masses, $\bar{M}_w$. $\bar{M}_w$* are related to $\bar{M}_w$ by[19]

$$\bar{M}_w^*/\bar{M}_w = \frac{1}{\nu^2}[\nu_1\nu_2 - (\nu_1\nu_2 - \nu_2^2)w_{PS}^2 - (\nu_1\nu_2 - \nu_1^2)(1 - w_{PS})^2] \qquad (6)$$

where ν_1 and ν_2, 0.938 and 0.112 mL/g, are the specific refractive index increments of PCEMA and PS, respectively; ν is that of a diblock. Using the above equation and ν computed from eq 4, we have calculated $\bar{M}_w$ of each diblock. The results are given in Table 2 for comparison with $\bar{M}_w$*. Equation 4 was used for calculating ν, as we believed that the calculated results were more accurate than those determined experimentally since eq 4 represents the best fit to ν of seven samples.

Summary of Polymer Characterization Results. Using $\bar{M}_w$ for diblocks determined by light scattering and n/m by NMR, we calculated the weight-average numbers of repeat units for styrene $\bar{n}_w$ and CEMA $\bar{m}_w$ of all diblocks. The $\bar{n}_w$ and $\bar{m}_w$ values have been given immediately after the structure of PS-*b*-PCEMA.

Since the synthesis of PS-*b*-PHEMA is a well-established procedure in our group,[18] we did not take samples of the PS block for the determination of their molar masses and polydispersities. Our previous studies have indicated that the PS block should generally have polydispersity indices below 1.10. Molecular weight analysis of the PS block in the past, using GPC, has indicated that the GPC $\bar{n}_w$ agreed, within ±10%, with those calculated from known diblock $\bar{M}_w$ and n/m values.[18]

Effect of f_c on the Adsorption of Polymers III and V. The equilibrium mass surface coverage σ_{eq} is defined as the amount of polymer adsorbed on the unit silica surface area after the equilibrium of polymer adsorption on silica has been achieved. This requires silica to be stirred with a coating solution for a prolonged period of time. To determine what was meant by this prolonged period, we initially used adsorption times of 24, 48, and 72 h. Since no differences in the adsorbed amounts of polymers were observed, within experimental error, using the three adsorption times, we later used adsorption times between 24 and 48 h.

Illustrated in Figures 5 and 6 are the changes in σ_{eq} for polymers III and V in different cyclohexane/THF mixtures as a function of the equilibrium concentration, c_{eq}, of polymer coating solutions. In constructing the adsorption isothermal curves, c_{eq} for the solution phase has been measured by UV spectrophotometry after the removal of coated silica by centrifuging. Other than at $f_c = 0.50$ and $f_c = 0.60$, respectively, for polymers III

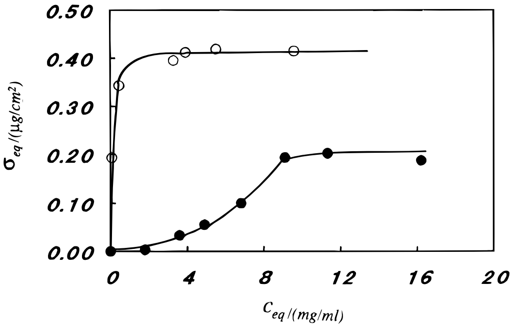


Figure 5. Isothermal curves of polymer III at different solvent compositions: (○) $f_c = 0.60$; (●) $f_c = 0.50$.

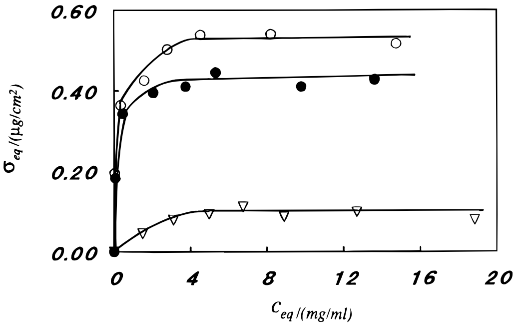


Figure 6. Isothermal curves for polymer V at different solvent compositions: (○) $f_c = 0.90$; (●) $f_c = 0.80$; (▽) $f_c = 0.60$.

