Short length-scale dynamics of polyisobutylene by molecular dynamics simulations

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Abstract

In this work we have performed fully atomistic MD simulations of bulk polyisobutylene (PIB), in order to extract detailed information on the relaxational mechanisms from short length-scale motions. Investigation of dynamics in terms of local reorientational correlation functions, dynamic structure factor, and calculation of relevant conformational jump rates, enable a direct comparison between observables of different experimental techniques such as NMR and neutron scattering. Moreover, the use of a full-atom model allows for a comparison between main-chain and side-group (methyl) dynamics.

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1. Introduction

Polyisobutylene (PIB) has long been attracting technological and scientific interest, due to its unusual physical properties among the linear chain polymers. Despite the steric hindrance by the methyl side groups, it exhibits a remarkably low glass transition temperature ($\approx$ 200 K) resulting in low cost processability, which when combined with its high packing efficiency and its low gas permeability, readily justifies the industrial interest and provides a strong motivation for a fundamental understanding of this behaviour.

A large number of experimental studies over the years, invoking rheological measurements [1] and a variety of spectroscopic techniques [2–14] have greatly contributed toward this purpose. On the other hand, modelling efforts for PIB utilizing energy minimization methods [15], rotational isomeric state (RIS) calculations [16], Monte Carlo[17,18] and molecular dynamics simulations [19,20], have provided valuable information (usually not accessible to experiment) on the energetics and the conformational characteristics of PIB. In this study, by adopting the more realistic approach of a full atomistic description, we aim to explore not only static/conformational features but also to perform a detailed analysis of the PIB dynamics. In the following, we present results related to short length-scale motions, in terms of dynamic observables linked to NMR and Neutron scattering experiments.

2. Simulation details

The system examined was comprised by 5 chains of 25 monomer units each. After the generation of

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Table 1

<table>
<thead>
<tr>
<th>Energy functions</th>
<th>Bond lengths</th>
<th>Bond angles</th>
<th>Torsional angles</th>
<th>Non-bonded interactions (Local: 1–4)</th>
<th>Non-bonded interactions (Non-local)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed</td>
<td>E(θ) = 1/2k_{θ}(θ - θ_0)^2</td>
<td>E(φ) = 1/2k_{φ}(1 - cos3φ)</td>
<td>E_{ij}(d) = x_{ij}/d^{12} - b_{ij}/d^6</td>
<td>E_{ij}(d) = Ae^{-r_{ij}/ρ} - C/r_{ij}^{12}</td>
<td></td>
</tr>
</tbody>
</table>

the starting configuration and the initial equilibration by a Monte Carlo procedure (see Ref. [21] for more details), the atomistic force field was switched on and 1 ns of additional equilibration under conditions of constant temperature and pressure (NPT ensemble) allowed the system to accommodate the local scale conformational changes due to the introduction of the force field. Subsequently, production runs of 1–2 ns in the constant energy and volume (NVE) ensemble were generated\(^1\) utilizing a time-step of 1 fs, with configurations being stored every 0.5 ps. Following this procedure, trajectories at 4 temperatures (300, 388, 446, 496 K) well above the experimental glass transition temperature were obtained.

Force field parameters controlling the local (up to 3 bonds apart) interactions were adapted from previous Monte Carlo simulational efforts, where it was shown that the resulting local structure of PIB was in good agreement with experiments [18]. Intra-molecular non-local (more than 3 bonds apart) and inter-molecular non-bonded interaction parameters, were derived from earlier studies of hydrocarbon polymers [23,24]. Tables 1 and 2 list the set of parameters used. The potential parameterization adopted, yielded a satisfactory prediction of the volumetric properties of PIB [25] as shown in Fig. 1.

3. Statics

Although a detailed account of the static behaviour of the examined model will be presented elsewhere [26], we quote here some characteristic features of the conformational state of the system. Fig. 2a shows the distribution of skeletal angles for the central portion of the chains at \( T = 496 \) K. In harmony with previous computational and experimental studies (see Refs. [18,19] and references therein), the methine-centered angle assumes a broader distribution and prefers a value close to the tetrahedral one, while the most probable methylene-centered angle is approximately 126° as a result of the methyl–methyl interactions. At the same temperature, probability distribution (symmetrized) of central backbone dihedrals is depicted in Fig. 2b. The splitting of the rotational isomer (trans) at 180° and the indication of two (though not well separated) gauche states located approximately at a 120° shift from the trans, is in close agreement with earlier RIS [16] and numerical energy minimization calculations [15], as well as with previous simulations in other PIB models [18,19].

