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Secondary Johari–Goldstein relaxation in linear polymer melts represented by a simple bead-necklace model

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ABSTRACT

Molecular dynamics simulations of linear polymer melts represented using simple bead-necklace models showed for the first time a distinct separation between primary α- and secondary Johari–Goldstein β-processes. The split is observed only for models where the bead diameter is much larger than the bond length connecting the beads. The overlap of neighboring (along the chain) beads results in a mismatch between local intramolecular correlations and intermolecular packing (cage size), which leads to two processes in segmental relaxation characterized by torsional autocorrelation function. The observed β-process shows all characteristics and correlations expected for the true Johari–Goldstein process.

1. Introduction

The mechanism(s) of the Johari–Goldstein (JG) secondary relaxation processes (also known as β-relaxation) in amorphous polymers and its relationship to the primary α- or glass relaxation remain a topic of ongoing research and discussions [1,2]. While it is generally agreed that in linear chains the JG 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] and a subject of ongoing research [3]. Ideally, molecular dynamics (MD) simulations are well suited to help elucidate the mechanism(s) of relaxations in polymers. However, the bifurcation of the α- and β-processes in polymers typically occurs on time scales inaccessible to MD simulations using chemically realistic, atomistically detailed models or force fields. For example, the relaxation times for the α- and β-processes in 1,4-polybutadiene (PBD) measured by dielectric relaxation are well resolved only on time scales approaching milliseconds [4,5]. Clearly accessing such times using brute force MD simulations and chemically realistic models is impractical.

Nevertheless, in our recent works [6–8] we demonstrated that reduction or elimination of dihedral barriers in PBD significantly reduces glass transition of this polymer and promotes the separation between α- and β-relaxations allowing the observation of two well-separated relaxations on time scales accessible to MD simulations (less than a microsecond). Extensive simulations of melts [6–8] and blends [8–10] comprised of PBD chains with reduced dihedral barriers allowed us for the first time to use MD simulations to systematically investigate the mechanisms of the β-relaxation and its correlation with the α-relaxation as a function of thermodynamic conditions. While these works provided a great insight into understanding of secondary relaxations it is hard to determine which of the observed mechanisms/correlations are a generic characteristic of the β-relaxation and which are specific for the investigated polymer. Despite the fact that in those works we used a united atom model (a single bead representing CH_3, CH_2, or CH groups) all other details of the chemical realistic PBD were preserved to allow an accurate representation of structural and conformational properties of PBD melts. For example, the chains were comprised of two types of beads with different diameters ($\sigma = 4.0$ and 3.4 Å), two different bond types, five types of bends, and eleven dihedral types. Each chain itself was a random sequence of *trans* and *cis* units with 10% of the units containing a vynil group to prevent crystallization. Therefore the structure of investigated PBD chains contained multiple intramolecular structural and conformational mismatches, all of which could be responsible for defining the JG relaxation observed in those systems.

To obtain a more universal and generic understanding of the β-relaxation and its correlation with the α-relaxation, simulations using simpler, more generic polymer models that do not contain chemical specificity are desirable. An excellent example of such models are the well known bead-spring or bead-necklace polymer models where polymer chains are represented as a collection of beads each representing a monomer or a statistical segment. Molecular simulations using these polymer models have been extremely useful in providing molecular level insight in a broad range of polymer physics areas as well as establishment of correlations between various physical, structural, dynamical and mechanical properties for a variety of polymeric systems (see e.g. ref. [11] and references therein). Molecular simulations using such models are several orders of

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magnitude faster than those with atomistically detailed models and therefore have been extensively used to sample dynamic relaxations in polymeric systems [11,12]. While MD simulations with bead-necklace models have been extensively used to understand chain and segmental relaxations for many polymeric systems near the glass transition, none of those simulations has reported an observation of a secondary relaxation process in linear polymer melts. This raises a fundamental question whether simple bead-necklace models, in principle, can possess enough structural or conformational characteristics that would allow them to show both α- and the JG β-segmental relaxations. In this work we address this problem and demonstrate that polymer melts comprised of simple bead-necklace chains can show two distinct relaxations, one of which possesses all known characteristics of the JG secondary relaxation.

