



LOCAL STRUCTURE AND GLASS TRANSITION OF POLYBUTADIENE UP TO 4GPa

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The glass transition can be induced by decreasing the thermal energy or by increasing the density. The usual way to investigate the glass transition is to cool a sample at ambient pressure, which not only reduces its thermal energy but also increases its density. The viscosity gets very high, the molecular relaxation time increases strongly: when these parameters get bigger than 10^{13} P or 10^3 s, the system can not reach equilibrium any more within the experimental time, the melt turns to glass. Let's point out that the glass transition is a kinetic transition, and not a thermodynamic one. Typically the density change during cooling between the high temperature melt and the glass transition temperature T_g is of the order of 6-10% depending on the system. This transition can be observed by many techniques. One of the simplest ones is to follow the density variation and consequently the mean peak position of the static structure factor with temperature: a change of slope occurs at the glass transition. The glass transition is still not fully understood in a fundamental point of view. For instance, it is difficult to disentangle the control parameters of the dynamics: is density or thermal energy mainly responsible of the slowing down of the dynamics occurring at the glass transition ?

It is observed that the characteristic slowing down of the molecular motions, when approaching the glass transition, depends more on thermal energy than on density; at T_g and normal pressure, we have shown that the temperature controls up to 80% of the phenomenon for the simple polymer, the polybutadiene [1]. However, the relative importance of thermal energy and density might change if a larger relative density change is imposed by the experimental conditions. For example one can impose a density change of 20–30% by applying high pressure at higher temperature and then the glass transition phenomena might be different with a glass of distinct properties. Furthermore by applying

external pressure one can separate the influence of density and thermal energy, and take the advantage of building isochors. These informations are reflected by the changes observed in the static structure factor $S(Q)$ under such conditions.

The main peak of the static structure factor in polymers is expected to be to a large part due to interchain correlations. At constant pressure the effect of increasing temperature on $S(Q)$ results essentially in a shift of the peak position towards lower Q -values. The shift is more pronounced above the glass transition than below, just like one would expect from the different thermal expansion below and above T_g . For deuterated polybutadiene the static structure factor $S(Q)$ was measured previously at several temperatures and moderate pressures, from atmospheric pressure up to 3 kbar, using neutron polarisation analysis of D7 at the ILL with a Niobium liquid pressure cell (from .2 to 2.5 \AA^{-1}) [2]. The range of pressure corresponds to a change in local density of about 6 to 10%, equivalent to the change observed at atmospheric pressure from room temperature down to the glass transition ($T_g=176\text{K}$ for $M_w=8000$). Recent experiments up to 4GPa [3], performed on G6.1 at the LLB, in an anvil sapphire cell, show a very good matching between the data obtained at lower pressure with D7 and the ones of G6.1 at the same temperature 295K (see Fig.1a). By these experiments we could extend the observation up to much higher pressures and have observed that the changes of $S(Q)$ with temperature and density affect mainly the Q -region near the first structure factor peak in the melt and in the glassy state as shown in Fig.1b at 160K. The main structure factor peak moves fast to higher Q at low pressures, an obvious sign of increasing local density, and more slowly at higher pressures. These measurements allow to estimate that at an isotherm of $T=295\text{K}$ the glass transition should appear in pressure range between 1.2-1.6 GPa, in agreement with calorimetric data (see Fig.2,3).

