Formation and Properties of Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) Brushes Studied by Surface-Enhanced Raman Scattering and Transmission Electron Microscopy

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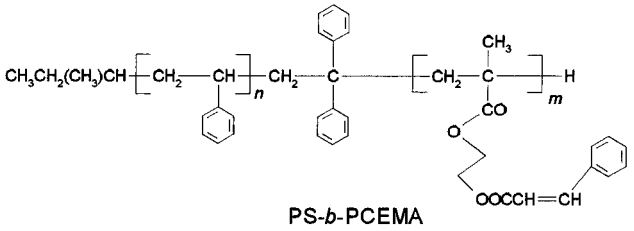
ABSTRACT: The aliphatic double bond of poly(2-cinnamoylethyl methacrylate) (PCEMA) displayed a characteristic surface-enhanced Raman scattering (SERS) peak at 1640 cm^{-1}. Polystyrene (PS), together with the phenyl rings of PCEMA, contributed to the peak at 1005 cm^{-1}. We determined the intensity ratio of these two peaks, i.e. I_{1640}/I_{1005}, for PS-*b*-PCEMA films deposited, from THF/cyclopentane (CP) mixtures, on silver and silicate-covered silver (or silica) surfaces. In THF/CP with CP volume fractions, f_{CP}, between 0.60 and 0.90, the I_{1640}/I_{1005} values were large. Since only these species which are in the immediate neighborhood of a roughened metal substrate, e.g. within ~100 Å, yield SERS responses, these data suggest that PS-*b*-PCEMA were adsorbed by silica and silver in the brush conformation, with PCEMA as the anchoring layer and PS as the buoy layer, in THF/CP with f_{CP} between 0.60 and 0.90. At low f_{CP}'s, PS-*b*-PCEMA samples did not adsorb on silica but did on silver. SERS results suggest that the adsorption on silver might be via either styrene or CEMA as the anchoring group. At high f_{CP}'s, PS-*b*-PCEMA micelles adsorbed. Brush formation at intermediate f_{CP} and micelle adsorption at high f_{CP} were directly confirmed by transmission electron microscopy for one of our PS-*b*-PCEMA samples. SERS results also suggest one of the possible mechanisms for PS-*b*-PCEMA adsorption was via the anchoring of micelles first. The micelles subsequently disintegrated on an adsorbate if f_{CP} was not too high and the rate for micelle dissociation was sufficiently fast.

I. Introduction

Analogous to conventional diblock copolymers, polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) self-assembles under appropriate conditions to form mesophasic structures such as micelles and polymer brushes. As the PCEMA block is photo-cross-



PS-*b*-PCEMA

linkable, these mesophasic structures can be cured by cross-linking the PCEMA block to produce nanostructures. Using this method, we have so far prepared star polymers,[1] nanospheres,[1] nanofibers,[2] and cross-linked polymer brushes.[3−6] Of all the nanostructures, cross-linked polymer brushes or monolayers may have immediate applications.[7] They can, for example, be used for modifying the surface properties of medical devices or coating silica particles as HPLC column packing materials.

Polymer brushes are prepared at solid/solution interfaces by the adsorption of a diblock copolymer dispersed in a block-selective solvent which solubilizes one, but not the other, block of a diblock copolymer. In a polymer brush, the insoluble block spreads on a solid substrate like a melt and the soluble block stretches into the solution phase like bristles in a brush.[8−9] A polymer brush forms only if the Gibbs free energy change accompanying the transfer of chains from the solution phase to the brush layer is negative. A favorable interaction between the insoluble block and the substrate will help to decrease the Gibbs free energy of the system. We have demonstrated previously that PS-*b*-PCEMA formed brushes on silica surfaces, with PCEMA as the anchoring layer and PS as the buoy layer, when THF/cyclopentane (THF/CP) with sufficiently high CP contents was used as the solvent, where CP was a block-selective solvent which solubilized PS but not PCEMA.[6] We established how the amount of polymer adsorbed was affected by changing the composition of the THF/CP mixtures. We also examined how the number of styrene and CEMA units in a chain affected the amount of polymer adsorbed and verified scaling relations derived by Marques et al.[10] for the buoy-dominated[6,11] and the van der Waals−buoy regimes.[12]

Our previous research has focused on the tuning of surface coverages by adjusting parameters such as solvent composition and molecular architecture. Solvent composition and molecular architecture may also affect the mode by which a PS-*b*-PCEMA polymer anchors on a solid substrate. As solvent composition such as the CP volume fraction, f_{CP}, in a THF/CP mixture changes, micelle formation in the solution phase may occur and this may cause micelle adsorption. Also, the solvent quality may play an important role in determining which block, PS or PCEMA, adsorbs preferentially. This study was initiated to elucidate the PS-*b*-PCEMA adsorption mechanism under different conditions and to optimize PS-*b*-PCEMA brush formation in THF/CP mixtures.

