ESRF	**Experiment title:** Glass transition at the surfaces of polymer films probed by GISAXS from gold/polymer samples	**Experiment number:** SI-651
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Report:

The aim of the experiment was to investigate *in situ* the structure of metal/polymer interfaces near the glass transition temperature (T_G) of polystyrene, in order to detect possible changes of T_G at the surface. Gold clusters deposited on a thin polymer film were used as a probe of the viscosity at the surface: when heated to temperatures in the region of T_G (for polystyrene, $T_G \simeq 100°C$), the clusters start to sink into the polymer since the viscosity is drastically reduced at T_G [1].

In this experiment, the lateral movement of the gold clusters (typical size of 30–100 Å) was in the focus of our research. It is only accessible using the GISAXS geometry. Four samples were investigated with different gold coverages (equivalent thickness of 1, 2 and 3 nm) and different molecular weights (M_W) of the polymer (3.8, 44 and 200 $kg\,mol^{-1}$). A furnace with a beryllium dome was used to heat the sample up to T_G. The out-of-plane diffuse scattered intensity was recorded with a CCD camera placed on a track in order to change the resolution for the different samples. In addition, the reflectivity profiles were also recorded using a position sensitive detector placed on the diffractometer detector arm. The experiment was carried out at a high energy of 18.27 keV in order to reduce radiation damage.

Figure 1-a presents the GISAXS patterns recorded for samples with the three different gold coverages (1, 2 and 3 nm, from the top to the bottom). The parallel and perpendicular components of the transfert vector ($q_{\|}$ and $q_{\perp}$, respectively) are indicated on the picture. The shadow of the beamstop appears in black in the middle of each pattern. The diffusely scattered intensity results from a mixture between the shape factor of the clusters and the inter-cluster correlation function: the side maxima along $q_{\|}$ are well pronounced and correspond to the cluster–cluster lateral correlation length. Oscillations along the $q_{\perp}$ direction results from the total thickness interference fringes in the transmission function.
The figure 1-b presents the cross section along $q_{\|}$ measured for different temperatures on the sample with low gold coverage. When increasing temperature, the correlation length in the system increases. This is probably due to a growing of the clusters by approximately 5% in diameter (which corresponds to a 16% increase in volume). A possible reason could be agglomeration or coalescence. For the measured samples, the size of the clusters is on the order of the distances between them which leads to a difficult data analysis.

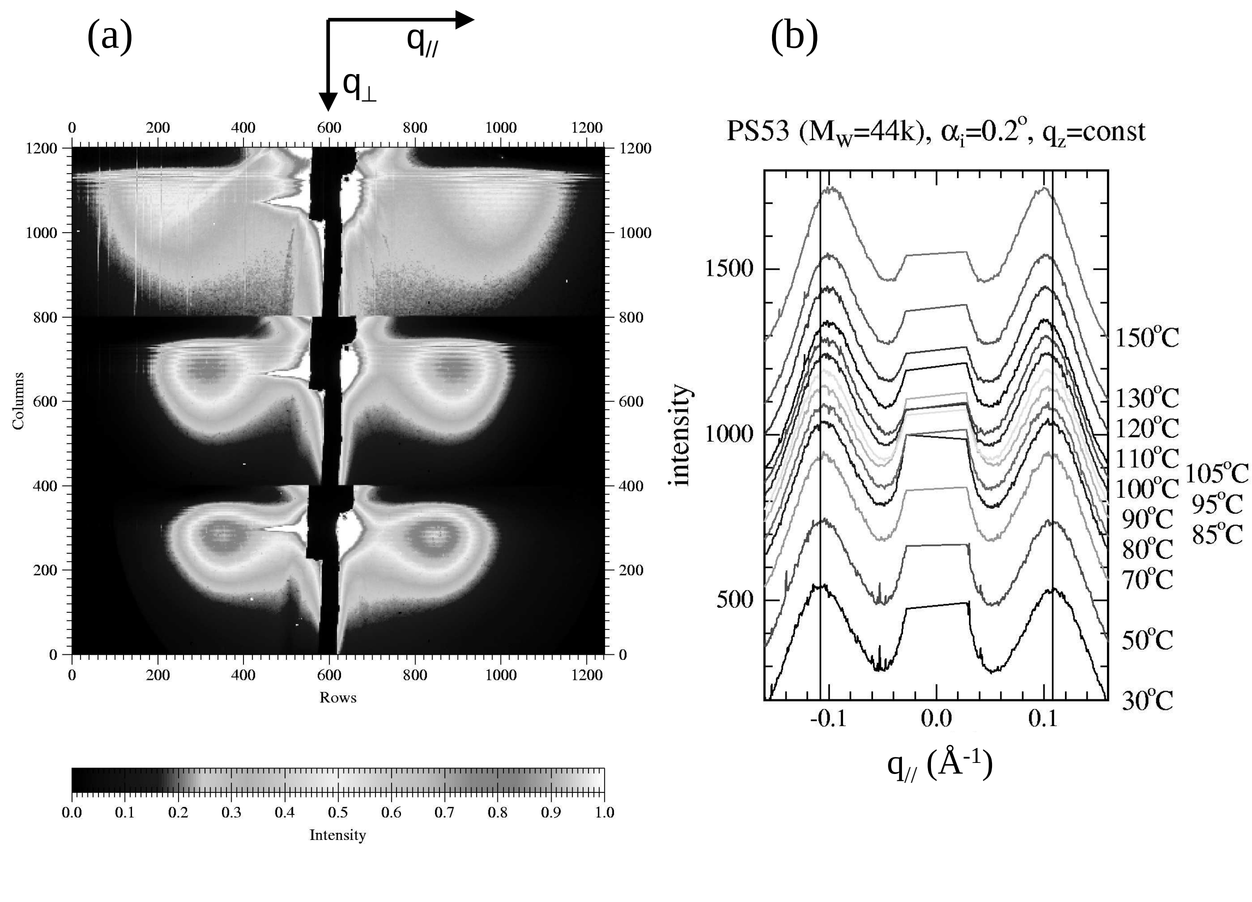

Figure 1: (a) GISAXS patterns measured for three samples with different gold coverages (equivalent thickness of 1, 2 and 3 nm, from the top to the bottom). (b) Cross section along $q_{\|}$ measured on the low gold coverage sample for increasing temperature indicated on the graph: a shift of the correlation maxima to small $q_{\|}$ values is visible for larger temperatures.

[1] R. Weber, K.-M. Zimmermann, M. Tolan, J. Stettner, W.Press, O.H. Seeck, J. Erichsen, V. Zaporojtchenko, T. Strunskus, and F. Faupel; Phys. Rev. E. **64**, 61508 (2001).