Observation of Surface Ordering of Alkyl Side Chains in Polystyrene/Polyelectrolytes Diblock Copolymer Langmuir Films

K. Shin,† M. H. Rafailovich,* J. Sokolov, and D. M. Chang‡

NSF-MRSEC, Department of Materials Science and Engineering, State University of New York at Stony Brook, New York 11794-2275, and Elwood/John Glenn High School, 478 Elwood Road, East Northport, New York 11731

J. K. Cox, R. B. Lennox,* and A. Eisenberg

Department of Chemistry, McGill University, 801 Sherbrooke Street W., Montreal, Quebec, Canada H3A2K6

A. Gibaud

Faculté des Sciences, Université du Maine, 72017 Le Mans Cedex, France

J. Huang and S. L. Hsu

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

S. K. Satija

National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562

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Block polyelectrolytes P(S_x-*b*-VP/RX_y) composed of polystyrene (PS) blocks ($x = 200$, 260) and alkylated ($R = C_n$) poly(vinylpyridine) (PVP) (X = I or Br; $y = 119-270$; $n = 4$, 10, and 18) have been studied using the Langmuir film balance technique and in situ X-ray and neutron reflectivity measurements. Previous studies showed that the self-assembled surface micelles (with PS core and RPV^+PX^- corona) at the air/water interface revealed a characteristic transition (when $n > 6$) without any significant hydration or the submersion of the corona chains. Combined X-ray and neutron reflectivity studies of P(S_x-*b*-VP/RX_y) polyelectrolytes show that although the polyelectrolyte block is water soluble, it remains adsorbed to the water surface. The thickness of the adsorbed layer measured by X-ray reflectivity is in agreement with that measured using neutron reflectivity. This agreement indicates that the counterions are closely associated with the alkylated PVP chains, localized at the air/water interface, and are not distributed into the subphase. Reduction of the water subphase surface tension (using 1−5 vol % *n*-butanol) yields no change in the two-dimensional ordering of the surface micelles but increases the thickness of the corona layer to ca. 100 Å during film compression, indicating that the alkylated blocks become submerged into the subphase under these conditions. In situ Fourier transform infrared spectroscopy performed at the air/water interface establishes that for $n = 10$ and 18, the alkyl chains adopt an ordered, all-trans state. However, no ordering is observed for $n = 4$. These results clearly indicate that transition observed in the $\pi-A$ isotherms is related to an order−disorder process of the alkyl side chains.

Introduction

The self-assembly process of diblock polyelectrolytes at the air/water interface, forming surface micelles, has been extensively studied.[1−5] The two-dimensional structure of diblock polyelectrolytes consisting of a polystyrene block and a fully quaternized polyvinylpyridine with alkyl side chains, P(S_x-*b*-VP/RX_y) (X = I or Br), has been investigated as a function of the chain length of quaternizing agent,[1a,4a] counterion,[4b] temperature,[1a] and pH.[5] Previous studies established that a distinct plateau occurs in the surface pressure−area ($\pi-A$) isotherm at $\pi = 35-40$ mN/m when the length of the alkyl chain is ≥ 5.[4b,5,6] Changing the counterion or pH shifts[5] the position of the plateau but

* Corresponding authors. Miriam Rafailovich: 631-632-8483 (phone), 631-632-5764 (fax), mrafailovich@sunysb.edu (e-mail). Bruce Lennox: 514-398-3638 (phone), 514-398-3797 (fax), bruce_lennox@maclan.mcgill.ca (e-mail).

† Present address: NCNR, NIST, Gaithersburg, MD 20899-8562.

‡ Elwood/John Glenn High School.

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Table 1. Characteristic Properties of Polyelectrolytes

polymer	$x(N_{PS})$	$y(N_{P4VP})$	M_w (g/mol)
$P(S_x\text{-}b\text{-}4VP/C_{18}I_y)$	260	240	142 800
$P(S_x\text{-}b\text{-}4VP/C_{10}Br)$	260	240	104 000
$P(S_x\text{-}b\text{-}4VP/d\text{-}C_4I_y)^a$	260	120	55 700
$P(4VPC_{18}I_y)$	0	480	179 000

[a] Deuterated *n*-butane ($C_4D_9^+I^-$).

does not affect the minimum alkyl chain length necessary for a plateau to be observed. It was proposed that the transition originates from the compression-induced submersion of surface-adsorbed $RPVP^+$ chains into the subphase.[3] This effect, dubbed a "starfish-to-jellyfish transition", would only occur when the hydrophobic alkyl chains were sufficiently long so as to initially pin the hydrophilic corona block chains to the air/water interface. Subsequent in situ X-ray specular and diffuse scattering of these Langmuir films[6] confirmed that the ordered surface micelle structure observed in ex situ Langmuir–Blodgett (LB) films also exists on the water surface. This study showed however that the corona ($RPVP^+$) blocks remain at the air/water interface even when the alkyl chain was as short as $n = 1$. Compression of the films slightly changes the intermicellar distances but does not apparently induce the submersion of the corona blocks. This was attributed to the effects of the high surface tension of the water. The X-ray results thus do not confirm the starfish-to-jellyfish model, nor do they suggest an alternative explanation for the $\pi-A$ plateau. The Langmuir films were also analyzed in situ with Brewster microscopy. For diblocks quaternized with $n > 4$, a rotation of the Brewster angle was observed on the film surface approximately at the onset of the plateau. This suggested that the surface phase transition was associated with a molecular reorientation rather than a change in conformation of the polymer chains. The studies described here are concerned with in situ neutron and X-ray reflectivity measurements. These were undertaken in order to determine (a) whether the associated ions are indeed localized within the corona block when the films are spread on the pure water surface and (b) whether the adsorbed alkylated polyelectrolyte blocks can be submerged into the water subphase when the subphase surface tension is reduced using *n*-butanol. Finally, in situ FTIR spectroscopy was used to determine whether molecular ordering of the alkyl side chains, when they are attached to a flexible polymer backbone, is associated with the observed surface phase transition in the pressure–area isotherm.

