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## On the morphology of a lamellar triblock copolymer film

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**Abstract.** — X-ray and neutron reflectivity are used to study the morphology of a triblock copolymer of d-poly(styrene) and poly(2-vinylpyridine) in the form P2VP<sub>30</sub>-dPS<sub>60</sub>-P2VP<sub>30</sub> deposited as a film on a silicon wafer. Microphase separation leads to a lamellar film which is strongly quantized in layers of about 300 Å each and with P2VP at the silicon substrate. The confinement of the polymer ends to the same plane leads for the top layer to a « looping » of the polymer, so that the middle PS part can still wet the air interface completely.

### 1. Introduction.

Block copolymers are macromolecules composed of blocks consisting of chemically distinct repeat units. The simplest case is an A-B diblock copolymer ; the next higher block copolymer is an A-B-A triblock copolymer. These polymers show « surfactant »-like behaviour due to the difference in chemical properties of the A- and B-blocks. The associated ability to modify interfacial properties also makes this class of synthetic materials important technologically. Below the order-disorder transition (ODT) various types of liquid-crystalline organization are observed. Just as in lyotropic liquid crystals, depending on the relative proportion and length of the constituent parts, lamellar structures, bicontinuous double diamond domains, hexagonal arrays of cylinders, and body-centered cubic arrays of spheres can be found [1, 2]. Such phase behaviour is in the simplest picture determined by three parameters : the total degree of polymerization  $N$ , the overall volume fraction  $f$  of the A component, and the A-B segment-segment (Flory-Huggins) interaction parameter  $\chi(T)$  [1-3]. The interaction parameter has a temperature dependence  $\chi = \alpha T^{-1} + \beta$ , where  $\alpha > 0$  and  $\beta$  are empirical coefficients describing the enthalpic part and an excess entropic part of the interactions. Increasing  $\chi$  (i.e.

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lowering the temperature) and/or increasing  $N$  leads to a reduction of A-B contacts. Since the enthalpic and main entropic contributions to the free energy scale as  $\chi$  and  $N^{-1}$ , respectively, the block copolymer phase behaviour is determined by the product  $\chi N$ . At temperatures below the ODT the enthalpic interactions dominate, leading to local phase segregation. For  $f = 1/2$  a transition to a lamellar structure can be observed. In that case the A-B joints of the block copolymer molecules are thought to be confined to the interfaces between the lamellae [4-6]. The constraint of separation of A and B layers may lead to significant distortions of the chain conformation away from the Gaussian state found in the disordered melt.

The morphology near surfaces can be dramatically affected by the different affinity of the various blocks for the substrate, and by their difference in surface free energies. In thin films the local packing of the lamellar microdomains — which in the bulk are randomly oriented — becomes uniformly parallel to the substrate over large areas [7]. In recent years this situation has been rather well studied for diblock copolymer layers [8, 9], where the technique of neutron reflectivity has proved to be very valuable. For diblock copolymers wetting of the substrate and the air interface by the A- and the B-block, respectively, can be accommodated in a simple lamellar structure. This is not the case anymore for an A-B-A triblock copolymer. In the bulk the microphase separation of a  $A_n B_{2n} A_n$  triblock and a  $A_n B_n$  diblock system are very much the same, and the triblock can be approximated as two combined diblock copolymers [10]. Nevertheless a fundamental difference arises because of the possibility in the lamellar triblock structure of bridging of the A-domains by B-blocks. At a surface this means that the A-blocks would prevent wetting of the air interface by the B-block. In this paper we present a combined X-ray and neutron reflectivity study of such a frustrated system.

## 2. Experimental.

The system under consideration consists of blocks of d-poly(styrene) and poly(2-vinylpyridine) in the form  $P2VP_{30}$ -dPS<sub>60</sub>-P2VP<sub>30</sub>, where the subscripts indicate the molecular mass in kg/mol. The structural units are sketched in figure 1. Note the steric similarity of the two types of blocks leading to the same statistical segment length  $a = 6.8 \text{ \AA}$  [11, 12]. The polymers have a very narrow polydispersity with  $M_w/M_n = 1.1$  for dPS and 1.2 for P2VP. Using the nominal molecular masses we calculate  $N = 1108$  repetitions over the full triblock, while  $N_{PS} = 536$  leading to  $f_{PS} = 0.48$ . Layers of this triblock copolymer on a Si(111) substrate were obtained by spin-coating from a solution in toluene and subsequent drying. The samples were annealed for 5.5 hours at 165 °C, and then quenched at room temperature, which is well below the glass transition temperature of the blocks (about 100 °C). The value of  $\chi$  of the present system is 0.08-0.1 [11, 13], of which the smaller value is probably the most appropriate one at the annealing temperature used.

