Discovery of anisotropy in Johari–Goldstein-β process of stretched crosslinked polybutadiene by time-domain interferometry

Polymers are essential to our daily lives. Improving fracture strength is particularly important for safety and resource conservation, and understanding the mechanism of fracture progression is key to this improvement. Additionally, imparting directionality to fracture strength is important. For example, materials that are rigid in the stretching direction but flexible in the perpendicular direction can meet various market demands.

The fundamental source of many material properties is the atomic/molecular structure and dynamics. In glass-forming systems, such as polymers, the α process and Johari–Goldstein (JG)-β process are common. The microscopic origin of the α process is cooperative diffusive motions within the polymer chains, while its sub-process, whose origin is elusive, is responsible for the JG-β process. Below the glass transition temperature, the α process is effectively frozen, while the JG-β process occurs much more frequently. Therefore, the JG-β process is often the major source of stress relaxation and is the dominant contributor to the failure strength of amorphous systems. As fracturing occurs at the end of stress-induced deformation, the JG-β process under stretching determines the fracture properties. We have found that stretching facilitates the JG-β process, indicating that the system strengthens against fracture [1]. Because the polymer is oriented by stretching, changes in the molecular environment can cause its dynamics to be directionally dependent. However, this directional dependence is poorly understood, despite its importance in various applications.

In this study, we measured the strain dependence of the JG-β relaxation time under stretching in detail and determined its directional dependence for crosslinked polybutadiene (PB). The cross-linked PB was prepared using a literature method [1]. Microscopic dynamics were studied using quasi-elastic gamma ray scattering (QEGS) with time-domain interferometry (TDI) [2,3]. A normalized intermediate scattering function was observed using the temporal beat pattern of the TDI time spectra. The QEGS measurements were performed at SPring-8 **BL35XU**. The sample was stretched to a target strain value of $\lambda = (l - l_0)/l_0$, where l_0 and l are the lengths of the sample before and after stretching, respectively. QEGS measurements on uniaxial stretching in the λ range between 0 and 1 were conducted at $q = 29$ nm^{-1} and 215 K, the conditions at which the JG-β process has been observed [1].

Figure 1 shows the obtained TDI time spectra, which were analyzed using a literature method [1].

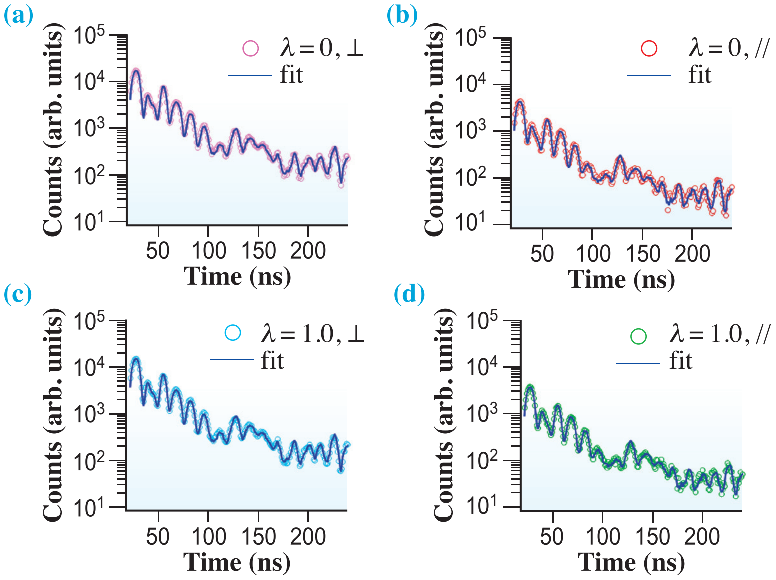

Fig. 1. TDI time spectra of the crosslinked PB on uniaxial stretching at 215 K **(a)** perpendicular to the stretching direction at $\lambda = 0$, **(b)** parallel to the stretching direction at $\lambda = 0$, **(c)** perpendicular to the stretching direction at $\lambda = 1.0$, and **(d)** parallel to the stretching direction at $\lambda = 1.0$ at $q = 29$ nm^{-1}. The solid lines in (a)–(d) represent the fitting curves. [4]

Figure 2 shows the strain dependence of the mean JG-β relaxation time perpendicular ($\langle\tau_\perp\rangle_{\text{JG-}\beta}$) and parallel ($\langle\tau_{//}\rangle_{\text{JG-}\beta}$) to the stretching direction. These relaxation times reflect the average timescale of the local few-angstrom-scale motions. Notably, $\langle\tau_\perp\rangle_{\text{JG-}\beta}$ tended to decrease with the increase in stretching, as reported previously [1]. By contrast, we found that $\langle\tau_{//}\rangle_{\text{JG-}\beta}$ did not change significantly on stretching. Thus, the strain dependence of the JG-β relaxation time was deemed to be anisotropic.