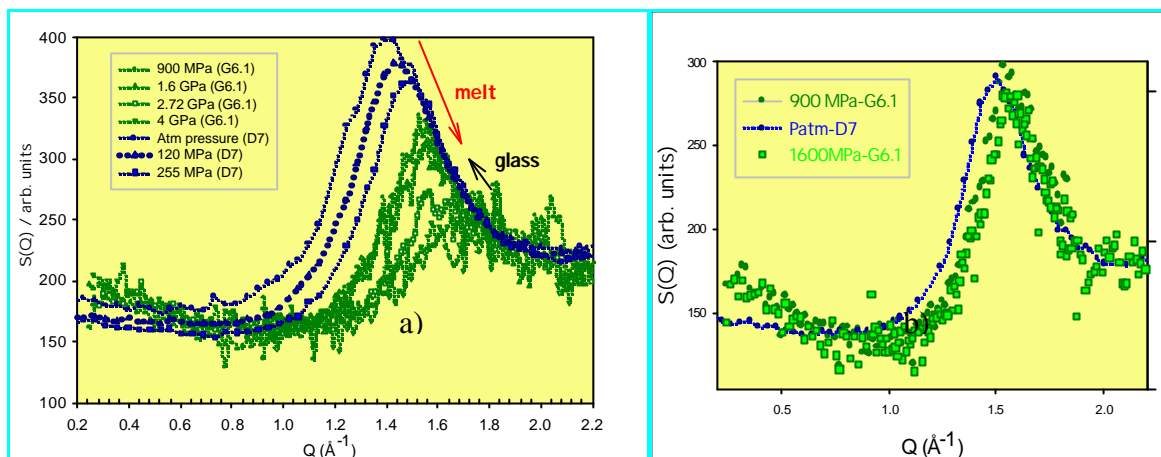


Figure 1. $S(Q)$ of PB as a function of pressure under isothermal conditions: a) at 295K from the melt to the glass; b) at 160K, but the system was quenched from 295K to 160K in order to avoid any pressure gradient.

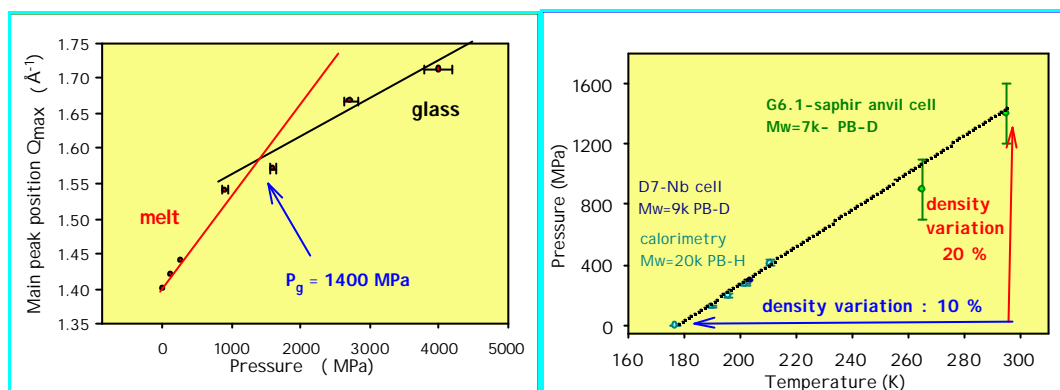


Figure 2. peak position of the first peak in $S(Q)$ as a function of pressure. The arrow shows the glass transition

Figure 3. glass transition line in a P-T phase diagram, with the corresponding density changes. Comparison of data obtained under different conditions

Moreover, we observe that the static structure factor $S(Q)$ does not change along macroscopic isochors which can be determined by calorimetric measurements and P-V-T under high pressure [2,3]. The behaviour of the structure is found to be contrary to the dynamics, where the relaxations observed by the dynamic incoherent scattering law $S(Q, \omega)$ in the ns- to ps-time scale differ strongly along the same thermodynamic path [2]. We conclude that the static behaviour, i.e. $S(Q)$, is dominated by macroscopic density changes, similar to the vibrational excitations in the meV-range.

But the most striking result in figure 1 concerns the

height of the peak, which dramatically decreases with pressure; in particular, at 4 GPa, while the system is in the glass region, a tremendous effect is observed. This phenomenon had already been observed in mineral glasses : in the case of SiO_2 and GeO_2 , the coordination number of Si and Ge was found to increase with pressure. In our case, when local density increases, the voids size decreases (inducing a lower contrast), and the inter and intra-chain distances tend to match, leading to a more homogeneous system. This point will be discussed in the future with the changes of the Boson peak observed after densification.

References

- [1] Ferrer M-L, Kivelson D., Alba-Simionesco C., Tarjus G., *J. Chem. Phys.* **109** (1998) 8010.
- [2] Frick B., Alba-Simionesco C., Anderse, K. Willner L. (2003) *Phys.Rev E*, in presse (May).
- [3] Cailliaux A., Alba-Simionesco C., Frick B., Willner L., Goncharenko, I., *Phys.Rev.E (Rapid Comm.)*, **67** (2003) (010802).