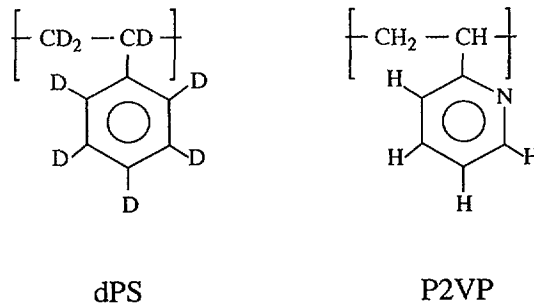


Fig. 1. — Structural elements of the P2VP-dPS-P2VP triblock copolymer. The PS units are deuterated to obtain neutron scattering contrast.

X-ray reflectivity measurements were performed using the  $\text{CuK}_{\alpha 1}$  line ( $\lambda = 1.5406 \text{ \AA}$ ) from a rotating anode generator and the triple-axis reflectometer described in reference [14]. The resolution normal to the surface was a Lorentzian with a FWHM of  $5 \times 10^{-4} \text{ \AA}^{-1}$  as determined by two Ge(111) single crystals at the monochromator and analyzer positions. As X-rays are sensitive to the electron densities — which are barely different for dPS and P2VP — they only scatter from the two limiting interfaces. Hence the experiment gives an accurate determination of the total film thickness. Neutrons have a very different sensitivity for hydrogen and deuterium, respectively, but are not very sensitive to a hydrocarbon-Si interface. Hence due to the deuteration of the PS-blocks they are ideal to probe the internal structure. Neutron reflectivity measurements were carried out at  $\lambda = 4.8414 \text{ \AA}$  using the reflectometer described in reference [15]. The resolution normal to the surface was approximately  $2 \times 10^{-3} \text{ \AA}^{-1}$  (FWHM), as determined by the two collimating slits and the spread in wavelength. These slits were kept at a constant width of 0.4 mm at a separation of 40 cm.

### 3. Results and modelling.

The application of X-ray and neutron reflectivity to the study of polymer films has recently been reviewed [9]. The reflectivity profile is a function of the momentum transfer  $Q = (4 \pi / \lambda) \sin \theta$  perpendicular to the film surface ( $z$  direction), where  $\theta$  is the angle of incidence with the surface. Below  $Q_c$  corresponding to the critical  $\theta_c$  of the order of  $0.2^\circ$  (Si) there is total reflection; beyond  $Q_c$  for a single sharp interface the reflectivity  $R_F(Q)$  follows the Fresnel law. The information about the density profile in the  $z$ -direction is contained in the deviations from  $R_F(Q)$ . For example, the rms roughness of an interface can be described by a Gaussian with a halfwidth given by  $\sigma$ . Then the reflectivity is modified to

$$R(Q) = R_F(Q) \exp(-Q^2 \sigma^2). \quad (1)$$

In the case of several interfaces the reflectivity profile can be calculated using the multilayer matrix method due to Parratt [16]. The segment density profile is approximated by a histogram

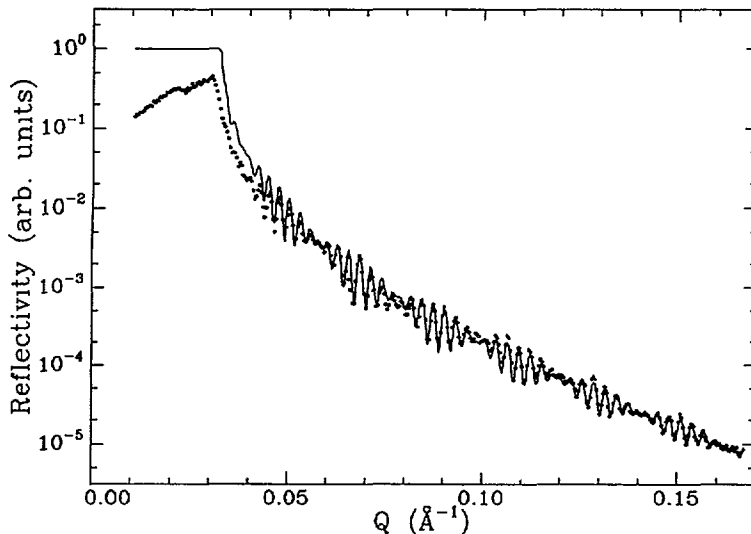


Fig. 2. — Results for the X-ray reflectivity of the triblock sample. The full line is a fit to the model described in the text.