Surface-enhanced Raman scattering (SERS) was the primary technique used here to identify the anchoring group on a solid substrate. This technique is based on the principle that only functional groups which are in the immediate neighborhood of a curved metal surface

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Table 1. Characteristics of the PS-*b*-PCEMA Samples Used in This Study

lab code	(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	$10^{-3}n$	$10^{-2}m$
1077−1158	0.93	1.10	32	41	1.08	11.6
1321−383	3.5	1.08	18.5	23.7	1.32	3.8

may display a greatly enhanced Raman signal.[13] This immediate neighborhood may represent different distances for different systems. It should, however, generally fall below 100 Å as was found for poly(styrenesulfonate) (PSS) deposited on silver.[13b]

The augmentation of Raman signals on a curved metal surface is partially caused by the enhancement in the electromagnetic field of the light at such a surface.[13a] Then, an adsorbed molecule may form charge-transfer complexes with a metal surface. This may greatly increase the polarizability of the compound and thus Raman scattering. The anchoring of PS-*b*-PCEMA via PCEMA can be immediately identified, as PCEMA has a characteristic aliphatic double bond vibrational band at 1640 cm^{-1}.

Although SERS was first discovered some 20 years ago and has been widely used in other disciplines,[13] it was used for studying polymer brush formation only recently. Boerio and co-workers have, for example, used SERS to establish that vinylpyridine groups of polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) were the anchoring groups on silver when deposited from toluene.[14,15] The SERS technique is very convenient and affordable. However, its drawback lies in its indirectness; i.e. one has to infer the structure of an adsorbed layer from relative peak intensity measurements. In this study, transmission electron microscopy (TEM) was used to confirm the conclusions inferred from SERS for a polymer brush formed from one of our samples.

II. Experimental Section

Materials. Cyclopentane (95%) was purchased from Aldrich. THF was freshly distilled before use to remove stabilizers.

Polymer Synthesis and Characterization. The synthesis and characterization of PS-*b*-PCEMA samples have been described in detail previously.[1,16] The precursor polymers to PS-*b*-PCEMA, polystyrene-*block*-poly(2-hydroxyethyl methacrylate) or PS-*b*-PHEMA, were synthesized by sequential anionic polymerization of styrene and (trimethylsilyl)ethyl methacrylate (TMSEMA) followed by hydrolysis in acidic methanol. The final product, PS-*b*-PCEMA, was obtained by reacting PS-*b*-PHEMA with cinnamoyl chloride in pyridine.

A PS-*b*-PCEMA sample in this paper is represented by two numbers separated by a hyphen, with the first number denoting the number of styrene units, n, and the second representing the number of CEMA units, m. The samples were characterized by NMR to determine the n/m values, GPC to determine the PS-equivalent molar masses and polydispersity indices, and light scattering to determine the weight-average molar masses. The characteristics of the samples used are tabulated in Table 1.

The polystyrene homopolymer (9.0×10^4 g/mol, $\bar{M}_w/\bar{M}_n = 1.04$) used was purchased from Pressure Chemicals. The PCEMA was synthesized by cinnamating a commercial PHEMA polymer (Polysciences). The PCEMA has a PS-equivalent $\bar{M}_w$ of 6.5×10^4 and a polydispersity index of 1.94.

SERS Studies. Silver foils (Aldrich, 0.025 mm thick, 99.9%) were roughened by dipping them in an aqueous mixture of 3 M nitric acid and 4 M sulfuric acid for 5−8 min. The foils were then rinsed with distilled water and dried with a gust of nitrogen before use. To coat the silver surfaces with a thin film of SiO_2, roughened silver foils were immersed in a 1.0 mg/mL tetraethyl orthosilicate (Aldrich, 98%) solution in 95% ethanol for 2 h, rinsed with the solvent, and dried in open air for 1 day.[17] A PS-*b*-PCEMA film on these substrates was obtained by equilibrating the substrate with a PS-*b*-PCEMA solution, typically between 1.0 and 5.0 mg/mL, for a designated period of time and then drying the withdrawn substrate surface by blowing nitrogen on it.

All SERS spectra were recorded on Jarrell-Ash Model 25-100 instrument. The slits were so set to provide a 5 cm^{-1} resolution. The excitation used was a 4-W argon ion laser (Coherent) emitting at 514.5 nm. The incidence angle on SERS specimens was ∼60° and the incident energy was ∼80 mW at the sample. Silver foils were placed against a metal block to facilitate quick heat dissipation. Plasma lines were removed by placing a narrow band-pass filter between the laser and the sample. SERS spectra of polymer films were obtained by subtracting the background spectrum of the bare substrate from those of polymer-coated substrates. This operation made the baseline smoother and the determination of the heights of different peaks more accurate.

Adsorption Studies. A given amount of silica (∼20 mg, Areosil Ox 50, Degussa, specific surface area = 50 m^2/g) or nickel spheres covered with silver (∼400 mg, Alfa, specific surface area = 0.11 m^2/g) was equilibrated with a 1321-383 solution, at ∼5.0 mg/mL for silica and 1.0 mg/mL for silver, for 72 h. The amount of polymer adsorbed by silica and silver was then determined spectrophotometrically, as PCEMA absorbed strongly at 274 nm. Surface coverages, σ_∞ in terms of $\mu g/cm^2$, were calculated by ratioing the amount of polymer adsorbed to the total surface area of the adsorbent used.

