ESRF	**Experiment title:** Probing the glass transition of a polymer surface by XPCS	**Experiment number:** SI-1239
Beamline: ID10A	**Date of experiment:** from: 7-9-2005 to: 12-9-2005	**Date of report:** 6-3-2006
Shifts: 18	**Local contact(s):** A. Madsen	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
T. Seydel[*,1], C. Caronna[*,2], A. Madsen[*,2], S. Streit[*,3], M. Tolan[3]
[1]ILL, [2]ESRF, [3]Univ. Dortmund

Report:

This experiment was a continuation of SI-1082 with the aim to measure the gradual slowing down of surface dynamics as the glass transition of poly-propyleneglycol (PPG) was approached. The experimental method was grazing incidence XPCS performed at ID10A using a partially coherent 8keV X-ray beam. The samples were prepared and stabilized in the sample environment we have constructed for such experiments [1]. The fluctuating signal scattered from the supercooled surfaces was detected by a CCD and subsequently the time-correlation function of the intensity was calculated vs the momentum transfer q. We were in particular interested in verifying the saturation of the damping constants observed previously: When a certain critical momentum transfer is passed the damping constant is not increasing in a linear fashion any more but seem to saturate. This deviation from a linear dispersion is not predicted by the standard capillary wave theory. Our experiment confirmed again this behavior and we explored the temperature dependence of the phenomenon. In particular we checked for any ageing and temperature hysteresis but did not observe significant effects in the explored temperature regime. Unfortunately, there was not time enough to investigate the influence of changing the molecular weight of the polymer, and we will propose to do that in a later experiment. In order to explain the deviation from simple capillary wave behavior we have attempted to include the effect of elasticity (solid like behavior) in the hydrodynamic equations as the glassy state is approached. This has proven to be a difficult task with only few models on the market.

A model developed by J. Jackle and K. Kawasaki [2] can indeed reproduce the slowing down of the surface fluctuations as observed (figure 1), but the fits point towards a decreasing shear modulus G as T_G is approached. This is absurd from a physical point of view and hence the model is not suitable to describe our data. This is maybe not surprisingly since the model is based on a classical Maxwell-Debye description of viscoelasticity which is known to be too simplistic for many complex fluids. Instead we seek to use molecular dynamics based models for the polymer viscoelasticity [3] in the expression for the surface wave dispersion, but hitherto we have not been successful. A real challenge is the difficulty in determining independently $G'(\omega)$ and $G''(\omega)$, the storage and loss components of the complex shear modulus in the relevant frequency and temperature range. We plan to attack this problem shortly by XPCS microrheology [4], light scattering [5] and possibly mechanical rheology. In addition we plan to ask for beamtime shortly to investigate the effect of varying the polymer chain-length and thereby the molecular weight.

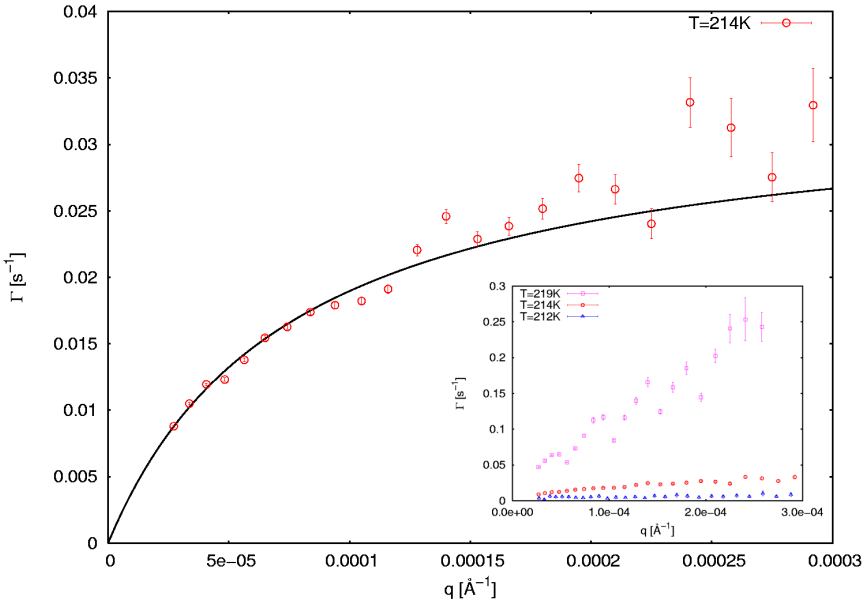

Figure 1. Damping constants extracted from the XPCS measurements at various temperatures. The deviation from a simple linear behavior $\Gamma \propto q$ is evident. The solid line is a fit with the model derived in Ref. [2].

References

[1] T. Seydel *et al.*, *Rev. Sci. Instr.* **74**, 4033 (2003)

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

[3] Y.-H. Lin, *Polymer Viscoelasticity*, World Scientific Publishing (Singapore, 2003)

[4] A. Papagiannopoulos *et al.*, *J. Phys Condens. Matter* **17**, L279 (2005)

[5] T.G. Mason and D.A. Weitz, *Phys. Rev. Lett.* **74**, 1250 (1995)