Observation of X-Ray Speckle by Coherent Scattering at Grazing Incidence

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We have observed x-ray speckle at grazing incidence from gold-coated films of symmetric diblock copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA). The polymer films consisted of micron-sized islands on a uniform surface. Coherent 6-keV photons were selected by monochromatizing and collimating the x-ray beam from a bending magnet synchrotron source. The visibility of the speckle patterns was enhanced with increasing degrees of spatial coherence of the photons. Speckles due to coherent scattering from islands with length scales up to 100 μm were clearly identified.

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Investigations of speckle can be traced to Fraunhofer's diffraction rings, which are produced when partially coherent light is diffracted by a glass plate covered with small particles [1]. A speckle pattern is formed when a medium with a randomly varying refractive index is illuminated with coherent or partially coherent light. The resulting pattern is due to interference between waves which undergo various optical path differences or phase shifts after being scattered by different parts of the medium. As such, the speckle pattern can provide unique structural information about the medium.

Speckle and related techniques such as dynamical light scattering [2, 3] have been used widely within the visible light region to study diffusion and critical phenomena in fluids. X-ray speckle can, presumably, extend these capabilities to length scales commensurate with x-ray wavelengths. Speckle patterns are not usually seen in x-ray experiments because of the low coherent flux available. X-ray speckle has only recently been observed in the Bragg-reflected beam from a single crystal of Cu_3Au with randomly arranged antiphase domains [4]. In this Letter, we report and x-ray speckle measurement at grazing incidence on annealed thin films of symmetric diblock copolymers. These film surfaces were covered with micron-sized islands or holes (domains) of uniform height. The lateral size of the domains can be varied by the initial film thickness and the extent of the annealing time.

The foremost requirement for observing a speckle pattern is a spatially and temporally coherent beam. However, it is possible to use an incoherent source such as a synchrotron bending magnet to form speckle patterns if the beam is sufficiently collimated and monochromated. Our experiment was carried out at the X-6B bending magnet beamline at the National Syncrotron Light Source (NSLS). The scattering geometry is shown in Fig. 1. Monochromatic x rays of 6 keV (2.067 Å) were selected using a double Si(111) crystal monochromator. A spatially coherent beam was obtained from the monochromatic beam by selecting the coherent photons with a small pinhole, 24 m from the source. The collimated x rays were directed at a grazing angle of $\theta_i = 0.4°$ onto the sample (10 cm behind the pinhole), which was mounted on the θ-rotation axis of a six-circle goniometer. A charge coupled device (CCD) camera with low dark current ($<2e^-/\mathrm{h}$) and low read-out noise ($5e^-$ rms) was mounted on the 2θ arm of the goniometer, 115 cm from the sample. The CCD chip has 1024 × 1024 pixels and covers an area of 1.95 × 1.95 cm^2. Thus, the angular resolution of each pixel is about 17 μrad. Scattering intensities can be measured along α and β, where $\beta = \theta_f - \theta_i$ (see Fig. 1).

To observe speckle, the transverse coherence width of the incident beam should be equal to or greater than (i) the beam size and (ii) the length scales of the inhomogeneities of the system to be studied [5]. The first condition is necessary to prevent incoherent averaging of many overlapping speckle patterns. The second condition

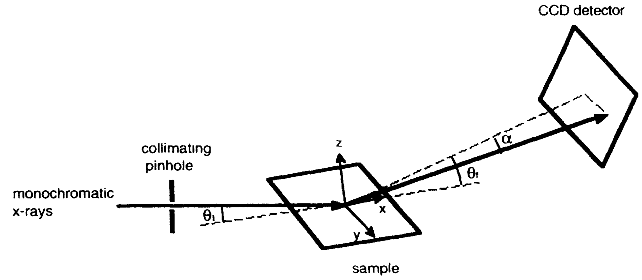

FIG. 1. Schematic illustration of the scattering geometry.

