Analysis of x-ray reflectivity data from low-contrast polymer bilayer systems using a Fourier method

O. H. Seeck[a] and I. D. Kaendler
XFD/APS Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

M. Tolan
Institut für Experimentelle und Angewandte Physik der Universität Kiel, 24098 Kiel, Germany

K. Shin, M. H. Rafailovich, and J. Sokolov
Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794-2275

R. Kolb
Exxon Research and Engineering Company, Annadale, New Jersey 08801

(Received 29 December 1999; accepted for publication 17 March 2000)

X-ray reflectivity data of polymer bilayer systems have been analyzed using a Fourier method which takes into account different limits of integration in q-space. It is demonstrated that the interfacial parameters can be determined with high accuracy although the difference in the electron density (the contrast) of the two polymers is extremely small. This method is not restricted to soft-matter thin films. It can be applied to any reflectivity data from low-contrast layer systems. © *2000 American Institute of Physics.* [S0003-6951(00)03719-0]

Thin-film layer systems are often studied by x-ray or neutron specular reflectivity (RF). The RF is determined by the density profile $\rho(z)$ perpendicular to the sample surface, in particular, by the thicknesses d_j, the interfacial rms roughnesses σ_j, and the densities ρ_j of the layers denoted by j.[1] Using x-ray photons $\rho(z)$ means the electron density, for neutrons it is the scattering length density. In Born approximation the reflected intensity is given by

$$I(q_z) \sim \frac{1}{q_z^4} \left| \int \frac{d\rho(z)}{dz} \exp(-iq_z z) dz \right|^2,$$

where q_z is the wave-vector transfer.[2] Thus, it is hard to study interfaces with small density contrasts (given by $|\rho_i - \rho_j|/\rho_i$) because $I(q_z)$ is determined by the Fourier transformation (FT) of the gradient of $\rho(z)$. We present a practical way to overcome the ''contrast problem.''

There are many interesting ''small-contrast'' layer systems, such as magnetic multilayers (see, e.g., Ref. 3) or polymer bilayers.[4,5] In the latter case, the x-ray contrast is essentially less than 10%. Therefore, neutron scattering is preferred to investigate polymer–polymer interfaces since the scattering contrast can be enhanced by deuterating one of the two polymers. However, deuteration may change the chemical behavior of the polymer. Furthermore, neutron RF data often suffer from low intensity and q_z-space resolution, which yield large error bars.

Figure 1 depicts RFs calculated using the Parratt algorithm.[1] A bilayer system with maximum contrast was taken for curve (A). The oscillations corresponding to both layers are easily visible in the pronounced beating. Curve (B) represents a RF of a bilayer system with only 5% contrast. It is almost identical to curve (C), for which a monolayer was used with the thickness equal to the whole thickness of the bilayer. To analyze the low-contrast interface of bilayer (B) quite laborious methods such as maximum entropy fitting can be used. However, a more straightforward way to obtain the information exists and is outlined in the following.

The right-hand side of Fig. 1 also depicts the FTs of the RFs. They are related to the corresponding one-dimensional Patterson functions and occasionally have been used to analyze RF data.[6,7] In the following, we discuss

$$F(d, q_{z,\mathrm{low}}) = \left| \int_{q_z,\mathrm{low}}^{q_z,\mathrm{up}} q_z^4 I(q_z) \exp(iq_z d) dq_z \right|^2, \qquad (1)$$

as a function of the lower limit $q_{z,\mathrm{low}}$. The upper limit $q_{z,\mathrm{up}}$ is given by the q_z-range of the data. It can clearly be seen that even the low-contrast layer system (B) shows the signature of a bilayer system: two small peaks at the position of the thicknesses of each layer and one large peak at the total thickness. The small peaks contain the information about the low-contrast interface.

The shape of the FTs strongly depends on the ratio of the roughnesses and the choice of $q_{z,\mathrm{low}}$ (see Fig. 2). If σ_1 (film–

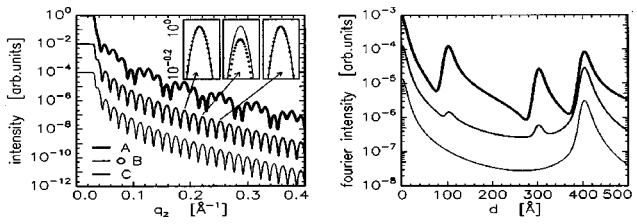

FIG. 1. Calculated RFs (left) and FTs (right). (A) bilayer on silicon with maximum contrast ($\rho_1 = 2\rho_2$) and $d_1 = 100$ Å and $d_2 = 300$ Å. (B) bilayer with 5% contrast, $d_1 = 100$ Å, and $d_2 = 300$ Å. (C) monolayer, $d_1 = 400$ Å. All σ_j are 5 Å, the q_z limits are $q_{z,\mathrm{low}} = 0.065$ Å^{-1} and $q_{z,\mathrm{up}} = 0.8$ Å^{-1}. For clarity, the RFs are only shown up to 0.4 Å^{-1}. The insets show that curve (B) still exhibits a tiny modulation.