Experimental Section

Langmuir Monolayer. Diblock polyelectrolytes $P(S_{260}\text{-}b\text{-}4VP/C_4I_{112})$, $P(S_{260}\text{-}b\text{-}4VP/C_{10}Br_{240})$, and $P(S_{260}\text{-}b\text{-}4VP/C_{18}I_{240})$ were synthesized by anionic polymerization as described previously.[4,6,7] To access deuterated analogues of $P(S\text{-}b\text{-}VP/C_4I)$, the 4-pyridyl moieties were alkylated using deuterated *n*-butyl iodide (Cambridge Isotopes, 99.9% D). The product is designated $P(S\text{-}b\text{-}VP/d\text{-}C_4I)$. Poly(4-vinylpyridine) homopolymer (designated $P(VP_{480}/C_{10}I)$ having 480 residues per chain was perdecylated and isolated as described previously. The characteristics of these materials are tabulated in Table 1.

The diblock copolymer samples were spread on the water surface from a 3:1 (v/v) chloroform/2-propanol solution. In each experiment, a known volume (80–120 μL) of the diblock solution was carefully added to the surface in 5–10 μL increments using a Hamilton microsyringe. To ensure complete evaporation of the solvent, sufficient time (~30 min) was allowed before the start of the measurements. Surface pressure (π)–area (A) isotherms were recorded at a compression rate of ~5 cm²/min using a KSV 3000 Langmuir trough with two moving barriers and a total compression area of 720.0 cm². A 25 mm wide platinum Wilhelmy plate suspended from a microbalance was used to measure the surface pressure. Milli-Q water ($\gamma = 72.1$ dyn/cm²) was used as the subphase. Before the polymer solution was spread, the cleanliness of the water subphase was monitored by a full compression cycle. The surface tension of the subphase was controlled by making water/*n*-butanol (1.1–5 vol % butanol, v/v) mixtures. These were stirred vigorously for 24 h before being used in the film balance experiment.

X-ray and Neutron Reflectivity. In situ specular X-ray and neutron reflectivity studies were performed to obtain the thicknesses and density profiles of the Langmuir films as a function of surface pressure and area.

X-ray reflectivity (XR) using a 8 keV beam was performed on Beam line X22B at the Brookhaven National Laboratory National Synchrotron Light Source (Upton, NY). The polymer solution was spread on the subphase, and the incoming and reflected beams were detected through Kapton-covered windows. The Langmuir film balance was enclosed in a plexiglass box with Kapton windows. To reduce evaporation of the subphase during the measurements, water-saturated N_2 gas was bubbled through the chamber. The apparatus is described in greater detail in ref 6.

Neutron reflectivity (NR) measurements were performed on $P(S\text{-}b\text{-}P4VP/d\text{-}C_4I)$ copolymers, where the alkyl chain was deuterated. The techniques and experimental setup of NR are similar to those for the XR. The polymer solution was spread on a minitrough, with an area of 200 cm² and a single barrier. Specular NR was performed at a fixed wavelength ($\lambda = 4.76$ Å) on the National Institute of Standards and Technology NG7 reflectometer (Gaithersburg, MD). $\Delta\lambda/\lambda$ was ca. 2.5%. The vertical slits were adjusted as a function of the scattering wave-vector transfer, q_z, to fix the resolution at a constant value of $\Delta q/q \approx 0.03$. The horizontal slits were set to 30 mm. A one-dimensional position sensitive detector (PSD) having the 255 channels oriented perpendicular to the sample surface enables one to simultaneously record both a specular intensity and an incoherent background scattering. The reflected intensity was obtained by integrating the peak channels. The angular difference of ±0.156° from the specular peak, where the flat incoherent scattering was shown, was chosen in order to obtain the background intensity, which was subtracted from the reflected intensity. The measured intensity has been then converted to the absolute reflectivity by normalization with the detector/monitor ratio below the critical angle, where total external reflection occurs. The detailed setup of the neutron liquid reflectometer is described elsewhere.[8]

