Pressure-Induced In-Glass Structural Transformation in the Amorphous Polymer Poly(methylmethacrylate)

A. Mermet,¹ A. Cunsolo,¹ E. Duval,² M. Krisch,¹ C. Masciovecchio,¹ S. Perghem,³ G. Ruocco,⁴ F. Sette,¹

R. Verbeni,¹ and G. Viliani³

¹European Synchrotron Radiation Facility, B.P. 220 F-38043 Grenoble, France

²L.P.C.M.L., Université Lyon I, UMR-CNRS 5620, 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne, France

³Universitá di Trento and Istituto Nazionale di Fisica della Materia, I-38050, Povo, Trento, Italy

⁴Universitá di L'Aquila and Istituto Nazionale di Fisica della Materia, I-67100, L'Aquila, Italy

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Inelastic x-ray scattering data have been collected in the polymeric glass poly(methylmethacrylate) in the P = 0-4.5 kbar and Q = 1-15 nm⁻¹ pressure and momentum transfer regions. At $P = P_0 \approx 1.6$ kbar, the elastic intensity at Q values smaller than ≈ 5 nm⁻¹ and the sound excitation energy at Q = 2 nm⁻¹ show a cusp behavior in their pressure dependences. These findings could indicate a pressure-induced structural transition in this polymeric glass, which does not affect, however, interparticle static correlations with length scales shorter than $L_0 \approx 1$ nm. [S0031-9007(98)06057-8]

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The dynamics of disordered solids shows very specific behaviors such as two-level systems, thermal conductivity plateau, and *excess* of vibrational density of states [1], which strikingly contrast with the absence of any obvious feature in their static characteristics at the nanometer scale. Incidentally, the question of whether these dynamical anomalies are rooted into some specificity of the static structural disorder is highly debated and a unifying picture relating the glassy structure to the collective dynamics still awaits to be settled. Theoretical arguments, molecular dynamics simulations in both the supercooled and glassy states [2-4], and even diffraction measurements [5,6] suggest that the *medium range order* of disordered systems is characterized by a correlation length of a few nanometers. The physical significance of such a length scale, and, more important, its relevance to collective excitations and their propagating nature is still unclear.

Recently, dynamic structure factor, S(Q, E), measurements, at energies E and momentum transfers Q relevant to density fluctuations approaching the interparticle distances, have been performed on strong, intermediate, and fragile glasses [7-11] using the inelastic x-ray scattering (IXS) method. Most of them point out the existence of acousticlike excitations [7,8,10,11]; the energy of these modes, $\Omega(Q)$, has been found to disperse linearly with Q, while their energy broadening, $\Gamma(Q)$, increases proportionally to Q^2 . Therefore, a value of Q, Q_m exists at which $\Gamma(Q) \approx \Omega(Q)$, and where it is no longer possible to describe the inelastic part of S(Q, E)in terms of propagating excitations. In these systems, a relation between Q_m and the microscopic structure has not yet been established. It is possible, therefore, that Q_m is a physical quantity connecting the high frequency dynamics to the mesoscopic structural properties. Obviously, further studies aiming to better identify these issues are highly needed. Among others, a possible direction

of investigation is the study of the pressure dependence of the high frequency glass dynamics at pressures that may start to modify the glass bonding network. The effect of hydrostatic pressure on the nanoscopic glassy structure and its inherent dynamics has already been investigated in various materials with different techniques. Low temperature measurements on a semicrystalline polymer [12] showed a considerable decrease of the excess specific heat on increasing pressure, thus suggesting a strong perturbation of the acoustic phonon pattern with pressure. Brillouin visible light experiments on amorphous poly(methylmethacrylate), PMMA, evidenced around 1.1 kbar an abrupt change in the shear elastic constant and in the intensity of the transverse phonon lines, thus indicating a *weak* glass transition within the glass [13]. Recently, nonlinear optical measurements on several amorphous polymers confirmed the existence of a marked change in the local structure at pressures in the 1.1-1.5 kbar range [14].

