Nanomosaic Surfaces by Lateral Phase Separation of a Diblock Copolymer

Joachim P. Spatz,[†] **Martin Möller,***[,†] **Michael Noeske,**[‡]
R. Jürgen Behm,[‡] **and Martin Pietralla**[§]

Organische Chemie III—Makromolekulare Chemie, Universität Ulm,
D-89069 Ulm, Germany, Oberflächenchemie und Katalyse, Universität Ulm,
D-89069 Ulm, Germany, and Experimentelle Physik, Universität Ulm,
D-89069 Ulm, Germany

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ABSTRACT: Ultrathin films of a symmetrical polystyrene-*block*-poly(2-vinylpyridine) diblock copolymer with a degree of polymerization of 600 were prepared by spin coating from a nonselective solvent, i.e., $CHCl_3$, on mica. The concentration of the casting solutions was chosen to be too low to allow homogeneous coverage of the substrate without significant stretching of the macromolecules. Scanning force microscopy demonstrated the formation of uniform polystyrene clusters with a height of about 5 nm and a distance of about 100 nm between them. In between the substrate was covered by ≈1 nm thick film of poly(2-vinylpyridine). The large periodicity of the two-dimensional phase pattern is explained by the strong interaction of poly(2-vinylpyridine) with mica, favoring a highly stretched conformation. X-ray photoelectron spectroscopy showed that about every third poly(2-vinylpyridine) unit was in chemical contact with the substrate. When the film thickness was increased, the X-ray photoelectron spectroscopy N(1s) signal decreased in comparison to the C(1s) signal indicating that the adsorbed poly(2-vinylpyridine) got increasingly covered by polystyrene. An estimation of the free energy indicates that the lateral phase separation is mainly controlled by the length of the polystyrene blocks affecting the incompatibility of the polystyrene and the poly(2-vinylpyridine) covered mica.

Introduction

A−B diblock copolymers organize in microdomains if the gain in enthalpy by reducing the contacts between A and B segments exceeds the penalty in entropy (i) by demixing of the A and B segments and (ii) by stretching the chains at the phase boundary.[1] Upon phase separation, the linkages between the blocks get arranged along the border line of the phases and a brush type structure is formed. Steric crowding causes some stretching of the chains resulting in a repulsive elastic contribution to the free energy.[2] The phase state has been shown to depend on the product of the Flory parameter χ_{A-B} and the number of monomer units N, i.e. $\chi_{A-B}N$. For small values of the product $\chi_{A-B}N < 10$ (weak segregation regime) the blocks mix and the chain conformation is Gaussian. For $\chi_{A-B}N >> 10$ (strong segregation limit) nearly pure microdomains are formed separated by narrow interfaces of width $\propto\chi_{A-B}^{-1/2}$. The Gaussian chain conformation becomes more stretched. The shape and size of the structure formed in the strong segregation limit are primarily controlled by the volume fraction of the constituent blocks.[1]

The proximity of a macroscopic phase boundary can affect the orientation of the microdomains as well as their structure. Parallel orientation of lamellae to the substrate was observed in thin films of a symmetrical polystyrene-*block*-poly(methyl methacrylate) on a polar substrate. The polar substrate was first covered by poly(methyl methacrylate) (PMMA) followed by an alternating sequence of polystyrene (PS) and PMMA layers with a periodicity L which corresponded to the bulk structure.[3−5] Because of its low surface energy, PS formed the top layer at the air interface. Significant mismatching of the layer thickness and the bulk periodicity has been shown to result in the formation of holes or islands with a thickness comparable to the bulk period.

The phase morphology of a block copolymer is also strongly affected by the confinement between two walls.[5,6] In the case of a lamellar structure, the lamellae get compressed or thickened in order to satisfy the geometric constraints. If the mismatch of the periodicity and the film thickness is too large, cylinders or lamellae are formed which are oriented perpendicular to the surface.[7,8]

Only recently, first attempts have been described on the preparation of chemically heterogeneous nanomosaic surfaces (NMS) by lateral phase separation of a block copolymer in ultrathin films.[9,10] Within this context, we reported on the structure of an ultrathin film of a symmetrical polystyrene-*block*-poly(2-vinylpyridine) block copolymer film which was cast from a non-selective solvent onto mica.[9] The casting conditions were chosen in such a way that the amount of polymer which formed the film was not sufficient in order to form a monomolecular film without significant stretching of the block copolymer chains. Scanning force microscopy data indicated the formation of a chemically heterogeneous, highly ordered surface. The experimental data have been explained assuming that the P2VP blocks strongly wet the mica surface as an ultrathin layer whereby the coil formation gets strongly deformed. The penalty in conformational entropy is balanced by the adsorption energy. The PS blocks dewet the poly(2-vinylpyridine) (P2VP) layer because it cannot gain sufficient energy by PS−P2VP contacts which would compensate for the necessary stretching of the PS blocks. The model is depicted in Chart 1.[9]

In this work we demonstrate the validity of the described model by varying the thickness of the nanomosaic surfaces and by combining scanning force mi-