NR and XR were used to obtain complementary information[8b,9] about the polymer system. Both were measured as a function of the scattering wave-vector transfer, q_z ($= 4\pi/\lambda \sin(\theta)$), where θ is the incident angle, when the X-ray or neutron beam was reflected at an interface with a contrast between two media. In the Born approximation,[8b,10] the reflectivity $R_F(q_z)$ is given by

$$R(q_z) \propto \frac{1}{q_z^4}\left|\int \frac{d\rho(z)}{dz}\exp(-iq_z z)\right|^2 \qquad (1)$$

where $d\rho(z)/d(z)$ is the contrast of the sample along the surface normal. In X-ray experiments, neglecting absorption, the calculated indices of refraction $n = 1 - \delta$ with dispersion δ, given linearly in terms of the electron density, ρ_e, by $\delta = \lambda^2 r_0 \rho_e/2\pi$ where r_0 is the classical electron radius. In contrast, the δ is given linearly in terms of the scattering length density, SLD, by $\delta = \lambda^2 \mathrm{SLD}/2\pi$ in neutron experiments. In this case, $d\rho(z)/d(z)$ is the gradient of SLD of the sample along the surface normal and implies that the reflected intensity at the intensity is sensitive to the SLD. Despite the fact that Synchrotron X-ray sources are

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more intense and better focused than neutron beams, the X-ray contrast is rather small between the block copolymer and the aqueous subphase. Most of the X-ray contrast is achieved from the counterions (Br^- or I^-).[6] To profile the copolymer chains with neutron reflectivity, isotopic substitution is necessary to provide contrast.[11] Samples using deuterated alkyl side chains were thus synthesized and used in neutron reflectivity studies.

To extract the density profiles from the reflectivity measurements, we used the box model analysis, where each box is parametrized as consisting of different slabs with ρ_e (or SLD), thickness (t), and roughness (σ). Two slabs were used to model the P(S_x-*b*-VP/RX_y), one for the PS core and another for the corona tails diffused into the subphase. Gaussian distributions have been used to describe the smeared interfaces. We systematically varied and then optimized fitting parameters ρ_e (or SLD), t, and σ until χ^2 was minimized. The details of this model used here can be found in the previous paper.[6]

FT-IR Spectroscopy. A Langmuir trough equipped with a Cahn electrobalance (ATI Instruments) coupled to a Fourier transform infrared spectrometer (Perkin-Elmer System 2000) was used to investigate the Langmuir films. A Hamilton microsyringe was used to spread the monolayer films on the surface of water. Characteristic infrared bands of the spreading solvents ($CHCl_3$, 2-propanol) used were monitored until they disappeared. Monolayer films were then compressed, and external reflectance infrared spectra were acquired as a function of molecular area and surface pressure. The isotherms were recorded by continuously compressing the monolayer films at a compression rate of 3.0 cm^2/min. Temperature was controlled using an Isotemp circulating water bath. The external reflection−absorption infrared spectra were obtained by recording 512 scans with a resolution of 2 cm^{-1}. The absorbance units of the spectra were defined as $-\log(R/R_0)$, where R_0 and R were the reflectivities of pure and film-covered water surfaces, respectively.[12] Because the hydrocarbon chain may play an important role in the phase transition,[4a,6] the IR spectra in the ~3100 cm^{-1} (symmetric mode, d^+) and ~3300 cm^{-1} (asymmetric mode, d^-) regions were monitored.

Results and Discussion

X-ray and Neutron Reflectivity. Figure 1 summarizes the $\pi-A$ isotherms for the block polyelectrolytes studied. As previously reported,[6] a well-defined plateau exists for the $n = 10$ and $n = 18$ block copolymers. No plateau is evident for the $n = 4$ copolymers. A plateau is observed even for the PVP/C_{18}I homopolymer, indicating that only the length of the alkyl chains determines the existence of a phase transition; the PS blocks are not necessary for a $\pi-A$ transition to be expressed. These data also show that it is possible to obtain a Langmuir film of the PVP/C_{18}I homopolymer although each residue is ionic. On the other hand, when n is short ($n < 6$) it was suggested[4b] that the pinning of the shorter alkyl groups may be insufficient to maintain the chains at the air/water interface at high surface pressure values. Subsequent XR data indicated[6] that a high surface pressure was in fact insufficient to completely submerge the chains into the subphase. The $\pi-A$ isotherm of the C_4-derivatized diblock on a 3.3 vol % butanol subphase ($\gamma = 65.2$ mN/m) is qualitatively similar to that on a pure water subphase. No information regarding the structure of the alkyl side chains can thus be determined from the $\pi-A$ isotherms alone.

Figure 2 shows the XR of P(S-*b*-4VP/*d*-C_4) Langmuir films at two different surface pressure values. The measured reflectivities (symbols) and fits (solid lines) are plotted as Rq_z^4 to compensate q^{-4} decay in eq 1 from Fresnel's law, so then the oscillations, which are directly related to the layer thickness, can be easily distinguished.