The observed anisotropy contrasts with the isotropic strain dependence of the α-relaxation time found previously [1]. Therefore, our finding hints at the origin of the mysterious JG-β process in polymeric materials. The activation energy, E_a, of the JG-β process is known to be ≈35 kJ/mol [1,4], approximately 2–3-fold higher than that of carbon–carbon torsional or vibrational motions, which occur mainly in the direction perpendicular to the main chain. The high activation energy indicates that several segments rotate or translate cooperatively, rather than individually. With respect to cooperativity, the observed anisotropy of the JG-β relaxation time can be explained as follows. Before stretching, the segments in the randomly oriented main chains are in collective local motion, as shown in the left panel of Fig. 3. Upon stretching, the main chains became slightly more aligned, facilitating collective motion in a direction perpendicular to the main chains. The right panel in Fig. 3 shows a schematic of the structure and dynamics proposed in our study, depicting the decrease in relaxation time $\langle\tau_\perp\rangle_{\text{JG-}\beta}$. It can be seen that the dynamics of the polymer chains remain relatively unaffected by stretching in the parallel direction, which explains the insensitivity of $\langle\tau_{//}\rangle_{\text{JG-}\beta}$ to stretching.

Thus, we directly observed that the anisotropic mobility of the polymer chains is dominated by the JG-β process during stretching. Anisotropy is essential to understanding the origin of the JG-β process and the mechanism of how the JG-β process relates to the material property under stretching.

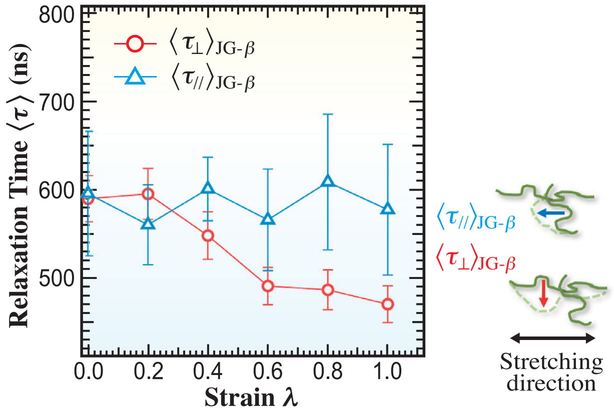

Fig. 2. Strain dependences of the mean relaxation times $\langle\tau\rangle$ of the crosslinked PB at $q = 29$ nm^{-1} and $T = 215$ K perpendicular and parallel to the stretching direction. On the right side, the dark green curves represent polymer chains. The red and blue arrows represent the direction of polymer chain motions, which are the origin of the relaxations occurring perpendicular and parallel to the stretching direction, respectively. [4]

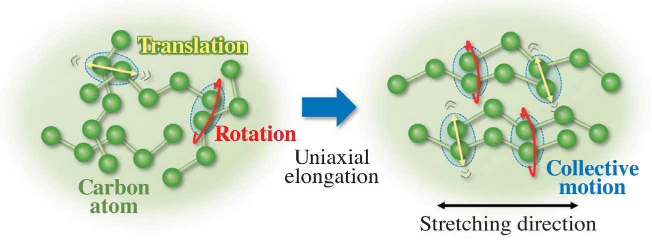

Fig. 3. Schematic of the JG-β process in crosslinked polybutadiene under uniaxial elongation (with the example of cooperative motion of two units). [4]

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References

[1] R. Mashita *et al*.: J. Synchrotron Rad. **29** (2022) 1180.
[2] A. Q. R. Baron *et al*.: Phys. Rev. Lett. **79** (1997) 2823.
[3] M. Saito *et al*.: Sci. Rep. **7** (2017) 12558.
[4] *R. Mashita, M. Saito, Y. Yoda, N. Nagasawa, Y. Bito, T. Kikuchi, H. Kishimoto, M. Seto, T. Kanaya: ACS Macro Lett.* ***13*** *(2024) 847.*