



Fast dynamics and the Boson peak in polymers under high pressure

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Report:

The purpose of the experiment was to study collective dynamics of the polymer Poly-iso-butylene by using pressure and molecular weight as control parameters. The sample was three different molecular weights of the polymer poly-iso-butylene (PIB). A very low molecular sample $M_w = 680$ (PIB680) which is in fact more like an oligomer than an actual polymer. A standard polymeric sample $M_w = 500.000$ (PIB500k) which is well above the entanglement size, and in general a weight where other chain length dependencies are saturated. Finally we included a measurement on an intermediate molecular weight $M_w = 4000$ (PIB4000), which is a molecular weight around which most molecular weight dependencies saturate. The lowest and the highest molecular weight were studied at ambient pressure and at 3kbar. The diamond windows were broken in an attempt to reach 4kbar, and the measurement on an intermediate molecular weight at ambient pressure was included as it was not possible to have the pressure cell fixed within due time. All experiments were performed at room temperature (295 ± 1 K). Hence we took five sets of spectra, PIB500k Patm, PIB500k 3kbar, PIB4000 Patm, PIB680 Patm and PIB680 3kbar.

The PIB680 and PIB4000 samples are not available in large amounts, and we have therefore constructed a small teflon cell that fits inside the pressure cell to reduce the sample volume. The teflon cell has an opening covered by a very thin teflon film at the position of the diamond window. The pressure was imposed by using ethanol as medium after checking that PIB did not dissolve in the ethanol. An empty cell measurement was taken with diamond windows, the teflon cell and ethanol (corresponding to the ethanol used to impose the pressure). Finally an "inverse" background was made for PIB500K,

that is a measurement with sample but without fluor diamant. The inelastic spectra were for all five setups and for the background measurements taken at 4 settings with Q values up to 25nm^{-1} . An $S(Q)$ was taken for each sample at the same conditions as the inelastic spectra (see figure 1). The $S(Q)$ is important in interpreting the the inelastic data, moreover the $S(Q)$ spectra were used to monitor the samples reaction to the imposed pressure. An $S(Q)$ was taken both before and after the measurements at 3kbar. There was no visible change in the $S(Q)$ spectra which demonstrates that the polymer has not relaxed on the segmental scale due to the pressure during the measurement. Additionally an $S(Q)$ was taken at Patm before imposing and after releasing the pressure. We found no visible change in the structure factor which shows that the effects of the pressure were reversible with regard to the length scales we study.

It is generally found that the segmental dynamics of polymers correspond to the dynamics of molecular glass forming liquids and it is this aspect of the polymer dynamics which interests us. In the structure factor the characteristic segmental distance is that which corresponds to the first structure factor peak. From DHO-fits (performed with the ID28 software, with a lorentzian for the central peak and a convolution with the resolution function) we find a dispersion which when compared to the structure factor corresponds to that found for a liquid (see figure 2). This indicates that the modes studied by IXS are in fact related to the segmental dynamics, and hence related to the same scale as that which is interesting in the study of the glass transition.

A speed of sound is determined from the low Q linear part of the dispersion relation (see figure 3). The density increases with increasing molecular weight as well with increasing pressure. In both cases this is followed by an increase in the speed of sound. It is found that the intensity of the Brillouin line increases along with the increase in speed of sound.

The study is preliminary as no cryostat was granted, and low temperature measurements (as we asked for in the original proposal) would be of great interest in order to test the proposed relations between the acoustic modes the boson peak and the glass transition by using molecular weight and pressure as controlling parameters. However this study is important for the future work as it demonstrates that significant changes can be seen within the pressure range accessible, and that the molecular weight dependence is seen in the same range as for other properties.

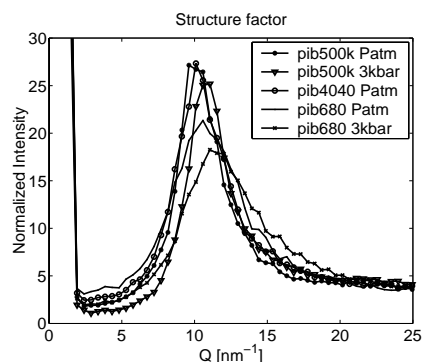


figure 1

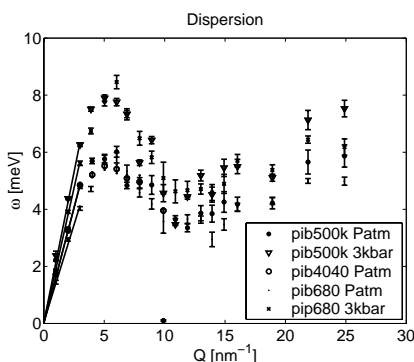


figure 2

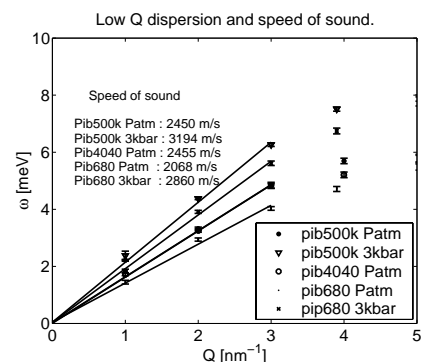


figure 3