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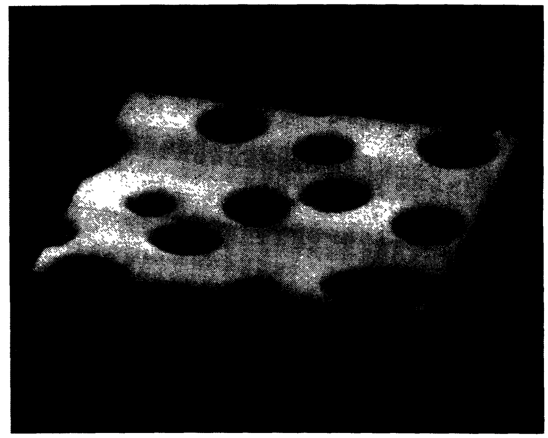
is necessary to observe interference of scattering on the different length scales of interest. In addition, the optical path differences of the scattered rays must not be greater than the longitudinal coherence length of the beam.

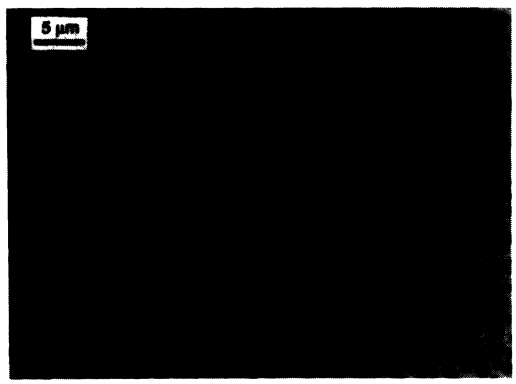
The transverse coherence width of the x-ray beam at a distance L from a source of size a is $\sim\lambda L/a$ [6], where λ is the wavelength of the radiation. We define the coherence width by the first zero of the coherence function [7]. Typical vertical and horizontal source sizes (2σ) of NSLS bending magnets are 0.3 and 0.7 mm. The corresponding coherence widths for 2-Å x rays at the location of the pinhole are 16 and 6.9 μm, respectively. To satisfy the first requirement for a speckle measurement, a platinum pinhole of 5 μm in diameter was used to select a highly coherent x-ray beam. Pinholes of 12 and 60 μm were also used to select partially coherent beams to study the influence of coherence on the speckle patterns.

When collimated by the 5-μm pinhole, the projection of the x-ray beam onto the sample surface at 0.4° was about 850 μm, satisfying the second condition above. Also, at this grazing angle, the maximum optical path difference was an order of magnitude less than the longitudinal coherence length $\lambda^2/\Delta\lambda$ [8] of the x-ray beam, where $\Delta\lambda$ is wavelength spread of the beam. For a Si(111) crystal monochromator, the longitudinal coherence length is about 1 μm at the wavelength of 2 Å. In our geometry, the optical path difference for a pair of surface domains separated by a distance h, observed at an angle θ_f from the sample surface, is $h(\cos\theta_i - \cos\theta_f)$. For $h = 850$ μm and $\theta_f = 1.0°$, which was the largest angle subtended by the CCD detector, the largest optical path difference was 0.11 μm.

The copolymers used in this experiment were purified symmetric diblock copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA) with a total molecular weight of 100 000 g/mole. Films of the copolymers were prepared by spin-coating techniques, followed by heating to 170 °C under vacuum for about 70 h to form surface domains. In order to increase the scattering contrast, a 200-Å gold layer was deposited on the surfaces of the annealed films. Figure 2(a) shows a typical atomic force microscope (AFM) image of an annealed PS/PMMA film on which surface domains are formed. Note that both islands and holes could be formed depending on the initial thickness of the film before annealing [9, 10]. Figure 2(b) shows an optical micrograph of the surface of an annealed and gold-covered copolymer film on which x-ray measurements were actually carried out. Scanning electron microscope measurements on the same surface (not shown) suggest that the domains consist of islands. The domain sizes range from 0.5 to 1.5 μm, and the distance between nearest domains is $\sim$2 μm. The domain height is uniquely determined by the molecular weight of the copolymers and is measured by AFM to be 415 Å



(a)



(b)

FIG. 2. (a) AFM image of typical domains on the surface of an annealed PS/PMMA diblock copolymer film. (b) Micrograph of the surface structure of a gold-coated diblock copolymer film from which x-ray speckle patterns were taken.

