ESRF	**Experiment title:** Vibrational dynamics and the boson peak in polymer melts and glasses under pressure	**Experiment number:** HS - 2683
Beamline: ID16	**Date of experiment:** from: 07.03.2005 to: 13.03.2006	**Date of report:** 27.02.2007
Shifts:	**Local contact(s):** Giulio MONACO	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
Kristine NISS and Christiane ALBA-SIMIONESCO and Cecile Dalle-Ferrier
Laboratoire Chimie Physique, UMR CNRS 8000, Bat 349 Universite de Paris-Sud, 91405 Orsay, Paris, France
Bernhard FRICK
Institut Laue Langevin, 6 rue Jules Horowitz, BP 156 - 38042 Grenoble, France
Giulio MONACO
ESRF

Report:
The aim ot the experiemnt was to study the pressure and temperature dependence of the dynamical coherent structure factor in the liquid and the glass of the molecular Van der Waals bonded system cumene.
Experiements were performed along two different isobars; atmospheric pressure and 3 kbar. In both cases cooling from the liquid into the glass. Experiments were all in all performed at 11 different experimental conditions. This allows us to map out the pressure, temperature and the IXS spectra of cumene. The general features of the spectra and the found dispersion does not change with pressure nor temperature. It has therefore been possible for us to investigate the behavior by focusing on a limited number of q-values. The temperatures chosen where such that we at both pressures have a spectra at $T_g(P)$ and at least two temperatures above and below the glass transition. The analyzers were set to give the Q values 2 nm^{-1}, 1 nm^{-1}, 4 nm^{-1} 7 nm $^{-1}$ and 10 nm^{-1}. The integration time per point was minimum 60 s per point and was increased by a factor 2 or 3 at lower temperatures where the inelastic intensity is lower.
The experiment was performed using the cryostat and the large volume diamond window cell of the beamline. The sample itself was used as pressurerizing medium. The pressure was alway imposed at room temperature, that is above the glass transition temperature, and cooling was done isobarically by adjusting the imposed pressure upon cooling. An S(Q) was taken at all the experimental conditions where IXS spectra where taken.

Figure 1 shows the dispersion of cumene at T=160 K at ambient pressure (red) and at 300 MPa (blue). The dashed lines are guides to the eye. The sample is in the liquid phase at both pressures at this temperature. The points at values 2 nm^{-1} and 4 nm^{-1} fall on a straight line indicating that the dispersion is linear in this region. The corresponding sound speed is 2200 m/s at atmospheric pressure and 2900 m/s at 300 MPa. Thus the sound speed increases with ∼30 % with the increase of pressure. The sound speed increases with cooling at atmospheric pressure and is about 2700 m/s at 50 K. At 300 MPa on the other hand the sound speed appears essentially temperature independent. This also means that the pressure dependence of the sound speed at 50 K is small changing only from 2700 m/s to 2900 m/s (7%). This is seen in figure 2 which shows the sound speeds at different T and P calculated 2 nm^{-1} and 4 nm^{-1} respectively. Unlike the sound speed the sound attenuation factor, Γ does not show any dependence of pressure nor temperature. This is illustrated in figure 3 which shows Γ/Q^2 at different conditions.

Figure 4 shows the temperature dependence of the non-ergodicity factor measured at 2 nm^{-1} at atmospheric pressure and 300 MPa. It is seen that non-ergodicity factor increases with pressure above T_g while it is pressure independent within the errorbars in the glassy phase. The pressure independence of the non-ergodicity factor corresponds to an increase with pressure of the parameter α defined by T.Scopigno *et al.* (Science **302**, 849 (2003)]. Figure 5 shows the inverse non-ergodicity factor as a function of temperature normalized to T_g. The parameter α is given by the slope of this type of plot in the T=0 limit. The increase of α with pressure is in contradiction with the expectation based on the result of T.Scopigno *et al.*

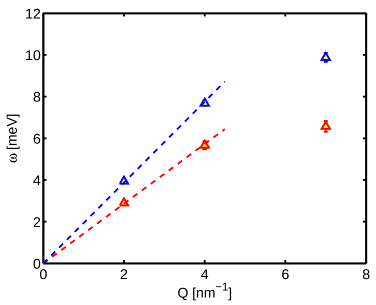

figure 1

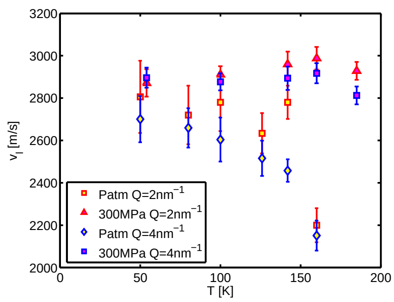

figure 2

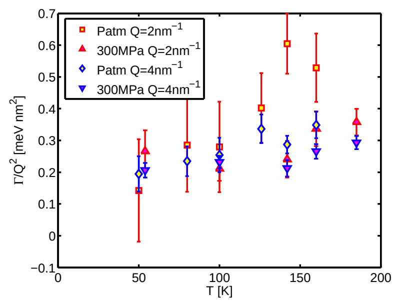

figure 3

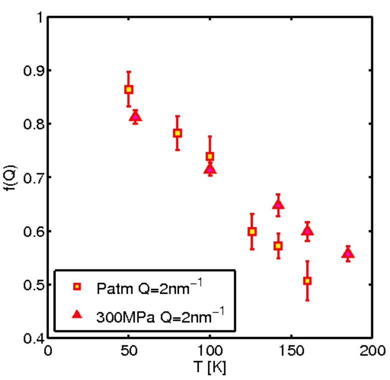

figure 4

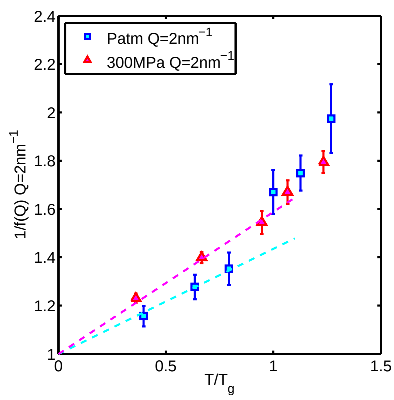

figure 5