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Report:

The surface morphology of ultra-thin block-copolymer films on top of solid substrates was investigated with grazing incidence small angle scattering. The films were prepared by spin-coating. We used as model system a symmetric polystyrene-block-polyparamethylstyrene P(S-b-pMS) with a molecular weight of 230k. The mean lamella spacing installable with this polymer is L_o=45nm. Due to the large molecular weight, despite the small polymer-polymer interaction parameter between PS and PpMS, it exhibits strong segregation. Thus the resulting lamellae are markedly shaped for film thicknesses above L_o. We investigated films with smaller film thicknesses $d<L_o$.

Depending on the installable long range correlations, a part of the roughness spectrum of the silicon substrate is transferred and determines the morphology of the polymer film. With **static measurements** the part of the correlated roughness spectrum is examined as a function of the film thickness. Due to the chosen set-up (Si(111) analyzer crystal together with a linear position sensitive detector) a large q-range is accessible which enables the determination of roughness correlation down to extremely small film thicknesses. In addition the q_y-resolution is very high. In a single measurement the roughness correlation is detected from the resulting fringes in the diffuse scattering. Figure 1A shows as an example films of different film thicknesses right after prepartion. From the bottom to the top the film thickness increases (d= 3nm, 22nm, 35nm and for reference 100nm). For samples with $d<L_o$ fringes are well resolved.

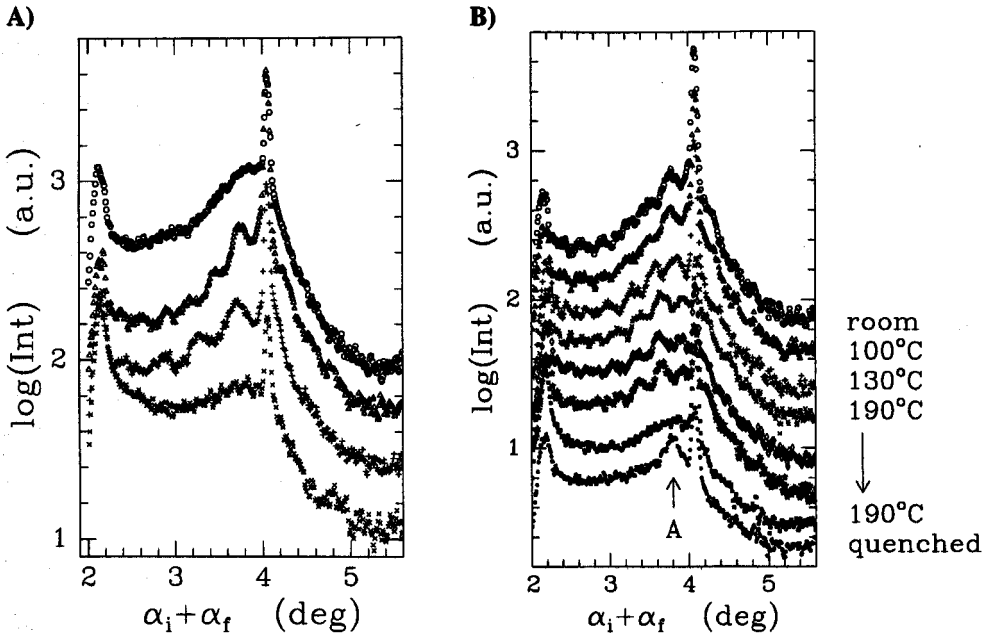

Figure 1: *A) Cuts at q_y=0, frequently called detector-scans, showing the Yoneda-peak, the specular peak and modulations in the intensity due to resonsnat diffuse scattering. The wavelength of the modulation is determined by the thickness d of the correlated film $\Delta q_z=2\pi/d$. B) Kinetic investigation of decaying long range correlations at temperatures near the glass transition temperature, below and above T_{ODT}.*

In figure 1B an example of **kinetic measurements** is shown. For a fixed film thickness of d= 35nm the as prepared sample (denoted room) is annealed at different temperatures near the glass transition temperature T_g=100°C, below and above the order-disorder transition temperature T_{ODT}=153°C and again quenched down to room temperature (denoted quenched). An annealing near the glass transition temperature only slightly weakens the long range correlation, while annealing at 130°C starts to built up an internal morphology, because the movability of the polymer molecules is increased but the system is still not miscible. Due to the chemical linking of the two weakly immiscible components PS and PpMS internal order is installed between T_g and T_{ODT} in an temperature interval of 53°C (UCST behavior). The energetically unfavorable highly correlated surface morphology is destroyed by the creation of an internal order. After sufficient long annealing at 190°C the modulations resulting from the roughness correlation vanished and no sign of internal order, like a bragg peak becomes visible. After quenching below the order-disorder transition, an additional peak (denoted with "A" in figure 1B) was detected again. Because in the plotted detector-scans not the pure q_z information is detected, the presence of the additional peak pictures the imperfection of the internal ordering, which gives rise to a smearing of the theoretically small bragg peak. The distance from the q_x=0 position probes the lateral length scale at which deviations are introduced.