[11]. From microscopic images of the polymer films before and after gold coating, it was found that the surface topography was preserved.

Figure 3 shows the scattering patterns recorded as the incident x rays became progressively more coherent when the 60-, 12-, and 5-μm pinholes were used. The scattering patterns obtained using the 5- and 12-μm pinholes clearly show the granular structure typical of visible light speckle patterns. Despite the low coherent flux from the bending magnet and the narrow bandwidth selected by monochromator (about 2×10^3 photons s^{-1} when collimated through the 5-μm pinhole), two-dimensional speckle patterns were obtained with 10-min exposures. In the center of each image is the shadow of a beam stop that prevents the specularly reflected beam from saturating the detector. Three line profiles of these scattering patterns along θ_f are shown in Fig. 4. As the beam becomes more coherent, the speckle pattern obtained using the 5-μm pinhole shows higher visibility than those obtained

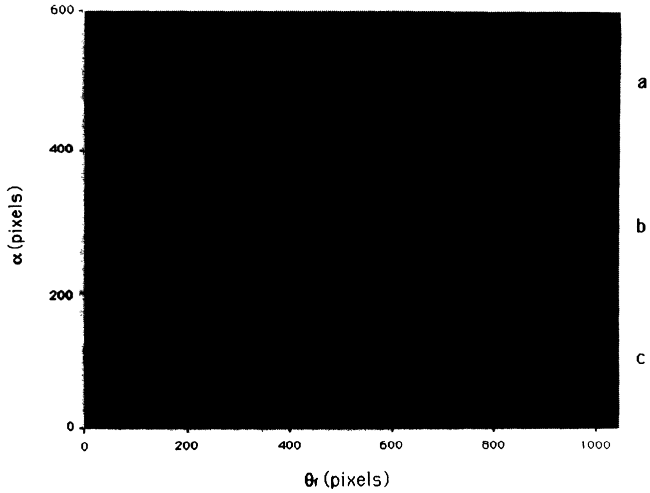


FIG. 3. Two-dimensional speckle patterns recorded with a CCD camera from an annealed thin film of diblock copolymers of PS and PMMA. The film was covered with 200 Å of gold. The incident angle was 0.4° and the collimating pinholes were 5 μm (a), 12 μm (b), and 60 μm (c).

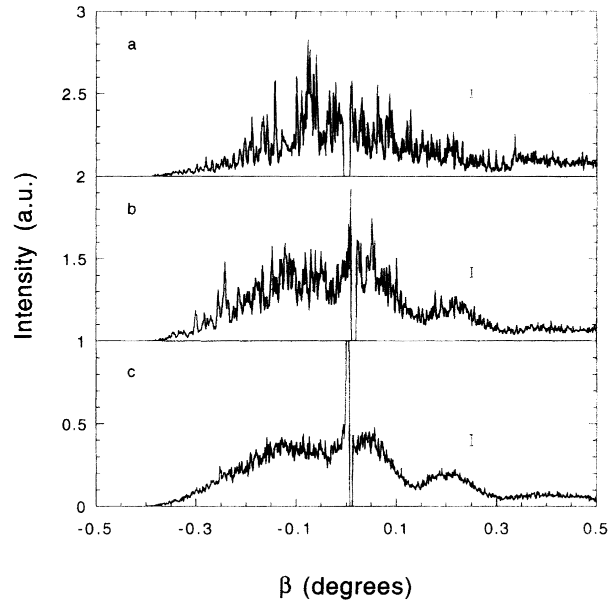


FIG. 4. Line profiles of the speckle patterns in Fig. 3 along the takeoff angle direction. The displayed intensities were normalized to have the same background level. The error bars indicate the shot noise due to the finite number of recorded photons.

