

Characterization of the Drastic Increase in Molecular Mobility of a Deformed Amorphous Polymer

Etienne Munch, Jean-Marc Pelletier, Bruno Sixou, and Gérard Vigier
GEMPPM, UMR CNRS 5510, INSA de Lyon, 69621 Villeurbanne Cedex, France
(Received 5 April 2006; published 14 November 2006)

Original experiments of dynamic mechanical analysis and small angle x-ray scattering on a deformed amorphous polymer below its glass transition temperature are reported. The mechanical treatment reveals high mobility zones induced by shearing and leads to a drastic increase in the molecular mobility of the system. These domains are evidenced by small angle x-ray scattering measurements, and their geometrical characteristics are independent of the applied deformation. An experimental procedure is proposed to determine an apparent activation energy associated with high mobility domains. The energy values obtained for intermediate modes rise from the β to the α relaxation ones.

DOI: [10.1103/PhysRevLett.97.207801](https://doi.org/10.1103/PhysRevLett.97.207801)

PACS numbers: 61.41.+e, 36.20.Ey, 81.40.Cd

Amorphous polymers present general characteristics of glass forming systems. Below the glass transition (T_g), they are in an out-of-equilibrium state and subject to the physical aging phenomenon. Their physical properties evolve slowly and continuously with time. This implies that the thermodynamic state of the system depends on both its age, i.e., the time spent in the glassy state, and the time elapsed since the measurement started. Above the glass transition, these systems are in a metastable equilibrium, and a complete erasure of the thermal history can be achieved.

Viasnoff and Lequeux have shown experimentally that mechanical solicitation on glasses has nontrivial consequences on the relaxation behavior and the kinetic of physical aging [1]. These results have been confirmed recently by a simulation performed by Wallace and Joos [2]. The deformation of glasses appears to be associated with both overaging and a rejuvenation of the system. Based on molecular simulations and an energy landscape analysis, Lacks and Osborne have shown that the balance between overaging and rejuvenation depends on the thermal history and the nature and amplitude of the mechanical solicitation [3].

Glassy polymers exhibit a molecular mobility below T_g that expresses itself through several relaxations. These relaxations reveal the heterogeneous nature of the system's dynamics [4]. If amorphous polymers are known for their capacity to support relatively high plastic deformation below T_g , the models describing the physics of their plasticity remain mainly phenomenological [5–7]. There is still a lack of experimental results that include microstructural information to reach a more physical description of a polymer's mechanical behavior.

Polycarbonate (PC) has been chosen for supporting a large homogeneous deformation in compression and because a wide temperature range separates its secondary relaxation (180 K at 1 Hz) and its main α relaxation (430 K at 1 Hz). A standard stress vs strain curve of an

amorphous polymer presents a maximum of stress, known as the yield point. It corresponds to a critical phenomenon where the system enters a transient regime. In this regime, a reversible part (elastic and viscoelastic deformation) and the very beginning of a plastic deformation coexist [8]. We chose to deform the system thanks to a plain strain compression test at room temperature (300 K) and a strain rate around $8 \times 10^{-5} \text{ s}^{-1}$. This test insures a homogeneous state of deformation in the central part of the sample, which can be isolated and submitted to various characterization tests.

This effect is observed thanks to a classical low frequency and high-resolution mechanical spectrometer [dynamic mechanical analysis (DMA)] [9,10]. The DMA experiments consist in a periodic deformation of the system in the linear regime (maximum deformation $\gamma = 10^{-5}$). As a consequence, the properties of the system are not affected by the mechanical solicitation. The deformation induced by DMA experiments is instantaneously recovered by the material. The parameter taken into consideration is the loss tangent $\tan\delta = G''/G'$, measured as a function of temperature (G' and G'' are the real and imaginary parts, respectively, of the complex modulus G^*). This parameter is independent of the sample geometry.