Table 3. Effect of Cyclohexane Content, f_C, on the Adsorbed Amount

f_C	σ_∞ (μg/cm^2)	$10^{-12}\rho_\infty$ (chains/cm^2)	ρ_∞/ρ^*
	Polymer III ($\rho^* = 1.14 \times 10^{12}$ chains/cm^2)		
0.50	0.20	1.3	1.1
0.60	0.42	2.7	2.4
	Polymer V ($\rho^* = 1.14 \times 10^{12}$ chains/cm^2)		
0.60	0.10	1.2	1.1
0.80	0.42	5.1	4.5
0.90	0.52	6.3	5.5

and V, the other isothermal curves all have the normal shapes, as observed previously.[10] That is, σ_{eq} increased rapidly with c_{eq} first and then leveled off quickly. The isothermal curves for polymers III and V at $f_c = 0.50$ and $f_c = 0.60$ exhibited a slower increase in σ_{eq} with c_{eq}. This is due to the fact that at these solvent compositions, the deposition of the polymers is not as energetically favored as in solvents with higher f_c values.

Figures 5 and 6 also show that the maximum σ_{eq} value or the level-off σ_{eq} value, σ_∞, increased as f_c increased. For polymer V, σ_∞ increased from 0.10 to 0.52 μg/cm^2 as f_c increased from 0.60 to 0.90. We did not increase f_c beyond 0.60 for polymer III as the polymer precipitated out at $f_c \approx 0.70$. All σ_∞ for polymers III and V at different f_c values are shown in Table 3.

The observed increase in σ_∞ with f_c is reasonable. As f_c increases, the solvent mixture gets poorer for the anchoring block, the thermodynamic force driving the PCEMA block out of the solution phase increases, and the surface coverage increases.

From a practical point of view, changing the binary solvent composition of a coating solution represents a convenient way for tuning the surface coverages of a diblock monolayer.

Adsorption of PS-*b*-PCEMA in the Brush Conformation. A polymer brush is formed only if (1) a diblock copolymer is adsorbed via the anchoring of the insoluble block and (2) the surface coverage is sufficiently high so that the chains of the soluble buoy layer are crowded and repel one another. We will next explain that these criteria were met by our systems and that PS-*b*-PCEMA chains were adsorbed in the brush conformation.

To show that PS-*b*-PCEMA was adsorbed via the PCEMA block, we prepared 2.0 mL of a THF/cyclohexane ($f_c = 0.90$) solution of a PS sample ($\bar{M}_w = 3.0 \times 10^4$ g/mol and $\bar{M}_w/\bar{M}_n = 1.05$) and equilibrated 0.040 g of silica with this solution overnight. Analysis of the supernatant after separating the silica showed that the amount of PS adsorbed was 0.23 mg or $\sigma_{eq} = 0.011$ μg/cm^2, which was the same as zero within experimental error. Under similar experimental conditions, 8.0 mg of polymer V was adsorbed. The drastic increase in the adsorbed amount must have derived from the deposition of the PCEMA block.

That PS at the molar mass ~30 000 g/mol would adsorbe negligibly onto silica from a THF/cyclohexane mixture is in agreement with the experimental results of Takahashi et al.[20] Takahashi et al. determined, at room temperature, a silica surface coverage of 0.045 μg/cm^2 for a PS sample with $\bar{M}_w = 3.7 \times 10^4$ g/mol in cyclohexane, a Θ solvent for PS at 34.5 °C. In a THF/cyclohexane mixture, where THF is a good solvent of PS, we expect that the tendency for PS adsorption by silica will be even lower, as was observed experimentally.

