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Report:

Measurements of the dynamic structure factor $S(Q,\omega)$ of a polymeric glass, poly(methy methacrylate) (PMMA) were done as a function of hydrostatic pressure up to 4.5 kbars. These works aimed at enlightening the origin of the so-called glass "universal" features like the "excess" of vibrational density of states or the boson peak and see whether the concept of a non-homogeneous polymeric glass structure were of relevance in this highly debated field of research.

The energy resolution used for this experiment was 1.5 meV and the newly installed ID16 five analyzer setup allowed us to investigate a Q-range lying between approximately 1 and 14 nm^{-1}. Pressure was applied using a piston-and-cylinder device, with ethanol as the pressure transmitting medium.

Similarly to previously investigated glasses, we found an inelastic signal that disperses up to to 2-2.5 nm^{-1}, in an energy range that is compatible with the above cited "universal" features. A first set of measurements aimed at measuring the Q-dispersion of the observed inelastic signal at ambient pressure as well as at 4.5 kbars. Best fits of the measured dispersion curves were found to be linear, yielding a sound velocity of about 2500 m/s at ambient pressure and 3300 m/s at 4.5 kbars, in reasonable agreement with Brillouin visible light results, at least within the error bars. The energy width of the excitation appeared to increase with Q but no specific Q-dependence could be reliably determined because of its too narrow range of observation (beyond 2-2.5 nm^{-1} no inelastic signal can be trustfully detected).

In a second round of experiment, we focused our attention on the pressure dependence of the observed exitation, by measuring the scattering spectra at the fixed Q-value of 2 nm^{-1} at six different pressures: 0, 800, 1200, 2000, 3000 and 4020 bars. Two illustrative examples of the obtained spectra are displayed in Figure 1. The derived pressure dependence of the excitation energy, as deduced from Lorentzian fits of the data, is displayed in Figure 2. This plot unveils the existence of a crossover pressure $P_0 \simeq 1600 \pm 150$ bars, that separates two different regimes with two different slopes. As shown in Figure 3, the occurence of a singularity at P_0 is also seen in the pressure dependence of the elastic peak intensity at that particlular Q-value of 2 nm^{-1}.
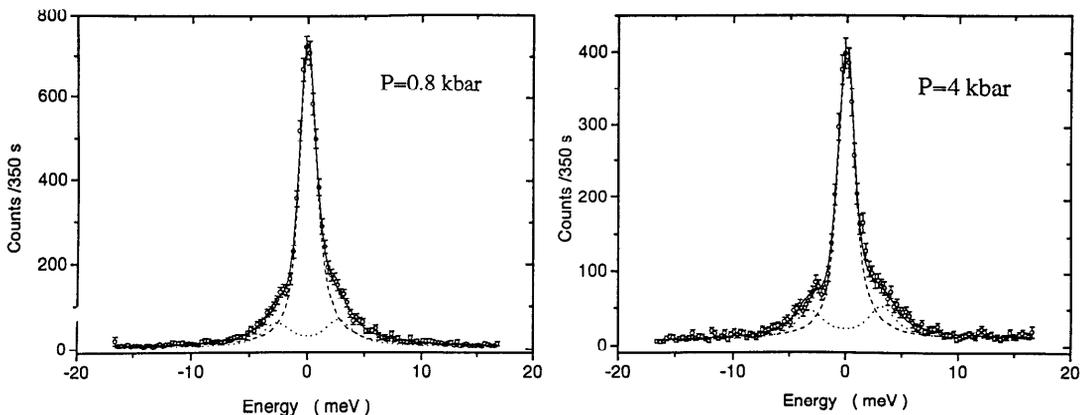
Figure 1: IXS spectra of PMMA at 800 and 4020 bars. Solid, dashed and dotted lines are respectively total, Lorentzian elastic and Lorentzian inelastic fits.

The elastic peak intensities recorded with the other four analyzers, placed at $Q \geq 5$ nm^{-1}, did not show such typical behavior; instead they exhibited a monotonic decrease upon pressure increase.

The non-continuous variations observed in the pressure dependences of both the excitation energy and the elastic peak intensity at $Q = 2$ nm^{-1} straightforwardly suggest that the amorphous polymeric structure is not continuous at the nanometer scale (unlike the short range order). As revealed by the application of a hydrostatic pressure, a disruption in the static disordered network at about $2\pi/2 \sim 3$ nm is seen to strongly inlfuence the observed dynamics. These results give strong support to models in which the dynamics of the glassy nanostructure integrate size effects, as the one proposed by some of us (Duval et al, J. Phys. : Condens Matter 2, 10227 (1993); Mermet *et* al, Europhys. Lett. 36, 277 (1996)) which actually motivated the hereby reported experiment. Observations of remarkably close crossover pressures in other dynamical properties of amorphous polymers (Weishaupt *et al*, Polymer 36, 3267 (1995); Hayden *et* al, Macromolecules 30, 2734 (1997)) openly call for the identification of this "in-glass" transition in a more generalized way.
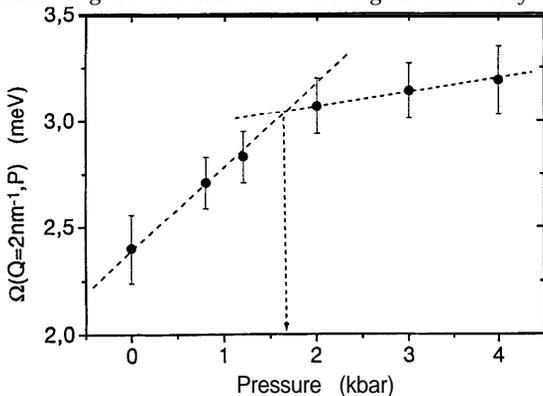

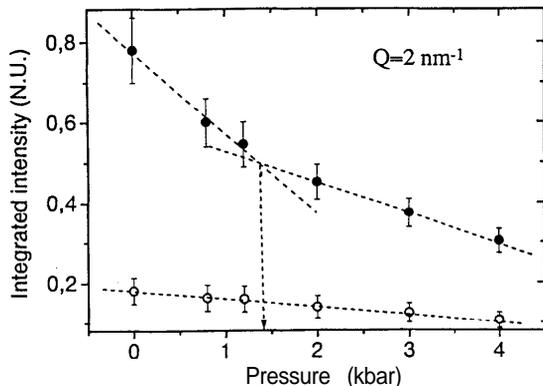Figure 2: Pressure dependence of the excitation energy at $Q = 2$ nm^{-1}.

Figure 3: Pressure dependences of the integrated elastic (solid symbols) and inelastic (open symbols) contributions at $Q = 2$ nm^{-1}.