TEM Studies. Silica particles were equilibrated with a 10 mg/mL 1077-1158 solution in THF/CP with $f_{CP} = 0.82$ for 3 days. The silica particles were then centrifuged and rinsed with THF/CP with $f_{CP} = 0.82$. The rinsing procedure was repeated three times, and the coated particles were then irradiated for 30 min while dispersed in THF/CP with $f_{CP} = 0.82$ with light passing through a 260-nm cut off filter from a 500-W Hg lamp. Irradiated particles were centrifuged, separated from solvent, redispersed in cyclopentane, and then sprayed onto a TEM grid coated with a carbon film before viewed with a Hitachi 7000 electron microscope operated at 100 kV.

III. Results and Discussion

The primary objective of this study has been to optimize PS-*b*-PCEMA brush formation in THF/CP mixtures. Since THF/CP mixtures with sufficiently high CP contents solubilize PS but not PCEMA, a polymer brush formed from such a solvent should have PCEMA as the anchoring layer and PS as the buoy layer. In this section, two SERS peaks are chosen so that their intensity ratio will serve as a convenient "marker" for quantifying the relative amount of PCEMA present in the "vicinity" of a substrate. The amount of random error expected of this marker under a given set of experimental conditions will then be examined. Using this marker, the effect of solvent composition and polymer solution/substrate equilibration time on brush formation will be investigated. The principal conclusions of SERS will be confirmed by TEM results. This section concludes by examining the application of SERS in probing certain properties of PS-*b*-PCEMA brushes.

Bulk and Surface-Enhanced Raman Scattering Spectra of PS, PCEMA, and PS-*b*-PCEMA. Illustrated in Figure 1 are the Raman spectra of PS, PCEMA, and PS-*b*-PCEMA powder samples. These are compared with their SERS spectra when deposited on silver in Figure 2. Similar SERS spectra were obtained on "silica surfaces", i.e. surfaces prepared by depositing a thin layer of silicate on roughened silver surfaces, as described in the Experimental Section.

Since the emphasis here is on SERS and the application of SERS for probing the preferential anchoring of the PCEMA block, we will not attempt assignments of all peaks of the PS and PCEMA bulk samples. Interested readers are referred to Boerio for PS peak assign-

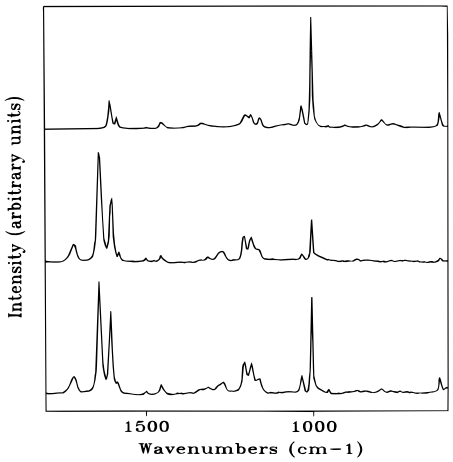

Figure 1. Comparison of the Raman spectra of PS (top), PCEMA, and 1321-383 (bottom) powders.

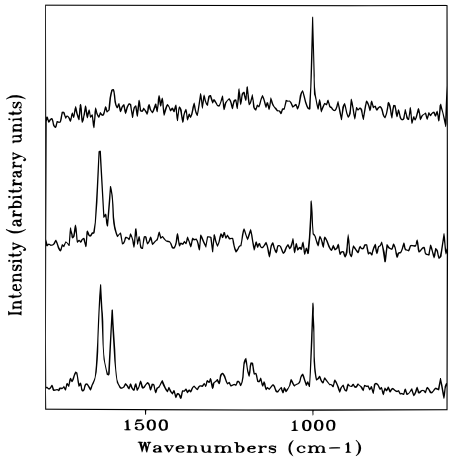

Figure 2. Comparison of SERS spectra of PS (top), PCEMA, and 1321-383 (bottom) films on silver. The PS and PCEMA films were all prepared from THF solutions of the polymers at the concentration of 3.0 mg/mL. The 1321-383 film was prepared from a THF/CP solution with $f_{CP} = 0.86$ at the 1321-383 concentration of 1.0 mg/mL.

ments.[15] PCEMA peak assignments can be made based on previous studies of ethylene, benzene, and benzoic acid.[13]

Of the thirteen observed peaks of PS in the normal spectra, only three were detected in the SERS mode between 600 and 1800 cm^{-1}. These were the peaks at 1005, 1035, and 1605 cm^{-1} associated with the symmetric ring breathing $\nu(1)$, in-plane C−H bending $\nu(18a)$, and ring stretching $\nu(8a)$ motions of pheny rings. Of the three peaks, the peak at 1005 cm^{-1} is the strongest. PCEMA bulk samples show seven strong peaks. The outstanding ones in the SERS mode are at 1005, 1605, and 1640 cm^{-1}, respectively. The peak at 1640 cm^{-1} is characteristic of the stretching vibration of the aliphatic double bond of PCEMA. The other two peaks, overlapping with those of PS, are due to $\nu(1)$ and $\nu(8a)$ vibrational modes of the phenyl rings of PCEMA.

A closer comparison of the bulk Raman and SERS spectra shows that there is no significant shift in the positions of any of the peaks. The relative intensities of the peaks are different in the two types of spectra. For bulk PCEMA samples, the intensity ratio, $(I_{1640}/I_{1005})_0$, between peaks at 1640 and 1005 cm^{-1} is 3.6. This ratio is reduced to 1.9 and 1.5 when PCEMA is casted from a THF solution on silver and silica, respectively. The insignificant peak position shift suggests that both PS and PCEMA are adsorbed physically on silver and silica surfaces.