2. Model description and simulation details

Taking into account the successful observation of distinct α- and β-relaxations in our previous simulations of PBD chains with reduced dihedrals, we focus our investigation on a coarse-grained model with parameters that are similar to those used for PBD. In our bead-necklace model polymer chains are represented by a collection of identical beads interacting via Lennard–Jones (LJ) potential with $\sigma = 4.0$ Å and $\varepsilon = 0.0959$ kcal/mol. These parameters are similar to those used to describe CH_3 groups in PBD as well as other realistic polymers using a united atom representation. This specific choice of σ and ε was done purely for convenience of comparing the results for the bead-necklace model with previous PBD simulations as well as helping to identify the range of thermodynamic conditions where the potential separation of α- and β-relaxations can be expected. The beads were connected by rigid (constrained) bonds of the same length *l*. Systems with different *l* have been investigated, ranging from $l = 1.4$ Å, therefore allowing a σ/l ratio of 2.85 which is similar to the corresponding value in PBD and other realistic polymers, to $l = 4.0$ Å ($\sigma/l = 1.0$) which corresponds to a typical coarse-grained representation of polymer chains. In order to minimize contamination of the short time dynamics by the high frequency modes created by intramolecular interactions of close neighbors, the LJ interactions between atoms separated by three bonds or less were excluded. However, to preclude the complete overlap of close neighbors we also introduced bends all of which were kept rigid at 120°. No dihedral potentials were applied. Therefore, the selected bead-necklace model has a very simplistic representation of the polymer (compared to e.g. united atom model of PBD) and consists of one type of beads, bonds, and bends as illustrated in Fig. 1 for the two limiting cases $\sigma/l = 2.85$ and 1.0.

All systems contained 100 chains and each chain was comprised of 76 beads. Simulations of polymer melts were performed using an NPT ensemble at specified temperatures and pressures. A time step of 1.0 or 2.0 fs (corresponding to 0.0004 or 0.0008 in reduced time units defined as $(\varepsilon/m\sigma^2)^{1/2}t$) was used depending on the temperature. Equilibration runs over 5 ns were followed by production runs with total trajectory length ranging from 40 to 300 ns (or from 16,000 to 120,000 in reduced units). A cutoff radius of 10.0 Å (2.5σ) was used for truncation of the LJ interactions. Bonds and bends were constrained using the velocity-Verlet form of the SHAKE algorithm [13].

In this work the segmental dynamics/relaxations have been characterized by torsional autocorrelation function (TACF):

$$TACF(t) = \frac{\langle|\theta(t)||\theta(0)|\rangle - \langle|\theta(0)|\rangle^2}{\langle|\theta(0)|^2\rangle - \langle|\theta(0)|\rangle^2} \tag{1}$$

Here $|\theta(t)|$ is the (absolute) value [14] of the conformational angle for a given dihedral at time *t* and the ensemble average is taken over all dihedrals. The TACF decays as backbone dihedrals explore conformational space through conformational transitions. We have shown previously that the decay of the TACF in PBD closely reflects segmental relaxation as probed by dynamic neutron scattering [15,16], NMR T_1 relaxation [17], and dielectric relaxations [18]. We also showed that in simulations of freely-rotated and lower-barrier PBD, where a clear separation of α- and β-relaxations has been observed, the corresponding relaxation times for these processes obtained from TACF, dipole moment autocorrelation function, and incoherent dynamic structure factor were very similar [6–8]; further illustrating that the TACF is a representative characteristic of segmental relaxation in polymeric systems.

We fit the TACF with a single relaxation process or a sum of two processes, labeled β (short-time) and α (long-time) using

$$TACF(t) = A_\beta f_\beta(t) + A_\alpha f_\alpha(t) \tag{2}$$

Here $f_\alpha(t)$ and $f_\beta(t)$ are functions representing the α- and β-relaxations, respectively, while A_α and A_β are amplitudes of these processes with the constraint $A_\alpha + A_\beta \leq 1.0$. We assume that the contribution of each relaxation process to the (partial) decay of TACF, resulting from segmental motion associated with the relaxation process, can be represented by the Kohlrausch–Williams–Watts (KWW) function [19,20]

$$f_i(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \tag{3}$$

where τ is an apparent relaxation parameter and β is a stretching exponent. When fitting with a single relaxation process we set $A_\beta = 0$ Relaxation times for the α-relaxation (τ_α) and β-relaxation (τ_β) processes were determined from the time integral of the corresponding relaxation function ($f_\alpha(t)$ and $f_\beta(t)$) obtained from fitting. Temperature dependences of τ_α and τ_β were described by either a Vogel–Fulcher dependence [21,22]

$$\ln[\tau_i(T)] = C_1 + \frac{C_2}{T - T_0} \tag{4}$$

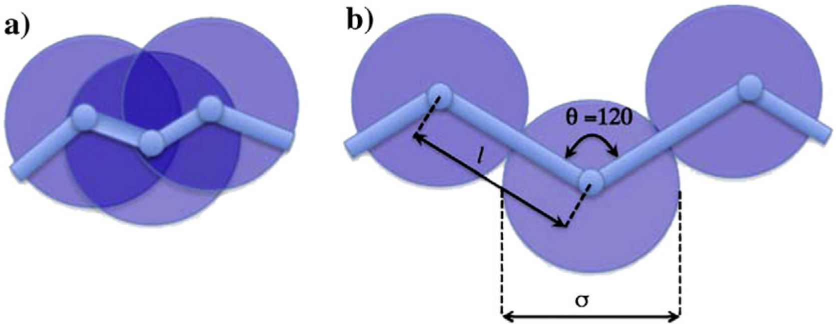

Fig. 1. Schematic representation of the bead-necklace model used in this work a) $\sigma/l = 2.85$, and b) $\sigma/l = 1.0$.