Macromolecules **1993,** *26,* 4973-4974

Observation of an Expanded Top Layer in a Lamellar Diblock Copolymer Film

Wim H. de Jeu[*,†] **and Peter Lambooy**[‡]

FOM-Institute for Atomic and Molecular Physics,
Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

David Vaknin[§]

Risø National Laboratory, P.O. Box 49,
4000-Roskilde, Denmark

Received March 12, 1993
Revised Manuscript Received June 16, 1993

An A–B diblock copolymer is composed of blocks derived from chemically distinct repeat units and shows "surfactant-like" behavior due to the difference in chemical and physical properties of the A- and B-blocks. The resulting phase behavior is, in the simplest picture, determined by the total degree of polymerization N, the overall volume fraction of the A component f_A, and the A–B segment–segment (Flory–Huggins) interaction parameter $\chi(T)$.[1–3] At temperatures below the order–disorder transition the enthalpic interactions dominate, leading to local phase segregation. For $f = {}^1/_2$ this results in a transition to a lamellar structure.[4–6] Interestingly, in thin films these lamellae become uniformly parallel to the substrate over large areas.[7] This particular morphology has been extensively studied for diblock copolymer layers,[8,9] while recently an extension to a triblock copolymer system has been made.[10] In the modeling of the results, usually a quantized lamellar structure of thickness $(n + {}^1/_2)L$ is taken, where n is an integer and L the periodicity of the ABBA double layer. In this note we report on a diblock copolymer film for which the combination of neutron reflectivity and an accurate determination of the total film thickness by X-ray reflectivity allows one to establish an expansion of the top layer by about 5%.

The system under consideration consists of blocks of d-poly(styrene) and poly(2-vinylpyridine) in the form $\mathrm{P2VP_{50K}\text{-}dPS_{50K}}$, where the subscripts indicate the molecular mass in kg/mol. Both blocks have the same statistical segment length a = 6.8 Å.[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 $N = 922$ full repetitions and $N_{dPS} = 446$ leading to $f_{dPS} = 0.48$. Layers of this diblock copolymer on a Si(111) substrate were obtained by spin-coating from a solution in toluene and subsequent drying. The samples were annealed for 3 h at 178 °C and then quenched to room temperature, which is well below the glass transition temperature of the blocks (about 100 °C).

X-ray reflectivity measurements were performed using the Cu Kα_1 line (λ = 1.5406 Å) from a rotating anode generator and the triple-axis reflectometer described in ref 13. The resolution normal to the surface was a Lorentzian with a fwhm of 5×10^{-4} Å^{-1} as determined by two Ge(111) single crystals at the monochromator and analyzer positions. Neutron reflectivity measurements were carried out at λ = 4.8414 Å using the reflectometer described in ref 14. The resolution normal to the surface was approximately 2×10^{-3} Å^{-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.

The X-ray or neutron reflectivity profile is a function of the momentum transfer $Q = (4\pi/\lambda) \sin \theta$ perpendicular to the film surface (z direction), where θ is the angle of incidence with the surface.[9] Below Q_c corresponding to the critical angle θ_c of the order of 0.2° (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 $R_F(Q)$. In the case of several interfaces the reflectivity profile can be calculated using the multilayer recursion formalism due to Parratt.[15] The segment density profile is approximated by a histogram 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. The root-mean-square roughness of each interface is described by a Gaussian with a half-width given by σ. This model density profile perpendicular to the surface is convoluted with the resolution function and fitted to the experimental data. In practice only three different values for σ were used: for each of the two limiting interfaces air/polymer (σ_{air}) and polymer/substrate (σ_{sub}) and one for the PS/P2VP interfaces (σ_{int}).

The results for the X-ray reflectivity show the expected series of oscillations characteristic of the total film thickness, which is equal to 1804 Å. The roughness at the top and bottom interface can be characterized by σ_{air} = 7 Å and σ_{sub} = 7 Å, respectively. The value for the optical density of the substrate was estimated from Q_c and the optical density of the film from the refraction at Q-values near Q_c. The results are $d_{film} = 3.66 \times 10^{-6}$ and $d_{Si} = 7.44 \times 10^{-6}$. They are essentially equal to the values obtained from the literature.[8,9] Results for the neutron reflectivity are shown in Figure 1. At least six orders in Bragg peaks appear; their positions correspond to a periodicity of L = 512 ± 1 Å. The full line in Figure 1 is a fit to the data for the model given in Figure 2 and with the parameter values of Table I, indicating an approximately $3^1/_2$ period. Variation of L outside the range indicated gives a systematic shift in the peak positions that makes the corresponding fit unacceptable. The ratio of the lengths is $L_{dPS}/L = 0.45$, slightly smaller than the nominal value of 0.48.