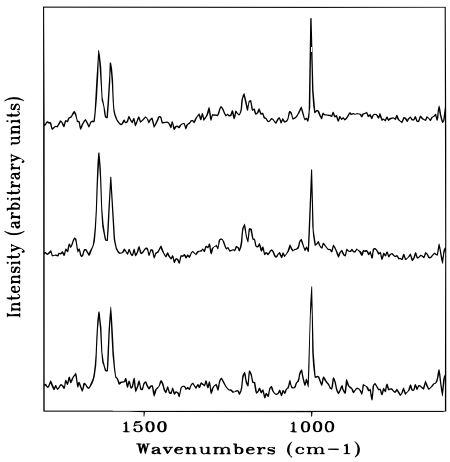

Figure 3. Comparison of SERS spectra of 1321-383 films on silver prepared from 1.0 mg/mL solutions in THF (top), THF/CP with $f_{CP} = 0.86$ (middle), and CP (bottom).

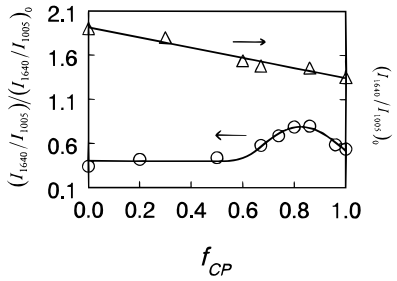

Figure 4. Plot of $(I_{1640}/I_{1605})_0$ of PCEMA films as a function of f_{CP} (top), where the PCEMA films were prepared on silver from a 3.0 mg/mL THF solution and then equilibrated in THF/CP mixtures with CP volume fractions equal to f_{CP}. Also shown is the plot of $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ as a function of f_{CP}, where I_{1635}/I_{1000} stands for the intensity ratio for peaks of 1321-383 films, prepared on silver from 1.0 mg/mL solutions of 1321-383 in THF/CP mixtures, at 1640 and 1005 cm^{-1}, respectively.

$(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ as a Measure for the Relative PCEMA Content in the Neighborhood of a Solid Substrate. To quantify the relative amount PCEMA in the neighborhood of a solid substrate, the double ratio $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ has been chosen as the "marker", where I_{1640}/I_{1005} represents the SERS intensity ratio measured for the peaks of a PS-*b*-PCEMA coating at 1640 and 1605 cm^{-1}, respectively, and $(I_{1640}/I_{1005})_0$ is the SERS intensity ratio for the peaks of a PCEMA coating at the two wavenumbers under identical sample preparation conditions. A double ratio is used here to normalize the (I_{1640}/I_{1005}) values for cases when there are no PS chains in the vicinity of a solid substrate. The peak at 1640 cm^{-1} was chosen as it is characteristic of PCEMA scattering. The characteristic peak of PS at 1035 cm^{-1} was not used because the signal to noise ratio for this peak was low. The use of the peak intensities at 1005 cm^{-1} helped to improve the precision in the determined double ratios. The difficulty has been in obtaining the absolute percentage of PCEMA in the vicinity of a solid substrate from $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$, because both PS and PCEMA contributed to the peak at 1005 cm^{-1}. This, however, did not present an obstacle to achieving our main objective, which was to establish the optimal conditions for PS-*b*-PCEMA brush formation or the maximization of $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ by changing the coating conditions.

Illustrated in Figure 3 is the change in the SERS spectra of 1321-383 on silver with f_{CP}. The overall trend is that I_{1640}/I_{1005} increased, peaked, and then decreased with f_{CP}. The calculation of the double ratio required

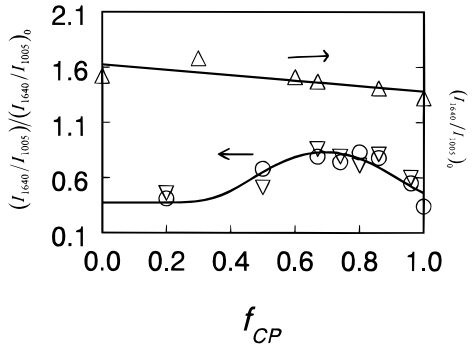

Figure 5. Plot of $(I_{1640}/I_{1605})_0$ of PCEMA films as a function of f_{CP} (top), where the PCEMA films were prepared on silica from a 3.0 mg/mL THF solution and then equilibrated in THF/CP mixtures with CP volume fractions equal to f_{CP}. Also shown is the plot of $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ as a function of f_{CP}, where I_{1640}/I_{1005} stands for the intensity ratios for peaks of 1321-383 films, prepared on silica from 1.0 (○) and 5.0 (△) mg/mL solutions of 1321-383 in THF/CP mixtures, at 1640 and 1005 cm^{-1}, respectively.

