

Glass Transition and Fast Process of Picosecond Order in Amorphous Polybutadiene

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Dynamics of amorphous polybutadiene has been investigated near the glass transition temperature T_g from microscopic viewpoints using a quasielastic neutron scattering technique in an energy range of 0.01 meV to 10 meV, which corresponds to a time range of $\sim 4 \times 10^{-10}$ to $\sim 4 \times 10^{-13}$ s. It was found that a very fast motion of picosecond order appears at the so-called Vogel-Fulcher temperature T_0 , suggesting that the fast process is a precursor of the glass transition. This *fast process* has been assigned to a damped vibrational motion in the C-C torsional potential well. In addition to the *fast process*, a slow motion of 10^{-10} s order is observed above T_g . This slow process has been assigned to an elementary process of conformational transition in a polymer chain, leading to structural relaxation above T_g .

Keywords: Glass Transition / Amorphous polybutadiene / Neutron scattering / Vogel-Fulcher temperature / Fast process of picosecond order / Damped vibrational motion

Glass transition is one of the most important phenomena in polymer science as well as in materials science because various properties of polymers such as thermal and mechanical properties change drastically below and above the glass transition temperature T_g . Therefore, lots of investigations have been made on amorphous polymers using various kinds of methods. Most of the investigations have been performed in macroscopic or mesoscopic time and spatial scales using thermal, mechanical and dielectric measurements. Stimulated by the recent microscopic theory, the so-called mode coupling theory (MCT) [1], lots of microscopic measurements have been made on various kinds of glass-forming materials such as organic and inorganic materials and polymers using quasielastic neutron and light scattering, NMR and dielectric relaxation techniques. From microscopic viewpoints, contributions of quasielastic neutron scattering are outstanding. One of the most important contributions is a find-

ing of the *fast process* of picosecond order, which has been observed for most glass-forming materials so far studied. We will report the characteristic features of the *fast process* of picosecond order for cis-1,4-polybutadiene having no side groups, and discuss the role in the glass transition phenomena [2-5].

Figure 1 shows the dynamic scattering laws $S(Q, \omega)$ observed with an energy resolution of ~ 0.2 meV in a temperature range of 50 K to 260 K covering the glass transition temperature T_g (~ 170 K). A very broad excitation peak, the so-called *low-energy excitation* peak, is observed at ~ 1.7 meV at low temperatures somewhat below T_g . The *low-energy excitation* is a universal feature for all amorphous materials so far examined and believed to be an origin of anomalous excess heat capacity of amorphous materials at low temperatures. The intensity of the *low-energy excitation* increases according to the Bose-Einstein population factor at low temperatures, indicating that the motion is vibrational.

FUNDAMENTAL MATERIAL PROPERTIES — Polymer Materials Science —

Scope of research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with the intention of solving fundamentally important problems in polymer science. The main projects are: the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation process and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.



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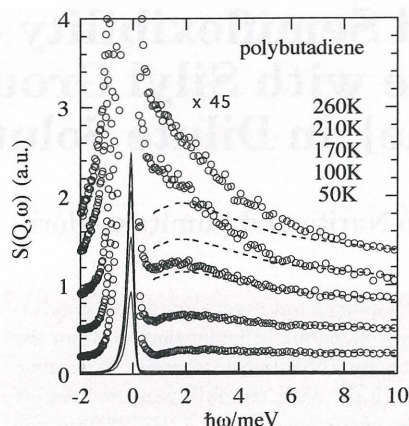


Figure 1. Dynamic scattering laws $S(Q, \omega)$ of polybutadiene. Dashed lines are the expected spectra from the Bose factor.

The dashed lines in the figure are the expected spectra calculated by applying the Bose-Einstein factor to the spectra at 50K; as seen in the case at 100K, the expected spectra agree well with the observed ones while above 120 K some excess quasielastic scattering is observed in an energy range below ~ 4 meV and the intensity increases with temperature. This excess quasielastic scattering is caused by the *fast process*.

