

Molecular dynamics simulation study of the α - and β -relaxation processes in a realistic model polymer

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(Received 2 November 2004; published 31 May 2005)

Molecular dynamics simulations of a melt of freely rotating chains of 1,4-polybutadiene (FRC-PBD) have been performed over a wide range of temperature. Removal of the dihedral barriers in FRC-PBD allows for complete resolution of the Johari-Goldstein β process from the primary α process in the simulation time window. We find that relaxation in the β regime occurs as the result of large-angle excursions of all backbone dihedrals. While during the β process each dihedral visits all available states, the complete relaxation of torsional autocorrelation function (α process) occurs only when the polymer matrix shows significant motion and each dihedral populates all states with equilibrium probability.

DOI: 10.1103/PhysRevE.71.050801

PACS number(s): 61.41.+e

Despite extensive experimental simulation and theoretical interest and study, the mechanism of the Johari-Goldstein β -relaxation process in amorphous polymers and its relationship to the primary α or glass relaxation remains poorly understood [1,2]. While it is generally agreed that the Johari-Goldstein β process involves local motion of the polymer chain backbone, the nature of these motions, whether they are spatially and temporally homogeneous or heterogeneous, and the relationship between molecular motions responsible for the β and α processes, remain controversial [2]. Ideally, molecular dynamics (MD) simulations are well suited to help elucidate the mechanism of relaxations in polymers. MD simulations utilizing validated potentials have been demonstrated to accurately reproduce the structural and dynamic properties, including relaxation processes, for a wide variety of polymers [3]. Unfortunately, the bifurcation of the α and β processes in polymers typically occurs on a time scale inaccessible to MD simulations. For example, Fig. 1 reveals that the relaxation times for the dielectric α and β processes in 1,4-polybutadiene (1,4-PBD) [4,5] are well resolved only on time scales approaching milliseconds. The same difficulty is faced in dynamic neutron studies, where the length-scale dependence of the dynamics probed by neutrons at different momentum transfers could provide invaluable information into the nature of the β and α relaxations but where time scales are currently limited to submicroseconds.

In order to further resolve the α and β processes in the dynamic range of experimental probes, particularly dielectric spectroscopy and perhaps ultimately dynamic neutron scattering, there has been increasing interest in performing experiments on glass forming liquids under high pressure [6]. Increasing pressure can result in a large shift in the relaxation time of the cooperative α process relative to that of the local β process that is relatively insensitive to pressure. As a result, the bifurcation of the relaxation processes is moved into a shorter time window at a higher temperature. In MD simulations the effect of raising pressure can be mimicked by reducing intramolecular energy barriers for dihedral transitions of the polymer backbone. In such an exercise, the intramolecular energetic effects are reduced while leaving the

intermolecular packing essentially unperturbed, similar to the effect of raising pressure and temperature. Reducing dihedral barriers should therefore move the bifurcation into a shorter time window at lower temperature.

We have performed MD simulations of 1,4-PBD melts using our quantum chemistry based potential [7] (chemically realistic chains, or CRC-PBD) and a freely rotating chain model (FRC-PBD) at temperatures (T) ranging from 500 to 70 K. A detailed description of the CRC-PBD model and extensive comparison of melt simulations with NMR spin-lattice relaxation [8], dynamic neutron scattering [9], and dielectric relaxation [10] measurements can be found in the literature. The FRC-PBD model is described in [11] and is identical to the CRC-PBD model except that the dihedral potential terms have been eliminated, yielding an almost flat conformational energy surface for rotations about individual dihedrals. We have already demonstrated that the FRC-PBD melt has structural properties essentially identical to those obtained using the CRC-PBD model—only dynamic properties are influenced by removal of the dihedral barriers [11].