4. Dynamics

In order to facilitate comparison with NMR experiments, local reorientational dynamics were probed by means of the following second order Legendre polynomial order parameter:

\[
\langle P_2(\hat{h}(t) \cdot \hat{h}(0)) \rangle = \frac{1}{2} [6 \langle \cos^2 \theta(t) \rangle - 1] \tag{1}
\]

(henceforth, referred to as \( P_2(t) \)) where \( \hat{h} \) represents a unit vector along the selected bond species (i.e. methylene or methine C–H bond). Calculation of the dynamic incoherent structure factor of \( N \) hydrogen atoms (in the isotropically averaged form)

\[
S(q, t) = \frac{1}{\sqrt{N}} \left( \sum_{t=1}^{N} \sin(q\Delta r(t)) \right) \tag{2}
\]

was used for a direct connection to neutron scattering experiments. In Eq. (2) \( q \) is the magnitude of the scattering vector and \( \Delta r(t) = || \vec{r}(0) - \vec{r}(t) || \) is the magnitude of the displacement of the relevant (skeletal or methyl) hydrogen atom.

Single bond gauche to trans jumps were monitored by evaluation of the transition rates between the relevant potential wells (see Fig. 2b). Methyl...
rotational jumps were found to be driven by a three-fold potential, offering support to this commonly invoked assumption in modelling methyl dynamics [27]. Fig. 3 depicts the activation map for the transition rates (per ps per dihedral) between the trans–gauche states as well as the methyl jumps. In the same plot NMR relaxation times describing backbone dynamics ($\tau_1$) for bulk PIB extracted from fits to the DLM model [7] are shown for comparison. Although simulation transition rates appear slower than the $\tau_1$ data, they seem to follow a similar temperature dependence implying a common underlying motional mechanism. The barrier height $E^*$ for the trans–

<table>
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<th>Table 2</th>
<th>Geometry and energy parameters</th>
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<tr>
<td>Bond type</td>
<td>Bond length (Å)</td>
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<tr>
<td>C–C</td>
<td>1.53</td>
</tr>
<tr>
<td>C–H</td>
<td>1.10</td>
</tr>
<tr>
<td>Bond Angle</td>
<td>$10^3 k_o/(\text{kcal/Å}^2/\text{mol})$</td>
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<tr>
<td>C–C–C</td>
<td>115.3</td>
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<tr>
<td>C–C–H</td>
<td>87.8</td>
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<tr>
<td>H–C–H</td>
<td>73.2</td>
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<tr>
<td>Interacting pair (local)</td>
<td>$10^{-7} z_{ij}/(\text{kcal/Å}^{12}/\text{mol})$</td>
</tr>
<tr>
<td>C, C</td>
<td>398.3</td>
</tr>
<tr>
<td>C, H</td>
<td>56.8</td>
</tr>
<tr>
<td>H, H</td>
<td>7.3</td>
</tr>
<tr>
<td>Interacting pair (non-local)</td>
<td>$A/(\text{kcal/mol})$</td>
</tr>
<tr>
<td>C, C</td>
<td>61861.09</td>
</tr>
<tr>
<td>C, H</td>
<td>10986.91</td>
</tr>
<tr>
<td>H, H</td>
<td>2627.30</td>
</tr>
</tbody>
</table>

Fig. 1. Temperature dependence of the specific volume as calculated by our model (■). The solid line denotes the experimental behaviour as found by Eichinger and Flory [25].

Fig. 2. $T = 496$ K. (a) distributions of the backbone angles; (b) distribution of the skeletal dihedral angles.
gauche conformational jumps as evaluated from the effective dihedral potential is $5.1 \pm 0.1$ kcal/mol in the examined temperature range. This value can be compared to $E^* \approx 5$ kcal/mol estimated by NMR measurements of PIB in solution [7], as well as to theoretical predictions [15] yielding $E^* \approx 4.5$ kcal/mol at $T = 400$ K, and to the rotational barrier of $E^* \approx 4.4$ kcal/mol about the CH$_3$–C(CH$_3$)$_3$ bond in 2,2-dimethylpentane as determined from infrared spectroscopy [28]. Calculation of the apparent activation energy from the slope of Fig. 3 yields a value of $E = 7.4 \pm 0.3$ kcal/mol consistent to NMR measurements [7,10], where analysis in the context of various models concluded that $E$ lied between 6.9 and 8.6 kcal/mol in a temperature range partially overlapping the one examined in this work.

The methyl rotational motion is described by an activation energy of $3.5 \pm 0.1$ kcal/mol, in close agreement with an estimation of $3.4$ kcal/mol for methyl dynamics in atactic polypropylene from recent QENS measurements in the sub-$T_g$ regime [29]. The weaker temperature dependence of the methyl jump rates will be discussed in detail in a forthcoming publication [26].

