

Local structure and glass transition of polybutadiene up to 4 GPa

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This communication presents a determination of the glass transition of polybutadiene under very high pressure, and raises the problem of the determination of the relative effects of temperature and density on the glass transition, depending on the pressure and temperature conditions. Local structure and slow dynamics were studied, by neutron scattering and calorimetry. To the best of our knowledge in neutron diffraction on soft matter such a high pressure, up to 4 GPa, was achieved.

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I. INTRODUCTION

The glass transition can be induced by a decrease of the temperature or an increase of the pressure. At ambient pressure (this is the case of most experimental investigations), the slowing down of the motions, characteristic of the glass transition, depends essentially on thermal energy, more than on density [1]. However, the relative importance of those two factors might change if the experiment imposes a higher relative change of density. Actually, at atmospheric pressure, the change of density between high T and T_g is around 10%. If we impose, thanks to high pressure, a change of 20–30 % of density, the glass transition might be driven by different factors, implying more density than thermal energy. The whole phenomenon of the glass transition might be different at much higher densities.

Structural and dynamics studies can be found in the literature. However, none of them covers such a density range, allowing an isotherm variation of the relaxation time along almost 12 decades (from 10^{-9} to 10^3). That is what we propose here, presenting a way to study the glass transition of polymers, polybutadiene in our case, at very high pressures (up to 4 GPa).

Hence, in a general study aiming to separate the pressure and temperature effects on dynamics, we present here the results obtained on the effect of pressure on local structure and slow dynamics related to the α process, on polybutadiene. We used two different experimental techniques at high pressure, calorimetry, and neutron diffraction, applied at very high pressure to polymers.

1,4-polybutadiene was studied. In the calorimetry experiments, we used high molecular weight samples ($M_w = 20\,000$ g/mol), purchased from Aldrich. In the neutron scattering experiments, we used a deuterated sample ($M_w = 7000$ g/mol), made by anionic polymerization. The range of temperature studied did not affect the chemical structure

of the polymer as cross-checked by size exclusion chromatography after the experiment.

II. CALORIMETRY

The glass transition can be easily determined, experimentally, either looking at the change of slope of the volume or of the enthalpy. This kinetic transition can also be observed thanks to their first derivatives (the thermal expansion and heat capacity), the change of slope then becomes a jump. In this home-made experimental setup, we measured the thermal expansion times the volume, αV , and we were then able to detect this jump.

The system [2] is based on the following Maxwell relation: $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$. Since the thermal expansion is defined as $\alpha = (1/V)(\partial V/\partial T)_P$, we then have, in a reversible transformation, held at constant temperature,

$$\delta q = T dS = T \left(\frac{\partial S}{\partial P} \right)_T dP = -T \left(\frac{\partial V}{\partial T} \right)_P dP,$$

$$\delta q = -\alpha V T dP.$$

Hence, the measure at constant T , of the heat exchange following a change of pressure dP can lead to the quantity αV .

Practically, the sample is put in a teflon cell, under pressure (resolution: 0.5 MPa). Pressure is decreased by steps of $\Delta P = 10$ MPa. The system measures the heat exchange due to this decrease of pressure, through the resultant change of pressure in surrounding gas containers. The measure is done thanks to a compensation-regulation system. The raw signal is then corrected by the tabulated signal due to the teflon container, and by the compressing fluid (pentane).

Hence, keeping the sample at one temperature, we were able to measure αV at each pressure step. The pressure where the jump is observed is the glass transition pressure. The results are presented in Fig. 1.