Figure 1 presents the secondary and the main relaxation peaks, classically observed during low frequency DMA measurements. The secondary relaxation (β) corresponds to movements at a very local scale. The α relaxation is related to larger scale displacements, which involve several repeating units of the macromolecule. The initial deformation treatment of the material induces the appearance of a pseudorelaxation peak lying between the β and α relaxations. Similar mechanical measurements have been published before in a different context [11–13]. At the deformation temperature, the peak starts like a classical relaxation, then turns into a plateau, with progressive and irreversible erasure of the phenomenon as the mobility increases. The plateau height increases with an increase

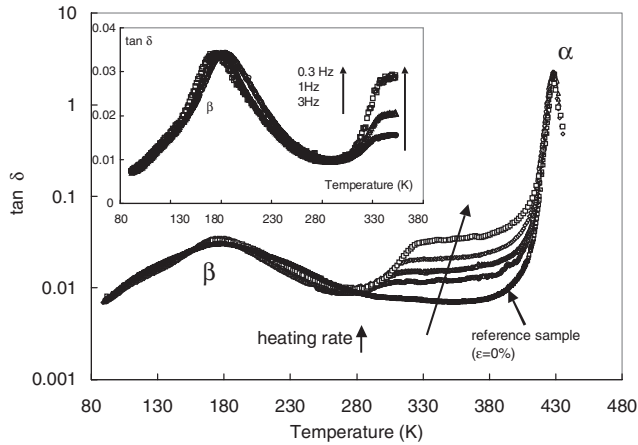


FIG. 1. $\tan\delta$ versus temperature at 1 Hz and various heating ramps (0.3, 1, 3, and 10 K/min) on bisphenol-A (BP-A) PC samples deformed at 20%. A curve of a nondeformed sample is added as a reference. The effect of the testing frequency for samples deformed at 20% is presented in the inset.

in the heating rate (Fig. 1), the decrease in testing frequency (Fig. 1), and the increase in deformation ratio imposed to the material (Fig. 2). The peak height reaches a saturation value for deformation ratios around 30%. It is sensitive to frequency, heating rate, and physical aging and should be seen as an unstable relaxation phenomenon which corresponds to a drastic increase in molecular mobility.

The microstructural impact of the deformation is related to the appearance of small zones undergoing shear transformations and inducing local positive or negative modifications of density without any significant mean volume change [14,15]. The sheared zones can be detected by small angle x-ray scattering (SAXS) through measurements of the electronic density fluctuations [16–18]. Local density variations in fluid and solid systems arise as results of thermal motions. They can be described using

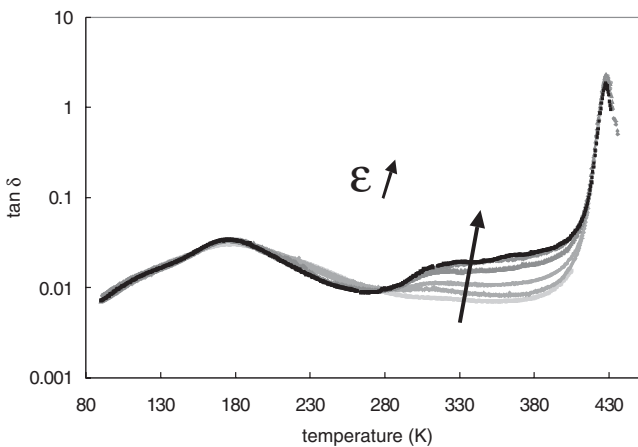


FIG. 2. $\tan\delta$ at 1 K/min and 1 Hz on BP-A PC samples deformed at 0%, 6%, 10%, 20%, 30%, and 40%.

the particle density fluctuation function. In the case of electronic density fluctuations, it leads to the following expression:

$$\psi(V_\infty) = \frac{\langle(N - \langle N \rangle)^2\rangle}{\langle N \rangle} = \lim_{q \rightarrow 0} \frac{I(q)}{Nf(q^2)},$$

where N corresponds to the number of particles included in a reference volume at a given time, $f(q)$ is the atomic structure factor, and $\langle \rangle$ denotes spatial averaging as the reference volume is moved around the sample. Below T_g , this equation is no longer expected to hold since the glass is in an out-of-equilibrium state [19]. Wiegand and Ruland proposed an empirical equation to approximate $I(q)$ for small q values [20]:

$$I(q) = I_0 \exp(bq^2).$$

Several attempts have been achieved to find a physical basis for this empirical equation, using, for example, the Percus Yevick approximation [21]. If these approaches remain qualitative interpretations, they enable one to connect the parameter b to the size of the diffusing objects.

