ESRF	**Experiment title:** Diffusion of very dilute gold clusters in thin polymer films studied in situ with GISAXS	**Experiment number:** SI807
Beamline: ID1	**Date of experiment:** from: 20/11/02 to: 20/11/02	**Date of report:** 06/09/04
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Report:

The aim of this experiment is the investigation of the metal/polymer interface as a function of the temperature, by the study of the lateral and vertical distribution of gold clusters at the polymer film surface using grazing incidence small angle x-ray scattering (GISAXS).

The samples are obtained by the evaporation of gold atoms onto a spin-coated polystyrene film in a high vacuum chamber. As the surface tension of the metal is much higher than the one of the polymer, the gold atoms diffuse on the surface before forming almost spherical clusters with typical size of 1–10 nm. At the glass transition of the polymer film, the viscosity decreases and the clusters are then able to sink in order to lower the Gibbs free energy (the metal/polymer interface tension is much smaller than the metal surface tension).

In a previous experiment, we already proved that the clusters distribution at the polymer surface can be monitored *in situ* using GISAXS (report SI651). In this geometry, the sample surface is illuminated with a monochromatic x-ray beam for an incidence angle α_i in the order of the angle of total external reflection (typically a few tenths of a degree). The diffuse signal scattered by the nano-particles out of the incidence plane around the specularly reflected beam is recorded with a 2D detector. Both form factor and structure factor of the cluster assembly are measured.

For this GISAXS experiment, we used an optimized set-up with the sample lying horizontally in the ID1 furnace equipped with a Be dome and a CCD detector on the track for resolution adjustment. The x-ray path between the sample and the CCD was evacuated. The temperature at the surface of the film was monitored by a PID

thermo-controller and was known within 1 K accuracy. A particular care was taken in order to avoid overshooting. A beam energy of 18 keV was used in order to reduce possible radiation damage. 10 samples with different polystyrene molecular weights, film thicknesses and gold coverages have been investigated for temperatures ranging from 300 to 500 K.

The Fig. (1) presents GISAXS patterns measured for an increasing gold coverage. The horizontal and vertical axis corresponds to the parallel ($q_{\|}$) and perpendicular ($q_{\perp}$) wavevector transfers, respectively. The dark stripe at $q_{\|} = 0$ is the beamstop shadow hiding the in-plane specular reflection. Lateral correlation maxima are developing when the gold coverage increases. At larger gold coverage, it is enhanced in the vertical direction by the particle form factor. The Fig. 2 presents GISAXS cross sections along the $q_{\perp}$ direction measured as a function of the temperature. The lines are the best fits leading to the particle radius values presented on the graph on the right. Near the glass transition, an increase of the mean particle size is observed which is only temperature dependent (and not time). This result is confirmed by the analysis of the GISAXS intensity distribution along the $q_{\|}$ direction. Further analysis are currently on the way.

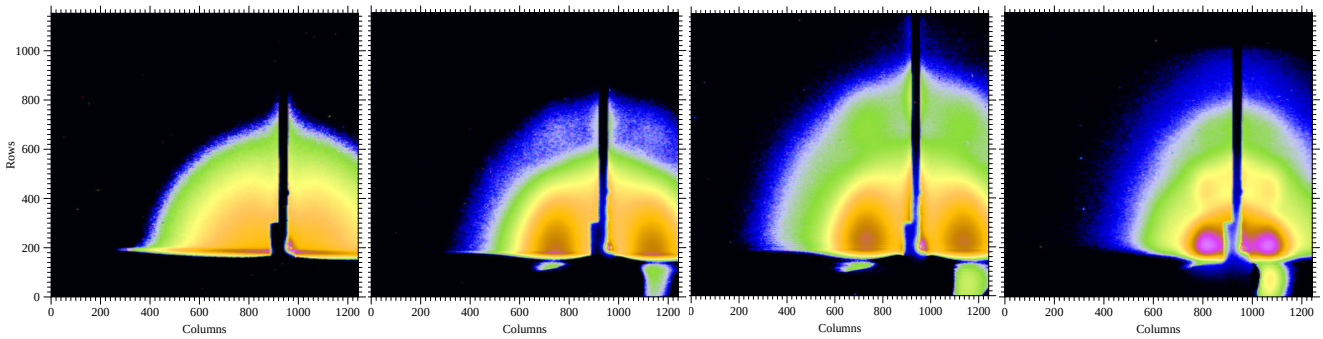

Figure 1: GISAXS patterns measured at room temperature for different gold coverages of 2, 10, 20 and 30 Å, respectively from left to right (molecular weight and film thickness are 220 kg/Mole and 100 nm, respectively). The distance between the sample and detector (1000 2000 cm) is adjusted in order to achieve the chosen resolution.

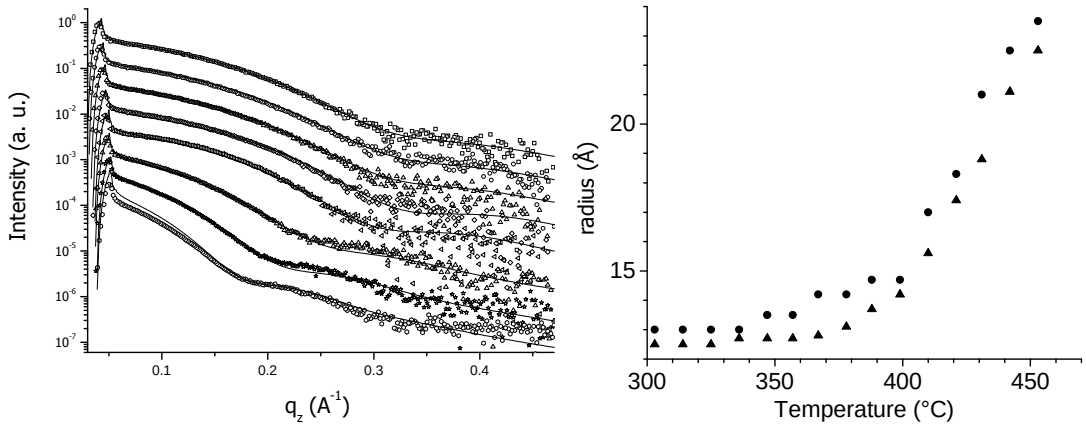

Figure 2: (*left*) GISAXS cross sections measured along the $q_{\perp}$ direction as a function of the temperature (300 to 450 K from top to bottom) for a 4 Å gold coverage. (*right*) Radii of the spherical particles obtained from the best fits along the $q_{\perp}$ (triangles) and $q_{\|}$ (circles) directions.