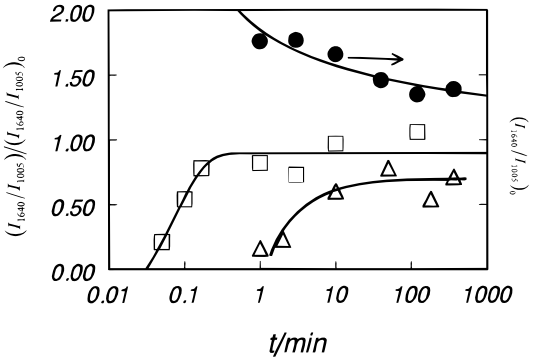

Figure 6. Decay in $(I_{1640}/I_{1605})_0$ of PCEMA films prepared on silver from a 3.0 mg/mL THF solution but equilibrated in CP as a function of their immersion time in CP (top). Also plotted is the increase in $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ of 1321-383 films prepared on silver surfaces as a function of the substrate's equilibration time with the coating solution. The slower rising curve represents results obtained using CP as the solvent for the 1321-383 coating solution. The faster rising curve denotes data obtained using THF/CP with $f_{CP} = 0.86$ as the solvent. In both cases, the 1321-383 coating solution concentration was 3.0 mg/mL.

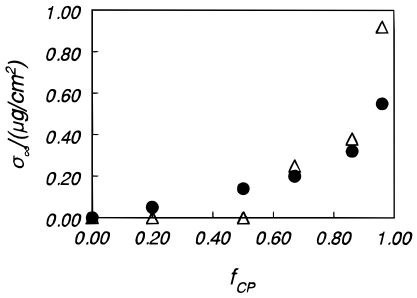

Figure 7. Plot of surface coverages of silica (△) and silver (●) by 1321-383 as a function of f_{CP}.

that $(I_{1640}/I_{1005})_0$ be determined for PCEMA as a function of CP volume fraction, f_{CP}. PCEMA did not dissolve in THF/CP mixtures with f_{CP} greater than ~30% and we could not prepare PCEMA films directly from PCEMA solutions in THF/CP mixtures with f_{CP} greater than ~30%. This problem was circumvented by immersing a silver or silica substrate in a PCEMA solution (3.0 mg/mL) in THF for 10 min and then immediately transferring the withdrawn substrate, now covered with a PCEMA film, into a THF/CP mixture for 2 h. This causes the different functional groups of CEMA in the film to undergo orientation adjustment in accordance with the new medium, and the I_{1640}/I_{1005} values obtained this way for PCEMA were taken as the $(I_{1640}/I_{1005})_0$ values. The $(I_{1640}/I_{1005})_0$ values determined using this method for PCEMA films on silver and silica surfaces are plotted in Figures 4 and 5 as a function of f_{CP}. Linear regression analysis of the data yielded

$$(I_{1635}/I_{1000})_0 = 1.92 - 0.57f_{CP} \quad (1)$$

for silver surfaces and

$$(I_{1635}/I_{1000})_0 = 1.63 - 0.25f_{CP} \quad (2)$$

for silica surfaces.

An equilibration time of 2 h in THF/CP mixtures was used for PCEMA films prepared in THF, because most of the orientation readjustment was expected to be complete in the first 2 h. This is indicated by the results shown in Figure 6, in which $(I_{1640}/I_{1005})_0$ of a PCEMA film prepared from a THF solution on silver surfaces was plotted as a function of the equilibration time of the film with CP.

Since the intensity ratios I_{1640}/I_{1005} were used as a measure of the relative PCEMA content near a solid substrate, we examined the error margin of the measured I_{1640}/I_{1005}. For five specimens of 1321-383 on silver prepared in a 5.0 mg/mL solution in THF/CP with $f_{CP} = 0.86$; the I_{1640}/I_{1005} values determined are 1.04, 1.09, 1.02, 1.09, and 1.00, respectively. The standard deviation, σ, in the data is 0.04, which represents a relative error, $\sigma/\langle I_{1640}/I_{1605}\rangle$ of 4%. This error should be characteristic of all of the samples examined in this study.

Effect of Solvent Composition on PS-*b*-PCEMA Brush Formation. Films of PS-*b*-PCEMA were prepared on solid substrates for SERS measurements from different THF/CP mixtures by equilibrating the solid substrates with diblock solutions for ~12 h. The substrate was then withdrawn from the coating solution and blown dry with nitrogen. 1321-383 films prepared this way on silver and silica surfaces were used to measure their I_{1640}/I_{1005} values. Using eqs 1 and 2 and the measured I_{1640}/I_{1005} values, $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ were calculated as a function of f_{CP}. The results were plotted in Figures 4 and 5 for silver and silica substrates, respectively.

The general trend observed is that $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ on both silica and silver surfaces peak at f_{CP} between 0.67 and 0.86 but are low at both high and low f_{CP} values. One explanation for this is that PS-*b*-PCEMA films prepared from 1321-383 solutions with high and low f_{CP}'s contain both PCEMA and PS in the layer which is within 100 Å of the substrate. However, in the f_{CP} range between 0.6 and 0.9, the films have a layered structure, with more PCEMA next to a solid substrate.

Low $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ Values at Low f_{CP}'s. That the 1321-383 polymer formed films containing more PS near the silica substrate from mixtures with low f_{CP}'s is quite understandable. Figure 7 shows how the surface coverage of silica and silver by 1321-383 varies with f_{CP}. At low f_{CP}'s, 1321-383 was not adsorbed by silica. A film of PS-*b*-PCEMA could be prepared using our method for the SERS study, only because it was derived from the evaporation of solvent from a solution film left on the substrate surface after its withdrawal from a coating solution. Due to the fast solvent evaporation rate and the fact that the chains in the solution phase were randomized (as the solvent mixture was good for both blocks), the film formed due

to solvent evaporation should have an overall random PS or PCEMA concentration distribution along the normal direction of a substrate, although one could not rule out local phase separation.

