Names and affiliations of applicants (*indicates experimentalists):
L. David*, A. Fake*, R. Vassoille, G. Vigier*
Groupe d'Etude de Métallurgie Physique et de Physique des Matériaux,
UMR CNRS 5510, Institut National des Sciences Appliquées de Lyon,
20, av. A. Einstein
69621 Villeurbanne Cedex   E-mail: david@gemppm.insa-lyon.fr
S. Etienne*
Laboratoire de Métallurgie Physique et Science des Matériaux,
URA CNRS 155 Ecole des mines de Nancy,
Parc de Saurupt,
54042 Nancy Cedex.

Report:

Aim of the work.
The microstructural state of glasses and liquids can be characterized by the the fluctuation function

$$\psi(v) = \frac{<N^2>-<N>^2}{<N>}$$

where N is the number of electrons in the reference volume v, and $<>$ means averaging over all volumes v in the large sample volume. For exemple, for a pperfect gaz, this value is 1 and for a crystal, it is zero as soon as v is large enough. The limit $\psi(v=\infty)$ can be measured by SAXS experiment because the intensity scattered at zero angle, $I(q \rightarrow 0)$ is proportionnal to it.
Moreover, $\psi(v)$ can be divided into a static component ('frozen-in' fluctuations) and a dynamic component (fluctuations arising from atomic/molecular mobility).
Thus,

$$\psi(v) = \psi_{stat}(v) + \psi_{dyn}(v)$$

In the liquid state, the value of $\psi(\infty)$ is given by statistical thermodynamics as:
$$\psi(\infty) = \psi_{dyn}(\infty) = \rho\, kT\, \chi(T)$$
where $\chi(T)$ is the isothermal compressibility, and ρ the electronic density.
In the glassy state, there is no exact relation involving the properties of the glass for the prediction of $\psi(\infty)$.

This work is a contribution to the identification of the dynamic and static components of the fluctuation function in the glassy state, as the microstructure is varied. To this goal, the effect of a thermal treatment (annealing below the glass transition temperature Tg and quenching from above Tg) was considered in our previous studies. The resent experiment is devoted to the study of the effects of plastic deformation, which leads to a specific microstructural state, m terms of density fluctuations.

Effect of plastic deformation

The extrapolated values of the scattered intensity at zero angle were measured for deformed PMMA samples with applied strain in the range from 20% up to 50% in compression mode, as a function of temperature and orientation of the sample.

All samples were kept in liquid nitrogen before the experiment, so that minimum microstructural reorganization occurs before the scattering experiment. The presented figure shows two successive heating runs, for a sample with applied strain close to *50%*.
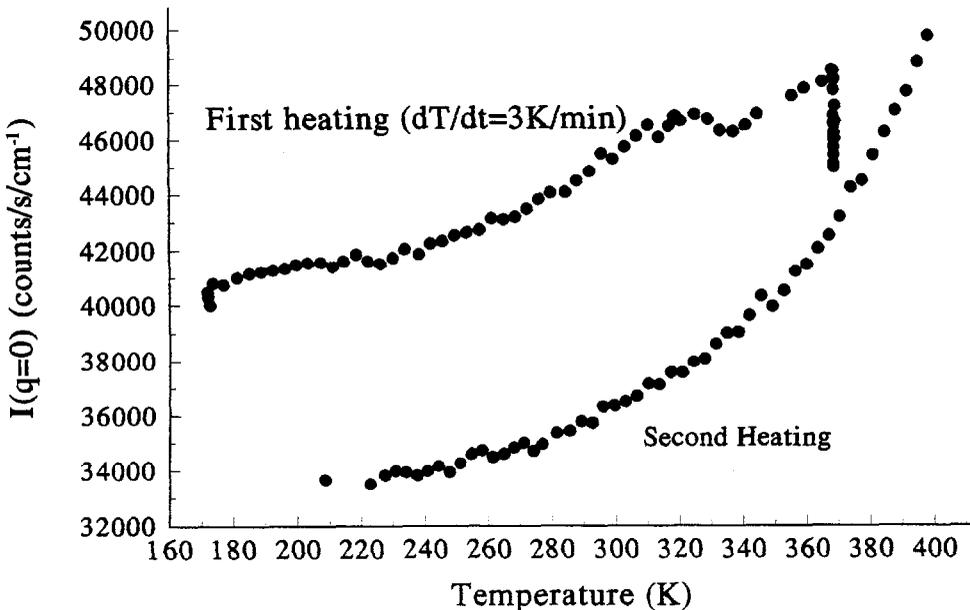
There is a large difference in *I(q=0)* at low temperature between the two successive ex periments. Consequently, there is a large static fluctuation contribution in the deformed glassy state. This static component also induces a shoulder below *Tg,* which is related to dynamic fluctuations.

When the temperature is maintained at 95°C for 2 hours, the static and dynamic contributions decrease with tune, as well as deformation as shown by the evolution of the transmission factor.

As a conclusion, deformation induces fluctuations with static nature, which is not the case for a quenching treatment [1]. ,The disorder associated with these static fluctuations induces dynamic fluctuations which manifest themselves at higher temperature. As soon as the anelastic part of deformation is recovered, the static/dynamic fluctuations disappear. These results, collected here for the first time, are in agreement with the basic h othesis of several models of non elastic deformation of glassy polymers, accor ing to which the applied strain results in the reversible formation of 'sheared microdomains' 2] [3], or 'plastically transformed zones' [4] associated with an increase of energy an6 molecular mobility.

References:

[1] Faivre, A. L,; David, L.; Vassoille, R.; Vigier G.; Geissler, E.; Vigier, G.; *Macromolecules,* m press.
[2] Argon, A., S.; *Phil. Mag., 1973, 28, 839.*
    Argon, A., S.; Kuo, H., Y.; *Mat.Sci. Engng, 1979, 39, 110.*
[3] Perez, J.; Physique et Mécanique des Polymeres Amorphes, Technique et Documentation - Lavoisier, 1992, ISBN 2-85206-787-o
[4] Oleinick, E. F.; *Prog. Coll. Polym. Sci., 1989, 80, 140*
    Oleinick, E. F.; *Polym. Sci., 1993, 35, 1532*