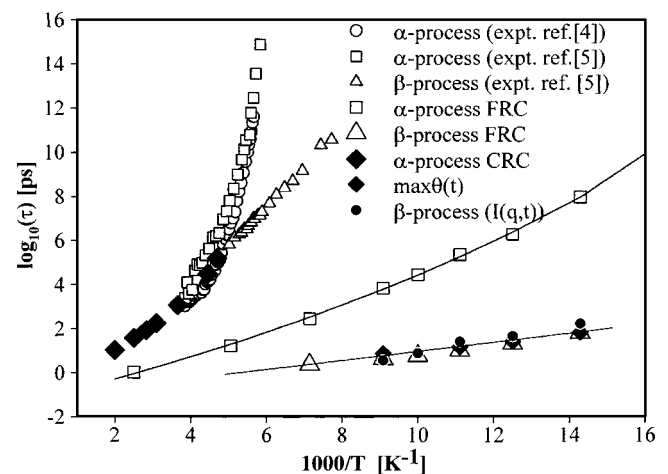


FIG. 1. Relaxation map for 1,4-polybutadiene. The solid lines are a Vogel-Fulcher fit to the α process and an Arrhenius fit to the β process in FRC-PBD.

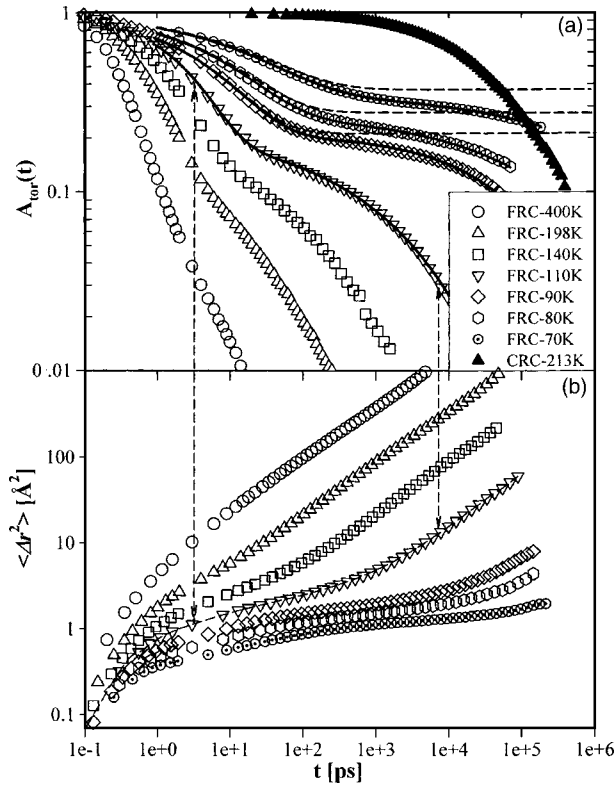


FIG. 2. (a) TACF in FRC-PBD at various temperatures and CRC-PBD at 213 K. The solid lines show the fits to the TACF in the data range where the data were fitted for $T \leq 110$ K. The vertical dash arrows indicate α - and β -processes relaxation times at 110 K. Dash curves show the contribution of the β process to the TACF. (b) Bead mean-square displacement for backbone atoms in FRC-PBD melts at various temperatures.

The torsional autocorrelation (TACF), defined as

$$A_{\text{tor}}(t) = \frac{\langle \theta(t)\theta(0) \rangle - \langle \theta(0) \rangle^2}{\langle \theta(0)^2 \rangle - \langle \theta(0) \rangle^2} \quad (1)$$

was determined for $C(sp^2)-C(sp^3)-C(sp^3)-C(sp^2)$ dihedrals in the CRC-PBD and FRC-PBD melts. For polymers with local dipole moments perpendicular to the chain backbone, such as 1,4-PBD, dielectric relaxation is closely related to the decay of the TACF [10]. The TACF at selected temperatures for the CRC-PBD and FRC-PBD melts is shown in Fig. 2(a). For the FRC-PBD melts a clear two-step decay can be seen in the TACF with decreasing temperature, while no such effect can be seen in the CRC-PBD melts even at the lowest temperatures simulated (213 K). At temperatures of 110 K and below it was possible to clearly resolve two relaxation processes in the FRC-PBD melts, and the TACF was fitted with

$$A_{\text{tor}}(t) = A_1 \exp\left[-\left(\frac{t}{\tau_1}\right)^{\beta_1}\right] + A_2 \exp\left[-\left(\frac{t}{\tau_2}\right)^{\beta_2}\right], \quad (2)$$

where $A_1 + A_2 \leq 1.0$. All data for $t > 1$ ps was utilized in the fit with weighting inversely proportional to the value of the TACF. At higher temperatures where the two processes significantly overlap, fitting with Eq. (2) became unsatisfactory.