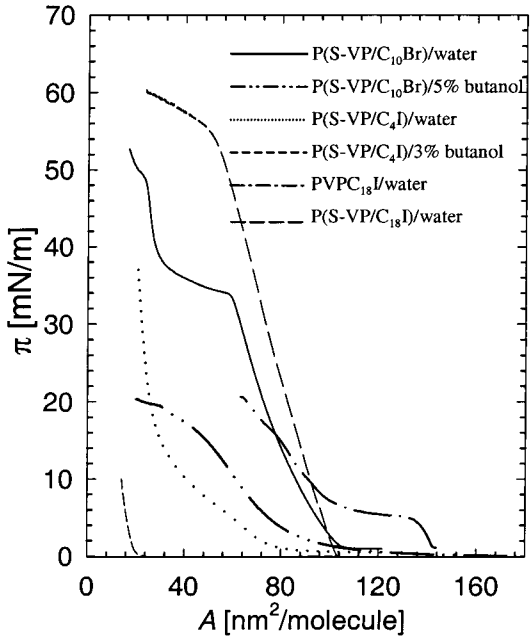

Figure 1. Isotherms of P(S-*b*-VP-C_nI) (or Br) diblock copolymers and P(4VP-C_{18}I)$_{480}$ homopolymer for Langmuir films on a water or water/*n*-butanol surface.

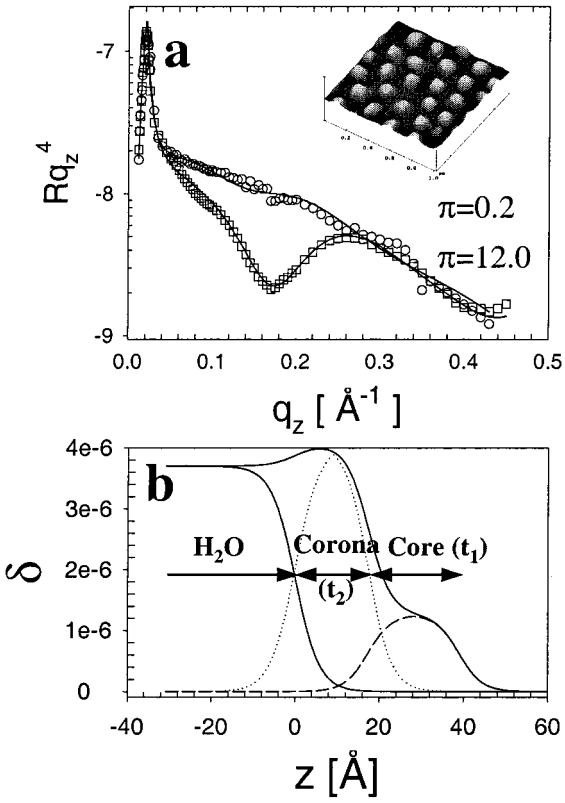

Figure 2. (a) X-ray specular reflectivity measurements of a P(S_{260}-*b*-VPC_4I_{120}) monolayer spread ($V = 120$ mL) on the air/water interface. The solid lines are the least-squares fits, and (b) is the corresponding two layer model at $\pi = 12$ mN/m. t_1 and t_2 are representing the thickness of core and corona, respectively, and root mean square roughnesses σ_1, σ_2, and σ_3 in Table 2 are from the air/core, core/corona, and corona/subphase interfaces, respectively. The bold line represents the dispersion profile $\delta(z)$ convoluted with the profiles of subphase (line), corona (dots), and core (dashes).

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Table 2. Fitting Parameters[a] from XR and NR of Diblock Polyelectrolytes at the Air/Water Interface

π (mN/m)	t_1 (Å)	t_2 (Å)	σ_1 (Å)	σ_2 (Å)	σ_3 (Å)	δ_1	δ_2
			Figure 2				
0.2	20.0	6.7	7.3	3.8	3.0	0.7	4.4
12.0	20.8	20.4	7.0	4.4	5.3	1.9	4.1
			Figure 3[b] (Reference 15)				
0.2	19	11	10	4	10	0.5	1.3
3.4	19	13	9	4	13	0.7	1.7
4.5	18	21	4	4	13	0.7	1.0
6.1	18	28	4	3	12	0.8	0.9
9.9	19	33	2	3	12	0.9	0.7
19.7	18	35	2	2	15	0.8	0.7
			Figure 5a				
0.2	22.4	15.9	7.1	3.3	7.0	0.5	4.5
25.0	22.4	16.9	7.1	3.4	6.5	0.7	3.4
30.0	22.4	18.4	7.1	3.5	4.7	0.9	4.8
33.0	22.4	19.7	7.1	3.7	3.6	1.0	4.0
34.0	22.4	21.1	7.1	4.3	3.2	1.1	4.1

[a] The parameters of the PS cores were initially calculated from previous studies; see ref 6. For X-ray experiments, the uncertainty for thicknesses was less than ±2 Å and the average uncertainty for roughnesses was about 15% of those values. [b] SLD_1 and SLD_2 ($\times 10^{-6}$ Å^{-2}) of the materials have been listed instead of δ_1 and δ_2, respectively.