In this Letter we report new evidence on the possible existence of an in-glass transition in PMMA: we show IXS data pointing towards a structural transformation that takes place over a length scale which is larger than the typical interparticle distances, and which reflects onto the longitudinal collective dynamics. The dynamic structure factor S(Q, E) of this polymeric glass shows an inelastic feature that disperses with Q. By increasing the hydrostatic pressure up to 4.5 kbar the energy position of this excitation linearly increases, with a change of slope around $P_0 \simeq 1.6$ kbar. Concurrently, around P_0 , the pressure dependence of the elastic signal at $Q = 2 \text{ nm}^{-1}$ shows a comparatively stronger cusp, a behavior which is not observed in the higher O region. In spite of the absence of any characteristic feature in the static structure factor S(Q), these results unveil the occurrence of a pronounced structural rearrangement within the amorphous state at P_0 , affecting most dramatically the interparticle correlations at a length scale larger than ≈ 1 nm.

The experiment was carried out at the new very high energy resolution inelastic x-ray scattering beam line (BL21-ID16) at the European Synchrotron Radiation Facility [15-17]. The instrument was used at the Si(11 11 11) reflection in backscattering geometry. At the incident energy of $\simeq 21748$ eV, the total instrumental resolution function, measured from the elastic scattering of PMMA at the maximum of its static structure factor $(Q = 10 \text{ nm}^{-1})$, was $1.5 \pm 0.1 \text{ meV}$ full width at half maximum (FWHM). A five analyzer setup allows the simultaneous recording of scattering spectra at five different Q values spaced by $\approx 3 \text{ nm}^{-1}$, each with a Q resolution of 0.4 nm⁻¹ FWHM. Energy scans, performed by varying the monochromator temperature with respect to that of the analyzer crystals, took about 150 min, and each Q point was obtained by typically averaging five scans. The data were normalized to the intensity of the incident beam. The PMMA, manufactured by Norsolor Company (France), has a number average molecular weight of 58000 g mol⁻¹, and a glass transition temperature $T_g \approx 390$ K, as determined by differential scanning calorimetry. A 9 mm long, 8 mm diameter cylindrical sample was placed into a cylindrical stainless steel high pressure cell, sealed at both ends by 1 mm thick diamond windows with a 2.2 mm diameter aperture. The crystalline windows allowed the passage of incident and scattered beams with negligible scattering. Pressure was applied using a piston-and-cylinder device equipped with a pressure gauge of ± 20 bar precision (Nova-Swiss). Ethanol was used as the pressure transmitting medium, and its amount in the x-ray beam was less than 1 mm. Its contribution to the total scattering was estimated to be less than 10%, and it was neglected in the data analysis. All pressure points investigated in this study were reached on pressure increase to avoid possible hysteresis effects, and all measurements were made at room temperature, i.e., well below T_g . The reported transformations were observed to be reversible by reproducing the ambient pressure S(Q) data at the end of the experimental runs.

The IXS spectra of PMMA were measured as a function of Q and pressure P. The Q dependence was investigated at the fixed pressure of 0 and 4.5 kbar [Fig. 1(a)] and the pressure dependence was measured at the Q values of 1, 2, 5, 8, and 11 nm⁻¹. The results at $Q = 2 \text{ nm}^{-1}$ are reported in Fig. 1(b). In Fig. 1(a) we observe an inelastic signal with an average energy position that increases with Q. The lines represent the results of a fitting procedure used to determine the energy position, $\Omega(Q)$, and the width, $\Gamma(Q)$, of these excitations. We modeled the line shape with the function F(Q, E) consisting of three Lorentzians, respectively, one for the central peak and the others for the two side peaks:



FIG. 1. IXS spectra of PMMA at P = 4.5 kbar as a function of Q (a), and at $Q = 2 \text{ nm}^{-1}$ as a function of P (b). The data (\bigcirc) are shown together with the Lorentzian fits discussed in the text. The total fit result (solid lines), and the elastic (dashed lines) and inelastic (dotted lines) contributions are individually shown. The data have been normalized to the elastic peak intensity. Here, the typical total intensity was 300–500 counts. The inset shows the Q dependence of the Ω and Γ parameters obtained from the fit. The line is a linear fit to the $\Omega(q)$ values, and the corresponding velocity of sound is indicated.

$$F(Q, E) = I_{c}(Q) \frac{\Gamma_{c}(Q)^{2}}{E^{2} + \Gamma_{c}(Q)^{2}} \times [n(E) + 1]I(Q) \frac{\Gamma(Q)^{2}}{[\Omega(Q) - E]^{2} + \Gamma(Q)^{2}}.$$
(1)