[a]Postal address: HASYLAB am DESY, Notkestraße 85, 22603 Hamburg, Germany; electronic mail: ohseeck@mail.desy.de

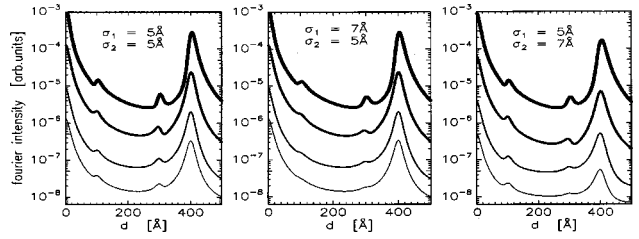

FIG. 2. Effect of different roughnesses and lower limits $q_{z,\mathrm{low}}$ on the FTs. From top to bottom: $q_{z,\mathrm{low}}=[0.064;0.18;0.25;0.367]$ Å^{-1}. The upper limit of integration is $q_{z,\mathrm{up}}=0.8$ Å^{-1}. The roughness of the film–film interface is denoted by σ_1 and of the film–air interface by σ_2. The substrate–film roughness was set to 5 Å for all calculations.

film interface) and σ_2 (film–air interface) are identical, the shape of the FTs is basically independent of $q_{z,\mathrm{low}}$.[8] In the case $\sigma_1>\sigma_2$ the small peaks disappear with increasing $q_{z,\mathrm{low}}$. The main peak remains unaffected. In the reverse case $\sigma_1<\sigma_2$ the small peaks stay visible while the large peak shrinks considerably.

This behavior can easily be explained: The scattered amplitude at each interface j is damped by a factor $\exp(-q_z^2\sigma_j^2/2)$. Thus, at large q_z the smoothest interface dominates $I(q_z)$. Small values of $q_{z,\mathrm{low}}$ yield FTs with all interfaces visible, larger values suppress rougher interfaces. By fitting the FTs using different $q_{z,\mathrm{low}}$ the sensitivity to the respective interfaces can be tuned.

In this letter we analyzed x-ray RFs of polymer bilayers (see Fig. 3) using the FT method. At the interface of two immiscible polymers enthalpic terms, which favor perfectly smooth interfaces, are balanced with entropic contributions which would lead to infinite roughness. The resulting equilibrium rms roughness σ_{pp} is given by the Helfand–Tagami theory,[9] which includes the Flory–Huggins interaction parameter χ_{pp} between the two polymers.[5] Additionally, capillary waves have to be taken into account. In the limit of high molecular weights[10] one yields

$$\sigma_{\mathrm{pp}}=\left[\frac{a^2}{3\pi\chi_{\mathrm{pp}}}+\frac{1}{4\pi a\rho}\sqrt{\frac{6}{\chi_{\mathrm{pp}}}}\ln\left(\frac{q_{\max}^2}{q_{\mathrm{coh}}^2+q_{\min}^2}\right)\right]^{1/2}, \qquad (2)$$

if the statistical segment lengths a and the monomer volumes $1/\rho$ are comparable for each polymer. The upper cutoff $q_{\max}=2\pi/\sigma_{\mathrm{intr}}$ is determined by the intrinsic roughness σ_{intr}, which is the square root of the first term in Eq. (2).[5] For thin-film systems the lower cutoff $q_{\min}$ depends on the temperature T and the van der Waals interaction between both polymers given by the effective Hamaker constant A_{eff} via $q_{\min}^2=A_{\mathrm{eff}}\sqrt{6/\chi_{\mathrm{pp}}}/(2\pi k_B T a\rho d^4)$.[5,11] If the film thickness of the bottom layer is sufficiently large, the effect of the substrate can be neglected and d stands for the thickness of the top layer. The finite coherence length of the x-ray photons is taken into account by q_{coh}, which is on the order of 1.25×10^{-5} Å^{-1} for our setup. From Eq. (2) follows that thin top layers cause slightly smoother polymer–polymer interfaces than thick top layers.[5]

