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1997 J. Phys.: Condens. Matter 9 L125

(http://iopscience.iop.org/0953-8984/9/9/003)

J. Phys.: Condens. Matter **9** (1997) L125–L130. Printed in the UK PII: S0953-8984(97)77582-9

LETTER TO THE EDITOR

An x-ray scattering study of laterally modulated structures: the example of diblock copolymers

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Received 4 September 1996

Abstract. A study of the specular and off-specular (diffuse) x-ray scattering of a diblock copolymer is presented. In the ordered state the surface of the diblock copolymer is covered with islands. It is shown that the periodicity in the ordered state in the direction normal to the surface in a specular scan differs from the periodicity in the same direction observed in an off-specular scan. This result is explained by an analytical calculation of the differential cross section. The introduction of the statistical properties of the island distribution allows a complete analytical calculation of the transverse scans yielding the determination of the mean distance between the islands and the average size of an island.

Since the pioneering work of Parratt [1], it is well known that x-ray and neutron specular reflectometry is a powerful non-destructive technique to study the electron density profile of a sample in a direction normal to its surface. Except for few early developments [2], off-specular x-ray scattering studies in reflection geometry have recently become used to investigate the morphology of surfaces [3–6]. While not yielding direct imaging information, as obtained from complementary techniques such as atomic force or optical microscopies, off-specular x-ray scattering allows the determination of quantitative statistical information about the spatial correlations observed parallel to the surface of a material over a large range of length scales (Ångströms to micrometres). Remarkable examples of application have been reported in liquids [7], multilayer materials [8] and in the laterally modulated structure of periodic gratings [9]. Similarly, Cai *et al* [10] using microscopy and x-ray scattering have reported an application to the study of the morphology of diblock copolymer (PS–PMMA) presenting a surface covered by islands or holes. They analysed their x-ray scattering data by using the domain–domain correlation functions obtained from microscopy images. In their analysis, they argued that the lack of perfect agreement between the calculation and the observed data was probably due to the fact that a surface studied by microscopy may be too small to represent the average property of the film surface.

It is the purpose of this letter to present a simple analytical model describing the specular and off-specular x-ray scattering from a surface covered by holes or islands. In this work, we include in the analytical expression of the scattering the Fourier transform of the shape of the islands and of the position distribution of the islands. The model is then compared to

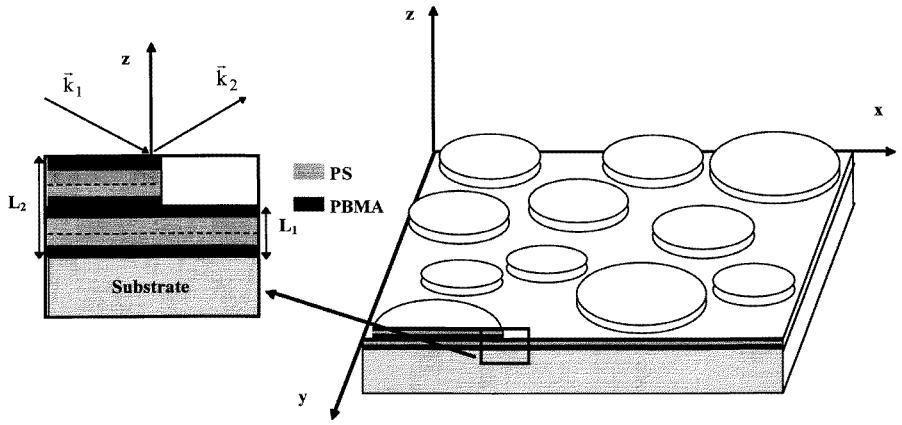

Figure 1. A schematic representation of the ordered surface of a symmetric diblock copolymer.

the experimental measurements performed on the surface of an ordered PS–PBMA diblock copolymer thin film.

Ordered diblock copolymer thin films present a stochastic but quantized morphology which is a consequence of the incompatible character of the two species A and B which compose the structure of the diblock. The two species A and B are linked by a covalent bond and form a diblock AB. Thin films are made by dissolving the diblock copolymer in a solvent (toluene) and by spin-coating the solution on the flat surface of a silicon wafer. The speed of rotation and the concentration of the solution determine the initial thickness of the film in the disordered state. In this state, the diblocks AB are mixed in a random way and the morphology of the film surface is essentially flat. When the system is heated above its ordering temperature, because of the incompatibility between the species A and B, the diblock copolymer adopts a lamellar structure provided that A and B are sufficiently symmetric. The lamallae consist of the association of two diblocks ABBA or BAAB (bilayers) of length L. Previous studies of diblock copolymers have been reported by several authors. For more details see for example [11] and [12] and references therein. In this study, we chose a symmetric PS–PBMA (AB) diblock copolymer with $L = 290$ Å for which the surface tension favours a BAAB sequence. We have chosen an initial thickness d in the disordered state of $d = 430$ Å so that $L < d < 2L$. The formation of the lamellar order gives rise to regions of thicknesses L and $2L$. The film thus adopts a quantized morphology characterized by the appearance of islands or holes depending on whether d is smaller or larger than $3L/2$.

