Macromol. Symp. **2007**, 249–250, 498–501 DOI: 10.1002/masy.200750426

Motional Coherency in Chain Dynamics of Glass-Forming Polymers

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Summary: Molecular dynamics (MD) simulations of 1,4-polybutadiene in bulk amorphous state were performed. To investigate motional coherency the relaxation rates for the collective and self motions, the collective and self relaxation rates, were evaluated for the short and long time regimes of the normalized intermediate scattering functions. The scattering vector dependence of the collective relaxation rates estimated for both fast and slow processes indicated a minimum at scattering vector $q = 1.3\ \text{Å}^{-1}$, corresponding to the position of a peak in the static structure factor. The self relaxation rates increased monotonously with q. A phenomenon known as de Gennes narrowing was reproduced well in the simulation and found to be originated from the inter-molecular correlation. The details of motional coherency and the distribution functions of relaxation time were evaluated.

Keywords: amorphous; molecular dynamics; motional coherency; polybutadiene; simulations

Introduction

The static and dynamic properties of amorphous polymers at the glass transition have been investigated. As the temperature of the system is approached to the glass transition temperature (T_g), molecules are localized and relaxation times increase by many orders of magnitude indicating a broad distribution. Cooperative motion is one of the keys to understand the dynamical behavior near T_g. However, the future of cooperative motion has not been fully understood. The de Gennes narrowing which is an example of motional coherency has been observed in amorphous materials such as polybutadiene (PB).[1,2] MD simulation is a powerful technique for studying dynamic property at atomic level. In this study, we performed MD simulations of PB molecules in bulk amorphous phase.[3] Motional coherency and distribution functions of relaxation times were investigated by analyzing the intermediate scattering functions.

Method of MD Simulation

All the MD calculations were performed using the Discover3/InsightII 400P (Accelrys Inc.) with the COMPASS force field. All atom models of 4 PB molecules consisting 50 monomer units and their periodic images are contained in a cubic MD cell. The chains are random copolymers of 47% 1,4-*cis*, 46% 1,4-*trans*, and 7% 1,2-vinyl units. The temperature of the system was set at 400 K for the initial equilibration. The density of the system at 400 K was also set at the observed density for the initial state. The temperature was lowered gradually down to 10 K. The equilibration runs at each temperature were performed for at least 2 ns under constant temperature and constant pressure. Temperature was controlled using velocity scaling method and pressure was controlled using Berendsen method.[4] The pressure of the MD system was kept at 0.1

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MPa. The sampling runs at each temperature were carried out under constant temperature and constant volume. The method proposed by Nosé and Hoover [5,6] to control temperature was employed for the sampling runs. The duration of the sampling run was over 10 ns. The time steps for the numerical integration of the Newtonian equation of motion were chosen to be 1 and 0.25 fs for the equilibration runs and the sampling runs, respectively. A cut-off radius of 12 Å for the van der Waals potential and for the electrostatic interactions was used.

Results and Discussion

The value of T_g obtained form MD simulations is 170 K, which is in good agreement with experimental value of 180 K. In order to investigate the static structure of the bulk amorphous phase, the coherent scattering differential cross section $(d\sigma/d\Omega)_{coh}$ is calculated by the Fourier transformation of the radial distribution function. A sharp peak at $q = 1.3$ Å^{-1} and a broad peak at $q = 2.9$ Å^{-1} are observed. The peak of static structure factor at $q = 1.3$ Å^{-1} is attributed to inter-molecular correlation, 2nd peak at $q = 2.9$ Å^{-1} originates from intra-molecular correlations.