The results for this diblock copolymer are to a large extent as anticipated.[8,9] The neutron results indicate unambiguously that PS segregates preferentially at the air interface and P2VP at the substrate. They are not very sensitive to the total film thickness D because of the relative small variation in scattering length density at the second interface. Similarly, inclusion of the thin SiO_x layer at the substrate does not affect the fits. However, as D is obtained accurately by X-ray reflectivity and the neutron results allow very little variation of L, we can calculate $D - 3L$ = 268 ± 5 Å. This value differs significantly from ${}^1/_2L$ = 256 Å. An expansion of the top dPS plus P2VP layer with 12 Å provides the optimum way to reconcile the X-ray and neutron results. We have also made fits with the extra 12 Å positioned at other places in the sample: in the middle, at the bottom layer near the substrate, and divided over top and bottom layer. In all cases the fits were worse compared to the one shown for an expanded top layer. An expanded surface layer is predicted in the recent theoretical treatment of Shull[6] for the slightly different situation of a diblock copolymer between two

---

[†] Also affiliated with the Open University, P.O. Box 2960, 6401 DL Heerlen, The Netherlands.

[‡] Present address: IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.

[§] Present address: Physics Department, Ames Laboratory, Iowa State University, Ames, IA 50011.

0024-9297/93/2226-4973$04.00/0

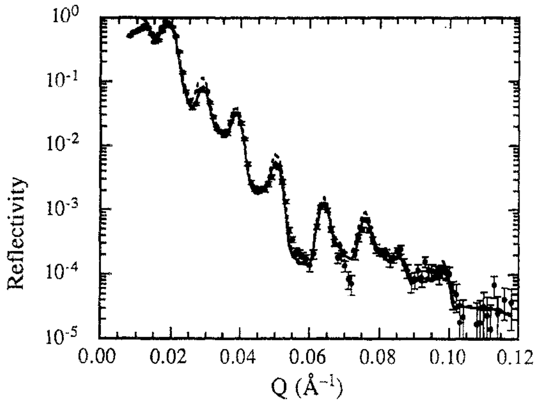

Figure 1. Results for the neutron reflectivity of the diblock sample. The full line is a fit with the parameter values given in Table I; the broken curve is according to the same model but with the bulk values $(b/V)_{\mathrm{dPS}} = 6.5 \times 10^{-6}$ Å^{-2} and $(b/V)_{\mathrm{P2VP}} = 1.4 \times 10^{-6}$ Å^{-2}.

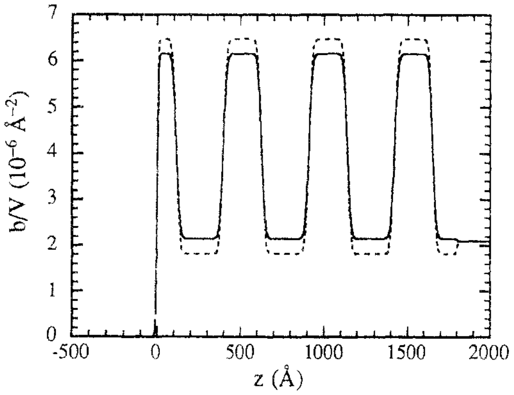

Figure 2. Scattering density profiles corresponding to the full and broken curves of Figure 1. dPS (high scattering length density) is at the air interface (left); P2VP (low scattering length density) is at the substrate (right).

Table I. Total Film Thickness (*D*), Layer Periodicities (*L*), Roughness Parameters (σ), and Scattering Length Densities (*b*/*V*) Used in Fitting the Data of Figure 1[a]

param	value	param	value
D	1804 ± 2 Å[b]	L_{dPS}	231 ± 2 Å[c]
L	512 ± 1 Å[c]	L_{P2VP}	281 ± 2 Å[c]
σ_{air}	7 ± 2 Å[b]	σ_{int}	15 ± 2 Å[c]
σ_{sub}	7 ± 2 Å[b]		
$(b/V)_{\mathrm{dPS}}$	6.15×10^{-6} Å^{-2} [c]	$(b/V)_{\mathrm{Si}}$	2.09×10^{-6} Å^{-2} [d]
$(b/V)_{\mathrm{P2VP}}$	2.15×10^{-6} Å^{-2} [c]		

[a] In addition a 12-Å expanded top layer was incorporated (see text). [b] From X-ray reflectivity data. [c] From neutron reflectivity data. [d] Bulk value.

equal surfaces. We conclude that these predictions are qualitatively in agreement with our experimental results.