of layers of different scattering length density (neutrons) or electron density (X-rays), and the total reflectance is obtained from recursion relations combining the various single-boundary reflectances. This model density profile perpendicular to the surface is convoluted with the resolution function and fitted to the experimental data. In principle each interface could have a different roughness. In practice, three different values for  $\sigma$  were used : for the two limiting interfaces air/polymer and polymer/substrate and for the « internal » PS/P2VP interfaces.

Results for the X-ray reflectivity are shown in figure 2. As the X-rays are not sensitive to the internal structure of the film the dominant feature is a series of oscillations characteristic of the total film thickness. The oscillations in the present sample show a beat frequency [9, 17] which can be interpreted as due to two different thicknesses of 1 935 and 2 229 Å. A good fit to the data can be obtained by adding the reflectivities due to these two thicknesses incoherently with approximately equal intensities. A coherent fit leads to an intensity of the nodes of the beats that is too low. This means that the top layer consists of about 50 % « elevations » and « depressions » [8a, b] with a difference in height of approximately 294 Å. A second sample gives thicknesses of 1 915 and 1 616 Å, respectively. Evidently, the total film thickness is approximately quantized as  $(n + 1/2)L$  with  $L \approx 294\text{-}300$  Å. This is substantiated by further data taken at the edge of the Si-wafer where the film is thinner due to the spin-coating process. The roughness at the top and bottom interface is characterized by  $\sigma = 13$  Å and  $\sigma = 7$  Å, respectively. The reflectivity at small  $Q$  is systematically lower than expected theoretically. This can be attributed to the depressions being partially « shadowed » at small  $\theta$  by the elevations due to scattering at the step-edges. The same phenomenon can be observed in the neutron-reflectivity data. We preferred not to present better-looking fits by incorporating this effect in an empirical way.

Results for the neutron-reflectivity of the sample after annealing are given in figure 3. Five orders in Bragg peaks appear and from their positions as a best compromise a periodicity  $L = 297$  Å is obtained for the « bulk » of the film. This value agrees nicely with the 294-300 Å found in the X-ray reflectivity as the difference between « elevations » and « depressions » in the sample. Depending on the total thickness of  $(n + 1/2)L$  this periodicity can be repeated six

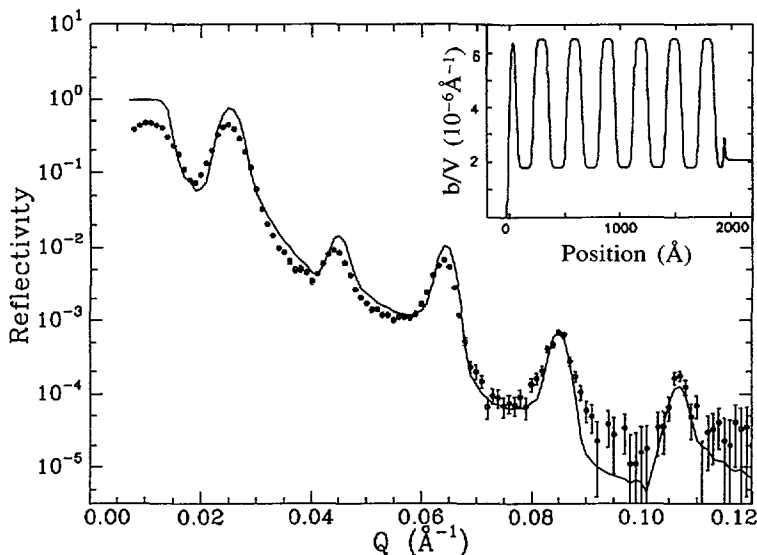


Fig. 3. — Results for the neutron reflectivity of the triblock sample. The full line is a fit with the parameter values given in table I; the inset gives the corresponding scattering density profile.