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* To whom correspondence should be sent.
[†] Organische Chemie III—Makromolekulare Chemie.
[‡] Oberflächenchemie und Katalyse.
[§] Experimentelle Physik.
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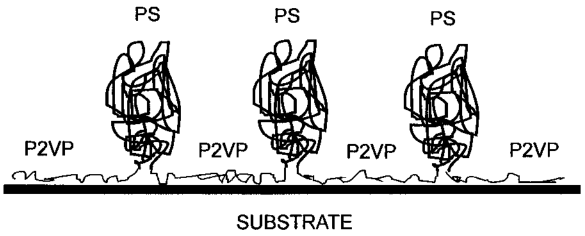
Chart 1



croscopy (SFM) experiments and X-ray photoelectron spectroscopy (XPS). XPS is known to be chemically selective within surface layers as thick as 10 nm depending on the specific electron free path in the investigated material.[11]

Experimental Section

Samples. Poly(styrene)-*block*-poly(2-vinylpyridine), PS-*b*-P2VP, with a monomer ratio of 300−300 was obtained by sequential anionic polymerization as described elsewhere.[12−14] A stock solution of the diblock copolymer was prepared in absolute chloroform (5 mg/mL). For casting the stock solution was diluted stepwise down to 0.01 mg/mL. Thin films were prepared on a freshly cleaved piece of mica by spin coating at 10 000 rpm. The concentration was varied between 0.1 and 0.01 mg/mL in order to control the surface coverage and the film thickness.

Scanning force microscopy was performed with a Nanoscope III (Digital Instruments, St. Barbara) operating in the tapping mode. The oscillation frequency was around 360 kHz depending on the Si cantilever, which had a spring constant of about 50 N/m. In order to minimize the interaction with the sample, the tapping frequency was chosen as far as possible on the low-frequency side of the noncontact resonance curve.[15] The layer thickness of the polymer films was determined by contact scanning force microscopy. A area of 1 μm × 1 μm was scanned for 20 min with maximum force resulting in the removal of all polymer in that particular section. Subsequently, a large scale image (5 μm × 5 μm) was scanned including the polymer scrubbed off area surounded by the unaffected layer.

X-ray photoelectron spectroscopy was performed with Mg Kα excitation ($h\nu = 1253.6$ eV) in an ultrahigh vacuum (UHV) system at a pass energy of 50 eV. The binding energy values reported are compensated for homogeneous electrostatic charging of the sample by referring to a binding energy of 293.75 ± 0.20eV of K(2p$_{3/2}$) resulting in a binding energy of 289.6 eV for the C(1s) electrons of the polymer film.[11,16,17] The emission angle was 90° with respect to the surface plane.

Results

Figure 1 shows a high magnification SF-micrograph of a film of a PS-*b*-P2VP block copolymer with 300 monomer units per block. The thin film was cast from a 0.05 mg/mL chloroform solution. Figure 1A shows the surface topology as formed upon casting. Figure 1B depicts the same film after it had been annealed for 24 h at 150 °C. The degree of ordering improved considerably. Clusters of about 5 nm in height are separated by a rather smooth, 1 nm thick layer.[9] The spacing of the pattern is about 100 nm. Figure 1C shows a large section which demonstrates a domain pattern. Inside the domains, the elevations are arranged hexagonally.

The ultrathin block copolymer film as depicted in Figure 1 has been studied by X-ray photoelectron spectroscopy in order to obtain information on the elemental composition and binding state. XPS is a powerful technique for distinguishing different chemical interactions of the nitrogen atom of the pyridine ring.[11,16,17] Figure 2a gives the intensity of the N(1s) signal versus the binding energy measured on a thick poly(2-vinylpyridine) film. No influence from the substrate is expected. The peak for the N(1s) electrons is fitted by a Gaussian function (solid line).

Table 1. XPS Intensities of C(1s) and N(1s) with P2VP Layer Thickness and PS Cluster Height

height of PS cluster[b] ±1 (nm)	thickness of adsorbed P2VP layer[b] ±1 (nm)	C(1s)/N(1s)[a] ±1	N(1s) (low energy) ±1 (counts·s^{-1}·eV)	N(1s) (high energy) ±1 (counts·s^{-1}·eV)
2	<1	16	50	25
5	1	16	50	30
7	3	21	60	30
11	5	25	121	

[a] Ratio is corrected with ASF: ASF(N(1s)) = 0.477, ASF(C(1s)) = 0.296. [b] Determined with contact scanning force microscope.

Figure 2b shows the XPS N(1s) signal of a thin film like the one of Figure 1. The experimental curve (squares) reveals two different interactions of the N(1s) photoelectrons and has been fitted by two Gaussian distributions (dotted and dashed line). The solid line presents the sum of both fits. The energy splitting is about 2.3 eV. The high-energy peak shows a quite smaller half-width than the low-energy peak. The integral ratio r of the two areas is about r=N(1s)(400.5 eV)/N(1s)(402.8 eV) = 0.58.

