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 $4 \times 10^{-10}$ to $4 \times 10^{-13}$ s. It was found that a very fast motion of picosecond order appears at the so-called Vogel-Fulcher temperature $T_F$, 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 finding 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.

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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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The dashed lines in the figure are expected spectra calculated by applying the Bose-Einstein factor to the spectra at 50 K; as seen in the fast process above 100 K, 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.

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, i.e., 50 K below Tg. The onset temperature of the fast process is 120 K and corresponds to the so-called Vogel-Fulcher temperature T0, which is 50 K below Tg for most amorphous polymers. The temperature T0 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 T0 is not affected by the time scale of the experiment, whereas the calorimetric glass transition temperature depends on the time scale. Therefore, T0 is considered to be a fundamental property of the sample. The present result implies that quasielastic neutron scattering can directly detect the temperature T0 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 t_f was evaluated from the spectral width, which was plotted against the length of the scattering vector Q for 210 and 260 K. The characteristic time t_f of picosecond order was almost independent of Q and T, suggesting that the fast process is a localized motion. The activation energy of t_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 Tg 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 new relaxational motion of 10^{-10} s order appeared as a quasielastic scattering above the glass transition temperature Tg. The motion is termed the slow process. The onset temperature of the slow process is around the glass transition temperature Tg (see Figure 2). The characteristic time t_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 Tg. 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-polybutadiene [8] 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 Tg. In the case of polystyrene, the fast process far below Tg has been assigned to phenyl ring motions using a deuteron 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**