Figure 1 shows the normalized collective and self intermediate scattering functions, $I(q,t)/I(q,0)$ and $I_s(q,t)/I_s(q,0)$, for several scattering vectors q at 200 K. The relaxation for $t < 1$ ps was defined as fast process, while the relaxation for $t < 1$ ps was defined as slow process. For $q = 1.26$ and 1.80 Å^{-1}, $I_s(q,t)/I_s(q,0)$ decays faster than $I(q,t)/I(q,0)$. While for $q = 2.20$, 2.92, and 3.40 Å^{-1}, $I_s(q,t)/I_s(q,0)$ and $I(q,t)/I(q,0)$ are almost same. As with previous neutron scattering studies,[2] the overall decay may be described by a two-step function: single exponential function for a fast process and a stretched exponential function for a slow process. The values of normalized intermediate scattering functions in the range of 5 to 500 ps were fitted with the stretched exponential function. While the single exponential function was used to fit normalized intermediate scattering functions in the range of 0.005 to 0.1 ps.

The relaxation rates for collective and self motion, $\Gamma(q)$ and $\Gamma_s(q)$, (or inverse of the relaxation times $\tau(q)^{-1}$) were obtained from the results of fits for the slow processes of $I(q,t)/I(q,0)$ and $I_s(q,t)/I_s(q,0)$, respectively. In Figure 2, the relaxation rates $\Gamma(q)$ and $\Gamma_s(q)$ are compared with the calculated static structure factor $S(q)$ $(=I(q,0))$ at 200 K. It is obvious that the minimum of $\Gamma(q)$ correlates with the peak at 1.3 Å^{-1} observed in $S(q)$, a result which qualitatively could be understood in terms of the so-called de Gennes narrowing. While $\Gamma(q)$ monotonously increases with q in the region observed a peak at 2.9 Å^{-1} in $S(q)$. In order to evaluate the spatial

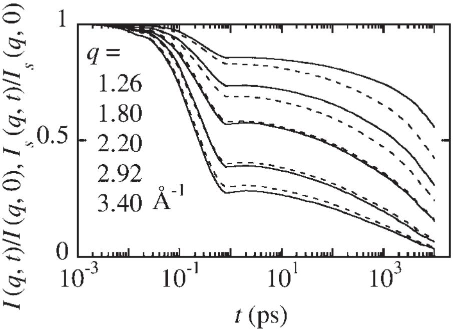

Figure 1.
Normalized intermediate scattering functions, $I(q,t)/I(q,0)$ (solid curves) and $I_s(q,t)/I_s(q,0)$ (broken curves), for several scattering vectors q at 200 K.

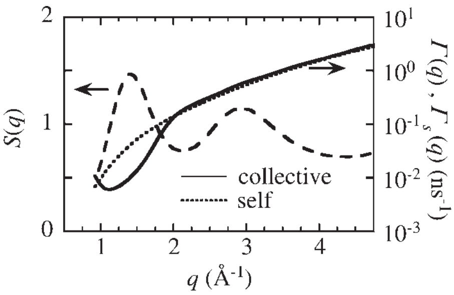

Figure 2.
Comparison between static structure factor (broken line) and collective (solid line) and self (dotted line) relaxation rates.

dependence of the observed $\Gamma(q)$ and $\Gamma_s(q)$ in terms of molecular correlations, the normalized collective and self intermediate scattering functions were separated into the contribution of the intra- and inter-molecular pairs. The results indicate that the minimum of Γ (q) is attributed to intermolecular correlation. The collective and self relaxation rates, $\Gamma^f(q)$ and $\Gamma_s^f(q)$, for fast process were evaluated and compared with $S(q)$. For short time regime ranging from 0.005 ps to 0.1 ps, the collective motion is found to be different form self motion and much sensitive to spatial correlations, inter and intra-molecular correlations.

The normalized collective and self intermediate scattering functions were analyzed with a kind of inverse Laplace transform method.[7] The normalized distribution functions $P(\ln\tau)$ of relaxation times were obtained. Figure 3 shows temperature and scattering vector q dependences of the distribution functions of relaxation times for collective and self motions. At $q = 3.40$ Å^{-1}, the shape of the distribution functions shows almost a single process situation with a short relaxation time at both 250 and 400 K. Comparing between collective and self motions, the shape of the distribution functions is similar at each temperature. While at $q = 1.26$ Å^{-1}, two or three relaxation processes can be identified at each temperature for both collective and self motions. The time range of the distribution functions is broadened to longer relaxation time as temperature decreases. The fraction of the peak at long relaxation time in the distribution functions of the collective relaxation time was larger than that in the distribution functions of the self relaxation time at each temperature.