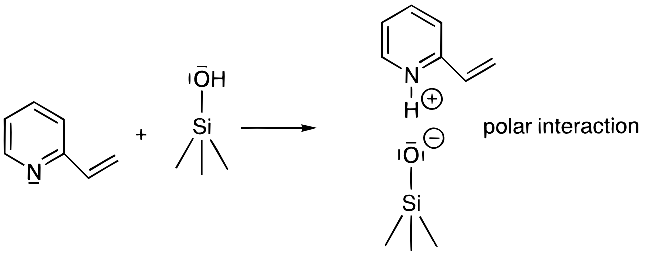
The carbon to nitrogen ratio in the surface layer was determined to be approximately $r = 16 \pm 1$ by comparison of the integrated C(1s) intensity with the sum of both N(1s) signals after correction by the corresponding atomic sensitivity factors (ASF[N(1s)] = 0.477, ASF[C(1s)] = 0.296). The stoichiometric C/N ratio in a symmetric PS-*b*-P2VP block copolymer of 15 is consistent with the XPS results.

Figure 3 shows a series of scanning force micrographs of annealed films which were cast from solutions differing in polymer concentration from that of Figure 1. The film thickness was measured by SFM after part of the film had been removed by scratching with the SFM tip at high normal force in the contact mode. Thickness values were taken as the height of the clusters (above the coating between the elevations) and as the thickness of the coating between the elevations (see Table 1). We estimate an uncertainty of at least 1 nm, which is mainly caused by the compliance of the polymer layer upon interaction with the tapping probe.

The film in parts A and B of Figure 3 was prepared from a 0.01 mg/mL solution. The elevations or polymer clusters are much less regularly arranged and vary also more strongly in size compared to Figure 1. Apparently the substrate was not entirely covered by the polymer (see also below). The average height of the clusters was determined to be about 2−3 nm.

The observed order was also less perfect when the concentration of the casting solution was increased compared to the sample of Figure 1. Increasingly larger, less regularly shaped clusters were observed in parts C and D of Figure 3 and parts E and F of Figure 3 which cover the ground more completely. The average height was determined to be 7 and 11 nm for parts C and D of Figure 3 and parts E and F of Figure 3, respectively.

Table 1 summarizes the XPS results in dependence of the film thickness. The intensity of the high-energy N(1s) signal disappeared for thicker films on the expense of the low-energy N(1s) signal. At the same time, the carbon to nitrogen ratio r = C(1s)/N(1s) increased from 16 (corresponding to Figure 3A/B) to about 25 (corresponding to Figure 3E/F). Thin films of homo poly(2-vinylpyridine) yielded the same thickness dependence for the ratio of the two N(1s) XPS peaks. While two N(1s) peaks were observed for a 1 nm thick P2VP film, thicker films showed only the low-energy peak of the N(1s) signal. Thus, there is clearly a correlation between the film thickness and the relative fraction of pyridine groups exposed to the surface as well as the occurrence of a second nitrogen peak. It can be concluded that the second nitrogen peak with a smaller half-width represents pyridine units which are chemisorbed to the OH groups at the surface of mica while the larger half-width of the low-energy peak indicates the influence of an interaction gradient between the surface and the pyridine units which are located at certain distances from the mica substrate.



Obviously the electrons which interact with the polar surface are more strongly bound. The energy shift of 2.3 eV of the binding energy of the N(1s) electron is consistent with an apparent charge transfer of one electron of the nitrogen atom to the Si−OH group, indicating the strong polar adhesive interaction of mica with the 2-VP units.[11,16,17] From the signal ratios for the first two samples in Table 1 it can be assumed that every second to third unit has direct contact to the mica substrate while the other units form loops.

So far the experimental results indicate strongly that the clusters or elevations are formed by the PS blocks, while the substrate surface in between is covered by strongly adhering poly(2-vinylpyridine) chains. The increase of the ratio $r = \mathrm{C(1s)/N(1s)}$ for thicker films is consistent with the SFM images of Figure 3E/F, demonstrating that the adsorbed poly(2-vinylpyridine) layer gets more and more covered by the clusters of polystyrene increasing in diameter.

Assuming a polymer density of 1.1 g/cm^3, the average amount of polystyrene chains per cluster can be estimated from the average volume of one cluster which can be evaluated from the SF micrographs. For the films shown in Figure 1B, the average number of polystyrene blocks per cluster was determined to be around 90 based on the volume average for a cylinder and a cone with the height of 5 nm and a radius of 24 nm. The number of poly(2-vinylpyridine) blocks which are adsorbed on the mica within a radius of 50 nm must be identical. Thus, the average surface area per vinylpyridine unit results to 40×10^{-20} m^2 corresponding to 8.3×10^{15} P2VP chains/m^2. Such a monomer coverage is consistent with the formation of trains and only small loops.[18−20]

On the basis of this interpretation, it appears worthwhile to have a closer look at the SFM images depicted in Figure 3A/B. Figure 3A shows the topography of the coating from ultradilute casting, Figure 3B presents the control signal of the amplitude of the tip oscillation.[15] In the latter case, small features are depicted as pronounced as larger ones. It appears that the images display bundles or even single poly(2-vinylpyridine) chains adsorbed on the surface of mica around the clusters of the polystyrene blocks, which are depicted as globular elevations. Observation of single molecules is certainly at the limit of the SFM technique and needs confirmation by other experimental data. However, the picture is remarkably consistent with our model. The block copolymers assemble to small polyp-like units which sit on the substrate. Between the adsorbed legs, we apparently see the uncovered surface of mica.