In PS–PBMA, the difference in electron density between the two species A and B is small enough to consider the film as having a uniform electron density ρ. The structure of the thin film in the direction normal to its surface is characterized by two specific thicknesses called L_1 and L_2 which are thicknesses of the bottom and top parts of the film with respect to the reference level of the flat substrate on which it has been deposited (see figure 1). We will assume that the islands or the holes have sharp edges although this assumption is not completely correct [13]. We describe the two-height system by a two-dimensional function $\alpha(X, Y)$ where $\alpha = 0$ for $0 \leqslant z \leqslant L_1$ and $\alpha = 1$ for $L_1 < z \leqslant L_2$, taking the origin of the z axis on the surface of the substrate. Assuming that the material is homogeneous, except for the presence of the surface, one can show that the differential cross section in the Born approximation may be separated into a specular $\mathrm{d}\sigma/\mathrm{d}\Omega_{spe.}$ and a diffuse part $\mathrm{d}\sigma/\mathrm{d}\Omega_{diff.}$ to

yield

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega_{spe.}} = \frac{4\pi^2 r_0^2 A}{q_z^2}\Big[\rho^2 + (\rho_s - \rho)^2 + 2(1-c_i)\rho(\rho_s - \rho)\cos(q_z L_1) + 2c_i\rho(\rho_s - \rho)\cos(q_z L_2) - 4c_i(1-c_i)\rho^2 \sin^2\left(\frac{q_z(L_2 - L_1)}{2}\right)\Big] \times \delta(q_x)\delta(q_y) \quad (1)$$

where ρ_s and ρ are respectively the electron density of the substrate and the film, r_0 is the classical electron radius and A is the illuminated surface and $\boldsymbol{q} = \boldsymbol{k}_2 - \boldsymbol{k}_1$ is the wave vector transfer with $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ the incident and scattered wave vectors. The symbol δ represents the Dirac distribution. After averaging over the surface, we obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega_{diff.}} = \frac{4\rho^2 r_0^2 A}{q_z^2}\sin^2\left(\frac{q_z(L_2 - L_1)}{2}\right)\int_S \mathrm{d}X\mathrm{d}Y < \alpha(0,\,0)\alpha(X,\,Y) > \mathrm{e}^{-\mathrm{i}(q_x X + q_y Y)} \quad (2)$$

where $c_i = (1/A)\iint_S \mathrm{d}x\mathrm{d}y\alpha(x,\,y)$ is the coverage of the islands. The above equations can be generalized to include the roughness of the substrate and those of the top and bottom parts of the islands [14].

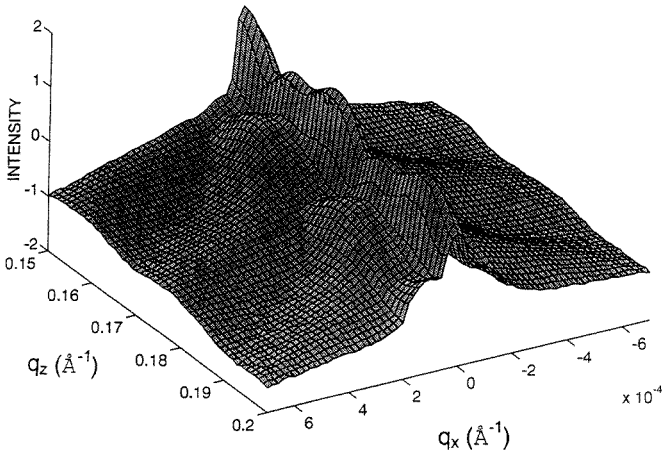

Figure 2. Mesh scan of a PS–PBMA diblock copolymer in the $(q_x,\,q_z)$ scattering plane showing the presence of different periodicities in the on- and off-specular q_z longitudinal direction and a structure in the q_x transverse scan parallel to the copolymer surface.

