



Vibrational dynamics and the boson peak in polymer melts and glasses under pressure

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Report:

The aim of the experiment was to study the pressure and molecular weight dependence of the dynamical coherent structure factor in the melt and the glass of the polymer isobutylene.

Experiments at room pressure were performed on four different samples with their molecular weights ranging from 680 to 500k. The samples of molecular weight 3580 and 500k were chosen for the studies under pressure, as these are the samples where we have the best INS and calorimetric data to compare with. In the case of these two samples we performed experiments at ambient pressure and at 3kbar. Experiments were all in all performed at 22 different experimental conditions. This allows us to completely map out the pressure, temperature and molecular weight dependence of the IXS spectra in PIB. The general features of the spectra and the found dispersion does not change with pressure nor molecular weight. It has therefore been possible for us to investigate the behavior by focusing on a limited number of q-values. We have in all cases studied $q=2\text{nm}^{-1}$ and $q=5^{-1}$, at central positions eg. at the Mw and pressure dependent T_g we also included the $q=3\text{nm}^{-1}$ and $q=6\text{nm}^{-1}$. The full dispersion was measured at room temperature in an earlier experiment.

The experiment was performed using the cryostat and the large volume diamond window cell of the beamline. Ethanol was used as pressurizing medium. The pressure was always 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 were taken.

Figure 1 shows the pressure dependence of the dispersion for the Mw 5580 sample in the glass ($T=140\text{K}$). The speed of sound increases with pressure and the bend over of the dispersion tends to move to higher q (consistent with the fact that structure factor peak moves to higher q upon compression.). Though the effect of pressure is seen clearly, it is still much weaker than shift of the boson peak which is observed when applying pressure [1]. Hence the correlation between IXS modes and boson peak which is suggested from temperature dependence in ref. [2] does not hold in this case. The temperature dependence of the speed of sound determined by the IXS measurements for PIB at different molecular weights is shown in figure 2. The general trend is that the speed of sound is larger in the high molecular weight samples, which also have larger density. It is moreover seen that the molecular weight has stronger influence on the speed of sound in the melt than in the glass. Figure 2 also includes the temperature dependence of a the speed of sound found from Brillouin scattering with visible light in a high molecular weight sample. It is seen that we find similar results but that the apparent speed of sound found by IXS at high frequencies is lower than the speed of sound found by light scattering.

Figure 3 shows the temperature dependence of the inverse non-ergodicity factor in the glass for different molecular weights. The slope gets significantly larger as molecular weight is increased. This is surprising because fragility decreases as molecular weight is increased [3]. The result is hence in contrast to relation which has been proposed between fragility and the non-ergodicity factor [4].

[1] B.Frick *et.al* Chem. Phys **292**, 311 (2003), K.Niss *et al.* in preperation (2005)[2] C.Masciovecchio *et al.* Philos Mag B **79**, 2013 (1999) [3] Y.Ding *et al.*, Macromolecules **37** 9264 (2004), [4] T.Scopigno *et al.*, Science **302**, 849 (2003),

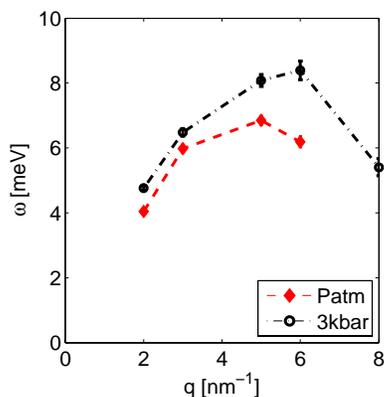


figure 1

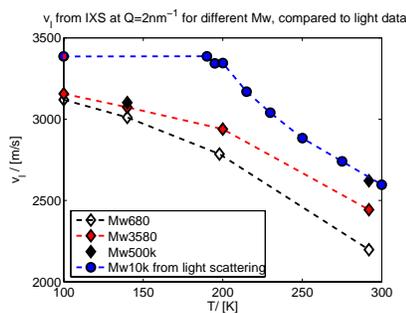


figure 2

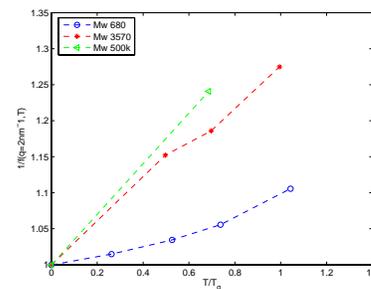


figure 3