Here, $I_c(Q)$ and I(Q) are the intensities of the elastic and inelastic contributions, respectively, $\Gamma_c(Q)$ is the energy width of the central line, and n(E) is the Bose factor. The choice of three Lorentzians was made to extract the spectroscopic parameters independently from a specific theory. The alternative use of a damped harmonic oscillator function to model the inelastic signal yields equally good fits to our data, and parameters with quantitatively similar Q and P dependences. The model function was fitted to the data by a standard χ^2 minimization routine after convolution with the experimentally determined resolution function. At both 0 and 4.5 kbar we find a linear dispersion relation between $\Omega(Q)$ and Q. The values $\Omega(Q)$ and $\Gamma(Q)$ are reported in the inset of Fig. 1 for P = 4.5 kbar. The corresponding sound velocity is 2950 ± 100 m/s, a value 20% smaller than that determined from the pressure dependence of the bulk modulus [13]. This difference in the sound velocities indicates the presence of structural effects inducing a bending of the dispersion relation, which underestimates the slope of the linear function obtained from the data points in the 1–2.5 nm⁻¹ Q region.

The data reported in Fig. 1(b), taken at constant Q_{1} , show a visible pressure dependence: with increasing pressure, there is an increase of both excitation energy and intensity ratio between the inelastic and elastic signals. The pressure dependences of $\Omega(Q = 2 \text{ nm}^{-1}, P)$ and $\Gamma(Q =$ 2 nm^{-1} , P), as derived from the Lorentzian fits shown in Fig. 1(b), are displayed in Fig. 2(a). Whereas the width of the excitation appears to remain approximately constant, the energy position $\Omega(Q = 2 \text{ nm}^{-1}, P)$ increases with pressure, thus revealing a stiffening of the detected vibration with increasing pressure. The rate of change is not constant, and a slope variation is most evident in the 1-2 kbar region. By interpolating the low and high pressure values of $\Omega(Q = 2 \text{ nm}^1, P)$ with linear functions, we find a crossover pressure P_0 of 1.6 \pm 0.2 kbar. The behavior of $\Omega(Q = 2 \text{ nm}^{-1}, P)$ cannot be explained by the pressure dependence of the density, ρ , and of the bulk modulus, c_{11} , as derived from Brillouin light scattering (BLS) data [13]. This is emphasized in Fig. 2(a) by the comparison of $\Omega(Q = 2 \text{ nm}^{-1}, P)$ with the solid line, which has been obtained scaling the low-Q sound velocity, $v_l(P) = \sqrt{c_{11}/\rho}$ to the ambient pressure value of Ω , $\Omega(2 \text{ nm}^{-1}, P = 0 \text{ kbar}) = 2.5 \text{ meV}$. This comparison shows that the ratio between the two curves is not constant, with a higher rate of variation for the high frequency excitation.

To get further insight into this change of the dynamics around P_0 , we studied the pressure dependence of the absolute scattered intensities at $Q = 2 \text{ nm}^{-1}$. Figure 2(b) displays the integrated intensities of the elastic and inelastic fits reported in Fig. 1(b) as a function of pressure (integrations were made from -17 to 17 meV). This plot shows a marked decrease of the elastic intensity, and a break at pressure values similar to P_0 , as inferred from $\Omega(Q = 2 \text{ nm}^{-1}, P)$. Such a break is not detectable in the inelastic signal, which is found to decrease with pressure at a comparatively smaller rate.

The peculiar pressure dependence of the elastic peak intensity at $Q = 2 \text{ nm}^{-1}$ has been further investigated by the determination of the static structure factor as a function of pressure in the 0.5–20 nm⁻¹ Q region, i.e., from the mesoscopic region up to, and above, the first maximum. The results, reported in Fig. 3(a), were obtained normalizing the measured intensity to that of the incident beam. One can see that there is no pressure-



FIG. 2. (a) Pressure dependences of the excitation energy $\Omega(Q = 2 \text{ nm}^{-1}, P)$ (solid circles) and of the excitation FWHM $2\Gamma(Q = 2 \text{ nm}^{-1}, P)$ (open circles). The error bars correspond to $\pm 1\sigma$ statistical error. The dashed lines on Ω are linear extrapolations of its low and high pressure values. The dashed line on Γ is a guide to the eye. The solid line has been obtained by scaling the zero frequency sound velocity, as obtained from BLS data [13], to the excitation energy at P = 0: $\Omega = 2.5 \text{ meV}$. (b) Pressure dependences of the elastic, $I_c(Q = 2 \text{ nm}^{-1}, P)$ (closed circles) and inelastic $I(Q = 2 \text{ nm}^{-1}, P)$ (open circles) integrated normalized intensities, as obtained from the Lorentzian fits shown in Fig. 1(b). The dashed lines on I_c were obtained as in (a).