The specular term (1) shows that one can expect scattering at positions corresponding to a periodicity $2\pi/L_1$, $2\pi/L_2$ and $2\pi/(L_2 - L_1)$ along q_z which will be resolution limited in the transverse direction. The diffuse part (2) produces peaks of periodicity $2\pi/(L_2 - L_1)$ along q_z in specular and off-specular directions provided that the Fourier transform of $\alpha(x,\,y)$ is not a delta function, i.e. that the surface presents two types of region of different thicknesses. Thus equations (1) and (2) demonstrate that the off-specular scans will be only sensitive to the difference of levels in the material (when the interfacial roughnesses are not considered). Specular scans will probe the presence of the two levels L_1, L_2 and the difference $L_1 - L_2$. Finally equation (2) also demonstrates that the only contribution which remains in an off-specular scan is the Fourier transform of the correlation function of the islands distribution modulated in the z-direction by the Fourier transform of the island height. Thus off-specular scans are only sensitive to the surface morphology of the film.

Diblock copolymers were prepared at the Institut Charles Sadron (Strasbourg, France). Experiments were performed at the ESRF (beam line 9/Troika) and at the NSLS (X10B Exxon beam line) with a wavelength of 1.2 Å. The collimation in both cases was adjusted so that the FWHM of the direct beam was reduced to 0.032°. This value together with the divergence of the outgoing beam fixes the resolution function of the instrument as shown in [15]. We present in figure 2 the results of a mesh scan in the q_x-range −0.0007–0.0007 Å^{-1} and in the q_z-range 0.15–0.2 Å^{-1}. This scan shows that there is a double periodicity along q_z in the specular condition, i.e. when $q_x = 0$, a single periodicity along q_x in the off-specular condition and a structure in the q_x direction parallel to the surface of the film. The first two points are consistent with what can be expected from equation (1).

We now discuss off-specular scattering by describing the statistical properties of the islands. We consider that the islands are cylindrical in shape, described by a shape factor $b(r)$, and they are distributed around averaged distances represented by a distribution function $p(r)$ which gives the position of islands. The two-dimensional distribution function $\alpha(x, y)$ is the convolution of the shape factor $b(r)$ with the distribution $p(r)$ of the islands. We then assume that the island distribution is isotropic in the plane of the sample surface. The distribution developed in Hosemann and Baghi for 'paracrystalline' systems in which the relevant parameters are the nearest-neighbour distance $\bar{d}$ and the r.m.s. (root mean square) deviation σ_n of the distribution [16] has been shown to be a powerful tool to deal with systems presenting a certain degree of disorder. In view of figure 3, it appears that such a distribution can be relevant to describe the statistical properties of the islands. The modulus square of the Fourier transform of the distribution function is then given by

$$\left|p(q_r)\right|^2 = \frac{1 - F^2(q_r)}{1 - 2F(q_r)\cos q_r\bar{d} + F^2(q_r)} \tag{3}$$

in which q_r is the component of the wave transfer $\boldsymbol{q}$ in the plane of the surface and $F(q_r)$, which plays the role of an attenuation factor, is the Fourier transform of the Gaussian distribution of the first neighbours, i.e. $F(q_r) = \mathrm{e}^{-q_r^2\sigma_n^2}$.

The factor $b(q_r)$ is the form factor of the islands. For circular and homodisperse islands of radius R, the form factor is $b(q_r) = \pi R^2 J_1(q_r R)/q_r R$, where J_1 is the Bessel function of order one. However since the islands are polydisperse as clearly shown in the inset of the optical micrograph of figure 3, we have weighted the factor form $b(q_r)$ by a log-normal distribution of radii: $p(R_k) = \exp(-(\log(R_k) - \log(R_0))^2/2\sigma_d^2)$, which yields

$$b_p(q_r) = \sum_k p(R_k)\pi R_k^2 \frac{J_1(q_r R_k)}{q_r R_k}. \tag{4}$$

The differential cross section for off-specular scattering becomes

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega_{diff.}} = \frac{4\rho^2 r_0^2 A}{q_z^2}\sin^2\left(\frac{q_z(L_2 - L_1)}{2}\right)\left|b_p(q_r)\right|^2 \frac{1 - F^2(q_r)}{1 - 2F(q_r)\cos q_r\bar{d} + F^2(q_r)}. \tag{5}$$

The measured intensity is then the convolution of the differential cross section with the Gaussian resolution function. The vertical instrumental resolution was poor if compared to the in-plane one. Therefore the in-plane resolution can be in a first approximation assimilated to a narrow two-dimensional Gaussian and the measured intensity in a transverse scan is then given by the integration of the differential cross section along the vertical aperture of the detector [17] and then convoluted with the in-plane resolution. This is performed numerically and the result is compared to the experimental data.