Table I. — Scattering length densities ( $b/V$ ), layer periodicities ( $L$ ) and roughness parameters ( $\sigma$ ) used in fitting the data of figure 3. The parameters are defined in figure 4.

| Parameter             | Value  |
|-----------------------|--|
| $n$                   | 6 and 7 <sup>(a)</sup>                               |
| $L$                   | $297 \pm 2 \text{ \AA}$ <sup>(b)</sup>               |
| $L_{\text{dPS}}$      | $137 \pm 5 \text{ \AA}$ <sup>(b)</sup>               |
| $L_{\text{P2VP}}$     | $160 \pm 5 \text{ \AA}$ <sup>(b)</sup>               |
| $\sigma_{\text{air}}$ | $13 \pm 1 \text{ \AA}$ <sup>(a)</sup>                |
| $\sigma_{\text{sub}}$ | $7 \pm 1 \text{ \AA}$ <sup>(a)</sup>                 |
| $\sigma$              | $15 \pm 1 \text{ \AA}$ <sup>(b)</sup>                |
| $(b/V)_{\text{dPS}}$  | $6.5 \times 10^{-6} \text{ \AA}^{-2}$ <sup>(c)</sup> |
| $(b/V)_{\text{P2VP}}$ | $1.4 \times 10^{-6} \text{ \AA}^{-2}$ <sup>(c)</sup> |
| $(b/V)_{\text{Si}}$   | $2.1 \times 10^{-6} \text{ \AA}^{-2}$ <sup>(c)</sup> |

<sup>(a)</sup> from X-ray reflectivity data,  
<sup>(b)</sup> from neutron reflectivity data,  
<sup>(c)</sup> bulk values.

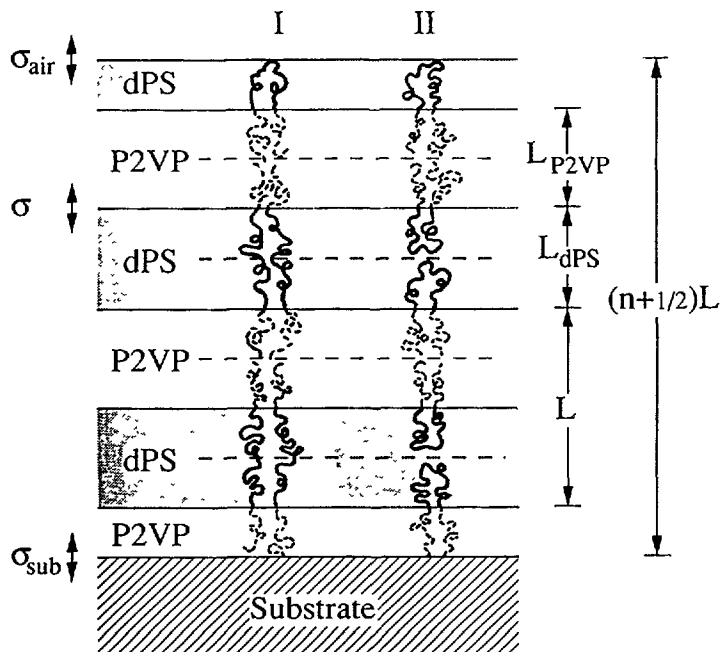


Fig. 4. — Schematic representation of two extreme models for the triblock copolymer ; I : looping occurs only in the surface layer, bridging everywhere else ; II : looping occurs in all the layers.

or seven times, leaving a top-layer that is within the experimental accuracy equal to  $L/2$ . The even orders of the Bragg peaks are observed to be less intense than the odd ones. In fact they would be absent if the PS- and P2VP-sublayers had thicknesses of exactly  $L/2$ . Hence the relative intensities of the various orders can be used to calculate  $L_{\text{PS}} = 137 \text{ \AA}$  and  $L_{\text{P2VP}} = 160 \text{ \AA}$ . This leads to  $f_{\text{PS}} = 0.46 \pm 0.02$  in agreement with the nominal calculated value of 0.48. The intensities for the second and fourth order peak are not fully consistent, and the value for  $f_{\text{PS}}$  is the best compromise. The scattering length densities of dPS and P2VP were fixed at the values calculated for the bulk homopolymer compounds. These ingredients were used for the model calculation shown as the full line in figure 3, and further summarized in table I and figure 4. Two final remarks are appropriate. The neutron reflectivity is rather insensitive to the termination of the polymer film at the substrate and in fact the same fitting curve is obtained for  $n = 6$  and  $n = 7$ . The relative intensities of the Bragg peaks are almost entirely determined by  $L_{\text{dPS}}/L$  and  $\sigma$  of the internal interfaces. Secondly, keeping the total film thickness fixed at the X-ray value the accumulated error in  $L$  allows the top PS plus P2VP layer to deviate slightly from  $L/2$ . However, within the experimental accuracy we can give no definite conclusion whether such a possible deviation, which has been predicted theoretically [6], indeed takes place.

