ESRF	**Experiment title:** Surface dynamics study of confined polymers using x-ray photon correlation spectroscopy	**Experiment number:** SC1179
Beamline: ID10a	**Date of experiment:** from: 18/06/03 to: 24/06/03	**Date of report:** 08/08/03
Shifts: 18	**Local contact(s):** Anders Madsen	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
V. Chamard*,a, M. Krämer*,a, J. Stettner*,b and M. Tolan*,a
(a) Experimentelle Physik IA, Universität Dortmund, Germany,
(b)Institut für Experimentelle und Angewandte Physik Universität Kiel, Germany.

Report:

The aim of the experiment is the study of the glass transition of confined viscoelastic liquids by measuring the surface dynamics of metal-decorated polymer thin films, using x-ray photon correlation spectroscopy (XPCS) in the grazing incidence small angle scattering (GISAXS) geometry.

Although physical properties of bulk polymers are well known, an anomalous behavior of the glass transition has been observed in thin polymer films a decade ago [1,2].

The surface of the viscoelastic liquid films are decorated with overdamped capillary waves [3]. The relaxation time τ of the process is related to the viscosity η, which increases near the glass transition leading to the freezing of the capillary waves and to an increase of the relaxation time [4,5]. By using XPCS we can directly monitor the dynamics at the surface of such liquids [4]. Previous XPCS measurements on polymer melt surfaces have reported the dispersion relation measured over the first 10 nm under the surface in the small q range (10^{-3} to 10^{-2} nm^{-1}) [6].

In the present experiment, we investigate the surface dynamics of metal cluster-decorated polymer thin films. The gold clusters with diameter of a few tens of Å are produced by evaporation at room temperature of some monolayers of gold on the spin-coated polystyrene thin films (100 nm). The resulting spherical clusters present a well defined correlation length in the surface plane, resulting in side correlation maxima at about 1 nm^{-1}. In addition, the scattering power of gold is much stronger than the polymer one. Therefore the clusters act as a marker of the surface. At the surface glass transition the clusters sink under the polymer surface.

In order to reduce the radiation damage, a beam energy of 10.64 keV was used. A coherent x-ray beam was produced using a 10×10 μm^2 pinhole and the beam was tilted vertically by a mirror in order get an angle of incidence of 0.1° at the sample surface. The sample was laying horizontally in the home-made furnace equipped with kapton windows. The out-of-plane scattering from the clusters was recorded with a NaI detector and the auto-correlation function was calculated on line with the intensity auto-correlator of ID10a beamline.

The measurements presented on figure 1(a) show the intensity autocorrelation functions recorded for temperatures ranging from 40 to 180°C on a 3.55 kg/mol polystyrene thin film covered by an equivalent thickness of gold of about 20 Å(the glass transition temperature is about 70°C). This investigation was done at the maximum of the cluster-cluster correlation at $q = 0.6$ nm^{-1}, corresponding to a real space length scale of 10 nm. Two time constants are observed : one in the 1-10 s range, attributed to the capillary waves (τ_{cw}) and a second one around 100-1000 s, corresponding to the Brownian motion of the clusters in the polymer matrix (τ_{Bm}).

Both are related to the viscosity through two independent relations. The viscosities deduced from τ_{cw} and τ_{Bm} are reported on the figure 1(b): they agree pretty well one with the other, which is a strong support to our dynamical model.

Although several questions arise with these measurements, this experiment demonstrates the feasibility of surface XPCS investigations in the *nanometer* range.

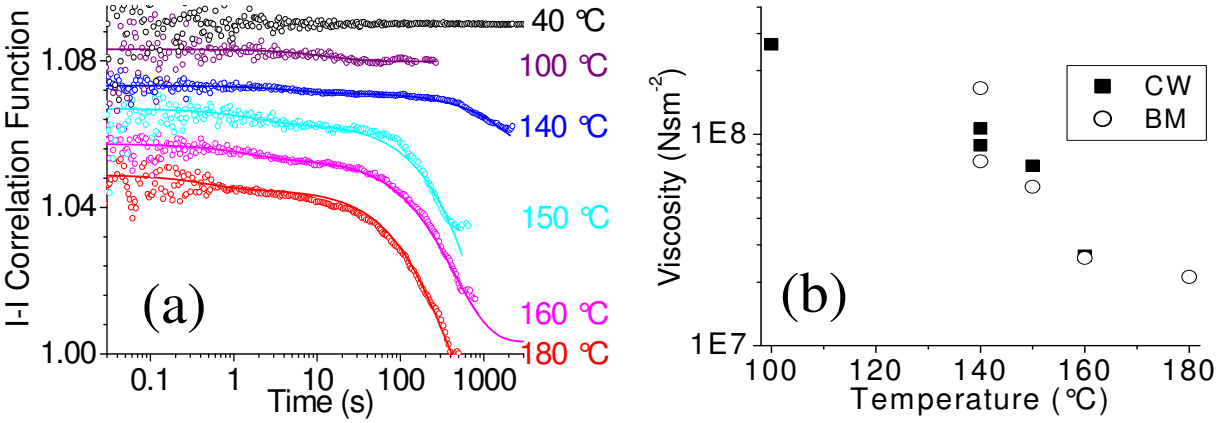

Figure 1: (a) XPCS measurements of the metal cluster decorated polymer thin film for different temperatures and their best fits. (b) Viscosities deduced from the capillary wave motion and the Brownian motion.

References:

[1] J. L. Keddie, R. A. L. Jones and R. A. Cory, Europhys. Lett. **27**, 59 (1994).

[2] M. Tolan, *X-Ray Scattering from Soft-Matter Thin Films*, Springer Tracts in Modern Physics Vol. **148**, Springer-Verlag, Berlin, Heidelberg (1999).

[3] J. Jäckle and K. Kawasaki, J. Phys: Condens. Matter **7**, 4351 (1995).

[4] T. Seydel, *et al.*, Phys. Rev. B **63**, 73409 (2001).

[5] T. Seydel, *et al.*, Phys. Rev. B **65**, 184207 (2002).

[6] Hyunjung Kim, *et al.*, Phys. Rev. Lett. **90**, 068302 (2003).