Chart 2

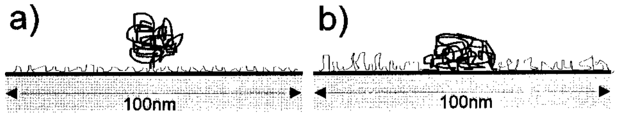
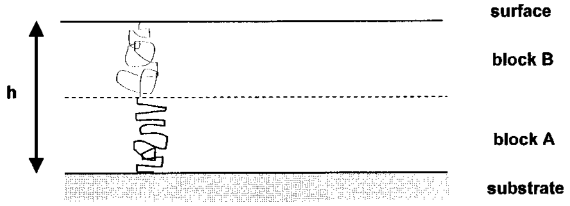


Chart 3



In average the adsorbed bundles have a height of 1 nm, which is in good agreement with the one-half to one-third ratio of substrate bound pyridine groups detected by XPS. An estimation of the number of polystyrene blocks per cluster results from 10 to 30 chains in average. Also this number is in agreement with the number of strings (adsorbed P2VP bundles) departing from the clusters. It is worth to emphasize that the smaller cluster shows less strings departing from the cluster (10 chains/cluster) than the bigger once (30 chains/cluster).

Discussion

From the SFM and XPS data on films of varying thickness it is evident that there is an optimum surface coverage or layer thickness for the development of an ordered pattern. If the coverage is too small or too high, the ability of the chains to organize to regular domains decreases.

The periodicity of about 100 nm is rather large for a block copolymer of twice 300 monomer units. The unperturbed end-to-end distance of a polystyrene chain $\langle r^2\rangle^{1/2} = (C_N{}^{\infty} n l^2)^{1/2}$ results in 13 nm corresponding to a radius of gyration of 5.5 nm.[21] The discrepancy is not changed if one accounts for the fact that part of the surface area might be covered by the polystyrene chains directly as shown by the situation b in Chart 2.

Also in this case stretching of the poly(2-vinylpyridine) chains results in several times the radius of gyration. Such a strong stretching of the poly(2-vinylpyridine) chains is, however, consistent with a strong interaction of the pyridine units and the substrate, as demonstrated by the XPS data with a 2.3 eV shift of the N(1s) signal to higher energies.[17] The interaction can be characterized as polar, which has to be correlated to strong adhesive energies. In comparison to other interfacial energies which take part in the system, $\gamma_{\mathrm{P2VP/mica}}$ can be neglected because of these high adhesive energies.

In the following we attempt a semiquantitative discussion of the free energy of the model depicted in Chart 1 in comparison to the formation of a homogeneous brush which corresponds to a lamella coating as depicted in Chart 3.