Silver does absorb a small amount of PS-*b*-PCEMA at low f_{CP} (Figure 7). The final film studied by SERS should have consisted of the film initially adsorbed on silver plus the overlayer formed from solvent evaporation. The film derived from the solvent evaporation should have an overall random PS and PCEMA distribution along the normal direction of a substrate as argued earlier. Our previous studies[12] have demonstrated that both PS and PCEMA compete for silver adsorption sites and that the adsorbed layer may also have an overall random PS and PCEMA concentration distribution along the normal direction. If not, low $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ values may still be expected, as the adsorbed layer is thin at low f_{CP}'s (Figure 7) and enhanced Raman scattering should be seen from a layer within ~100 Å of the silver surface. Furthermore, the adsorbed layer and the layer due to solvent evaporation may mix. All of these would lead to low $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ values.

High $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ Values at Intermediate f_{CP}'s. In the f_{CP} range of 0.60−0.90, the data for 1321-383 films (Figures 4 and 5) do suggest layered structures with more PCEMA close to the silica or silver surface. This suggests that polymer brushes formed from 1321-383 in these solvent mixtures and some of the features of the brush structure were retained in the solid film. Polymer brush formation on silica is not difficult to appreciate from the adsorption data shown in Figure 7. At low f_{CP}, silica essentially did not adsorb 1321-383 at all. As the solvent mixture became poorer for PCEMA by increasing f_{CP}, the amount of 1321-383 adsorbed suddenly increased. This jump must have been caused by the preferential deposition of PCEMA on the silica surface to minimize PCEMA/solvent contacts. This hypothesis is further supported by our previous study, which showed that PS did not adsorb significantly even in THF/CP mixtures with $f_{CP} = 0.96$.[6,12] The retention of the layered structure of a brush in the film studied by SERS can be appreciated by analyzing the properties of the brush layer and the formation of the film for the SERS study. The formed film for the SERS study should have consisted of the brush layer plus an overlayer formed by evaporation of the residual solution left on the brush layer after a substrate's withdrawal from the coating solution. During solvent evaporation, the buoy layer of the brush and the evaporated layer might have undergone some mixing. The PCEMA anchoring layer of the brush should not mix with the buoy and the evaporated layers, as the PCEMA anchoring layer should be essentially free of solvent even when in equilibrium with the coating solution.[8,9] Upon the withdrawal from a solution, the solvent evaporates rapidly, partially because the films prepared using our method were thin. During the short solvent evaporation time, the penetration of new chains into the highly viscous anchoring PCEMA layer was unlikely. After solvent evaporation, the mixing between glassy PCEMA and PS at room temperature became even more difficult. Thus, the structure of the PCEMA anchoring layer should be retained.

Since both PS and PCEMA can be adsorbed by silver, the formation of a PS-*b*-PCEMA brush on silver seemed to be more difficult and required a more selective solvent mixture, i.e. THF/CP mixtures with higher f_{CP}, to produce a layered film structure. On silica, the peaks for $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ were broader and the $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ value reached peak values at $f_{CP} \approx 0.67$. The $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ values on the silver surface peaked only at $f_{CP} \approx 0.82$.

We also examined the effect of polymer concentration on $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$. For 1321-383 on silica, the coating solution concentrations of 1.0 and 5.0 mg/mL did not seem to affect the $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ peak shape (Figure 5).

Decrease in $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ Values at High f_{CP}'s. The decrease in $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ at extremely high f_{CP} values, e.g. >0.90, was initially not expected. However, the trend seemed to be true and occurred with both silica and silver surfaces. The logical explanation is that micelles, with PCEMA as the core and PS as the corona, adsorbed at high f_{CP}'s and remained intact on the adsorbate surfaces after adsorption. For this picture to be reasonable, we first need to explain why micelles become more stable at high f_{CP}'s and then to explain why stable micelles compete with PCEMA for surface sites.

That micelles do become more stable in a more selective solvent has been shown by our past micelle chain exchange kinetic experiments. We demonstrated that the rate constant for chain expulsion from poly(methyl methacrylate)-*block*-poly(methacrylic acid) (PMMA-*b*-PMAA) micelles with PMAA as the core decreased as the ethyl acetate content increased in the methanol/ethyl acetate mixed solvent, where ethyl acetate was the poor solvent for PMAA.[18] A similar trend would be expected for PS-*b*-PCEMA micelles as f_{CP} increased. As f_{CP} increased, less solvent would be sorbed by the core. A glassy core of PCEMA not plasticized by THF should be rigid and the micelles should be more stable.