using the 12-μm and larger pinholes. For the 60-μm collimating pinhole, the fluctuations are within the photon statistical noise and the speckle is essentially lost. We have also repeated the measurements with a different part of the sample being coherently illuminated and found that the scattering patterns were much different in detail, indicating the dependence of speckle patterns on the sample area of illumination. When an annealed film of Au/PS/PMMA without surface domains was used, speckle was not observed, indicating that the speckle pattern arose only from the domain scattering.

Each speckle in the two-dimensional pattern is due to constructive interference of waves scattered by all the coherently illuminated domains with identical separation and orientation. The minimum width of the speckles is λ/s, where s is the beam size. However, the widths of the individual speckles also depend on both the spatial distribution of the domains within the illuminated sample area and the detector resolution.

When diffraction by the pinhole is considered, the beam size on the sample using the 5-μm pinhole is 6 μm, and the minimum angular width of the speckles should be about 35 μrad, twice that subtended by a CCD pixel. In the pattern shown in Fig. 4(c), except for those peaks that are too complex to be resolved clearly, the angular sizes of the speckles vary from 40 to 100 μrad, in good agreement with the minimum width that would be obtained using a 5-μm collimating pinhole. On the other hand, 100 μrad is still much smaller than the angular width, λ/p (about 280 μrad for the sample studied here, where p is the domain size), of the peak that would be obtained in conventional scattering with incoherent light. However, even narrower speckles were not found in the pattern obtained using the 12-μm collimating pinhole due to the limited detector resolution.

The critical angle of our samples varies with the degree of surface coverage. The experimental measurements reported in this paper were performed at an angle of incidence of 0.4°, which was about 0.1° above the measured critical angle of the film at 6 keV. We also observed speckle patterns at angles of incidence from 0.2° to 0.5°. We chose this angle because it limits the illuminated size of the sample, thus simplifying the pattern for interpretation, yet allows speckle patterns to be recorded within a reasonable time period.

For a scattering peak at (θ_f, α), the components of the scattering vector $\mathbf{q}$ defined in the geometry shown in Fig. 1 are given by

$$q_x = k(\cos\alpha\cos\theta_f - \cos\theta_i),$$
$$q_y = k\sin\alpha, \qquad (1)$$
$$q_z = k(\cos\alpha\sin\theta_f + \sin\theta_i),$$

where $k = 2\pi/\lambda$ is the wave vector of the incident beam. Thus, the lateral separation and orientation of the domains causing the peak can be determined from q_{para} [where $q_{\text{para}} = (q_x^2 + q_y^2)^{1/2}$]. Scattering along θ_f results in changes in both q_x and q_z. In order to interpret the broad features in Fig. 4(c), we carried out conventional reflectivity and off-specular measurements on the same sample. We believe that these features are due to coupling of the scattering characterizing the thickness of the gold layer and the height of the surface domains. For the films studied here, there is no other structure normal to the film surface that would result in sharp peaks in the scattering pattern.

At the angle of incidence $\theta_i = 0.4°$, a CCD image gives a q_y region of ± 0.026 Å^{-1} and a highly elongated q_x region from -3.9×10^{-4} to 7.4×10^{-5} Å^{-1}. Because of the extreme stretch in q_x, the scattering annulus becomes stripelike in Fig. 3(c). The angular spacing of the two stripes, which represents a 1.8-μm length in real space, is consistent with the average separation of neighboring domains. In scattering patterns taken from samples with different average domain separations, we found that the angular separation between the two stripes decreased when the average separation of neighboring domains increased.