The free energy of a surface grafted block copolymer can be calculated by

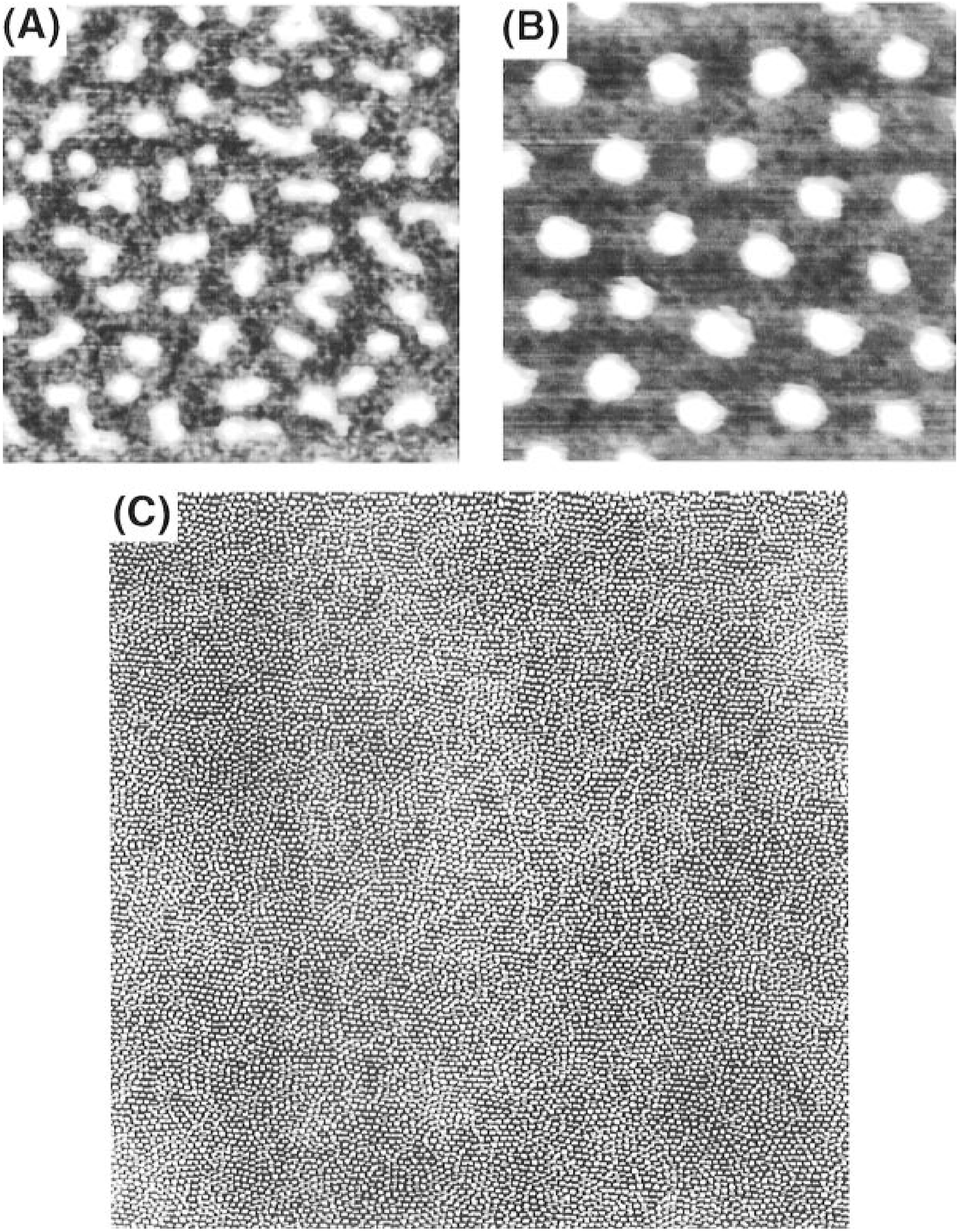


Figure 1. Scanning force micrographs of ultrathin PS-*b*-P2VP films: (A) directly after spin coating (length of the image corresponds to 550 nm); (B) after annealing (length of the image corresponds to 550 nm); (C) large scale image of the same film as shown in (B) (length of the image corresponds to 11 μm).

$$F_{\mathrm{LAM}} = S[\gamma_{\mathrm{B}} + \gamma_{\mathrm{B-A}} + \gamma_{\mathrm{A-S}} + E_{\mathrm{def}}] \qquad (1)$$

S corresponds to an unit area, γ_{B} is the surface tension of the polymer exposed to the air, $\gamma_{\mathrm{B-A}}$ is the interfacial energy between the polymer phases, and $\gamma_{\mathrm{A-S}}$ is the interfacial energy of contact between the second polymer with the substrate. Two principally different situations, shown in Chart 4, have to be distinguished for the "uncomplete coverage" discussed here if a lamellar structure is assumed. In case A the number of substrate contacts per poly(2-vinylpyridine) block is relatively small and the chains can adopt a favorable brush conformation. The thickness h of the lamellae corresponds to half of the periodicity of the bulk equilibrium structure, i.e., $h = L/2$. The consequence is, however, that the total amount of material is not sufficient to cover the substrate fully and part of the surface of mica remains exposed to the air.

In case B of Chart 4, the poly(2-vinylpyridine) chains are laid flat onto the substrate favoring a closed layer. In a second layer the poly(2-vinylpyridine) is covered by the polystyrene chains. Because of the equal block lengths also the polystyrene chains have to be pinned down and become strongly stretched parallel to the

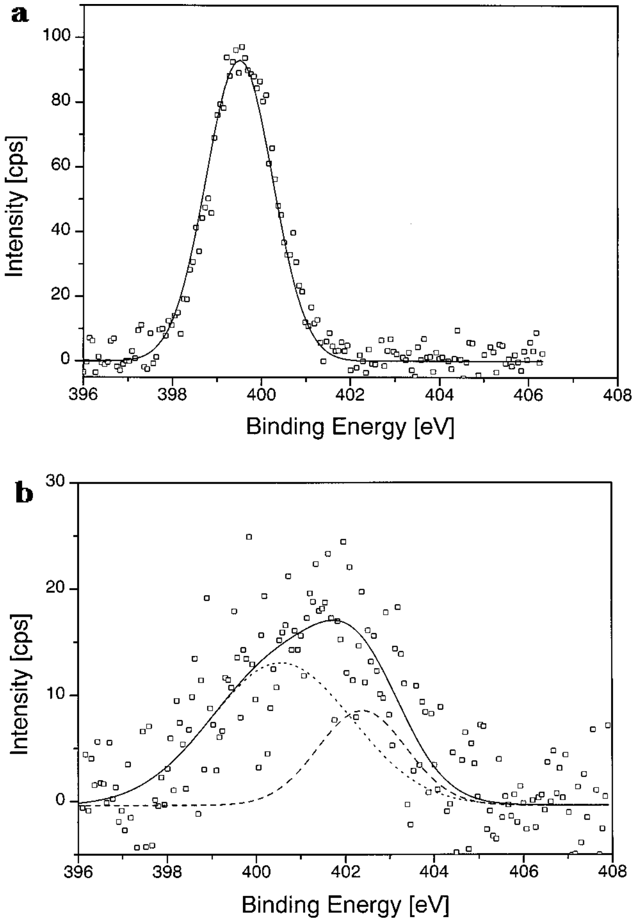


Figure 2. X-ray photoelectron spectroscopy signal of the N(1s) peak: (A) thick P2VP homopolymer film (the solid line presents a Gaussian fit) and (B) ultrathin PS-*b*-P2VP film like that shown in Figure 1(solid line is the sum of the two Gaussian fitted, dashed and dotted, lines). In (B) the high-energy peak indicates adsorption of 2VP units onto mica. The energy shift due to adsorption is about 2.3 eV.

substrate in order to cover the surface fully. The thicknesses of the lamellae are significantly smaller than those in the bulk equilibrium, i.e., $h << L/2$.