Stable micelles can be a competitive adsorbent, as each micelle contains many arms and many styrene units. In a THF/CP mixture with high f_{CP}'s, a single CEMA unit may be a better anchoring group than a styrene unit. But the number of styrene units in a micelle far surpasses that of CEMA units in a single PS-*b*-PCEMA chain. As the adsorption energy of each anchoring site in a micelle is additive, a stable micelle can be adsorbed by silica or silver in preference to a PS-*b*-PCEMA chain. This argument would be consistent with the well-established observation that the amount of PS adsorbed by a substrate under otherwise identical conditions increased with the PS molar mass.[19]

If the adsorption of stable micelles was indeed responsible for the decrease in $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ in Figure 4, it should be possible to increase this value by increasing the temperature at which the solid substrate was equilibrated with the coating solution, because micelle dissociation rate constants should increase with temperature. Silica substrates were coated by soaking silica in THF/CP solutions of 1321-383 with $f_{CP} = 0.96$ and $c = 1.0$ mg/mL. When two SERS samples were prepared from the solution at room temperature, the average $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ value obtained was 0.55. This value jumped to 0.63 when two SERS samples were prepared at 50 °C. While $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ did increase with temperature, this increase might still be within the experimental scatter.

In summary, SERS results suggest that PS-*b*-PCEMA brushes form only in solvent mixtures sufficiently poor for the anchoring block, but not so poor that the PS-*b*-PCEMA micelles will not disintegrate. This rule may well apply to brush formation processes for other diblock copolymers.

TEM Results. We inferred from our SERS results in the last subsection that PS-*b*-PCEMA should be adsorbed by silica in the brush conformation in THF/

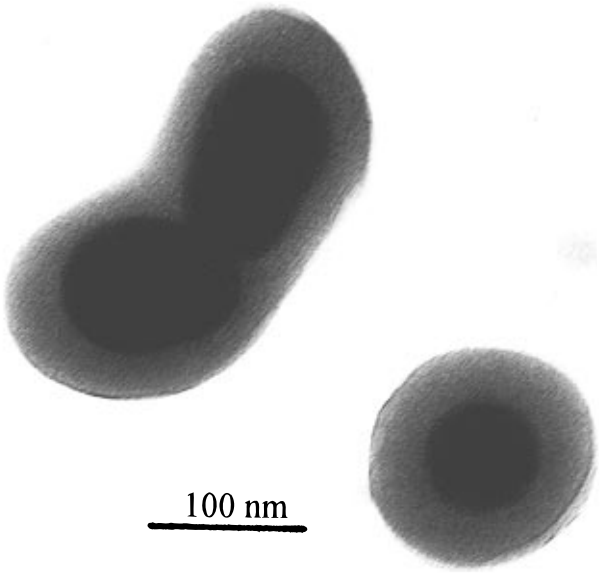

Figure 8. TEM micrograph of single and fused silica particles coated with 1077-1158 in THF/CP with $f_{CP} = 0.82$. The TEM specimen was not stained by OsO_4.

CP mixtures with f_{CP} between 0.76 and 0.90 and micelles were adsorbed at higher f_{CP}. In this subsection, we will show the validity of our SERS results by directly viewing, using TEM, the layered structure of 1077-1158 brushes formed on silica particles from THF/CP with $f_{CP} = 0.82$. This polymer was chosen, as it had a surface coverage of 2.7 μg/cm^2 on silica. This surface coverage would correspond to a dry PS-*b*-PCEMA film thickness of 27 nm, if the density of the PS-*b*-PCEMA film can be assumed to be 1.0 g/mL. Assuming clean phase separation between PS and PCEMA, the PS layer thickness would be 7 nm, as the PS weight fraction in the film is 0.27.

Illustrated in Figure 8 is a transmission electron micrograph of a 1077-1158-coated silica particle. The brush layer has a uniform thickness ~30 nm surrounding the dark silica core. We measured the thicknesses of the PS-*b*-PCEMA layer around 20 silica particles and obtain an average thickness of 29 nm and a standard deviation of 3.7 nm. The average thickness of 29 nm is in good agreement with the expected value of 27 nm.

The brush layer thickness distribution may be partially caused by the fact that there is a distribution in the size of the silica particles. The fact that surface curvature does affect the amount of polymer adsorbed has been well documented previously.[20] Shown in Figure 8 is also a coated silica particle aggregate. This clearly shows that a brush layer can form at a site with a large curvature change and also the contour of the substrate is closely mapped by the brush layer.

After staining with OsO_4, the TEM graph of another silica particle is shown in Figure 9. OsO_4 reacted selectively with PCEMA and made the PCEMA layer appear dark. The fact that a lighter polymer layer remained indicates that PS and PCEMA were well phase-separated. The fact that the lighter layer lied at the edge of the dark core suggests that PCEMA was situated immediately next to silica. If PCEMA were above the PS layer, one lighter region would have been seen between two dark shells. Averaging the PS thickness over 10 stained silica particles gave us an PS layer thickness of 11 nm, in good agreement with the expected value of 7 nm, considering that the PS chains might have partially retained the swollen configuration they assumed in cyclopentane before the particles were sprayed on copper grids.

Figure 9. TEM micrograph of a silica particle coated with 1077-1158 in THF/CP with $f_{CP} = 0.82$. The TEM specimen was stained by OsO_4.

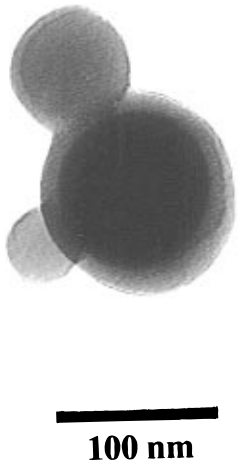

Figure 10. TEM micrograph of a silica particle coated with 1077-1158 in THF/CP with $f_{CP} = 0.92$. The TEM specimen was not stained by OsO_4.