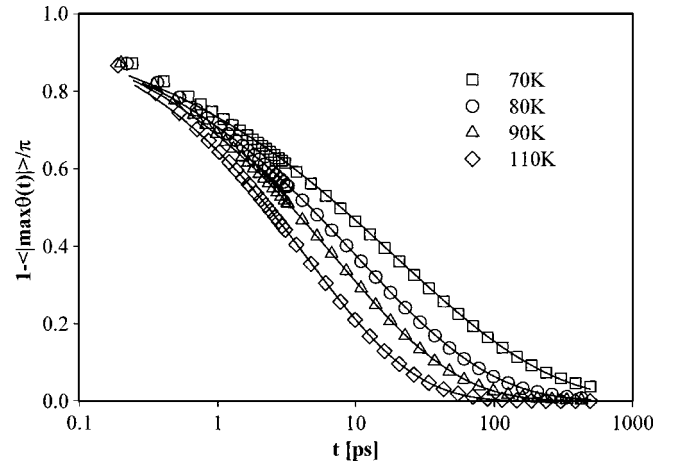


FIG. 3. Maximum angle excursion of the $C(sp^2)-C(sp^3)-C(sp^3)-C(sp^2)$ dihedrals in the FRC-PBD melts. The solid lines show fits using Eq. (3).

Therefore, for $T > 110$ K for the FRC-PBD melts and for all temperatures for the CRC-PBD melts where only one process is observed, we utilized

$$A_{\text{tor}}(t) = A_2 \exp\left[-\left(\frac{t}{\tau_2}\right)^{\beta_2}\right], \quad (3)$$

and fitted only the terminal relaxation (α process) ignoring times shorter than the final inflection point in the TACF.

Relaxation times for the nonbifurcated process in the CRC-PBD melt and α and β processes in the FRC-PBD melt, shown in Fig. 1, were determined from the time integral of the respective relaxation functions given in Eqs. (2) and (3). In FRC-PBD, the α relaxation times exhibit clear non-Arrhenius temperature dependence, while the relaxation times for the β process exhibit Arrhenius temperature dependence over the temperature range in which the process is resolvable, consistent with experimentally observed dielectric relaxations in 1,4-PBD [5].

In order to understand better mechanistically what leads to the β relaxation in FRC-PBD we calculated the maximum angular excursion $|\max \theta_i(t)|$ for each $C(sp^2)-C(sp^3)-C(sp^3)-C(sp^2)$ dihedral after time t and determined the average of this quantity over all dihedrals as a function of time. In Fig. 3 we show the decay of $1 - \langle |\max \theta(t)| \rangle / \pi$, illustrating the time evolution of the average maximum dihedral excursion. Fitting this excursion function with a stretched exponential, as illustrated in Fig. 3, provided us relaxation times that are also shown in Fig. 1. A clear correspondence between the time scales of large-angle conformational excursions and the β relaxation in FRC-PBD can be seen. What is also clear is that these large-angle excursions alone are not sufficient to result in the complete decay of the TACF, as shown in Fig. 2(a), where the contribution of the β process to the decay of the TACF is shown. The magnitude of the β process decreases with decreasing temperature, consistent with experimental observations of main-chain subglass relaxations [12]. Hence large-angle excursions, which are exhibited by *all* dihedrals thereby indicating a spatially

homogeneous process, become increasingly less effective in relaxing the TACF with decreasing temperature, resulting in a decrease in the magnitude of the β process and a corresponding increase in magnitude of the α process.

The final decay of the TACF, associated with the α relaxation, occurs on increasingly long time scales compared with that for the large-scale dihedral excursions (β process) with decreasing temperature, as illustrated in Fig. 1. The TACF can only completely decay, and hence complete polymer relaxation can only occur, when *each* dihedral populates *all* angles with equilibrium probability. A dihedral simply visiting all angles is not sufficient to equilibrate the population of that dihedral. Since this equilibration occurs at a much longer time scale than exploration of dihedral space by individual dihedrals (the β process), we can associate it with a memory effect imposed on the conformations of a chain by the surrounding matrix. If this is the case, we would expect to see a correspondence between the α process and the motion of the matrix indicative of an intermolecularly cooperative process, while the β process would be able to occur without significant matrix motion (initial relaxation due to dihedral excursions), indicative of a local process. This correspondence is illustrated in Fig. 2(b) where the mean-square displacement $\langle \Delta r^2 \rangle$ of the backbone atoms is shown for FRC-PBD melts at various temperatures. The β relaxation occurs on a time scale when polymer backbone motion is still restricted within the nearest-neighbor packing cage formed by neighboring chains [3], i.e., about 20% of the nearest-neighbor packing distance of 5 Å. The terminal relaxation of the TACF occurs only when the magnitude of the backbone motion is much greater, necessitating cooperative motion of neighboring chains.