If the coverage of the surface by patches of the polymer lamellae in case A of Chart 4 is expressed by S_{polymer}/S with S being the total surface area, the free energy of the system results to

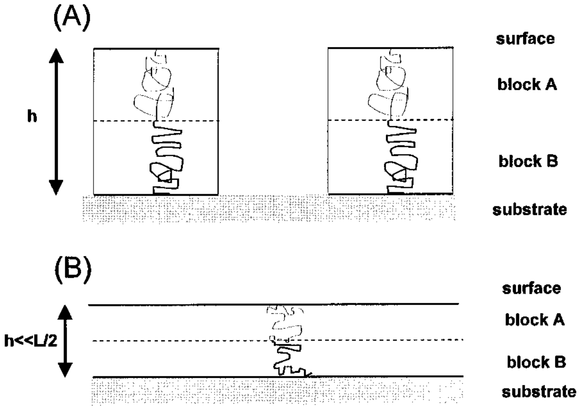
$$F_{\mathrm{LAM}}(A) = \left(\frac{S_{\mathrm{polymer}}}{S}\right) S[\gamma_{\mathrm{PS}} + \gamma_{\mathrm{PS-P2VP}} + \gamma_{\mathrm{P2VP-S}} + E_{\mathrm{def}}] + \left(1 - \frac{S_{\mathrm{polymer}}}{S}\right) S\gamma_{\mathrm{S}} \tag{2}$$

The free energy can be estimated assuming a relatively small deformation of the chains[22]

$$E_{\mathrm{def}} = \frac{3}{8} k_{\mathrm{B}} T \sigma_{\mathrm{lam}} \frac{h^2}{N l^2} \tag{3}$$

where k_{B} is the Boltzmann constant, T the absolute temperature, h the height of the film, N the degree of polymerization, l the monomer length, and σ_{lam} the number of block linkages at the polymer A−B interface per area. For $N = 600$ and a periodicity which corresponds to the bulk equilibrium structure $h = L/2 \cong 12$ nm [obtained from electron and scanning force microscopy] and $\sigma_{\mathrm{lam}} = 5 \times 10^{18}$ m^{-2},[7] $\gamma_{\mathrm{PS}} = 0.031$ J/m^2,[23] $\gamma_{\mathrm{PS-P2VP}} = 0.022$ J/m^2,[24] $\gamma_{\mathrm{P2VP-mica}} \cong 0$ (adhesive contributions are high as mentioned before), and $\gamma_{\mathrm{mica}} = 0.3$ J/m^2 ,[20] as well as a surface coverage of $S_{\mathrm{polymer}}/S = 0.13$ as suggested by the pattern in Figure 1, the free energy estimation results to $F_{\mathrm{LAM}}(A) = S{\cdot}0.27$ [J/m^2]. This value is about 3 times higher than the corresponding free energy estimation for the surface fully covered by a block copolymer film of the same height.

Chart 4



In a similar way an estimation of the free energy can be made for the situation depicted in Chart 4, case B. As a result of the reduced film thickness, $h << L/2$, the cross sectional area per chain, σ, has to be increased significantly. From the average film thickness in Figure 1, the number of chains per square meter results to $\sigma = 8.3 \times 10^{15}$ m^{-2}, compared to $\sigma = 5 \times 10^{18}$ m^{-2} for the situation in Chart 3. While in Chart 3 the chains stretch perpendicular with respect to the substrate because of steric crowding, in the latter case both blocks have to be stretched strongly lateral to the substrate. For strongly stretched chains as observed in the case of a dense polymer brush where the repulsive steric forces can result in a brush thickness $h = 10{\cdot}\langle s^2\rangle^{1/2}$,[18] the elastic energy for stretching is given by[25−27]

$$E_{\mathrm{def}}^{\mathrm{I}} = \frac{3}{2} k_{\mathrm{B}} T \sigma \frac{(h^*)^2}{N_{1/2} l^2} = 0.004\ [\mathrm{J/m^2}] \tag{4}$$

In the case discussed were the P2VP blocks of $N_{1/2} = 300$ units are strongly stretched in the lateral direction, $h^* = 50$ nm, i.e., half the periodicity of the observed pattern. For a quantitative estimation of the free energy

$$F_{\mathrm{LAM}}(B) = S[\gamma_{\mathrm{PS}} + \gamma_{\mathrm{PS-P2VP}} + \gamma_{\mathrm{P2VP-S}} + 2E_{\mathrm{def}}^{\mathrm{I}}] \tag{5}$$