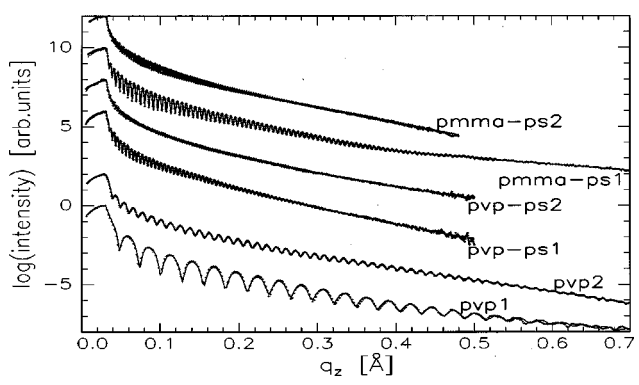

FIG. 3. Measured RFs (symbols) and refinements (solid lines) of the polymer films. The fits have been performed simultaneously using the respective FTs shown in Fig. 4.

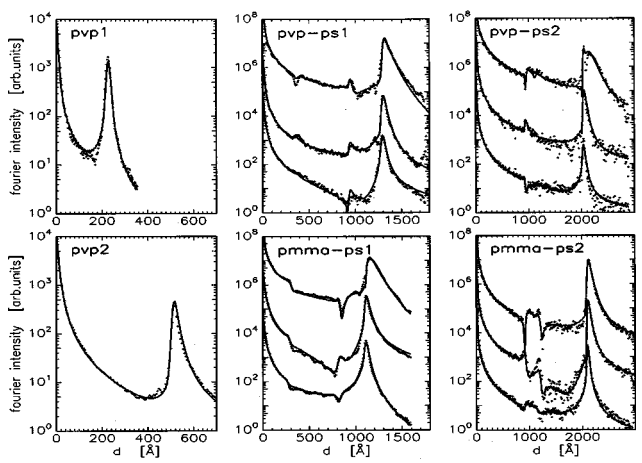

FIG. 4. FTs of measured (symbols) and calculated (solid lines) RFs. The values of $q_{z,\mathrm{low}}$ are typically (from the top to the bottom curves in each subplot) 0.05, 0.08 and 0.11 Å^{-1}. The precise values depend on the sample.

Thin-film bilayers of polystyrene (PS) on poly-2-vinylpyridine (PVP) and PS on polymethylmethacrylate (PMMA) have been investigated. The films were made by spin coating PVP (or PMMA, respectively) on commercial silicon wafers and covering them with PS afterwards. They were annealed for 24 h at $T=438$ K and then quenched to 300 K. We used molecular weights between 600 and 700 k with $a\approx6.7$ Å (Ref. 9) and $1/\rho\approx174$ Å^3.[5] The respective interaction parameters are $\chi_{\mathrm{PMMA-PS}}=0.037$ (Ref. 12) and $\chi_{\mathrm{PVP-PS}}=0.1$.[10] A sufficient estimate for the Hamaker constants of both systems is $A_{\mathrm{eff}}\approx2\times10^{-20}$ J.[5] The measurements took place at beamline X10B (Brookhaven National Laboratory) using a photon energy of 11 keV. Monolayers of PVP have also been prepared for comparison.

To analyze the data of a sample, the RF and the FTs have been refined simultaneously. The only fitting parameters were the thickness of the bottom and the top polymer film ($d_{\mathrm{bot,fit}}$ and $d_{\mathrm{top,fit}}$, respectively), and the roughnesses of the film–film interface $\sigma_{\mathrm{pp,fit}}$ and the film–air interface $\sigma_{\mathrm{top,fit}}$. The refraction indices of the polymers $n=1-\delta$ are determined by the electron densities and the photon energy and have not been fitted. The calculated dispersions are $\delta_{\mathrm{PVP}}=2.00\times10^{-6}$, $\delta_{\mathrm{PS}}=1.92\times10^{-6}$, and $\delta_{\mathrm{PMMA}}=2.17\times10^{-6}$.

Figure 4 shows, that only the FTs of the PVP monolayers (''pvp1'' and ''pvp2'') can be refined well using a monolayer model. All other FTs show the signatures of a bilayer system, which are more pronounced for PMMA–PS than for PVP–PS because of the larger contrast. To refine the bilayer data, three FTs with different $q_{z,\mathrm{low}}$ were used to be more sensitive to the polymer–polymer interface.

The results are summarized in Table I. For the

TABLE I. Results of polymer layer systems. The first two lines represent PVP monolayers, the last lines bilayers. All values are given in angstroms. The error of the thicknesses d is 1–2 Å. The errors of the roughnesses are 10%–15% of the value.