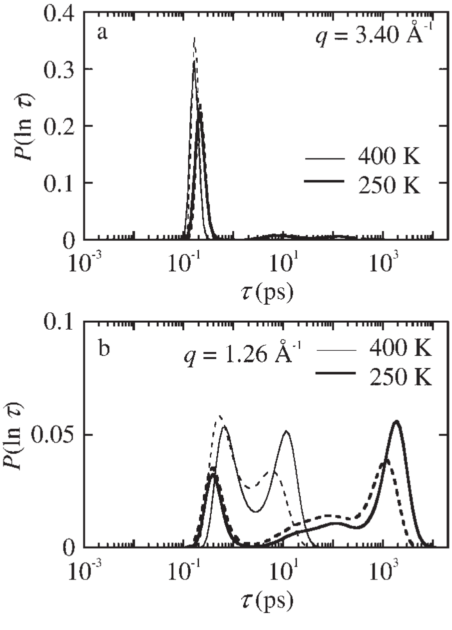

Figure 3.
The distribution functions of the relaxation times obtained from collective (solid curves) and self (dotted curves) intermediate scattering functions at 400 K (thin lines) and 250 K (thick lines) for (a) $q = 3.40$ Å^{-1} and (b) $q = 1.26$ Å^{-1}.

The details of the torsional motion for each dihedral angle were investigated by directly tracing the time evolutions of the dihedral angles for intra- or inter-molecular pairs. Time evolutions of dihedral angles around $CH–CH_2$ bonds for inter-molecular chain pair, ϕ_a and ϕ_b, at 200 K were shown in Figure 4. When the dihedral angle ϕ_a changes from −60° to +60°, the dihedral angle ϕ_b shifts from +60° to −60° cooperatively at the same moment. The distance for two dihedral angles of the intermolecular chain pair was found to remain constant at about 5 Å. When the temperature decreases to the glass transition temperature, PB chains move cooperatively by the inter-chain correlation.

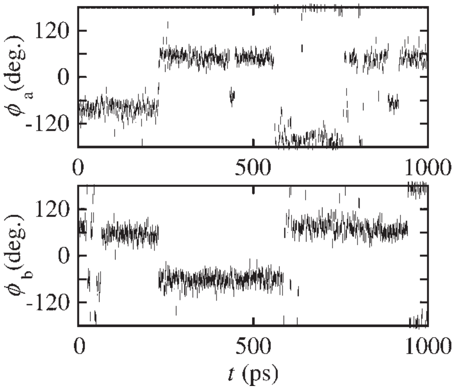

Figure 4.
Time evolutions of the dihedral angles of inter-chain pair, ϕ_a and ϕ_b, at 200 K.

Conclusions

We performed MD simulations of 1,4-polybutadiene in bulk amorphous state. The collective relaxation rates, $\Gamma^{f}(q)$ and $\Gamma(q)$, for both fast and slow relaxation processes pass through minimum at $q = 1.3$ Å^{-1}, corresponding to the position of the peak in the static structure factor, a phenomenon known as de Gennes narrowing. The motional coherency for inter-chain correlation of PB was intensively observed and found to be a key role for the de Gennes narrowing. The collective motion for fast process was slightly affected by intra-chain correlation. The distribution functions of the relaxation time were evaluated by the analysis of the intermediate scattering functions. It was revealed that motional coherency for the long relaxation time at lower q was enhanced on decreasing temperature. The details of the cooperative torsional transitions by inter-molecular correlation were found by the analysis of MD simulations.

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