ESRF	**Experiment title:** Fluctuations of density in polymers near Tg as a function of pressure: a saxs study.	**Experiment number:** SC145
Beamline: ID2BL4	**Date of Experiment:** from: 21-Apr-96 7:00 to: 23-Apr-96 7:00	**Date of Report:**
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Report:

Aim of the **work.**

The density fluctuations that are present in glasses and liquids lead to collective and cooperative molecular mobility near the glass transition. In the previous studies [1], we investigated the density fluctuations in various amorphous polymers as a function of temperature and microstructural state, by means of the determination of the scattered intensity extrapolated at zero angle. In the glassy state, the density fluctuations can be divided into the static component (frozen-in fluctuations) and the dynamic component (arising from molecular mobility). The amplitudes of these two components are functions of the sample history. Moreover, the dynamics of disordered systems is known to depend on the isostatic pressure. Thus, we are interested in the effect of such a pressure on the density fluctuations in the dynamic and eventually the static contribution.

Experimental details.

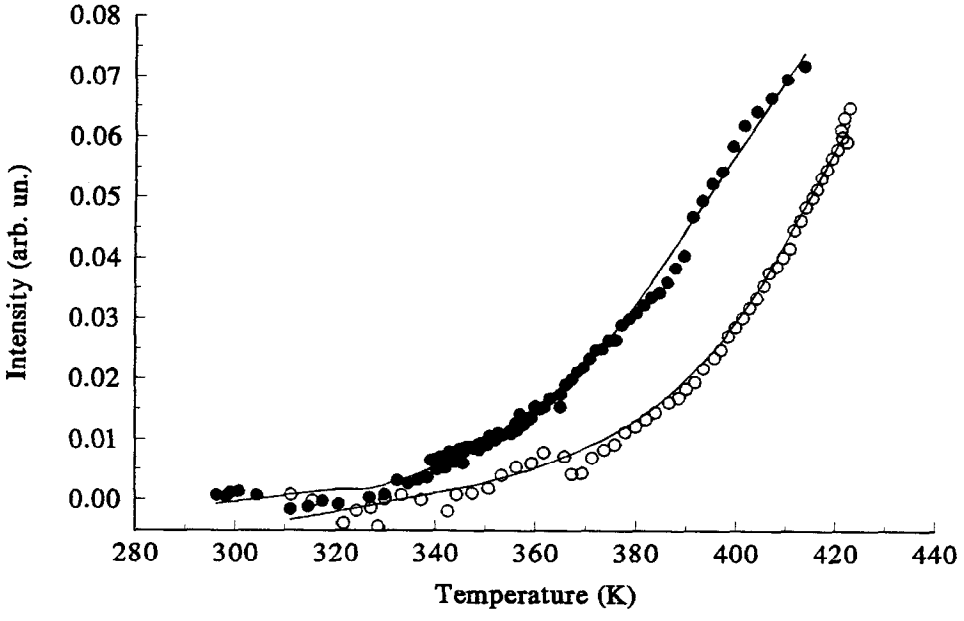
The polymer chosen for this study is poly methyl methacrylate. This polymer is known to exhibit a very apparent scattering pattern, and the dynamic behaviour of this polymer is well-known. The sample is placed in a high pressure cell with sebaccate oil. Unfortunately, the introduction of this fluid induces a large amount of pressure and temperature-dependent scattering, in comparison with the polymer sample.

The data processing mainly consisted in incident intensity attenuation correction and azimuthal averaging. As the transmission fluid stays liquid in the temperature/pressure range investigated, the contribution of sebaccate oil is a linear contribution on the

density fluctuation with temperature, for a constant pressure. The measurable quantity is thus proportional to the excess of density fluctuation with respect to ambient temperature. Consequently, the static/low temperature component is not assessable, and only the dynamic component can be measured.

Results.

Figure 1 displays the evolution with temperature of the extrapolated intensity *I(q=0)* for two different pressures namely about 64MPa (●) and 400MPa (○).



In the pressure range investigated, the calorimetric glass transition (Tg=105°C at ambient pressure) is shifted to high temperatures (well above 15O°C). Thus the increase in the density fluctuations that can observed with increasing temperatures is mainly related to secondary β molecular motions, with limited cooperative features.

As a consequence, the Roe's decomposition of the density fluctuations:

$$\psi_{total} = \psi_{dynamic} + \psi_{static}$$

can be shown to be further separated according to

$$\psi_{dynamic} = \psi_{\beta\ motions} + \psi_{\alpha\ motions}$$

where $\psi_{\alpha\ motions}$ is the (usually large) contribution of the collective motions involved in the glass transition, and $\psi_{\beta\ motions}$ the contribution to fluctuations arising from secondary relaxations.

Moreover, the value of the shifts between the two curves lead to the pressure dependence of the β -relaxation time, as given by:

$$\psi_{\beta motions} \sim 1/\tau_{\beta} \sim exp(-E_{\beta}/RT-\mu P)$$

The value found for μ (about $4\ 10^{-3}$ MPa^{-1}) is in agreement with the values found in literature [2] and confirms the dominant role played by β motions in the increase of density fluctuations in high pressure conditions.

Acknowledgements.

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References.

[I] ESRF experiences n°020419, N°SC197, N°SC229

[2] Williams, G.; Trans. Farad.Soc., 1966, 62, 2091