The preferential adsorption of the PCEMA can also be appreciated by observing the following two points. On one hand, the PS block is not as polar as the PCEMA block. Silica is a relatively polar substrate, and it will preferentially attract the ester groups of PCEMA. Furthermore, the PCEMA block prefers to deposit out as it is insoluble in the solvent mixture, i.e. THF/cyclohexane or THF/cyclopentane, used for preparing the diblock coating solutions.

We will perform a simple calculation to show that chains of the buoy PS layer in our case are crowded and assume elongated conformations like bristles in a brush. Under normal conditions, a well-solubilized PS coil in the solution phase would occupy a volume ~$(4/3)\pi R_G^3$ and possess a cross-section area of πR_G^2, where R_G is the radius of gyration of the coil. A brush is formed only if the allowed area on a surface for each PS chain is less than πR_G^2 or the number surface coverage ρ defined as the number of chains on unit silica surface area is above a critical value ρ^*. At ρ^* the allowed area for each PS chain is equal to πR_G^2, and ρ^* can be calculated using

$$\rho^* = \frac{1}{\pi {R_G}^2} \tag{7}$$

In our study, different cyclohexane/THF and cyclopentane/THF mixtures were used and the accurate scaling relations between R_G and the molar masses of PS are not known from the literature. To obtain an estimate of ρ^*, we used the following scaling relation established for PS in toluene,[21]

$$R_G = 1.86{n_w}^{0.595}\ (\text{Å}) \tag{8}$$

to calculate R_G of PS regardless of the solvent mixtures used. In eq 8, n_w is the weight-average degree of polymerization of a PS chain. Using eqs 7 and 8, we obtained the ρ^* value of 1.14×10^{12} chains/cm^2 for polymers III and V, respectively.

Table 4. Effect of the Length of Each Block on Surface Coverages

sample	σ_∞ (μg/cm^2)	$10^{-12}\rho_\infty$ (chains/cm^2)	β	$m^{-(13/25)}\beta^{-2}$
		Cyclopentane/THF = 2/1		
III	0.51	3.3	1.87	0.0164
IV	0.31	2.7	2.36	0.0135
V	0.19	2.2	3.07	0.0102
II	0.37	4.8	1.62	0.0311
		Cyclohexane/THF = 60/40		
III	0.42	2.8	1.87	0.0164
V	0.10	1.3	3.07	0.0102
II	0.38	4.9	1.62	0.0311

The maximum number surface coverages ρ_∞ for our samples at each f_c were calculated using

$$\rho_\infty = \frac{\sigma_\infty}{\bar{M}_w} N_A \tag{9}$$

where $\bar{M}_w$ is the molar mass of the polymer and N_A is Avogadro's number. Using eq 9, ρ_∞ values calculated for polymers III and V in different cyclohexane/THF mixtures were tabulated in Table 3. For cases when ρ_∞/ρ^* are larger than 2, polymer brushes would have definitely formed.

The ρ_∞/ρ^* values we observed are very reasonable, as ρ_∞/ρ^* values for other polymers have been previously seen to be between 1 and 8.[2] We have not determined ρ_∞/ρ^* for polymer V at f_c values higher than 0.90. We believe that we can push ρ_∞/ρ^* even higher, using solvent mixtures with greater f_c values such as $f_c = 0.95$.

Effect of Changing *n/m* on Polymer Adsorption. We obtained the adsorption isothermal curves for polymers II−V in a cyclopentane/THF mixture with a cyclopentane volume fraction f_{cp} of 67% and for polymers II, III, and V in a cyclohexane/THF mixture with f_c = 0.60. σ_∞ values evaluated from these isothermal curves have been shown in Table 4.