SAXS measurements are carried out with a wavelength of 1.54 Å, and the calculations are done after integrating the 2D SAXS patterns recorded. Special care is taken in results correction, taking into account the geometrical changes occurring in the samples during the heating ramps. All of the recorded patterns were isotropic for the deformation ratios applied. This observation confirms that the plain strain test leads to a homogeneous deformation state. All of the samples studied are submitted to a 1 K/min heating rate from room temperature to T_g , then to a 1 K/min cooling ramp back to room temperature. The same conditions were used during DMA measurements.

Figure 3 presents a log plot of the scattered intensity I as a function of q^2 obtained at room temperature for a non-deformed sample. A similar curve is obtained every 2 K

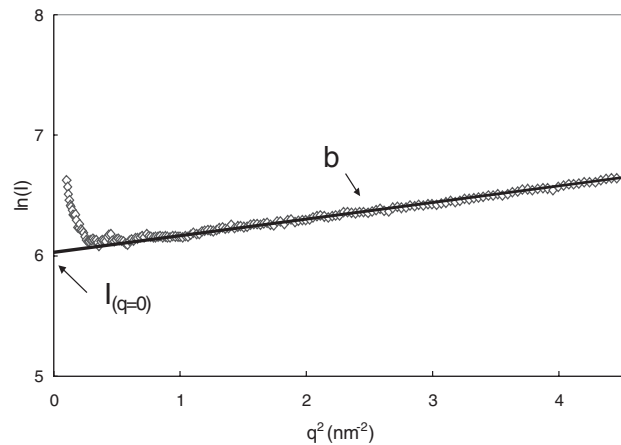


FIG. 3. log plot of I as a function of q^2 for a deformation of 20%. Parameters $I_{(q=0)}$ and b are extracted from a linear fit of the curve.

step during the thermal ramp imposed to the different samples and a couple of value $\{I_{(q=0)}, b\}_T$ is extracted.

We observe that the intensity scattered by electronic density fluctuations increases with an increase in deformation ratio imposed to the material (Fig. 4). The variations of the fluctuations appear significant for deformation ratios higher than 10%, beyond the yield point. The increase in the intensity scattered by fluctuations is progressively erased during heating, and all of the curves converge to the same point in the vicinity of T_g . This point corresponds to the merging point observed on the DMA results as well. At this temperature, the molecular mobility of the system is high enough to induce a short time annealing of all of the thermomechanical history of the material, and all curves obtained during the cooling process at a constant rate of 1 K/min are superposed.

It has also been observed that the values of b are independent of the deformation ratio and present a decreasing trend with an increase in temperature. This trend is related to a slight increase in fluctuation sizes. The values obtained are similar to those given by David *et al.* [17]. They considered that b was dependent on geometrical characteristics of fluctuations. Following this standpoint, our results would imply that the geometrical characteristics of the high mobility zones do not depend on the deformation ratio imposed to the material. This observation is in agreement with the results obtained by Hasan *et al.* in a positron annihilation study. They have concluded that plasticity increases the number of voids but not their sizes [22].

Several models consider that the local high mobility zones [5–7] appear in preferential sites of the native material and undergo nucleation-growth steps until an equilibrium state between recovery and coalescence. Our results seem to privilege an increase in number instead of a growth of the sheared zones size. Starting from this, it should be possible to simplify existing models of plasticity, by introducing percolation concepts.