The intensity profiles show that the scattering drops to zero at $\beta = -0.4°$. Scattering below this angle is truncated by the substrate. The most intense speckles appear within an angular region close to the specularly reflected beam, and the speckles are more pronounced at $\theta_f < \theta_i$. This is because the average scattering form factor peaks at $\beta = 0$, and the scattering intensity drops quickly as q_z increases [12]. The speckles in the patterns in Fig. 3 characterize length scales in the sample up to 100 μm. Speckles due to longer length scales are not seen because of the beam stop.

The main advantage of coherent scattering is that it enables one to obtain information about spatially uncorrelated distant domains [13]. This kind of information is not available in conventional scattering with incoherent light. As demonstrated here, x-ray speckle observed at grazing incidence can be used to study inhomogeneous systems where high surface and interfacial sensitivity is required. This technique may be applicable to a large group of noncrystalline materials. With an increase of 3 or 4 orders of magnitude in the coherent flux provided by new undulator source at the Advance Photon Source and the European Synchrotron Radiation Facility, speckle patterns could be taken within 0.1 s, permitting real-time studies of disordered structures. Studies of inhomogeneous systems with much shorter length scales, which are currently limited by low scattering intensities, will also become possible.

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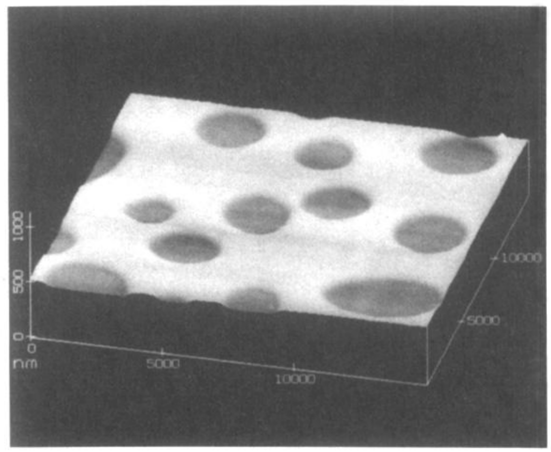
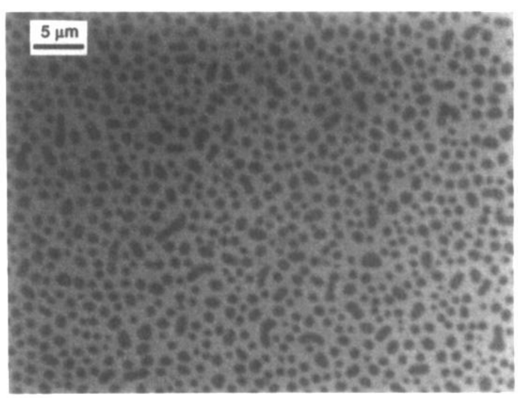


(a)



(b)

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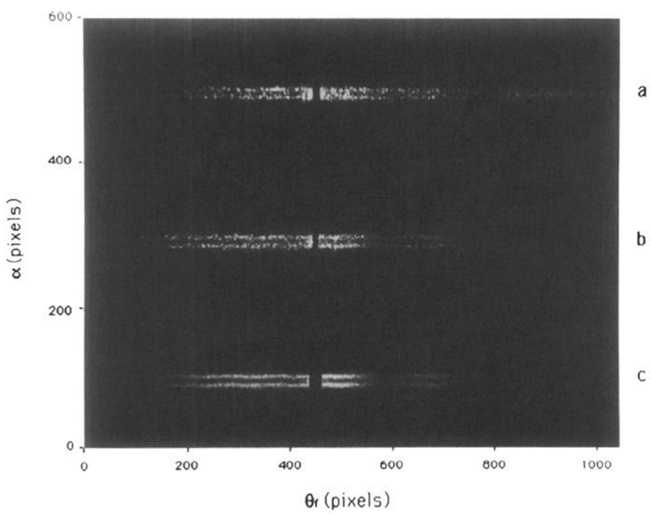

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