ESRF	**Experiment title: Inelastic X-ray scattering study of physical aging in a polymer glass**	**Experiment number**: HS 2594
Beamline: ID28	**Date of experiment**: from: Sept. 22, 2004 to: Sept. 29, 2004	**Date of report**:
Shifts: 18	**Local contact(s)**: Alexandre Beraud	*Received at ESRF:*

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Report:

The purpose of the experiment was to investigate the change of the mesoscopic collective dynamics induced by physical aging in the well known polymer glass polymethylmethacrylate (PMMA). In this polymer, low frequency Raman scattering measurements, together with inelastic neutron scattering measurements [1], indicated a reduction of the boson peak intensity with aging. Such observation reflects, to our view, an evolution towards a more homogeneous nanostructure of the amorphous polymer, similarly to the effect induced by hydrostatic pressure [2]. Since IXS allows to probe the collective dynamics inherent to the nanometric scale, changes in the IXS spectra were expected to be observed upon aging, in particular with respect to the excitations "propagating" characteristics.

Three PMMA (additive free, Tg=118C) samples were investigated. All three samples were initially brought at Tg+20 K then quenched downto room temperature. Subsequently, one sample was annealed at Tg-40 K for 1 month and another sample was aged at room temperature for several months. A third sample was re-quenched 15H before the IXS experiment. Prior to the IXS experiment, low frequency Raman spectra of the (1) quenched (2) aged at Tg-40 K and (3) aged at room temperature samples were recorded to ensure the observation of the aging effect on the boson peak (Figure 1).

IXS scans of the three samples were recorded at room temperature, using the Si (11 11 11) operating conditions of the instrument. Inelastic scans were recorded in the Q range 1.5 – 4.5 nm^{-1} with one same analyzer (#2). The dispersion curves $\Omega(Q)$ obtained from Damped Harmonic Oscillator (DHO) fits of the inelastic lineshapes for the three samples are reported in Figure 2; the corresponding $\Gamma(Q)$ curves (Γ being the HWHM of the inelastic excitations) are displayed in Figure 3. The observed variations of $\Omega(Q)$ and $\Gamma(Q)$ are typical of glassy systems, showing a linear relationship between Ω and Q over 1.5-4.5 nm^{-1} for PMMA, while Γ increases rapidly with Q. For Q values larger than 4.5 nm^{-1}, the excitations become extremely overdamped.

The speed of sound deduced from the linear interpolation of Ω(Q) yields a sound velocity of 2600 m/s, a value consistent (though somewhat slightly smaller) than its "macroscopic" counterpart deduced from Brillouin light scattering. Obviously, from Figure 2, no change of the excitations energies with aging could be detected within the error bars of the measurements. This confirms with the Raman measurements showing no seizable energy shift of the vibrational spectrum after aging, in particular in the region of the boson peak. Interestingly, Figure 3 shows that some systematic differences appear between the quenched sample and the aged ones : in the case of the aged samples, the DHO fits yield lower Γ values, with respect to those of the quenched sample. The reduced broadenings of the inelastic excitations in the aged samples reflect a lesser attenuation of the probed acoustic soundwaves. This observation may well be interpreted as a smoothening of the elastic topology at the nanometric scale, in agreement with our initial predictions : upon aging, the glass nanostructure evolves towards a more homogeneous state,where the elastic contrast between more cohesive domains and the surrounding less cohesive zones is lower than in the quenched state. The outcomes of the IXS experiment provide further valuable characterization of physical aging in polymer glasses.

Figure 1

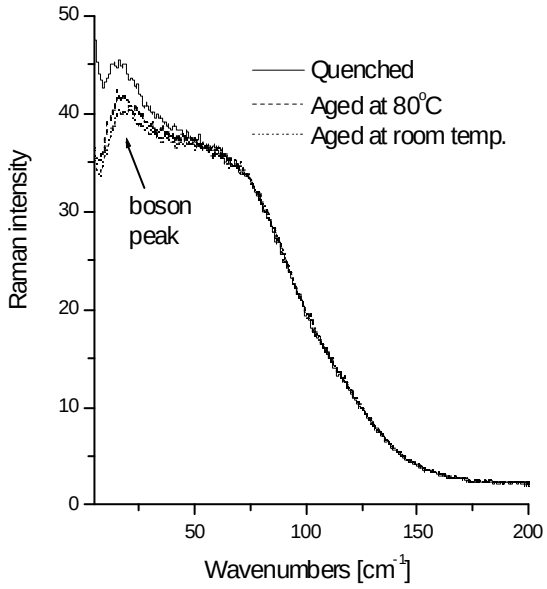


Figure 2

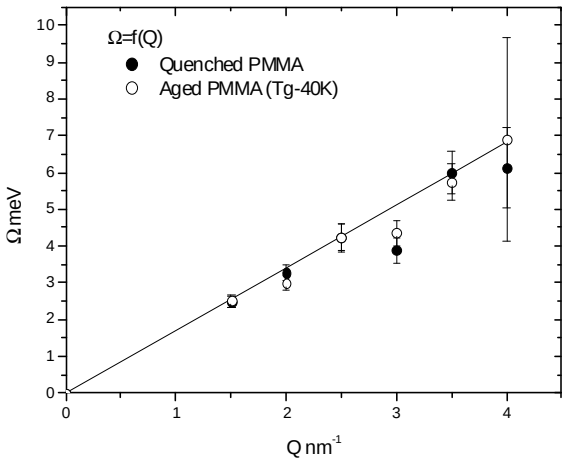
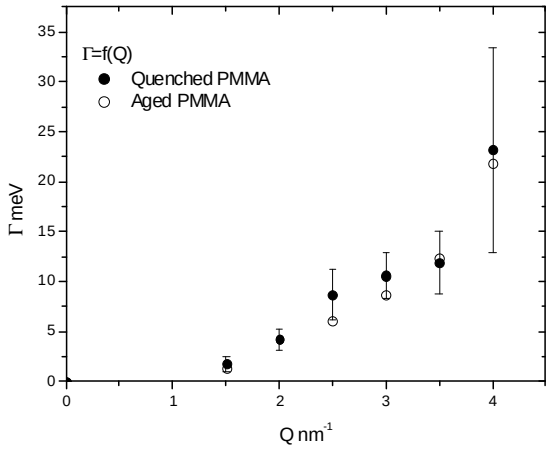


Figure 3



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[2] A. Mermet, A. Cunsolo, E. Duval, M. Krisch, C. Masciovecchio, S. Perghem, G. Ruocco, F. Sette, R. Verbeni and G. Viliani, Phys. Rev. Lett. 80 4205 (1998)