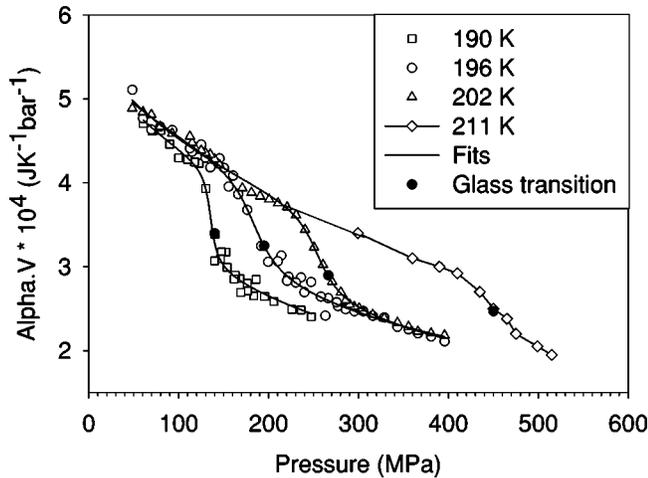


FIG. 1. Calorimetric determination of the pressure of glass transition.

The jump is shifted towards high pressures when the temperature increases. Reporting the pressure of glass transition at each temperature, we were able to determine, in the 0–600 MPa range, the line of glass transition in the P - T diagram. We found $P_g = -1865.67 + 10.54T$ (P_g , the glass transition pressure in MPa and T , the temperature in K). This gives a slope of around 0.095 K/MPa, very small compared to other well known polymers (PS, PMMA), whose slope is around 0.2 and 0.3 K/MPa. Let us note too that this is smaller than previous results on polybutadiene (PBD) [3], recent results showed that the local structure of linear polymers has a great influence on the pressure effects on T_g [4]. The differences found between our study and study of Huang *et al.* one could simply be due to the abundance of 1,2 PBD (1,2 PBD possesses lateral groups, whereas 1,4 does not), almost equal to zero in our case, and equal to 55% in their case.

III. NEUTRON SCATTERING

Experiments were carried out at the laboratoire Léon Brillouin (Saclay), on the diffractometer G6.1. The high pressure system is a sapphire anvil pressure cell [5], and the pressure is measured following the fluorescence frequency of ruby powder. This system gives the possibility to reach very high homogeneous pressure with a small amount of sample (from 0.5 to 0.9 mm³). The high flux resulting from the focusing supermirrors of G6.1 allows to have a well resolved signal, in a reasonably short time [5]. Let us point out the fact that this experiment implies some practical details; in order to keep a sufficient sample volume at high pressure, the gasket has to be adapted to each pressure range. In our experiment, we had to use three of them, hence three different weights of samples (the neutron scattering data were then normalized to the sample weight).

We studied PBD on one isotherm (295 K) with pressures of 0, 940, 1600, 2720, and 4050 MPa (pressure resolution: 50 MPa), and on two isobars (940 and 1600 MPa) with temperatures ranging from deep in the glass (100 K) up to the melt (310 K). The results are presented on Fig. 2. We included in this figure previous results, obtained on D7 (ILL,

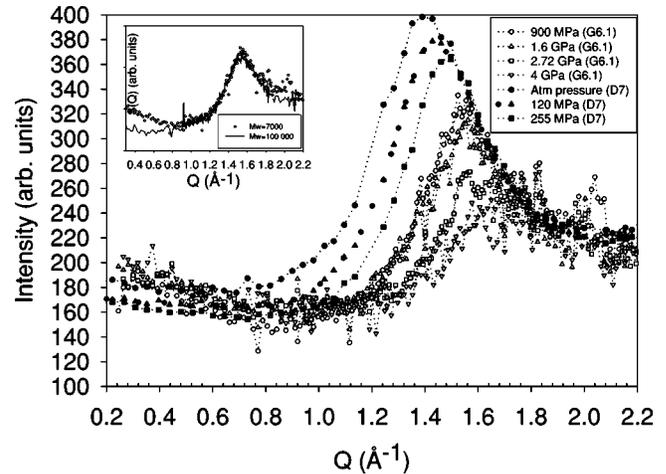


FIG. 2. Structure factors of deuterated polybutadiene at 295 K under pressure. In the inset, a comparison between high and low M_w , at 900 MPa, 295 K is shown.

Grenoble) [6], and put them on the same scale than the G6.1 data. Those experiments had been done with deuterated PBD of $M_w = 9000$ g/mol, with polarized neutrons, at lower pressure (from 0 to 255 MPa). The pressure cell used on D7 was an appropriate niobium cell [7]. Very good agreement was found between the two instruments at atmospheric pressure, after a mass rescaling, which allowed us to put all the results of those two experiments on the same graph.

