



	Experiment title: IXS investigation of dynamics in a photosensitive poly-azo-acrylate glass-former	Experiment number: HS-2672
Beamline: ID16	Date of experiment: from: 20/04/2005 to: 26/04/2005	Date of report: 15 July 2005
Shifts: 18	Local contact(s): Francesco Albergamo, Giulio Monaco	<i>Received at ESRF:</i>
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Report:

In the present experiment we have measured the Inelastic X-ray Scattering (IXS) from an azobenzene polyacrylate, with and without UV photoperturbation, in its glassy phase, i.e. below $T_g=20^\circ\text{C}$. The experiment was initially scheduled over the Easter period (23-30 March 2005), however the severe breakdown of the main storage ring interrupted the data acquisition just after beamline optimisation and sample alignment. The experiment was then successfully repeated on April 20-26, 2005.

In this non-standard experiment we needed to apply a strong UV photoperturbation to our sample. This imposed some constraints on the geometries: the sample was prepared as a parallelepiped with small thickness (size $20 \times 4 \times 0.2 \text{ mm}^3$) to achieve a reasonably uniform UV irradiation. Photoperturbation was applied by a high power 450 W Hg(Xe) lamp (Lot-Oriel #66142) filtered by a 320-380nm band-pass filter. We needed the new multilayer mirrors to focus the X-ray beam at the sample position with size $30 \times 100 \mu\text{m}^2$ (HxV). In doing so we were sure that the IXS signal was collected from the region of sample in which photoperturbation was uniformly applied. Sample temperature was routinely checked with and without UV radiation, in order to ensure that we were not observing obvious artifacts associated with temperature drifts. Si(11,11,11) reflection was used to monochromatize the incoming beam with energy $E=21.747 \text{ keV}$. Two different Q-sets were collected at each temperature spanning the range $2-15.5 \text{ nm}^{-1}$ in 1.5 nm^{-1} steps. Nominal Q-resolution was 0.45 nm^{-1} on each detector.

Resolution and background were measured on the same geometry of the experiment, with the sample kept at the base temperature of the CCR ($T=15\text{K}$). The resolution showed no appreciable difference from the standard resolution measured on a bulk PMMA sample. A typical spectrum measured at $T=273\text{K}$ in dark at $Q=5 \text{ nm}^{-1}$ is shown below, on the left. On the right we show the rough density of states $g(\omega)$ obtained from $S(Q, \omega)$ measured at $T=273\text{K}$ in dark, after background correction and applying the appropriate detailed energy balance factor.

By fitting the experimental $S(Q, \omega)$ with a sum of Damped Harmonic Oscillator (DHO) plus a flat background and a purely elastic term (elastic on the time scale determined by ID16 resolution) convoluted with the measured resolution, we could extract the sound velocity and we could measure the effects of photoperturbation on the v-DOS.