As we reported previously,[6] an overall off-specular intensity, which is considered as a background intensity for specular analysis, consists of off-specular scatterings both from a micelle lattice ($I_{micelle}$) and a capillary wave spectrum ($I_{capillary}$). However, the off-specular scattered intensity within our experimental q-range was at least 1 order of magnitude lower than the specularly reflected intensity.[13] An AFM topography image of the LB film (removed at π = 7.6 mN/m) is shown in the inset. The AFM image establishes that one obtains the expected two-dimensional ordering[6] of the surface micelles when the PVP is derivatized with the d-C_4 chains. Fits to the reflectivity data (solid lines) were obtained from a two-layer model (Figure 2b), which consists of an upper layer of PS hemimicelles and a lower layer of corona chains at the subphase interface. The thickness (t_1) of the PS cores used in the fitting was taken from AFM measurements and was kept constant while the thickness (t_2) of the polyelectrolyte corona was a free parameter. The y-axis represents a dispersion coefficient, the real part of the refractive index (n). The Parratt algorithm was applied for the fitting routine.[14] The parameters, including thicknesses (t), roughnesses (σ), and dispersion coefficients (δ), obtained from the fits are summarized in Table 2. The data demonstrate that at low π values, the counterions are concentrated at the air/water interface within a layer 6 Å thick. Increasing the surface pressure to 12.0 nm/m (which is well into the liquid condensed phase of the Langmuir film) increases the counterion layer to ca. 20 Å. This however is still far less than would be expected for an extended polymer brush in a good solvent (approximately 100−400 Å).[11a]

NR studies were performed in order to confirm that the polymer chains are not submerged when the counterions are isolated near the air/water interface. Because the contrast in the NR experiment arises from the deuterium substitution, NR data are insensitive to the spatial position of the counterions. The specular neutron reflectivity curves obtained from P(S-b-4VP/d-C_4) Langmuir films at different points along the isotherm are shown in Figure 3.

(13) For XR measurements, the specular scans were regarded as their reflectivities.

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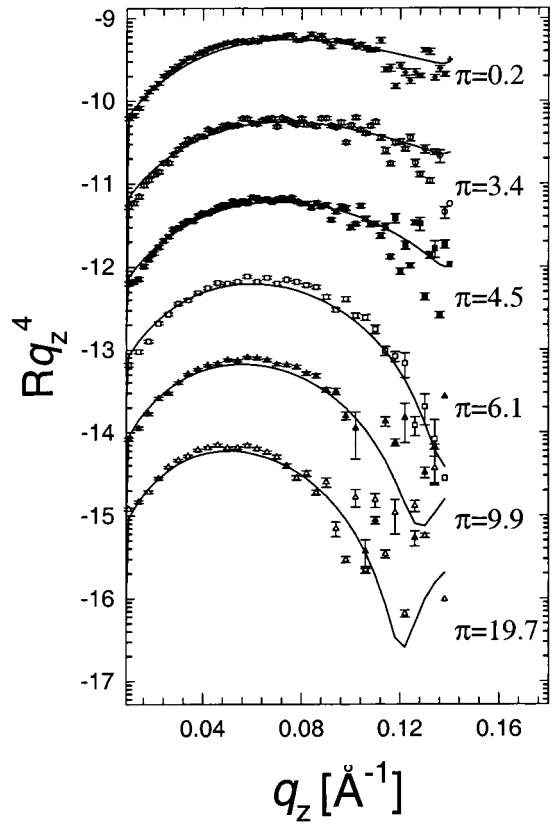

Figure 3. Neutron reflectivity of P(S_{260}-b-VPC_4I_{120}) vs wave transfer vector q_z on a water subphase. The solid lines are the least-squares fits to each experimental data obtained at different surface pressures. The curves are shifted by 1×10^{-1} of the y-axis for clarity.

The model used to fit the data (solid lines) is similar to the one derived for analysis of the XR data (Figure 2b). In this case, we can express the neutron scattering densities $\rho(z)$ of the deuterated polyelectrolyte chains in a direction to surface normal z by

$$\rho(z) = \lfloor b_{vp} n_{vp}(z) + b_{d\text{-}C_4} n_{d\text{-}C_4}(z) \rfloor \phi_{polymer}(z) + b_{H_2O}(1 - \sigma_{polymer}(z))$$

where b_i is the scattering length of species i (i = VP, d-C_4, and H_2O represent the monomer segments of vinylpyridine corona backbone, deuterated n-butane, and water subphase, respectively) with a number density n_i of species i in a direction to surface normal z. The $n_{polymer}(z)$ of the polymer chains can be expressed from the Gaussian distribution of the volume fraction ($\phi(z)_{polymer}$). Table 2 lists the parameters obtained from the fits. The data in Table 2 established that the thickness of the polyelectrolyte block ranges from 11.4 Å at π = 0.2 mN/m to 33.0 Å at π = 9.9 mN/m. These values are somewhat larger than the thicknesses obtained from XR (Table 2).[15] The roughness estimated from neutron reflectivity data of the polymer/H_2O interface is ∼11 Å, while it is 3 Å from X-ray reflectivity data. Both X-ray and neutron results confirm that the corona chains are submerged in the water subphase, with increasing surface pressure, by less than 1 radius of gyration (R_g ∼ 35 Å) of PVP/C_4I.

(15) The reflected intensity is directly related to surface excess, Γ, given by the product of t and SLD. Even without the unique reflectivity features, such as a critical edge and interfering fringes, varying the parameters of corona chains can give a good fit with accuracy; see: Penfold, J. *Physica B* **1991**, *173*, 1. We estimate an uncertainty of ±20% from the sensitivity of χ^2.