We observe a drastic change of the main peak of the structure factor, representative of the interchain interactions. The peak is shifted towards high momentum transfer Q . This is a clear and obvious sign of increasing local density. Furthermore, only the low Q part is shifted; the structure factors match very well in the high Q part. But the most striking result concerns the height of the peak, which dramatically decreases with pressure. At 4 GPa, while the system is in the glass region, a tremendous effect is observed.

In the data at very high pressure (G6.1), an increase of the intensity at low Q is observed. Wondering about the reason of this increase (it had not been observed in the previous experiments on D7), we checked the absence of impurities in our sample. Furthermore, the good matching of the structure factor peak with the high molecular weight sample's one (Fig. 2 inset) validated our results at higher Q . The increase at low Q in the low molecular weight sample is still unclear, but, thanks to the comparison of those two samples, we checked that it does not affect the Q region we are interested in.

We reported the position of the main peak of the structure factor, interested in the variation of the interchain distance [6]. At the glass transition, the change of slope of the volume can be detected thanks to this local effect, through the change of slope of $Q_{max} = f(P)$ or $Q_{max} = f(T)$ at the glass transition. The peak position reflects density, even if there is no direct relationship, and this allows the detection of the glass transition through Q_{max} .

The results of this report, done on the 295 K isotherm from the results of Fig. 2, are presented Fig. 3(a). We did the same with the results obtained from the isobars at 900 and

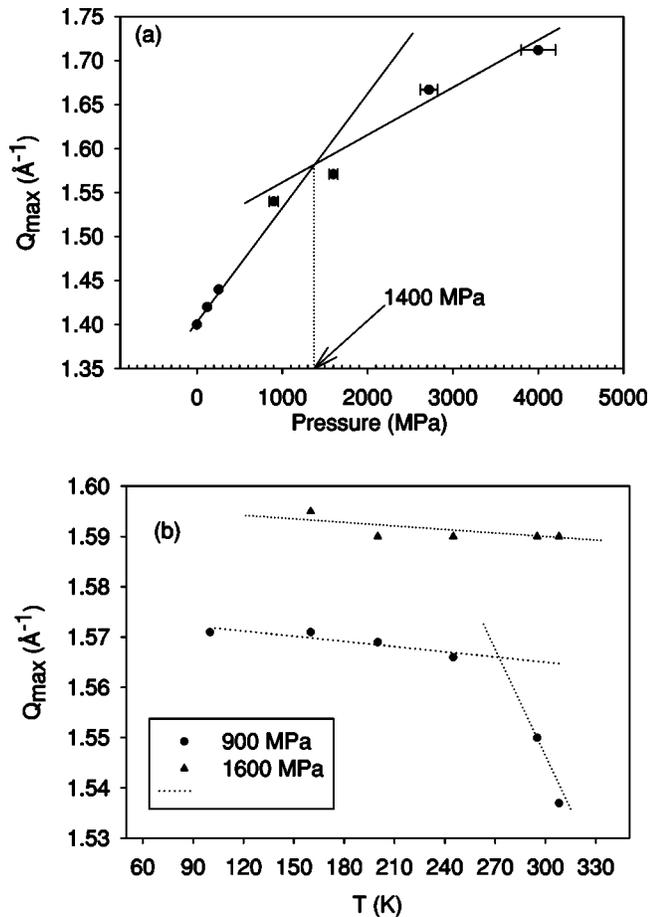


FIG. 3. Position of the main peak of the structure factor of PBD, on two isobars, as a function of temperature.

1600 MPa, and we show them on Fig. 3(b). The usual analysis of the width of the peak was not possible here, due to the great changes of the shape of the peak.

The evolution of Q with P or T allowed us to determine the glass transition at 295 K, as around 1400 MPa. On the isobars, the glass transition could be detected at 900 MPa, around 248 K, but not at 1600 MPa; the glass transition might occur at higher temperatures in this case.