That micelles may adsorb at $f_{CP} = 0.92$ is clearly seen from Figure 10, in which two micelles are seen to be fused with a silica particle. Micelles are distinguishable from coated silica particles as silica particles appear much darker than micellar cores. One may question the subjectiveness of this differentiation. The unambiguous evidence for micelle adsorption is that the thickness of the 1077-1158 layer, adsorbed from a THF/CP solution with $f_{CP} = 0.92$, in the regions free of micelles is only ~20 nm, which is considerably smaller than 29 nm observed at $f_{CP} = 0.82$. On the other hand, the surface coverage should increase with f_{CP} as was demonstrated for 1321-381 in Figure 7 and for other PS-*b*-PCEMA in previous studies.[1] The extra polymer adsorbed at $f_{CP} = 0.92$ did not increase the thickness of the adsorbed layer and had to be accounted for by micelle deposition.

The results described in this subsection represent the first direct observation of the layered structures of polymer brushes and their structures at a site where an abrupt change in surface curvature occurs. This also provides direct evidence for the thickness uniformity of polymer brushes. The results also confirmed the SERS results, which indicated that PS-*b*-PCEMA formed brushes at intermediate f_{CP}'s. Micelle adsorption occurred at higher at f_{CP}'s.

Micelle Disintegration on Solid Substrates as a Brush Formation Pathway. In another set of experiments, roughened silver foils were equilibrated with 1321-383 in CP (1.0 mg/mL) and in THF/CP (5.0 mg/mL) with $f_{CP} = 0.82$ for different periods of time and

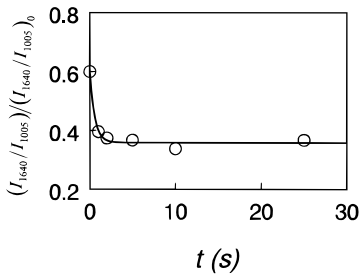

Figure 11. Plot of $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ of 1321-383 films on silver, prepared from a THF/CP solution with $f_{CP} = 0.96$ and $c = 1.0$ mg/mL, as a function of UV irradiation time.

then blown dry with nitrogen prior to SERS measurements. The $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ values for these samples are plotted as a function of the equilibration time in Figure 6. Also shown are two curves which were hand-drawn to fit the experimental data. The $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ values were initially low, increased with time, and eventually leveled off. This represents the same trend as observed by Boerio et al. for PS-*b*-P2VP adsorption from toluene, in which PVP SERS signals were seen to increase with time.[14]

Similar to Boerio et al.'s case, we believe that both the PS-*b*-PCEMA micelles and unimers are initially adsorbed. The adsorption of micelles via the PS block would have resulted in a high concentration of PS near the silver surface. As time progresses, unimers may replace the micelles or the micelles may disintegrate on the silver surface to increase the number of PCEMA/substrate contacts. The fact that $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ relaxed to their equilibrium values much faster for 1321-383 in THF/CP with $f_{CP} = 0.82$ further confirmed our previous hypothesis that the PS-*b*-PCEMA micelles disintegrate faster in a solvent which is less poor for the PCEMA block.

Another possible interpretation for our $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ relaxation data might have been that $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ initially increased with time, because the brush layer took time to build up and $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ relaxation was actually a reflection of brush construction kinetics. This argument may seem plausible if we had not compared $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ relaxation behaviors at two solvent compositions. Our previous adsorption kinetic data clearly illustrated that the rate of polymer adsorption by silica increased with f_{CP}.[6] The fact that the $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ relaxation rate decreased with increasing f_{CP} clearly shows that adsorption kinetics and the $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ relaxation were, in fact, not correlated.

Effect of UV Irradiation on $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$. Having optimized the conditions for brush formation from PS-*b*-PCEMA, we examined the effect of UV irradiation on $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ of a 1381-383 film prepared from THF/CP solution ($c = 1.0$ mg/mL) with $f_{CP} = 0.86$ on silver. Shown in Figure 11 is $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ as a function of UV irradiation time. $(I_{1640}/I_{1005})/(I_{1640}/I_{1005})_0$ initially decreases very rapidly with time but soon levels off. This suggests that the aliphatic double bond could not be completely converted. This might be due to the restricted mobility of the PCEMA groups next to the silver surface. Upon cross-linking, the mobility was further reduced and certain double bonds might not have the appropriate conformation to undergo dimerization with other double bonds.

IV. Conclusions

We have used SERS to optimize the conditions for PS-*b*-PCEMA brush formation from THF/CP mixtures. Our SERS and TEM results showed that polymer brushes formed only in solvent mixtures with f_{CP} between 0.60 and 0.90. At higher f_{CP}'s, PS-*b*-PCEMA micelles also adsorbed on silica and silver surfaces.

We also showed that one of the mechanisms for PS-*b*-PCEMA adsorption was via the deposition of PS-*b*-PCEMA micelles first. The micelles then disintegrated on the surface of an adsorbate or were replaced by unimer chains, if f_{CP} was between 0.60 and 0.90.

The layered structure of PS-*b*-PCEMA brushes and the structural transition of a brush at a site with an abrupt curvature change have been observed, for the first time, by TEM. The TEM results also confirmed the expected thickness uniformity of polymer brushes.

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