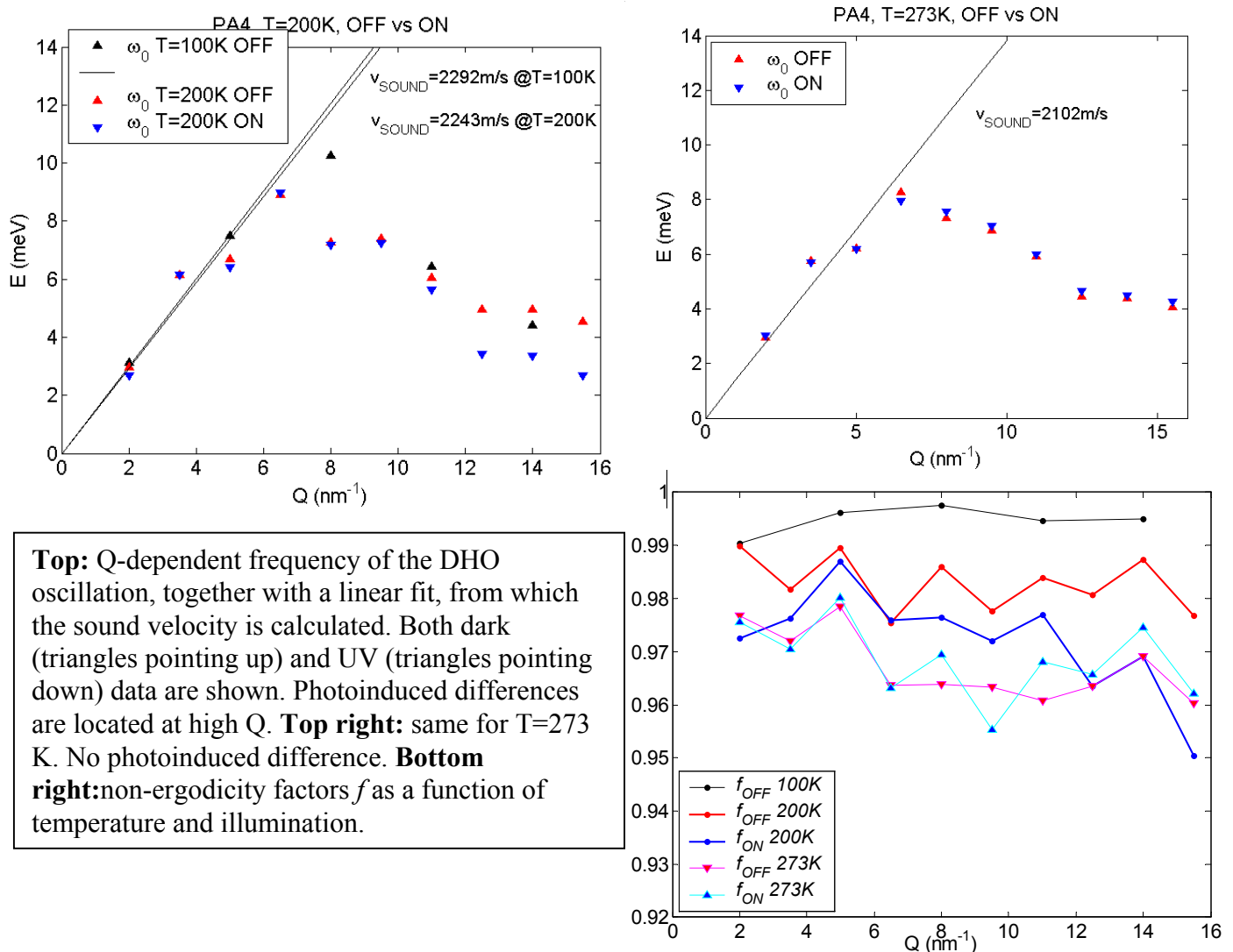
The sound velocity (2300 m/s at $T=100\text{K}$, 2200 m/s at $T=200 \text{ K}$, decreasing to 2100 m/s at $T=273 \text{ K}$), as in general all the low-Q features, resulted independent from UV photoperturbation at both the measured temperatures (200K and 273K), as it is apparent from the following figures. This is in agreement with the localized nature of the azobenzene moiety photo-isomerization, which does not affect, in first approximation, the large scale features of the system.

On the contrary, and in agreement with our previous findings by Inelastic Neutron Scattering [L. Cristofolini et al., Phys. Rev. E, 64 061803 (2001)], we have found a clear influence of UV photoperturbation on the high Q features of $S(Q,\omega)$ in the region of the first maximum in the static structure factor $S(Q)$, i.e. above $10\text{--}12\text{ nm}^{-1}$ which corresponds, in the direct space, to a typical intra-molecular distance for the two aromatic rings of the azobenzene moiety. In particular we have found a remarkable softening of the residual acoustic mode, and correspondingly an increase in the relative amplitude of the DHO signal with respect to the total scattering, which implies a photoinduced decrease of the system non-ergodicity, as shown in the 3rd following figure.

Our current findings seem to suggest that, at least in the low-T regime explored by the present experiment, azobenzene photoisomerization is a local process, which only induces changes in $(S(Q,\omega))$ located at large Q, however the effects of such localized process might extend to the macroscopic scale via a softening of a mode localized in Q-space at the first maximum in the static structure factor $S(Q)$. This can be put in relation with the observed macroscopic decrease of polymer viscosity. Moreover, our data are fully consistent with our previous Inelastic Neutron Scattering data, in which we found a photoinduced decrease of $g(\omega)$ in the region of the BP, which could be interpreted in the framework of a general softening of vibrational modes in the high-Q region, in a similar way to what we have presently found by IXS in which we observe that intensity is subtracted from the 5 meV region in favour of the 3 meV region.

The temperature dependence of the inelastic intensity seems not to follow the predictions of an harmonic oscillator. This points warrants further investigations, over a much more extended T range, which will be the subject of a separate proposal.

Full data analysis is in progress, also with a more detailed model including two modes: one pseudo longitudinal, propagating mode, plus a second non-propagating mode of transverse character. Given the relatively poor S/N ratio of our data this requires a global fit to the 10 different Q data-sets at the same time. A manuscript is in preparation.



Top: Q-dependent frequency of the DHO oscillation, together with a linear fit, from which the sound velocity is calculated. Both dark (triangles pointing up) and UV (triangles pointing down) data are shown. Photoinduced differences are located at high Q. **Top right:** same for T=273 K. No photoinduced difference. **Bottom right:** non-ergodicity factors f as a function of temperature and illumination.