induced characteristic feature in the considered Q region. At high Q values one sees a smooth intensity variation with increasing pressure, due to the pressure-induced shift in the maximum of the S(Q). On the contrary, in the 2 nm⁻¹ Q range, there is a steep intensity decrease between the 0 and 1 kbar spectra, followed by a much less pronounced variation in the 1-4 kbar range. This pressure behavior is qualitatively identical to that of the $Q = 2 \text{ nm}^{-1}$ elastic intensity in Fig. 2(b). In order to determine this anomalous behavior around P_0 , we performed a set of quasielastic scan measurements (from -5 to 5 meV) as a function of pressure. Their integrated intensities, together with those obtained from the Q = 2 nm^{-1} data, are reported in Fig. 3(b). Both sets of data were normalized to unity at ambient pressure. We observe again a crossover at the pressure P_0 : this is best visible in the $Q = 2 \text{ nm}^{-1}$ data, it can still be observed up to $Q = 5 \text{ nm}^{-1}$ (not shown for clarity), and it is no longer detectable at Q values larger than $Q = 8 \text{ nm}^{-1}$.

The pronounced break in the pressure dependence of the elastic intensity at low Q indicates that, at P_0 , there is a modification in PMMA that affects the structure most severely in the length scale range associated with momentum



FIG. 3. (a) Static structure factor, S(Q), measured at the indicated pressures in arbitrary normalized units. The shift of the peak at $\approx 10 \text{ nm}^{-1}$ reflects the pressure-induced density change. The inset emphasizes the absence of any characteristic feature in the $1-4 \text{ nm}^{-1} Q$ region. These latter data were taken with a Q resolution of 0.2 nm⁻¹ FWHM, and the rise at low Q is due to the tails of the incident beam. (b) Pressure dependences of the integrated intensities at the selected Q values indicated in the figure. Open symbols refer to integrations from -17 to 17 meV and full symbols refer to integrations from -5 to 5 meV. The dashed lines were obtained as in Fig. 2(a).

transfer values $Q \approx Q_0 = 2 \text{ nm}^{-1}$, i.e., with length scales $L \approx L_0 = 2\pi/Q_0 \approx 3 \text{ nm}$. Interestingly, this effect is observed in a quite wide Q region $(1-5 \text{ nm}^{-1})$ of the S(Q) without the appearance of any specific feature. It is possible that something could appear at Q values lower than 1 nm^{-1} , not accessible in the present experiment. The impact of this structural modification is also found in the pressure dependence of the excitation at $Q = 2 \text{ nm}^{-1}$.

The finding of a crossover at P_0 in the structural properties can be interpreted as evidence of a *glass-to-glass* structural transformation. This phenomenon has been recently suggested by Poole *et al.* as a possible feature existing in both liquid and glass materials [18]. The observation reported here in a polymeric glass such as PMMA indicates that the existence of distinct amorphous phases, differing from each other by their structures at mesoscopic length scales, could be a more general feature of glassy materials. One may speculate that the observed structural transformation is due to a change in the packing scheme of unmodified structural entities, which are characterized by a size comparable to L_0 . This transformation may couple to the dynamics considering that pressure-induced modifications of a nonhomogeneous glassy nanostructure will have the strongest effect on collective excitations at the length scale of the inhomogeneities. This could be in agreement with models relating size effects to the picosecond dynamics [19,20].

In conclusion, the cusps observed in some of the parameters describing the S(Q, E) spectra of amorphous PMMA at pressures around $P_0 = 1.6$ kbar, could be interpreted as evidence of an *in-glass* structural transition. The analysis reported here indicates that this transformation affects the high frequency collective dynamics, and the structure only down to a length scale of ≈ 3 nm, i.e., a length scale sensibly larger than the size of the monomers constituting this polymer. The investigation of these pressure effects as a function of temperature in the region around T_g , where the disordered system becomes ergodic, may give further information on the relation between dynamics and structural inhomogeneities at the nanometer scale.

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