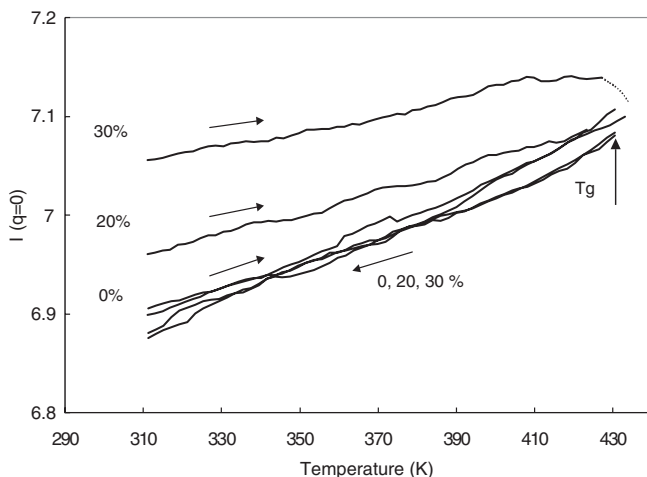


FIG. 4. Extrapolated value at $q = 0$ of the scattered intensity during SAXS measurements on deformed samples of BP-A PC.

The appearance of the pseudorelaxation peak is the result of the relaxation of high mobility zones with time and temperature. Regarding the irreversible nature of the unstable relaxation, an experimental protocol is built to determine the apparent activation energy of the affected zones at various steps of their evolution.

After compression, the deformed part of the sample is cut in an adiabatic way (homemade guillotine at the temperature of liquid nitrogen). The DMA sample thus obtained is cooled to 90 K just below the secondary relaxation peak. Then it is submitted to successive temperature ramps, leading to a progressive erasure of the unstable peak, as detected at two frequencies (0.3 and 3 Hz). As reported elsewhere [23], the apparent activation energy is determined from DMA measurements at these two frequencies with the hypothesis of an Arrhenius-type behavior of the phenomenon.

Three particular domains appear in Fig. 5. The first part A between 170 and 270 K corresponds to the middle and high temperature parts of the secondary relaxation. The values obtained for the apparent activation energy (around 1 eV) are consistent with values in the literature [24]. In the higher temperature range (part C), one can easily identify the main α relaxation, which coincides with T_g in the frequency range investigated. It corresponds to high values of apparent activation energy. The increase in the T_g temperature domain is large, and the merging point observed on the DMA and SAXS curves corresponds to the highest values of apparent energy.

Finally, in the intermediate range of temperature between 270 and 390 K (part B), lying between the main and the secondary relaxations, we obtain groups of apparent activation energy values corresponding to the unstable relaxation peak. Each of them is obtained for each heating ramp described in Fig. 5 (the sample being quenched to

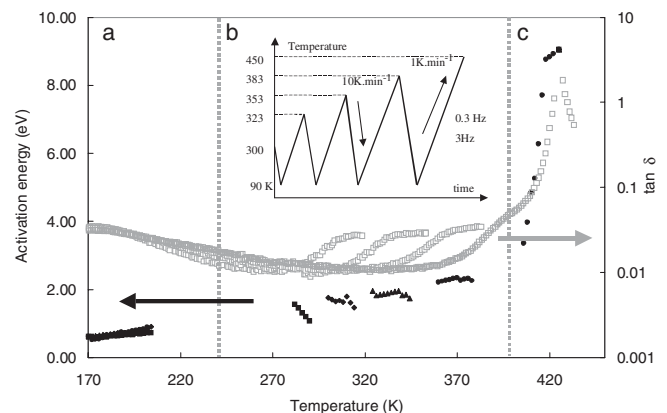


FIG. 5. Multiple ramp curves of $\tan \delta$ (for clarity, only the results at 3 Hz are presented; frequency effects are illustrated in Fig. 1) and the associated values of the apparent activation energy obtained with two different DMA (0.3 and 3 Hz) on a sample deformed at 20%. The experimental procedure realized for each frequency is schematized in the inset.

