



OBSERVATION OF SPECKLE PATTERNS BY COHERENT X-RAY SCATTERING FROM THIN POLYMER FILMS

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A speckle pattern is produced whenever a disordered material causes random phase shifts while scattering coherent incident light. Changes of the disordered structure with time lead to fluctuating speckle patterns. The observation of these intensity fluctuations at a single point in the speckle pattern provides a direct measure of the underlying dynamics.

In the wavelength regime of visible light this dynamic light scattering is a well-established technique [1, 2] capable of probing dynamics up to q -vectors of typically $4 \times 10^{-3} \text{ \AA}^{-1}$. This limitation has been overcome recently by correlation spectroscopy with x-rays (XPCS). Using a wide bandpath coherent x-ray beam [3], the translational dynamics of systems such as colloidal aggregates [4] or block copolymer micelles [5] could be studied. Motivated by the observation of static x-ray speckles in block copolymer systems [6, 7], we were interested in exploring the feasibility of XPCS for the study of surface and interface dynamics. Two types of polymer samples were chosen: On one sample the

diffusely scattered intensity, containing information about surface morphology, is created by an additional roughness introduced by small droplets on top of the surface (Figure 1a). The other sample of multilayer type scatters due to the density difference at internal interfaces which are strongly correlated (Figure 1b). This roughness correlation gives rise to resonant diffuse scattering, which concentrates the diffusely scattered intensity into narrow sheets in reciprocal space [8]. We show that these samples might be good candidates for measurements concerning the dynamics of surfaces, like capillary waves, by performing x-ray photon correlation spectroscopy.

The experiments were performed at beamline ID10A at the ESRF using a wide bandpath set-up [3] for coherent scattering in small-angle reflectivity geometry.

Polymer blends exhibit a complex behavior upon spin-coating due to the possibility of phase separation occurring during the film formation. We used polystyrene (PS) and polybromstyrene P(Br_xS) with a degree of bromination of $x = 0.72$. Figure 2 displays an optical micrograph of the sample surface with a magnification factor of 50, displaying droplets with a mean diameter of $2 \mu\text{m}$. They consist of PBrS in a matrix of PS. The laterally disordered domain structure is caused by the partial wetting behavior of the blend. PBrS entrapped in the PS phase during the rapid evaporation of the solvent, segregates to form droplets at the surface. In the investigated q -range, capillary waves have only little contributions compared to the contributions of the droplets, and the droplet motions on a polymer melt can be studied. With the increase of roughness the diffusely scattered intensity, which contained the information about the surface morphology [9], is increased too, providing an increased intensity for coherent experiments.

Installing the above described requirements for coherent x-ray scattering we measured the static speckle patterns by performing common 'detector-scans' (the sample is held fixed at one angle of incidence α_i and the detector angle α is varied). According to $\Delta q_x \sim \pm(2\pi/\lambda) \alpha \Delta\alpha$ and $\Delta q_z \sim \pm(2\pi/\lambda) \Delta\alpha$, changes in the exit angle $\Delta\alpha$ will mainly result in a change of q_z and only very small changes in q_x . Typical speckle patterns are presented in Figure 3. The exit angle equals the critical

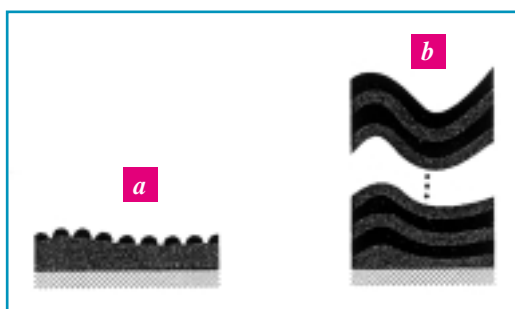


Fig. 1: Schematic drawing of the two sample types used in the coherent experiment: (a) droplets on a thin polymer blend film and (b) layered lamella of diblock copolymer (about 50 layers, not all shown).

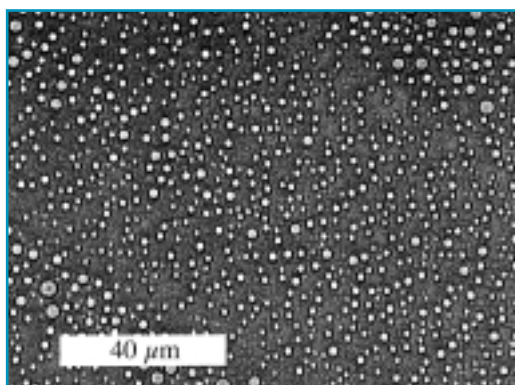


Fig. 2: Optical micrographs of the blend film sample (magnification 50 times) displaying the surface structure consisting of small droplets which were used for the surface labelling.