We used both cyclopentane and cyclohexane as the block-selective solvent, on one hand, to examine the effect of changing the block-selective solvent, cyclopentane vs cyclohexane, on polymer adsorption. The main reason for our use of cyclopentane was in the consideration that it would have allowed us to compare the adsorption behavior of all our five polymer samples at the same f_{cp}, as cyclopentane is a better solvent for polystyrene than cyclohexane.[22] While in a cyclohexane/THF mixture, polymer I at the concentration ~20 mg/mL precipitated at $f_c \approx 0.33$. With cyclopentane, we were able to push the polymer I precipitation point to $f_{cp} \approx 0.55$. However, we still failed to prepare a coating solution of polymer I at $f_{cp} = 0.67$. We did not attempt to compare the adsorption behavior of all our samples with $f_{cp} = 0.55$, as polymer V, possessing a short PCEMA block, would adsorb too little at this f_{cp} value.

Obviously from Table 4, σ_∞ increased as $\bar{n}_w/\bar{m}_w$ decreased in both cyclopentane/THF and cyclohexane/THF mixtures for polymers III−V. Thus, another practical way to increase σ_{eq} is to increase m while fixing n. However, as m increases at a fixed n, the f_c or f_{cp} value at which PS-*b*-PCEMA would precipitate out also decreases. We have found that polymer I at the concentration of 20 mg/mL would precipitate out at $f_c \approx 0.33$, polymer II would precipitate $f_c \approx 0.70$, and polymer V would not precipitate at $f_c = 0.95$. Since σ_∞ increases also with f_c, a lower n/m, overall, seems to favor the achievement of higher σ_∞ values.

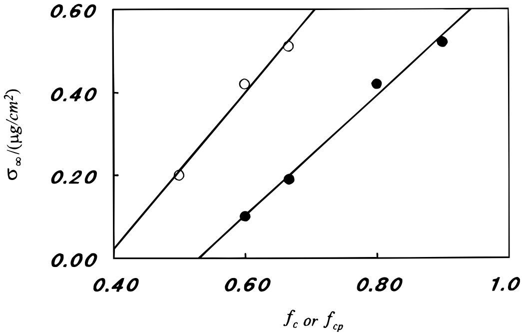


Figure 7. Increase in σ_∞ for polymers III (○) and V (●) as a function of f_c or f_{cp}.

Effect of Changing the Block Selective Solvent. In cyclopentane, the Θ temperature for PS is 20 °C, while that in cyclohexane is 34.5 °C.[22] Thus, at room temperature, cyclopentane is a better solvent for PS than cyclohexane.

In Figure 7, we have plotted σ_∞ of polymers III and V as a function of f_c or f_{cp}. The data at $f_{cp} = 0.67$ were obtained in a cyclopentane/THF mixture, and all others were obtained in cyclohexane/THF mixtures. Since no apparent discontinuity is observed when plotting σ_∞ vs f_c or f_{cp}, we conclude that the effect of changing from cyclohexane to cyclopentane had little effect on the adsorption of polymers III and V.

The trend that σ_∞ is higher in a cyclopentane/THF mixture with $f_{cp} = 0.67$ than in a cyclohexane/THF mixture with $f_c = 0.60$ is, however, not reproduced by polymer II. Table 4 clearly shows that σ_∞ for polymer II is the same, within experimental error, in the two mixtures. We do not know the explanation for this obvious contradiction.

Comparison of Adsorption Results ρ_∞ of Different Samples with Theoretical Predictions. At f_{cp} = 0.67 and $f_c = 0.60$, our polymers existed as micelles, as was clearly indicated by the typical bluish tinge of a micellar solution. Due to micelle formation, the theory of Marques et al.[14] for the adsorption of block copolymers from micellar solutions should be adopted for data analysis. Since all our samples possess β parameters close to 1 (Table 4), ρ_∞ should obey the scaling relation derived for the buoy-dominated regime, i.e.

$$\rho_\infty \propto m^{-13/25}\beta^{-2} \tag{10}$$

where m is the degree of polymerization for the insoluble block, which have been approximated by $\bar{m}_w$ in all our calculations.