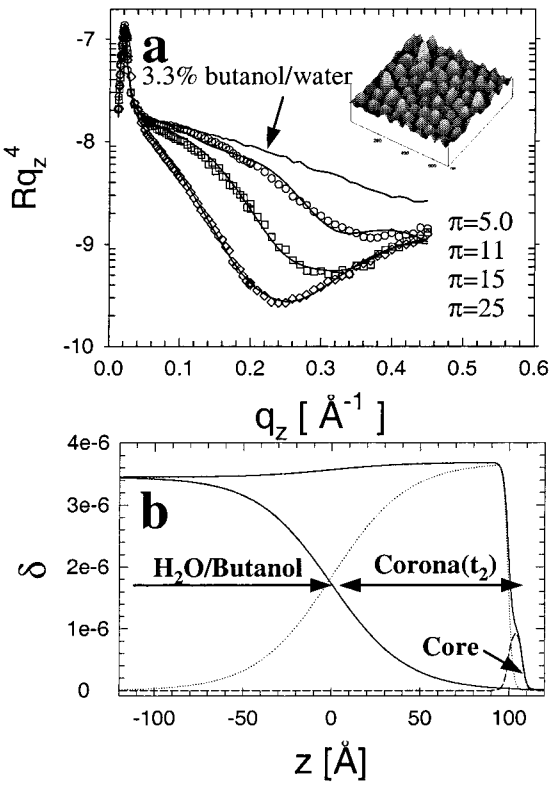

Figure 4. (a) X-ray reflectivity of a $P(S_{260}\text{-}b\text{-}VPC_4I_{120})$ monolayer spread at the air−butanol/water mixture interface at a subphase controlled at $\gamma = 69.1$ mN/m. The solid lines are the least-squares fits, and (b) is the corresponding two-layer model at $\pi = 11$ mN/m as described in Figure 2.

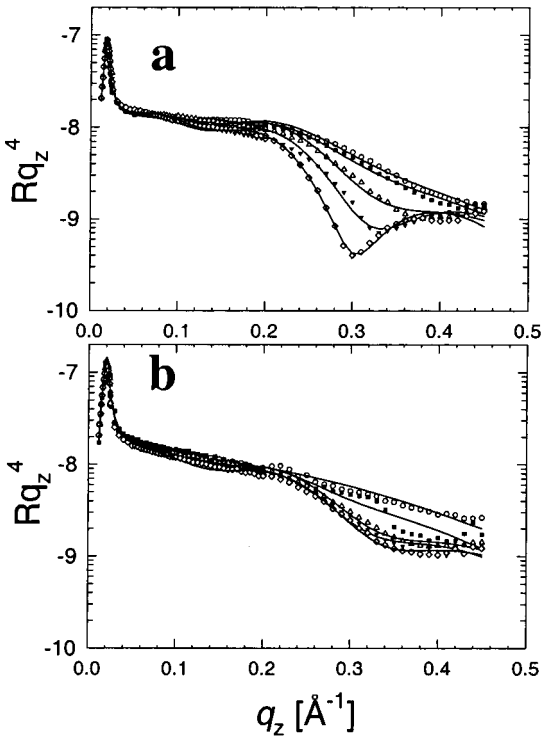

Figure 5. (a) X-ray specular reflectivity of a $P(S_{260}\text{-}b\text{-}VPC_{10}\text{-}Br_{240})$ monolayer spread ($V = 80$ mL) on (a) the air/3.3 vol % butanol−water interface ($\gamma = 65.2$ mN/m) and (b) (a) the air/5.0 vol % butanol−water interface ($\gamma = 61.2$ mN/m). The solid lines are the least-squares fits to each experimental data obtained at different surface pressures from the model profiles as shown in Figure 4b.

The surface tension of the water subphase can be decreased by the addition of *n*-butanol.[5] If the surface tension of the subphase is the origin of the strong localization of corona chains at the air/subphase interface, tuning the subphase surface tension might be an effective way to initiate chain submersion. For example, γ values of ~69.2 and 61.0 mN/m are accessible with *n*-butanol/water mixtures whose volume fractions ϕ of *n*-butanol in water are 1.1 and 5.0 vol %, respectively.[16] It is therefore interesting to investigate the thickness of the polyelectrolyte block as a function of subphase surface tension in order to determine whether a submersion process can be initiated.

Figure 4a is the specular XR data obtained when the subphase is 3.3 vol % *n*-butanol ($\gamma = 65.2$ mN/m, see ref 16). An AFM topography image (inset, Figure 4) of the corresponding LB film deposited on a Si surface results in the same highly ordered two-dimensional structure of surface micelles being formed when *n*-butanol is added to the subphase. Comparison of these data with the XR data obtained on pure water (Figure 2a) shows that the well-defined oscillation (at $q_z \sim 0.17$ Å^{-1}) disappears when *n*-butanol is added. The solid lines in Figure 4 are the fits obtained with the model shown in Figure 4b. At low π, the thickness of the layer (20 Å) is comparable to that on pure water ($t_2 = 6.7$ Å). As the surface pressure π is increased, the chains become submerged and the data are best fitted with a parabolic brushlike layer which is approximately >100 Å thick. Since the layer is highly diffuse, the X-ray contrast is significantly reduced, and the data fits are no longer sensitive to the exact functional form of the brush. Nonetheless, the polyelectrolyte chains clearly occupy a significant volume at the air/water interface.