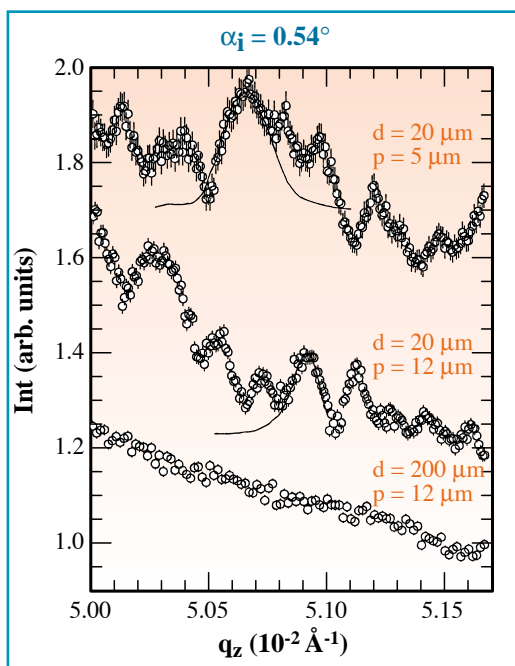


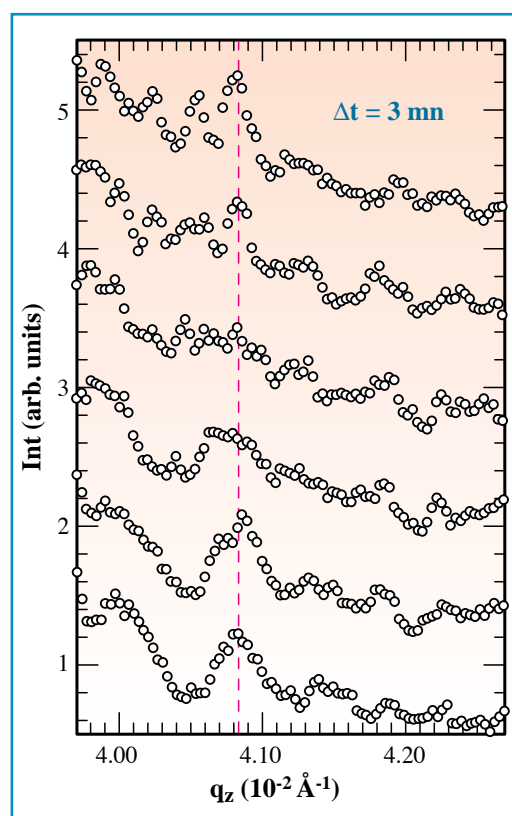
Fig. 3:
«Detector-scans»
measured at the angle of incidence $\alpha_i = 0.54^\circ$ of the blend film sample demonstrating the influence of the front pinhole p and the detector pinhole d . In each scan the q_x value is changed between $1.69 \times 10^{-4} \text{ \AA}^{-1}$ and $1.72 \times 10^{-4} \text{ \AA}^{-1}$. The solid line shows the width of the central peak of the Fraunhofer diffraction pattern as yielded by the measurement. For clarity the curves are shifted against each other.

angle of PS which corresponds to $\alpha_i = 0.54^\circ$. Therefore the measurements are performed through a Yoneda peak. The width of the speckles depends on the size of the front pinhole aperture p . The angular extent of each spot is comparable to that of the central peak of the Fraunhofer diffraction pattern λ/p of the pinhole. An enlarged pinhole aperture causes a narrower diffraction pattern and therefore narrower speckles. The solid lines in the two top curves (20 μm detector pinhole) show the width of the measured central peaks of the primary beam with the corresponding front pinhole for comparison. The good agreement shows that the observed intensity distribution is due to a static speckle pattern from the sample surface. Increasing the detector pinhole d by a factor of 10 averages out the sharp speckle structure corresponding to the observation of the ensemble averaged structure factor. Block copolymers are interesting materials due to their particular phase separation behavior. Because of the chemical connectivity of the components only microphase separation of mutually incompatible blocks takes place. Therefore phase separation occurs only on a molecular scale. This order-to-disorder (ODT) transition is controlled by the degree of polymerisation and the Flory-Huggins segment interaction parameter. Due to selective interactions surfaces can influence the structure formed during a phase separation process. One component may segregate to the surface of the film introducing a surface-induced order. In oriented films the

structures extend over large distances and for a symmetric block copolymer a lamellar ordering is induced. The characteristic periodicity d of these lamella is of the order of the radius of gyration.