Equation 4 yields an estimated free energy value of $F_{\mathrm{LAM}}(B) = S{\cdot}0.065$ [J/m^2]. This value is already considerably smaller than that estimated for case A. However, we have to consider that the reduced layer thickness affects the interaction forces between the layers. E.g., the interfacial width for a symmetrical, phase separated polystyrene-*block*-poly(methyl methacrylate) sample has been determined to be $a = 5.0 \pm 0.3$ nm,[3] which is more than the maximum film thickness in Figure 1. Segregation forces between the PS chains and the P2VP/mica sublayer as well as the surface tension values are expected to increase. Thus, long range van der Waals forces are expected to increase the free energy compared to the value calculated by eq 4.[28]

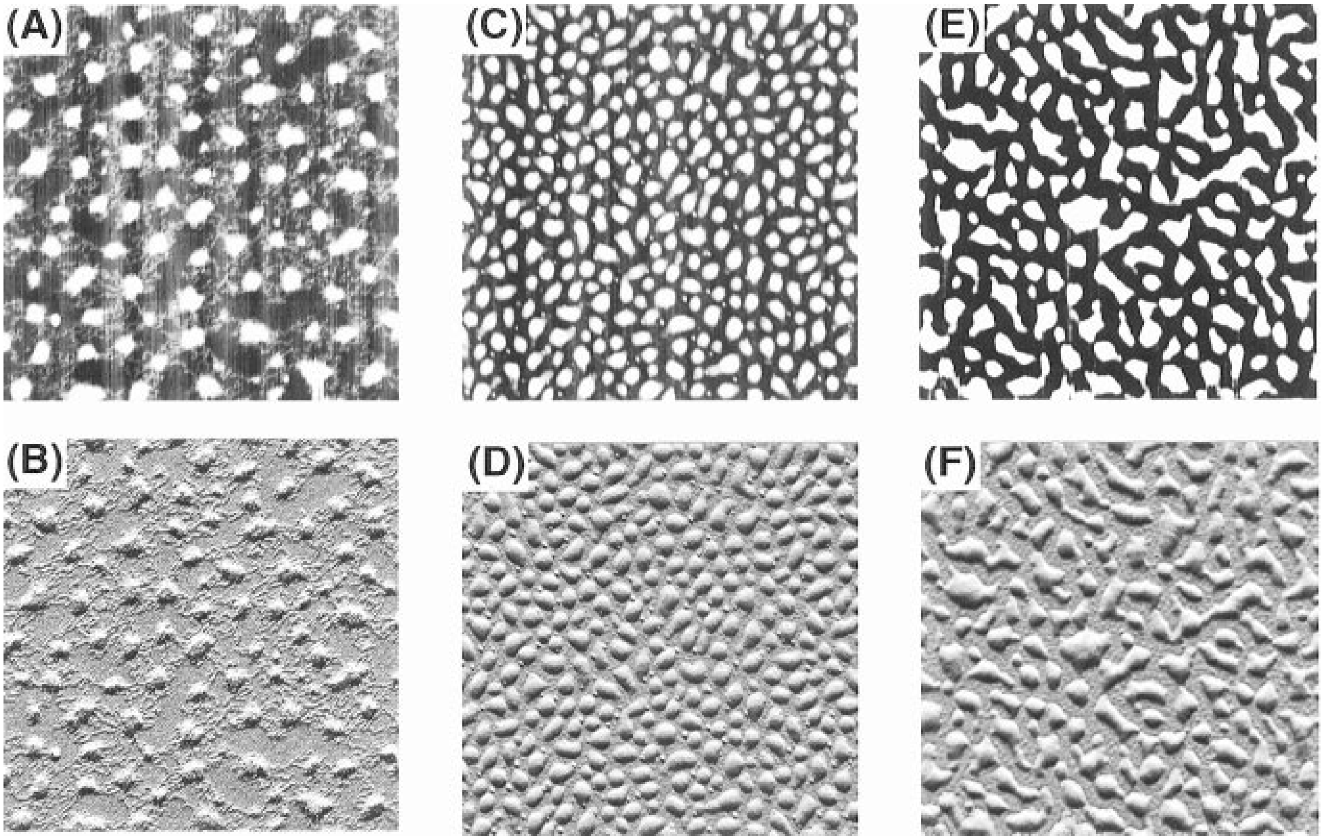


Figure 3. Scanning force micrographs of ultrathin PS-*b*-P2VP films. (A), (C), and (E) are showing the topography while (B), (D), and (F) are presenting the amplitude control signal emphasizing rather small features. While (A) shows bundles of molecule chains (600 × 600nm^2 scan size) or even single molecules, (B) and (C) represent increased layer thicknesses (both 1.1 × 1.1 μm^2).