90 K between each ramp). The decreasing trend observed for each group leads to a preliminary comment. It has been shown that the intermediate relaxation peak observed after deformation is sensitive to physical aging; thus, every attempt to measure its characteristics induces its disappearance and strong experimental errors. It is not possible to determine the apparent activation energy without errors, but they can be minimized by measuring the energy at the very beginning of the peak. It restrains the number of accessible values, and we observed that, even during the first times, the annealing effect tends to diminish them. Nevertheless, we observe that the apparent activation energy average value of the phenomenon increases from the value of the secondary relaxation to the value of the main α relaxation. This is a new insight brought to the understanding of the effect of deformation on the microstructure of amorphous material.

In conclusion, the modification of the energy barriers induced by the deformation of the system below T_g leads to a drastic increase in molecular mobility. Small zones of high mobility are created. These zones can be detected by SAXS measurements considering the electronic density fluctuations. Their relaxation characteristics correspond to movements observed during the β process and evolve to α -type relaxation movements as the temperature increases.

-
- [1] V. Viasnoff and F. Lequeux, Phys. Rev. Lett. **89**, 065701 (2002).
- [2] M. L. Wallace and B. Joos, Phys. Rev. Lett. **96**, 025501 (2006).
- [3] D. J. Lacks and M. J. Osborne, Phys. Rev. Lett. **93**, 255501 (2004).
- [4] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).
- [5] O. A. Hasan and M. C. Boyce, Polym. Eng. Sci. **35**, 331 (1995).
- [6] J. Perez, J. Y. Cavaille, and L. David, J. Mol. Struct. **479**, 183 (1999).
- [7] K. L. Ngai, R. W. Rendell, and D. J. Plazek, J. Chem. Phys. **94**, 3018 (1991).
- [8] R. Quinson, J. Perez, M. Rink, and A. Pavan, J. Mater. Sci. **31**, 4387 (1996).
- [9] C. Gauthier, J. M. Pelletier, L. David, G. Vigier, and J. Perez, J. Non-Cryst. Solids **274**, 181 (2000).
- [10] S. Etienne, C. Lamorlette, and L. David, J. Non-Cryst. Solids **237**, 628 (1998).
- [11] A. R. Berens and I. M. Hodge, Macromolecules **15**, 756 (1982).
- [12] A. Chudnovsky, Z. Zhou, C. P. Bosnyak, and K. Sehanobish, Polym. Eng. Sci. **35**, 304 (1995).
- [13] M. Trzadnel, T. Pakula, and M. Kryszewski, Polymer **29**, 619 (1988).
- [14] E. Oleynik, Prog. Colloid Polym. Sci. **80**, 140 (1989).
- [15] O. A. Hasan and M. C. Boyce, Polymer **34**, 5085 (1993).
- [16] A. Faivre, L. David, R. Vassoille, G. Vigier, S. Etienne, and E. Geissler, Macromolecules **29**, 8387 (1996).
- [17] L. David, G. Vigier, S. Etienne, A. Faivre, C. L. Soles, and A. F. Yee, J. Non-Cryst. Solids **235–237**, 383 (1998).
- [18] G. Floudas, T. Pakula, M. Stamm, and E. W. Fischer, Macromolecules **26**, 1671 (1993).
- [19] R. J. Roe and J. J. Curro, Macromolecules **16**, 428 (1983).
- [20] W. Wiegand and W. Ruland, Prog. Colloid Polym. Sci. **66**, 355 (1979).
- [21] Y. Tanabe, N. Müller, and E. W. Fischer, Polymer Journal **16**, 445 (1984).
- [22] O. A. Hasan, M. C. Boyce, X. S. Li, and S. Berko, J. Polym. Sci., Part B: Polym. Phys. **31**, 185 (1993).
- [23] J.-F. Blachot, L. Chazeau, and J.-Y. Cavaille, Polymer **43**, 881 (2002).
- [24] M. D. Shelby and G. L. Wilkes, J. Polym. Sci., Part B: Polym. Phys. **36**, 2111 (1998).