For the experiments presented here, polystyrene-block-polyisoprene (PS-*b*-PI) with a symmetric composition was used. For the bulk material an order-to-disorder transition temperature $T_{\text{ODT}} = 178 \text{ }^\circ\text{C}$ was obtained. For the dynamics of such systems one expects collective interfacial modes in which adjacent interfaces move in phase. In the case of full correlation the in-plane morphology of the upper layer would equal the one of the underlying layer through the whole

Fig. 4: Time series of «detector-scans» performed at $T = 125 \text{ }^\circ\text{C}$. The angle of incidence was $\alpha_i = 0.224^\circ$ for the examination of the diblock copolymer film sample ($p = 5 \text{ } \mu\text{m}$ and detector sided pinhole aperture of $20 \text{ } \mu\text{m}$). For clarity the curves are shifted against each other. The dashed line is a guide to the eye.



sample. Whereas for a sample with uncorrelated interfaces all interfaces scatter independently and the diffuse intensities of all individual interfaces superpose, the case of partially or fully correlated roughness gives rise to a coherent superposition of the contributions from individual interfaces leading to a much higher intensity. The intensity is concentrated in narrow sheets. These sheets of resonant diffuse scattering are oriented perpendicular to the q_z -axis with the center fulfilling the one dimensional Bragg-condition $\Delta q_z = 2\pi/d$ [9].

Static speckle patterns from this system were recorded by performing «detector-scans». The scans were taken around the q_z -value of the first order Bragg peak, however slightly off-peak in q_x (two times the full width half maximum of the Bragg peak) to avoid contamination of the signal from specular reflection. Again we measured a well-pronounced speckle pattern comparable to the ones of the blend sample. However they do not result from an increased intensity due to surface labeling but are due to an increased intensity by resonant diffuse scattering. Whereas at room temperature speckles are nearly independent of time, at $T = 125 \text{ }^\circ\text{C}$, above T_g of the PS-block, we observe speckle patterns fluctuating on the time scale of a few minutes.



As an example we show a time series of detector scans in Figure 4. Each scan was taken after three minutes delay time with a counting time of one second per point. In summary we presented experiments using coherent x-ray scattering in a reflection geometry to investigate thin polymer films. In the blend film system the scattering in the demanded q -range is enhanced by surface labelling, whereas in the diblock copolymer film system the roughness correlation of the multilayer interfaces provides the high intensity. Therefore both samples are well suited for experiments using x-ray photon correlation spectroscopy, because they deliver a good signal-to-noise ratio in the observed speckle patterns. Thus they are good candidates for further dynamic

measurements. This will enable the determination of the time correlation function of the surface and interface dynamics and will open up the door for examinations of capillary waves, surface diffusion processes and membrane dynamics. ■

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FIRST EXPERIMENTS ON TROIKA II

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The Troika II beamline (ID10B) started user operation on schedule in April 1998. This second branch of the Troika beamlines is again an open beamline with a flexible diffractometer which aims at providing additional beam time for demands in the soft-condensed matter community. Special emphasis to surface and interface studies using grazing-incidence diffraction and x-ray reflectivity is given.

Although Troika II uses the same undulator source as Troika I (ID10A), both stations can work independently in parallel. A thin diamond (111) crystal acts as monochromator and beam splitter (see Figure 1), a technique which has been

pioneered at the Troika beamline. A second (111) diamond crystal deflects the monochromatic beam at a constant offset from the white beam path. The energy range of this double-crystal monochromator is 8 to 12 keV. As a

further optical element, a plane double mirror for harmonic rejection is in preparation. Presently, harmonic rejection is achieved with two small mirrors in the experimental hut.

The Troika II eight-circle diffractometer with an additional beam deflector can operate both in horizontal and vertical scattering geometry. In horizontal geometry heavy and bulky sample environments can be handled. In combination with the deflector, a device that employs either a mirror or a Bragg crystal to deflect the beam out of the horizontal plane, the horizontal geometry

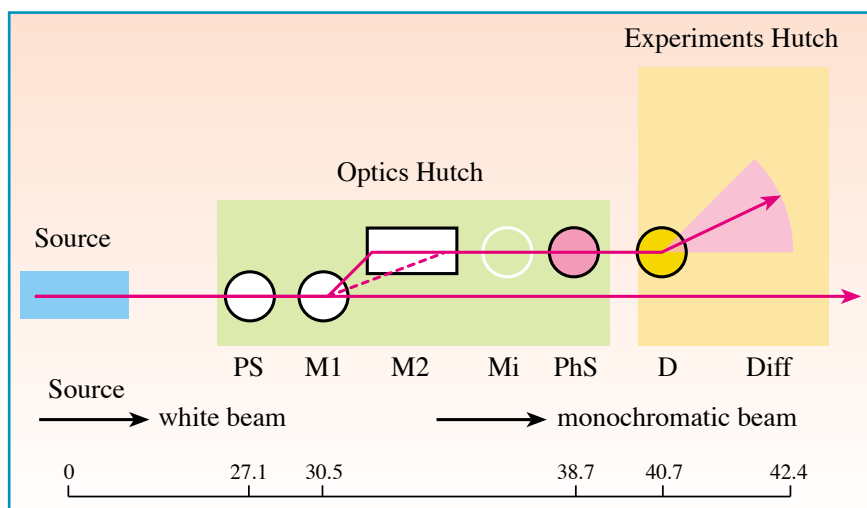


Fig. 1: Troika II layout: PS primary slits; M1, M2 diamond double-crystal monochromator; Mi planned double mirrors; PhS photon shutter, D deflector, Diff: eight-circle diffractometer.