Let us remark that the glass transition was more easily determined on the isobar experiment than on the isotherm one. Actually, in the isotherm, pressure modifies density, and what is observed (Q position) reflects density. Hence, observable quantity and controlling parameter are strongly related. This does not occur on the isobar, where temperature is the control parameter; this allows a better determination of the glass transition, since perturbation and observed quantity are not so close.

IV. DISCUSSION

What is the physical explanation to the neutron scattering results? The structure factor peak, in addition to its shift, presents a decreasing intensity with pressure. This phenomenon had already been observed in mineral glasses [8,9]; in the case of SiO_2 and GeO_2 , the coordination number of Si

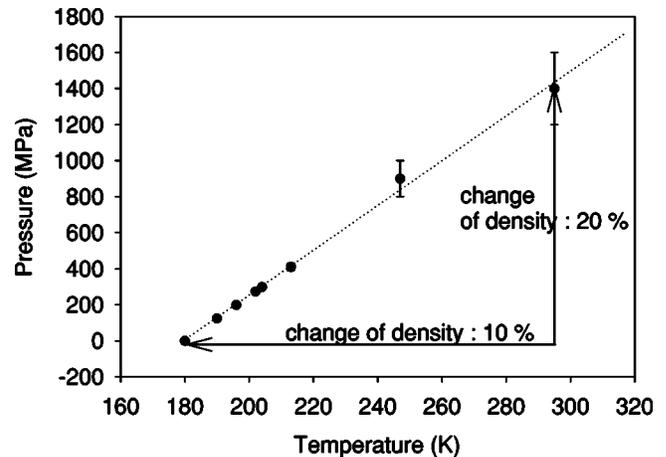


FIG. 4. Glass transition as a function of P and T (neutron scattering and calorimetry).

and Ge was found to increase with pressure. In our case, when local density increases, interchain and intrachain distances tend to match. The interchain distance, corresponding to the first peak of the structure factor, decreases considerably. However, the intrachain distance does not vary much, pressure does not have a great influence on the chemical bond distance. Hence, in a very high pressure limit, both distances will match; the first structure factor peak disappears, in favor of the second one that might increase. Let us note that this is in contradiction to what is usually observed in simulations of hard spheres or colloids [10], where only one distance is relevant.

Furthermore, those two sets of experiments gave us results concerning the glass transition under pressure over a large range of pressures. The error bars were much larger with the neutron scattering data. However, we tried to see how those two techniques could give us a global picture. The results are presented on Fig. 4.

We give the change of density between the melt and the glass [11] on Fig. 4. We notice that the change is twice bigger for the glass obtained on the isotherm than for the one obtained on the atmospheric pressure isobar. At ambient pressure, the glass transition occurs with a certain amount and distribution of free volume blocked by temperature (glass A), and the control parameter of the activated dynamics of PBD is the temperature. At higher pressure, the glass is formed at higher density, hence with a much smaller amount of free volume (glass B). This means, that glass A still possesses a reducible free volume, since glass B has less free volume. Hence, the glass A formation is not controlled by density. Otherwise, glass B would form much earlier. Under pressure, density induces an increase of the energy barriers. The thermal energy available at 295 K allows relaxation over those barriers for the system at a compression of 10%, whereas it was not possible any more at 180 K. When density still increases, barriers finally reach the point where they prevent those thermally activated processes at the studied temperature. Going back to our introduction, this indication leads to the point that those glasses are different, in density, and result of different freezing processes.

V. CONCLUSION

The results presented in this Rapid Communication show the great impact of pressure on slow dynamics and structure of polybutadiene. The pressure effect is very strong, and almost destroys the main peak of the structure factor when it gets very high. The tremendous effect of high pressure shows

that pressure still has a strong effect, even on very dense system, and no crystallization occurs, even if PBD has a very simple structure. The effect is in such an unexpected range, that we will soon continue, at higher temperatures, to get a more complete dataset, that will be completed by a numerical approach (Monte Carlo and reverse Monte Carlo methods), as well as performing dynamical studies.

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