	$d_{\mathrm{bot,fit}}$	$\sigma_{\mathrm{pp,fit}}$	$\sigma_{\mathrm{pp,theo}}$	$d_{\mathrm{top,fit}}$	$\sigma_{\mathrm{top,fit}}$
pvp1	226	⋯	⋯	⋯	5.2
pvp2	510	⋯	⋯	⋯	7.3
pvp-ps1	927	11.1	18.6	356	10.8
pvp-ps2	926	12.7	20.0	1091	12.5
pmma-ps1	813	20.4	23.6	287	11.4
pmma-ps2	910	22.3	26.1	1176	8.8

PMMA–PS systems (''pmma-ps1'' and ''pmma-ps2''), the roughnesses $\sigma_{\mathrm{PMMA-PS}}$ are identical to already published values,[5] where neutron-scattering methods have been used. However, the x-ray scattering results are two times more accurate. We also investigated PVP–PS interfaces (''pvp-ps1'' and ''pvp-ps2''), where the rms widths $\sigma_{\mathrm{PVP-PS}}$ turn out to be considerably smaller than for PMMA–PS. This is due to the larger χ_{pp} parameter of PVP–PS. Furthermore, it is evident that $\sigma_{\mathrm{PVP-PS}}$ is larger than $\sigma_{\mathrm{PVP-air}}$ for the PVP monolayers because in the latter cases the surface roughness is purely of capillary wave origin. Finally, the dependence of σ_{pp} on the film thickness can easily be identified for both systems, PMMA–PS and PVP–PS.

In addition, Table I lists the calculated values for $\sigma_{\mathrm{pp,theo}}$ using Eq. (2). For all bilayers they exceed $\sigma_{\mathrm{pp,fit}}$ by a constant offset. This finding was also observed by other authors.[5,13] The reason may be the finite thickness of the bottom layer which is not considered in the theory. Qualitatively, it would smoothen the interfaces by introducing additional cutoffs to the capillary wave spectra. Also, viscoelasticity may affect the interfacial properties,[14] especially in the case of PVP which strongly interacts with the Si substrate.

Summarizing, it is shown that for polymer bilayers x-ray reflectivity measurements, with the advantage of the large q_z-range and high resolution, yield very accurate results of polymer–polymer interfaces if the FT method is used to analyze the data. Generally, there is no restriction to polymers and any other low-contrast layer system can be studied similarly.

This work was supported by DOE under BES, Contract No. W-31-109-ENG-38; from NSF-MRSEC, Program No. DMR-9732230; and from FZ Jülich, IFF 8, 52425 Jülich (Germany).

[1] L. G. Parratt, Phys. Rev. **95**, 359 (1954).
[2] J. Als-Nielsen, *Topics in Current Physics. Structure and Dynamics of Surfaces* (Springer, Berlin, 1986).
[3] P. Grünberg, R. Schreiber, and Y. Pang, Phys. Rev. Lett. **57**, 2442 (1986).
[4] M. Sferrazza, M. Heppenstall-Butler, R. Cubitt, D. Bucknall, J. Webster, and R. A. L. Jones, Phys. Rev. Lett. **81**, 5173 (1998).
[5] M. Sferrazza, C. Xiao, R. A. L. Jones, D. G. Bucknall, J. Webster, and J. Penfold, Phys. Rev. Lett. **78**, 3693 (1997).
[6] G. Vignaud, A. Gibaud, G. Grübel, S. Joly, D. Ausseré, J. F. Legrand, and Y. Gallot, Physica B **248**, 250 (1998).
[7] C. J. Yu, A. G. Richter, A. Datta, M. K. Durbin, and P. Dutta, Phys. Rev. Lett. **82**, 2326 (1999).
[8] The damping of the peaks is due to the upper limit $q_{z,\mathrm{up}}$ which restricts the range of the integration in Eq. (1).
[9] E. Helfand and Y. Tagami, J. Chem. Phys. **56**, 3592 (1972).
[10] C. J. Clarke, A. Eisenberg, J. La Scala, M. Rafailovich, J. Sokolov, Z. Li, S. Qu, D. Nguyen, S. A. Schwarz, Y. Strzhemechny, and B. B. Bauer, Macromolecules **30**, 4184 (1997).
[11] M. Tolan, *X-ray Scattering from Soft Matter Thin Films* (Springer, Berlin, 1999).
[12] T. P. Russell, R. P. Hjelm, and P. A. Seeger, Macromolecules **23**, 890 (1990).
[13] J. Wang, M. Tolan, O. H. Seeck, S. K. Sinha, O. Bahr, M. Ravailovich, and J. Sokolov, Phys. Rev. Lett. **83**, 564 (1999).
[14] G. H. Fredrickson, A. Ajdari, L. Leibler, and J.-P. Carton, Macromolecules **25**, 2882 (1992).