Specular X-ray reflectivity curves were also obtained for PS−P4VP/C_{10}Br Langmuir films. These films exhibit a distinct plateau on both pure water and reduced surface tension subphases.[5] Figure 5a shows the specular reflectivity curves with a 1.1 vol % *n*-butanol/water ($\gamma = 69.1$ mN/m) mixed subphase. Compared to the pure water case,[6] whose maximum thickness of the PVP/C_{10}Br corona layer is 19.4 Å, the maximum thickness on a 1.1 vol % *n*-butanol/water subphase is 21.1 Å. This similarity indicates that a reduction in the subphase surface tension by 3.1 mN/m is insufficient to allow the alkyl chains to become fully submerged at modest surface pressure values.

A 5 vol % *n*-butanol ($\gamma = 61.7$ mN/m) subphase was also studied. The reflectivity profiles (Figure 5b) at different surface area values are fairly featureless, even at high compression. The scattering intensity is less than that of pure water (upper trace) making it difficult to determine the precise functional form of the concentration profiles. This indicates that the chains are already submerged even at low surface pressures. The model used to fit the data is shown in Figure 4b. When $t_2 > 100$ Å, the interfacial roughness between corona (t_2) and subphase becomes so large that little or no contrast exists between the layers.

These findings establish that the inter-relationships between the surface pressure, subphase surface tension, and nature of the polyelectrolyte are quite complex. Caution must be exercised in assuming where a surface-tethered polyelectrolyte is localized with respect to the air/water interface (for example, see ref 17). The XR experiment, as used here and in prior work,[6] clearly establishes that the P4VP-based polyelectrolytes do not form a brush structure except under special conditions.

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(17) Prinz, C.; Muller, P.; Maaloum, M. *Langmuir* **2000**, *16*, 6636.

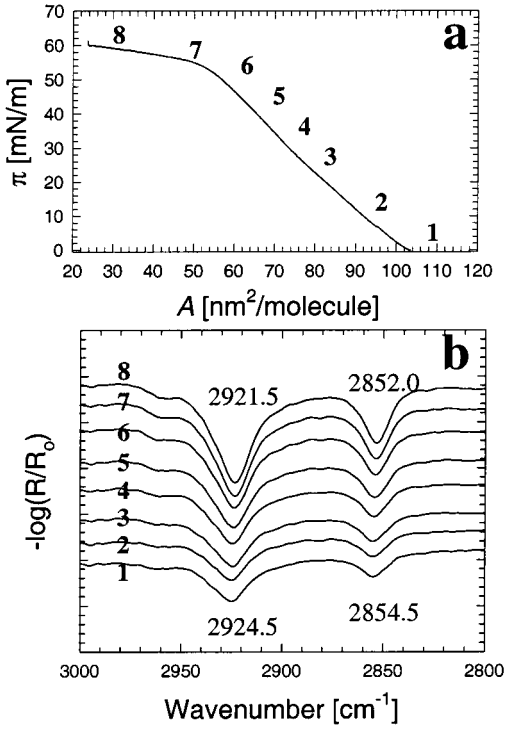

Figure 6. (a) Surface $\pi-A$ isotherm of a P(S_{260}-*b*-$VPC_{18}Br_{240}$) monolayer spread ($V = 100$ mL) on the air−water interface at $T = 24$ °C. The isotherm is recorded at the same time as the corresponding FTIR reflection−absorption spectra (b) in the range 2800−3000 cm^{-1} at areas corresponding to points 1−8 labeled on the isotherms.

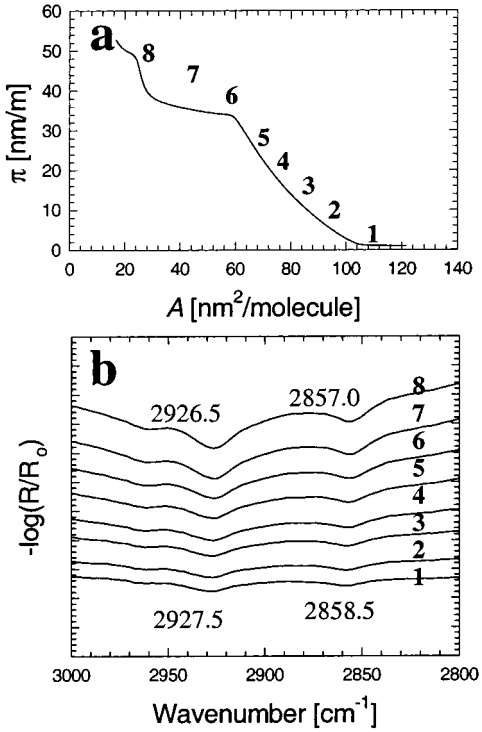

Figure 7. (a) Surface $\pi-A$ isotherm of a P(S_{260}-*b*-$VPC_{10}Br_{240}$) monolayer spread ($V = 80$ mL) on the air−water interface at $T = 24$ °C. The isotherm is recorded at the same time as the corresponding FTIR reflection−absorption spectra (b) in the range 2800−3000 cm^{-1} at areas corresponding to points 1−8 labeled on the isotherms.