We have calculated the ρ_∞ values of our samples using eq 9 at $f_{cp} = 0.67$ and $f_c = 0.60$, and the results are shown in Table 4. The variation of ρ_∞ with $m^{-13/25}\beta^{-2}$ for these samples is illustrated in Figure 8. Excluding the data point for polymer II at $f_{cp} = 0.67$, almost perfect straight lines are obtained, as expected, in both cases. This is the first observation of such a trend, i.e. that ρ_∞ increased with decreasing β, which contradicts the previously observed trend that ρ_∞ increased with β.

Unfortunately, the straight lines did not go through the origin as expected. There may be a few possible reasons for the nonideality. First of all, Marques et al. considered the case of polymer adsorption from solution of a single solvent. We used binary solvent mixtures where preferential adsorption of one solvent by the core or the corona is possible. Then, Marques et al. assumed that the block-selective solvent is a good solvent for the soluble block. Cyclohexane is definitely not a good

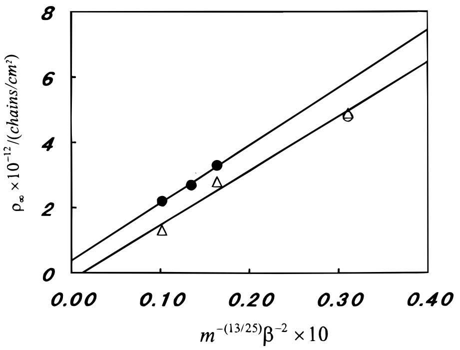


Figure 8. Increase in ρ_∞ as a function $m^{-(13/25)}\beta^{-2}$ for our samples at $f_{cp} = 0.67$ (●) and $f_c = 0.60$ (△), respectively. The point (○) represents the result for polymer II at $f_{cp} = 0.67$.

Table 5. Effect of the Length of Each Block on Anchoring Layer Thicknesses *e*

sample	σ_∞ (μg/cm^2)	w_{PCEMA}	e (Å)	$m^{(12/25)}\beta^{-2}$
	Cyclopentane/THF = 2/1			
III	0.51	0.69	35	3.99
IV	0.31	0.58	18	1.96
V	0.19	0.45	8.5	0.92
II	0.37	0.71	26	3.85
	Cyclohexane/THF = 60/40			
III	0.42	0.69	29	3.99
V	0.10	0.45	4.5	0.92
II	0.38	0.71	27	3.85

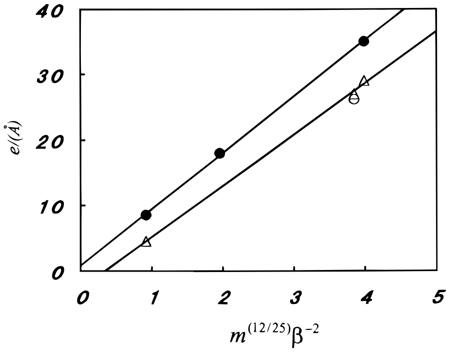


Figure 9. Increase of e of the anchoring layer as a function of $m^{(12/25)}\beta^{-2}$ for our samples at $f_{cp} = 0.67$ (●) and $f_c = 0.60$ (△), respectively. The point (○) represents the result for polymer II at $f_{cp} = 0.67$.

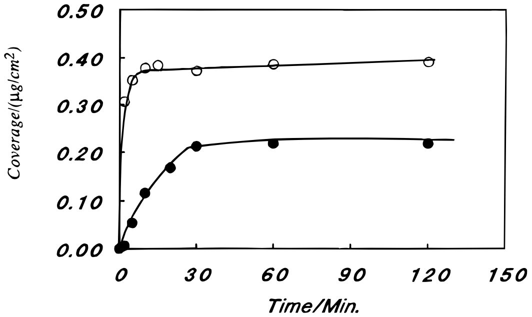


Figure 10. Increase in mass surface coverage σ of polymer III, at $f_c = 0.60$ (○) and $f_c = 0.50$ (●), as a function of the time of equilibration between silica and a polymer solution.