The result of such a calculation is presented in figure 4. One can see the very good agreement existing between the calculated and the measured intensity especially at very

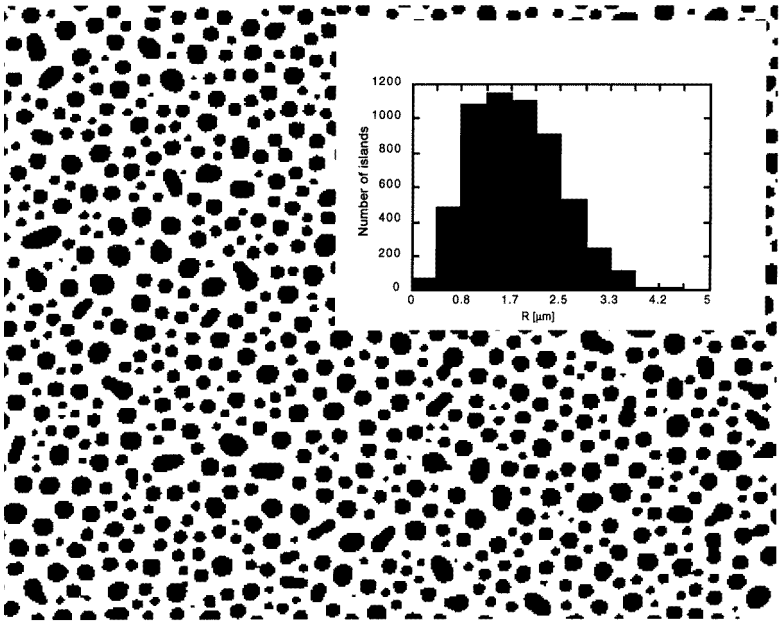

Figure 3. Optical micrographs of PS–PBMA (82000) copolymer film: islands appear as black on a white surface. The inset depicts the distribution function of radii assuming that the islands are circular. R is the radius in micrometres.

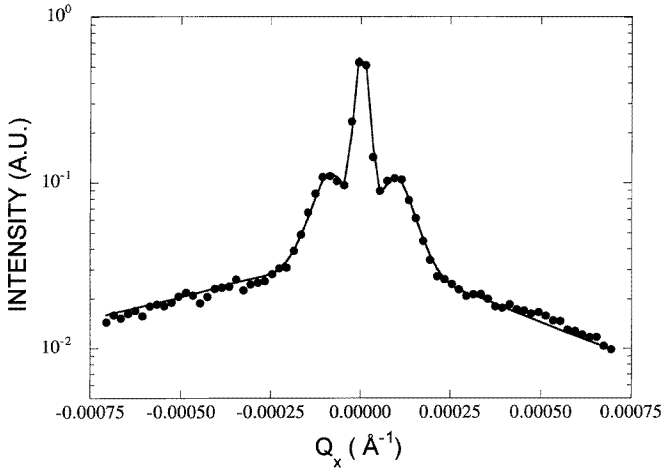

Figure 4. Observed and calculated intensity in a transverse scan parallel to the surface of the sample.

small q_x wave vector transfer where the interference term dominates the scattering. The very steep decrease of the intensity observed after the first ring is only well described if the vertical resolution is taken into account. The lineshape is well interpreted with $R_0 = 1.5\ \mu$m, $\bar{d} = 4.8\ \mu$m and $\sigma = 1.3\ \mu$m, values which are in good agreement with optical observations of the surface. The log-normal distribution is centred at $R_0 = 1.5\ \mu$m and has an r.m.s. $\sigma_d = 0.3\ \mu$m.

In conclusion, we have shown that x-ray scattering experiments are very sensitive to the morphology of the diblock copolymer surface. In the specular direction the quantized distribution of thickness which results from the lamellar order is clearly demonstrated. We observe in this direction a double oscillation which is the signature of the two heights L_1 and L_2 characteristic of the structure. In longitudinal off-specular scans, a single oscillation of period $2\pi/(L_2 - L_1)$ persists and probes the height of the islands. The transverse scans (in the q_x-direction) can be well interpreted in terms of the Fourier transform of the autocorrelation function of the island position (without roughness) which is determined analytically. In our next paper, we will develop a complete formalism for the analysis of the x-ray scattering measurements which takes into account the effect of the beam coherence and the implications of the roughness on the scattering features [14].

This work has been supported by the ESRF, the French MESR and ANL. The help of P Feder and H Gleyzolle at the ESRF is gratefully acknowledged and the authors are indebted to the members of the Exxon beam line for technical support during the course of the experiments at Brookhaven. Finally, two of us (GV and AG) wish to thank D Aussérré for initiating this work in Le Mans and T Salditt and H Metzger for useful discussions.

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