#### 4. Discussion.

Modelling of the results shows that P2VP preferentially segregates at the Si-interface. In addition PS is found to wet the air interface completely in spite of its non-terminal position in the triblock copolymer. To understand this structure we must assume a looping of the PS-block in the surface layer such that the junctions with P2VP are approximately confined to the same interface. As already noted the thickness of the top-layer is within the experimental accuracy equal to  $L/2$ . This is similar to the situation found in most diblock copolymer films (apart from very thin films) [8f]. This leads to two extreme models that are pictured in figure 4. Experimentally we cannot distinguish between the first model in which only the molecules in the top layer are looped and form bridges everywhere else (I), and the model in which all layers have a looped structure (II). Therefore we shall refrain in this paper from a further discussion of the actual amount of bridging, although this point is of considerable interest.

The theory of microphase separation of diblock copolymers is well developed, and in the strong segregation limit two effects are dominant [4-6]. (i) A contact enthalpy is associated with the narrow AB interface region, which can be written as  $\gamma_{\text{AB}} \Sigma$  where  $\gamma_{\text{AB}}$  is the surface tension and  $\Sigma$  the surface area per molecule. This effect tends to make the periodicity  $L$  as large as possible. (ii) There is an entropy loss connected with extended chain configurations which are needed to maintain a homogeneous density. This effect limits the growth of  $L$ . Recently, the theory has been extended to cover the full range of interactions between the weak and strong segregation limit [6], which enables  $L/R_g$  to be expressed as a function of  $\chi N$ . Here  $R_g$  is the radius of gyration in the unperturbed situation. No equivalently general result exists for triblock copolymers, but, of course, the physical mechanisms will be the same. Therefore we treat the triblock system under investigation as two P2VP<sub>30</sub>-PS<sub>30</sub> diblocks, which leads for these artificial diblocks to  $\chi N = 44$  and  $R_g = 65 \text{ \AA}$ . With this assumption we obtain according to reference [6]  $L = 307 \text{ \AA}$  and  $\sigma = 10.5 \text{ \AA}$ . The value for  $L$  is in excellent agreement with the experimental one; the value for the interfacial width is reasonable. It should be realized that although the system is already far away from the weak-segregation limit for which  $\chi N \approx 10$ , according to reference [6] it is still in the intermediate regime and the strong segregation (or narrow interface) limit is not yet fully applicable.

Next we come to a discussion of the looping in the top layer at the surface. The entropy loss associated with the looping of a polymer chain has been calculated by various authors within the context of micelle formation [18, 19]. Its contribution to the free energy can be written as

$$F_{\text{loop}} = \frac{1}{2} k_B T \ln (\pi \chi N_{\text{PS}}), \quad (2)$$

which is in our case approximately  $3 k_B T$  per molecule. As in deriving equation (2) the theory of weakly perturbed Gaussian chains is used, this value can be considered as a lower limit. For a looped top layer there will be a gain in surface energy which can be written as  $(\gamma_{\text{P2VP}} - \gamma_{\text{PS}}) \Sigma$ . Using  $\gamma_{\text{PS}} = 40 \text{ mN/m}$  [20],  $\gamma_{\text{P2VP}} = 50 \text{ mN/m}$  [21] and  $\Sigma = 6.1 \times 10^{-18} \text{ m}^2$  (taking  $1.01 \times 10^4 \text{ mole/m}^3$  and  $L$  from Tab. I), we calculate for this quantity  $30 \times 10^{-18} \text{ J}$ . At the annealing temperature this is of the order of  $10 k_B T$ , and thus can very well provide compensation for the entropy loss associated with looping of the top layer.

In conclusion we have investigated the lamellar structure of a PVP<sub>30</sub>-PS<sub>60</sub>-P2VP<sub>30</sub> triblock copolymer. For the top layer the confinement of the polymer ends to the same plane leads to a « looping » of the polymer so that the middle PS part can still wet the air interface completely. The films are quantized in multiple layers of about 300 Å each, as evident from « elevations » and « depressions » at the surface of the film. The amount of looping *versus* bridging in the rest of the film is experimentally still an open question.

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