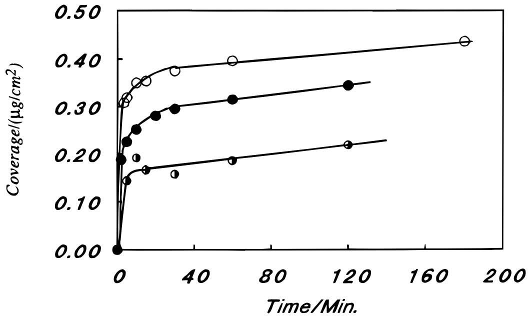


Figure 11. Increase in mass surface coverage σ of polymer V as a function of the time of equilibration between silica and a polymer solution. The rate of polymer uptake is the highest at $f_c = 0.90$ (○), intermediate at $f_c = 0.80$ (●), and the lowest at $f_c = 0.70$ (◑).

solvent for PS, as its Θ temperature for PS is 34.5 °C. Even cyclopentane hardly qualifies as a good solvent for PS, as the Θ temperature is 20 °C. When mixed with THF, the mixed solvents are probably better for PS than pure cyclopentane and cyclohexane but may still not be good solvents. Considering all this, we conclude that the agreement between experimental results and theory is good. As the variation in m of our samples is only 3-fold, an unambiguous verification of the scaling relation of Marques et al. would require the study of more samples encompassing a much larger range of m values.

We, however, do not know why the abnormality occurs with polymer II at $f_{cp} = 0.67$.

Thickness *e* of the Anchoring Layer. Assuming a density, d, of 1.00 g/cm^3 for the anchoring layer and that it was essentially free of solvent, as assumed in most theoretical models, the thickness, e, of the anchoring layer was calculated by

$$e = \frac{w_{\mathrm{PCEMA}}\sigma_\infty}{d} \tag{11}$$

where w_{PCEMA} is the mass fraction of the PCEMA block of a diblock. Using eq 11, we calculated e for polymers II–V at $f_{cp} = 0.67$ and $f_c = 0.60$ and summarized them in Table 5.

For diblock adsorption from a micellar solution in the buoy-dominated regime, e should scale according to

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

This e dependence is clearly seen in Figure 9 for our samples, except for polymer II, at $f_{cp} = 0.67$. This again supports the validity of the theory by Marques et al.[14]

Adsorption Kinetics. Illustrated in Figures 10 and 11 are the adsorption kinetic curves of polymers III and V in different cyclohexane/THF mixtures. As f_c increased, the rate of polymer adsorption increased. This is expected, because adsorption becomes more downhill and thus faster, as the binary solvent becomes poorer for the PCEMA block.

It is clear that the adsorption of polymer V can be divided into at least three regimes. In the first few minutes, polymer adsorption was very fast. It slowed down but continued to increase up to ~40 min. After 40 min, the surface coverage increased very slowly with time. This trend is, however, not conclusive for polymer III.

That the adsorption kinetics can be divided into a few regimes can be explained by the Ligoure and Leibler theory.[23] The initial adsorption rate is high, as adsorbed polymer chains are far away from one another on a surface and the rate is diffusion-controlled. As the surface coverage exceeds ρ^*, a chain from the solution phase now needs to penetrate the existing brush layer to be incorporated, and thus the rate of adsorption decreases. Ligoure and Leibler predicted extremely long times for reaching adsorption equilibrium depending on the lengths of the diblocks and the interaction energy between a surface and an anchoring layer.

In all cases, the near maximum surface coverages, e.g. $\sim 0.70\sigma_\infty$, were achieved for our samples within 5 min. This high brush formation rate is of critical importance in practical situations.