Finally the structure shown in Chart 1 can be discussed. If we assume that the P2VP chains are homogeneously stretched over the area S and the PS chains remain unperturbed, which is consistent with the experimental height of the polystyrene clusters in the range of $R_g = (Nl^2)^{1/2}$, the free energy results to

$$F_{\mathrm{LAT}} = \left(\frac{S_{\mathrm{cluster}}}{S}\right) S[\gamma_{\mathrm{PS}} + \gamma_{\mathrm{P2VP-PS}} + \gamma_{\mathrm{P2VP-S}}] + \left(1 - \frac{S_{\mathrm{cluster}}}{S}\right) S\gamma_{\mathrm{P2VP}} + SE_{\mathrm{def}}{}^{\mathrm{I}} \quad (6)$$

Using $\gamma_{\mathrm{P2VP}} = 0.05$ [J/m], the free energy value $F_{\mathrm{LAT}} = S{\cdot}0.056$ [J/m^2] is obtained.

The differences of the estimated free energy of case B in Chart 4 with that of Chart 1 is not sufficiently large to explain the experimentally observed preference of the cluster formation clearly. We regard this as an indication that long range interactions of PS with the substrate must not be neglected. Thus an extra term $\gamma^*_{\mathrm{PS/MICA}}$ must be introduced accounting for the long range van der Waals interaction of PS with the substrate. In this case, the sum of $\gamma^*_{\mathrm{PS/MICA}} + \gamma_{\mathrm{PS-P2VP}}$ will be the driving force for minimizing the PS−P2VP contacts. Assuming that the surface tensions in Chart 4 case B and Chart 1, i.e., γ_{PS} and γ_{P2VP}, are both affected by approximately the same amount because of the ultrathin films, the free energies of Chart 4 case B and Chart 1 result:

$$F_{\mathrm{LAM}}(B) = S[\gamma_{\mathrm{PS}} + \gamma_{\mathrm{PS-P2VP}} + \gamma_{\mathrm{P2VP-S}} + \gamma^*_{\mathrm{PS/MICA}} + 2E_{\mathrm{def}}{}^{\mathrm{I}}] \quad (7)$$

$$F_{\mathrm{LAT}} = \left(\frac{S_{\mathrm{cluster}}}{S}\right) S[\gamma_{\mathrm{PS}} + \gamma_{\mathrm{P2VP-PS}} + \gamma_{\mathrm{P2VP-S}} + \gamma^*_{\mathrm{PS/MICA}}] + \left(1 - \frac{S_{\mathrm{cluster}}}{S}\right) S\gamma_{\mathrm{P2VP}} + SE_{\mathrm{def}}{}^{\mathrm{I}} \quad (8)$$

Because the interfacial energy $\gamma^*_{\mathrm{PS/MICA}}$ is not known, a quantitative estimation is not possible. However, a comparison of the three structures (Chart 4 case A and case B and Chart 1) on a semiquantitative base is well possible. Case A, depicted in Chart 4 case A can be denied because of the extremely high interfacial tension of mica. Chart 1 succeeds over case B if

$$F_{\mathrm{LAT}} < F_{\mathrm{LAM}}(B) \quad (9)$$

which results as

$$\left(\frac{S_{\mathrm{cluster}}}{S} - 1\right)(\gamma_{\mathrm{PS}} + \gamma_{\mathrm{PS-P2VP}} + \gamma^*_{\mathrm{PS/MICA}} - \gamma_{\mathrm{P2VP}}) - E_{\mathrm{def}}{}^{\mathrm{I}} < 0 \quad (10)$$

Comparitive evaluation of eqs 4 and 5 has shown that the free energy contribution for the stretching of the PS block is not sufficient to yield the situation described by eqs 8 and 9. Consequently, $\gamma^*_{\mathrm{PS/MICA}} + \gamma_{\mathrm{PS-P2VP}}$ plays the important role for the dewetting of the P2VP layer by the PS blocks. It may be approximated

$$\gamma_{\mathrm{PS}} + \gamma_{\mathrm{PS-P2VP}} + \gamma^*_{\mathrm{PS/MICA}} - \gamma_{\mathrm{P2VP}} > 0 \quad (11)$$

i.e., the lateral phase separation is controlled by minimizing the interaction enthalpy of PS chains which becomes increasingly unfavorable with increasing length of the blocks. Because the entropy of the mixing also decreases for higher molecular weights, long range order as shown in Figure 1c is increasingly favored. In agreement with the bulk behavior of a phase separating diblock copolymer, an order−disorder transition of the surface mesophase must be expected if the length of the PS block is lowered significantly.[1]

Conclusions

Adsorption of a block copolymer as an ultrathin film can yield a periodic surface domain structure. The remarkably large spacing for a rather low molecular weight block copolymer has been explained by strong adsorption of the P2VP blocks and an increased segregation force between the PS blocks and the thin P2VP layer due to the affect of long range van der Waals forces originating from the substrate. Minimizing the enthalpy of the PS clusters controls the dewetting of the PS chains as well as the long range ordering. The PS enthalpy is estimated to be about 1 order of magnitude higher than the energy for stretching the blocks. An order−disorder transition on the surface of ultrathin diblock copolymer films is proposed in agreement with the mesophase behavior of a diblock copolymer in the bulk.

After this paper has been submitted we received notice of work by others where a similar surface structure has been discussed for a thin film of PS-*b*-P2VP.[10,29] However, in this work the film was cast from a solvent selective for PS which results in a situation similar to that described in refs 13 and 14 where we discussed deposition of solution assembled micelles on top of an adsorbed polymer brush.

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