As is clear from Figure 1, to obtain a good fit to the neutron reflectivity data it is necessary to adjust the scattering length densities away from the bulk values of the respective homopolymers. From the values in Table I we see that this amounts to about 10% interpenetration of the two blocks into each others domains. This could be an indication that the annealing is not complete. In addition or alternatively, it could be due to the system being close to but not yet fully in the strong segregation limit.

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; 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 to be expressed as a function of χN. Using $\chi = 0.08$,[11,16] we find in our situation $\chi N = 74$ leading according to ref 6 to $L/R_g = 5.39$. Calculating the radius of gyration $R_g = a\sqrt{N/6}$ to be 85 Å, we thus arrive at $L = 458$ Å and $\sigma_{\mathrm{int}} = 10$ Å, in reasonable agreement with the experimental values given in Table I.

In conclusion we have investigated the lamellar structure of a PVP$_{50}$-PS$_{50}$ diblock copolymer. Microphase separation leads to the usual structure of a quantized lamellar film with P2VP at the silicon substrate and PS wetting the air interface. The combination of neutron and X-ray reflectivity allows one to establish an expansion of the top layer in agreement with recent theoretical considerations.

Acknowledgment. We wish to thank Prof. G. Hadziioannou, Department of Chemistry, University of Groningen, The Netherlands, for providing us with the samples. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for the Fundamental Research of Matter, FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research, NWO) and from the Ministry of Economic Affairs of the Netherlands, within the framework of the Innovatief Onderzoekprogramma Polymeercomposieten en bijzondere Polymeren (IOP-PCBP).

References and Notes

(1) Bates, F. S. *Science* **1991**, *251*, 898.
(2) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(3) (a) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51. (b) Huggins, M. *J. Phys. Chem.* **1942**, *46*, 151; *J. Am. Chem. Soc.* **1942**, *64*, 1712.
(4) Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers*, Goodman, I., Ed.; Applied Science Publishers: London, 1982; Vol. 1, p 99.
(5) Semenov, A. N. *Sov. Phys-JETP* **1985**, *61*, 733.
(6) Shull, K. R. *Macromolecules* **1992**, *25*, 2122.
(7) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(8) (a) Ausserre, D.; Chatenay, D.; Coulon, G.; Collin, B. *J. Phys.* **1990**, *51*, 2571. (b) Coulon, G.; Ausserre, D.; Russell, T. P. *J. Phys.* **1990**, *51*, 777. (c) Anastasiadis, S. H.; Russell, T. P.; Satija; S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852. (d) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677. (e) Russell, T. P.; Anastasiadis, S. H.; Menelle, A.; Felcher, G. P.; Satija, S. K. *Macromolecules* **1991**, *24*, 1575. (f) Russell, T. P.; Menelle, A.; Anastasiadis, S. H.; Satija, S. K.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 6263.
(9) Russell, T. P. *Matter. Sci. Rep.* **1990**, *5*, 171.
(10) de Jeu, W. H.; Lambooy, P.; Hamley, I. W.; Vaknin, D.; Pedersen, J. K.; Kjaer, K.; Seyger, R.; van Hutten, P.; Hadziioannou, G. *J. Phys. II Fr.* **1993**, *3*, 139.
(11) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Wing Tang *Macromolecules* **1990**, *23*, 4780.
(12) Tangari, C.; King, J. S.; Summerfeld, G. C. *Macromolecules* **1985**, *15*, 132.
(13) Gierlotka, S.; Lambooy, P.; de Jeu, W. H. *Europhys. Lett.* **1990**, *12*, 341.
(14) Vaknin, D.; Kjaer, K.; Als-Nielsen, J.; Lösche, M. *Makromol. Chem. Macromol. Symp.* **1991**, *46*, 383.
(15) Parratt, L. G. *Phys. Rev.* **1954**, *95*, 359.
(16) Matsushita, Y.; Mori, K.; Saguchi, R.; Nakao, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1990**, *23*, 4313.