The appearance of the *fast process* above ~ 120 K involve an anomalous excess decrease of the elastic scattering intensity, which is the counter part of the quasielastic scattering, indicating that the onset temperature of the *fast process* is ~ 120 K, i.e., ~ 50 K below T_g . In Figure 2, the excess quasielastic scattering intensity is plotted against temperature T , confirming that the onset temperature of the *fast process* is ~ 120 K. It should be emphasized that the temperature 120K corresponds to the so-called Vogel-Fulcher temperature T_0 , which is 50 K below T_g for most amorphous polymers. The temperature T_0 is sometimes called as the "ideal" glass transition temperature, i.e., an experimentally inaccessible temperature in the limit of infinitely slow cooling. The value of T_0 is not affected by the time scale of the experiment, whereas the calorimetric glass transition temperature depends on the time scale. Therefore, T_0 is considered to be a fundamental property of the sample. The present result implies that quasielastic neutron scattering can directly detect the temperature T_0 and strongly suggests that the *fast process* is a precursor of the glass transition phenomena.

In order to see the nature of the *fast process*, its characteristic time τ_f was evaluated from the spectral width, which was plotted against the length of the scattering vector Q for 210 and 260K. The characteristic time τ_f of picosecond order was almost independent of Q and T , suggesting that the *fast process* is a localized motion. The activation energy of τ_f evaluated for the melt was ~ 0.5 kcal/mol, which is very small compared with the energy barrier height of the C-C torsional potential (2–3 kcal/mol), indicating that the *fast process* is not related to the conformational transition between rotational isomeric states (trans and gauche). In other words, the atomic groups or segments are trapped within the C-C torsional potential even above the onset temperature of the *fast process*. In this sense, the *fast process* can be called a cage motion. At a very low temperature, such motion must be vibrational but near T_g it is damped by thermal agitations. At the present stage, we conclude that the *fast process* is a damped vibrational motion in the C-C torsional potential well.

In the low energy range of 0.01 meV to 0.2 meV, a

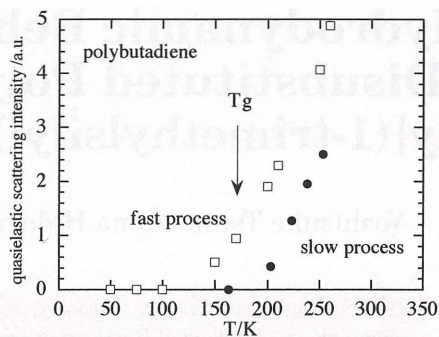


Figure 2. Temperature dependence of quasielastic scattering intensity of the fast and slow processes.

new relaxational motion of 10^{-10} s order appeared as a quasielastic scattering above the glass transition temperature T_g . The motion is termed the *slow process*. The onset temperature of the *slow process* is around the glass transition temperature T_g (see Figure 2). The characteristic time τ_s of the *slow process* depended on T in contrast to the *fast process* and the activation energy was ~ 2.9 kcal/mol. This value corresponds to the C-C torsional potential barrier height, indicating that the *slow process* includes an elementary process for conformational transition between rotational isomeric states such as trans and gauche, which leads to the structural relaxation above T_g . It is emphasized that the *slow process* must be assisted by the damped vibrational motion in the C-C torsional potential well (the *fast process*).

Similar results were obtained for trans-1,4-polychloroprene [6] which has no side groups. On the other hand, polymers with side groups or internal degrees of freedom such as polystyrene [7–9] and polycarbonate [10] show similar *fast processes* of picosecond order far below T_g . In the case of polystyrene, the *fast process* far below T_g has been assigned to phenyl ring motions using a deuterium labeling method [7,9]. Generally, it is rather difficult to distinguish the *fast process* of side groups from that of main chains. At the present stage, therefore, the picture presented here is valid only for polymers without side groups. Further investigations are now in progress.

References

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