IV. Conclusions

We have successfully synthesized several PS-*b*-PCEMA samples, and all of them possessed narrow molar mass distributions. The samples have been well characterized by NMR, GPC, and light scattering.

The adsorption of such polymers from cyclohexane/THF or cyclopentane/THF mixtures by silica has been demonstrated to occur via the anchoring of the PCEMA block. At relatively high cyclohexane and cyclopentane contents, polymer brush formation occurred.

Surface coverages ρ_∞ in a fixed solvent mixture for different samples and the thickness e of the anchoring PCEMA block have been found to follow scaling relations derived by Marquest et al.[14] for block copolymer adsorption from a micellar solution in the buoy-dominated regime. This represents the first experimental observation of such scaling relations. These scaling relations allow the convenient tuning of polymer brush surface coverages and thicknesses in practical applications.

Our preliminary kinetic results showed that polymer brush formation was fast, although the achievement of ρ_∞ could take a long time. The observed multiregime kinetic behavior could be qualitatively explaiend by the Ligoure and Leibler theory.[23]

Acknowledgment. The authors thank the Institute for Chemical Science and Technology and NSERC of Canada for financially sponsoring this research. PS-*b*-PHEMA have been synthesized by Dr. Nanxing Hu and Mr. Sean Stewart. Their contribution is gratefully acknowledged.

References and Notes

(1) Milner, S. *Science* **1991**, *251*, 905.
(2) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
(3) Gast, A. P. In *Scientific* Methods *for the Study of Polymer Colloids and Their Applications*; Candau, F., Ottewill, R. H., Eds.; Kluwer Academic Publishers: Amsterdam, 1990.
(4) Liu, G. In *The Polymeric Materials Encyclopedia—Synthesis, Properties, and Applications*; Salamone, J. C., Ed.; CRC Press (in press).
(5) See, for example: Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, U.K., 1986.
(6) Liu, G.; Hu, N.; Xu, X.; Yao, H. *Macromolecules* **1994**, *27*, 3892.
(7) Liu, G.; Hu, N. *J. Macromol. Sci., Pure Appl. Chem.*, in press.
(8) Liu, G.; Xu, X.; Skupinska, K.; Hu, N.; Yao, H. *J. Appl. Polym. Sci.* **1994**, *53*, 1699.
(9) Liu, G. U.S. patent 5,409,739, 1995.
(10) Bossé, F.; Schreiber, H. P.; Eisenberg, A. *Macromolecules* **1993**, *26*, 6447.
(11) Parsonage, E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. G. *Macromolecules* **1991**, *24*, 1987.
(12) Watanabe, H.; Tirrell, M. *Macromolecules* **1993**, *26*, 6455.
(13) Stouffer, J. M.; McCarthy, J. *Macromolecules* **1988**, *21*, 1204.
(14) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(15) Huguenard, C.; Varoqui, R.; Pefferkron, E. *Macromolecules* **1991**, *24*, 2226.
(16) Tassin, J. F.; Siemens, R. L.; Tang, W. T.; Hadziioannou, G.; Swalen, J. D.; Smith, B. A. *J. Phys. Chem.* **1989**, *93*, 2106.
(17) Munch, M. R.; Gast, A. P. *Macromolecules* **1990**, *23*, 2313.
(18) Liu, G.; Smith, C. K.; Hu, N.; Tao, J. *Macromolecules*, in press.
(19) Huglin, M. B. *Light Scattering from Polymer Solutions*; Academic Press: London, 1972.
(20) Takahashi, A.; Kawaguchi, M.; Hirota, H.; Kato, T. *Macromolecules* **1980**, *13*, 884.
(21) Higo, Y.; Ueno, N.; Noda, I. *Polym. J.* **1983**, *15*, 367.
(22) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989.
(23) Ligoure, C.; Liebler, L. *J. Phys. (Paris)* **1990**, *51*, 1313.

MA951305E