Finally, in Fig. 4 we show the incoherent structure factor $I(q,t)$ for FRC-PBD at $q=2.7 \text{ \AA}^{-1}$ corresponding to the position of the second peak in the static structure factor of 1,4-PBD [13]. This peak is entirely intramolecular in origin [13] and we can anticipate motions on this scale are sensitive to local polymer (i.e., conformational) dynamics. At high temperatures, a featureless one-step relaxation of $I(q,t)$ is observed. However for $T < 110 \text{ K}$ a three-step decay is clearly observed in $I(q,t)$, where the first-step relaxation is due to torsional librations that occur on a time scale of around 1 ps and independent of temperature. The second and third steps in the decay of $I(q,t)$ at low temperatures are very similar in nature to the relaxation of TACF [Fig. 2(a)] and can be associated with the β and α processes, respectively. Fitting data for $t > 1 \text{ ps}$ with Eq. (2) yields the fits that are also shown in Fig. 4. The integrated relaxation time for the β process from $I(q,t)$ is compared with that obtained from the TACF in Fig. 1. A very close correspondence of relaxation times and their temperature dependence can be seen, indicat-

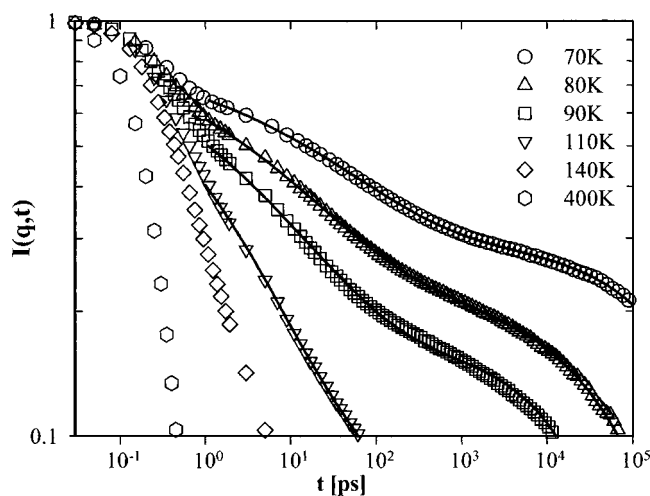


FIG. 4. Incoherent dynamic structure factor $I(q,t)$ at $q = 2.7 \text{ \AA}^{-1}$ for the FRC-PBD melt at various temperatures. The solid lines show fits using Eq. (2).

ing that the mechanism leading to the β process as observed in the TACF (large-angle excursions of backbone dihedrals) is also responsible for the β process observed in $I(q,t)$ at this q value. This is in contrast to a neutron scattering and dielectric relaxation study of 1,4-PBD [14], where the two orders of magnitude difference in the time scales of the β process obtained from these measurements was reported. Recently, we showed [15] that the relaxation time reported from neutron scattering was an artifact of the limited dynamic range of the experimental data.

In summary, we have observed a split of the α and β relaxations in MD simulations of a realistic polymer melt without dihedral barriers (FRC-PBD) in both the TACF, which corresponds to dielectric relaxation, and in $I(q,t)$. The elimination of dihedral barriers shifts the bifurcation of the α and β processes into the time window accessible to conventional MD simulations. Detailed mechanistic analysis of the β process indicates that the β relaxation occurs through large-angle excursions of *all* dihedral angles consistent with a spatially uniform picture of the β relaxation. However, these large-angle reorientations are biased by memory effects imposed by the surrounding matrix and cannot provide equilibrium sampling of conformational space. Therefore, the complete relaxation of dihedrals only occurs when cooperative intermolecular motion results in matrix relaxation (α process).

The authors would like to acknowledge support from the National Science Foundation through Grant No. ITR-CHE0312226

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