In Situ FTIR Spectroscopy. Since changes in the XR data do not correlate with the onset of the plateau in the $\pi-A$ diagram, it was previously proposed[6] that the transition might originate from a compression-induced organization of the alkyl chains into some type of a superstructure. Only indirect evidence for this hypothesis, based on the changes in the Brewster angle at the plateau, had previously been presented.

To directly observe if such a process was occurring, the block copolymers with the longest side chains were studied, as they are the most likely to order. Monolayers of P(S_{260}-*b*-4$VPC_{18}I_{240}$) were spread on the surface of water from 3:1 (v/v) chloroform/2-propanol solution at an initial surface area of 60 nm^2/molecule. The $\pi-A$ isotherm and the corresponding reflection−absorption infrared spectra obtained at 24 °C are displayed in Figure 6b for the spectral range 2800−3000 cm^{-1}. The corresponding isotherms (Figure 6a) whose labeled surface pressure values correspond to the infrared spectra are shown in Figure 6b.

The spectra in Figure 6b clearly indicate that the alkyl chains adopt an all-trans conformation when $n = 18$, given that CH_2 stretching vibrations are conformation sensitive.[12] For example, an asymmetric CH_2 stretching vibration (d^-) of 2920 cm^{-1} and a symmetric CH_2 stretching vibration (d^+) of 2850 cm^{-1} are characteristic of an all-trans chain.[12] A gauche conformation d^- stretch is ∼2924 cm^{-1}, and the d^+ stretch is ∼2853 cm^{-1}. Increasing compression of the film shifts both d^- and d^+ from 2924.5 and 2854.5 cm^{-1} to 2921.5 and 2852.0 cm^{-1}, respectively (Figure 6b). This indicates that the population of trans-chain segments increases as the surface pressure increases. Since the hydrocarbon chains are attached to a polymer backbone (which has its own degrees of freedom), the ordering can reach crystalline alkane levels. These data are acquired at 24 °C (near the bulk mp of $C_{18}H_{38}$ at ∼28 °C), so the extent of ordering is rather surprising. The pinning of the alkyl chains to the polymer backbone and the overall localization at the air/water interface probably play a role in the chain-ordering process. The increased intensity of the IR absorbance peak with increased surface pressure is consistent with the X-ray reflectivity data (that show that chains are not submerged) and the fact that the surface density increases with surface pressure.

The reflection−absorption infrared spectrum for a P(S_{260}-*b*-4VP/$C_{10}Br_{240}$) film spread on pure water at 24 °C is shown in Figure 7b. The corresponding pressures are labeled on the $\pi-A$ isotherm shown in Figure 7a. In Figure 7b, d^- and d^+ are shifted to lower frequencies by 1 and 1.5 cm^{-1}, respectively. These shifts are smaller than those observed for the C_{18} derivative and are consistent with a lesser degree of ordering, as is expected for shorter chains. As per the C_{18} case, however, the observed increase in intensity with surface pressure indicates that the C_{10} chains are not submerged. This is also in agreement with the X-ray reflectivity data. Some limited degree of chain ordering is observed at 24 °C, which is considerably greater than the bulk freezing temperature (−27 °C) of *n*-decane.[18] One possible explanation is that the C_{10} chains, being attached to the polymer backbone, have reduced entropy relative to free chains, thus allowing for ordering at higher temperatures. Nevertheless, the onset of the transition in the $\pi-A$ diagram, observed for both C_{18} and C_{10} side chains, correlates with the increased ordering of the side chains.[19] In contrast, no shift in d^+ or d^- was observed for

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(19) These results have been qualitatively confirmed by lateral force imaging of the LB films. A decrease in surface friction and adhesion occurs with increasing compression. Such changes are characteristic of an increasing rigidity in the film, which in turn corresponds to an increase in crystallinity.

the infrared absorbance spectra of $P(S_{260}$-*b*-$4VP/C_4I_{120})$ films at 24 °C. This suggests that no ordering of the C_4 side chains occurs upon compression. This is consistent with the C_{18} and C_{10} systems given that no plateau in the C_4 $\pi-A$ isotherms occurs.

Conclusions

Combined X-ray and neutron reflectivity studies of P(S-*b*-VP/RX) show that even though the $P(VP/R^+X^-)$ polyelectrolyte block is water soluble it remains adsorbed to the water surface throughout compression of the Langmuir film. The thickness of the adsorbed layer, as measured by X-ray reflectivity, is consistent with the results from neutron reflectivity measurements. This indicates that the counterions are associated with the copolymer chains at the air/water interface and exist as ion pairs with the pyridinium ions. The counterions do not diffuse into the subphase. Addition of *n*-butanol (1−5 vol %) to the water subphase decreases the surface tension of the water subphase; with this reduced surface tension, no change in the two-dimensional ordering was observed. The thickness of the polyelectrolyte corona layer does however increase to roughly 100 Å, indicating that the chains are submerged in the subphase, as was originally suggested.[6]

In situ FTIR spectroscopy was performed on the surface micelle Langmuir films. When $n = 10$ and 18, the population of alkyl chains with ordered, all-trans segments increases upon compression; no ordering is observed for $n = 4$ however. These results clearly indicate that the observed phase transition in the $\pi-A$ isotherms is associated with an order−disorder process arising from the alkyl side chains.

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