Fig. 4 shows $P_2$ auto-correlation functions for the backbone (solid lines) and the methyl (dotted lines) C–H bonds. Comparison of average relaxation times defined as $\tau_{av} = \int_0^\infty P_2(t) \, dt$, between backbone and methyl dynamics at the higher temperatures where decorrelation has advanced more, shows that methyl reorientation is at least one order of magnitude faster. Collating $P_2$ average times for backbone motion from simulations and from NMR (based on the functional form of the DLM model and the measured $\tau_1$ temperature dependence), indicates that the simulation times are approximately only a factor of 3 slower.

The dynamic behaviour as probed by $S(q, t)$ for the backbone and the methyl hydrogens, is presented in Figs. 5 and 6. The $q$ dependence of the dynamic structure factor at a constant temperature ($T = 496$ K) is shown in Fig. 5 for three different scattering vectors. An attempt to fit the data using a single exponential decay at short times (accounting for fast librational motions) and one stretched exponential function ($f(t) \propto e^{-(t/\tau)^\beta}$) was not successful, indicating that the scattering spectra is composed by multiple relaxation processes. These motional mechanisms appear to follow different $q$-dependencies, since a simple shift of the time axes (either between the scattering curves referring to methyl, or to backbone hydro-

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2The long time tail was fitted by a single exponential.
gens) does not collapse the data onto corresponding q-mastercurves.

Fig. 6 depicts \( S(q, t) \) as a function of temperature at a constant scattering vector \( (q = 0.95 \text{ Å}^{-1}) \). The observed temperature dependence of the structure factor bears a direct analogy to the corresponding \( P_2(t) \) behaviour. In an effort to investigate to which extent NMR and scattering experiments can probe dynamics on a similar time and/or length-scale we compared the \( P_2(t) \) and \( S(q, t) \) spectra for all the examined scattering vectors. It was found that at all temperatures, both skeletal and methyl C–H reorientation \( P_2(t) \) curves, were closely reproduced by the respective dynamic structure factor at \( q = 0.95 \text{ Å}^{-1} \). This occurrence is illustrated in the inset of Fig. 6. An immediate consequence of this observation is that for PIB a characteristic length-scale (~ \( 2\pi/q \)) on which local reorientation is realized, can be roughly estimated as \( 6 - 7 \text{ Å} \). In the context of this prediction, direct comparison between neutron scattering and NMR experiments is in order.

We finally proceed to examine the applicability of the time-temperature superposition (TTS) for our model. Rheological experiments \([1]\) revealed that PIB is a thermo-rheologically simple polymer. The temperature dependence of the shift factors extracted from rheology (expressed by a Williams–Landel–Ferry law (WLF))

\[
\log[\tau_f(T)] = - \frac{9.08(T - 298.2)}{209 + T - 298.2} \tag{3}
\]

were shown to apply to local PIB dynamics \([11]\). Fig. 7 shows the \( P_2(t) \) curves in the examined temperature range shifted in order to superpose. In inset (a) the temperature dependence of the extracted shift factors is compared to the dependence of the rheological shift factors \([1]\) and to the behaviour of the NMR \( \tau_1 \) correlation times. As evidenced, the simulation shift factors follow the same dependence as from rheology. The same shift factors can be applied to the \( S(q, t) \) as shown in inset (b) for \( q = 0.95 \text{ Å}^{-1} \). Superposition remains satisfactory for all the examined \( q \) values. The discrepancy between the \( \tau_1 \) and the rheological shift factors’ behaviour, explicitly pointed out by the authors of Ref. \([7]\), seems to be an exceptional case which was interpreted by suggesting that in PIB NMR does not probe exactly the same motional mechanism responsible for the glass transition phenomena. In order to resolve this issue we are currently performing a detailed analysis of the simulation data, planned to be extended to a broader temperature range.
5. Conclusions

In this paper, we presented molecular dynamics simulation results of local scale dynamics in a PIB melt, using a fully atomistic model. The static picture is in agreement with previous simulation studies and experimental results. Short-scale motion was probed by means of local reorientational functions $P_2(t)$ and the incoherent structure factor, describing both backbone and methyl dynamics. Energetic parameters characterizing conformational changes related to skeletal or side group (methyl) motions, are found (within the error) to comply with NMR and other spectroscopic results. Quantitative comparison of average relaxation times associated with backbone motion to NMR based average times, results in a reasonable agreement within a factor of 3 (the simulation times being slower). Combining information from $P_2$ reorientational functions and incoherent dynamic structure factors, it was possible to find a close correspondence of the observed dynamics at $q \approx 1 \text{ Å}^{-1}$, setting therefore a characteristic spatial scale for the realization of local (backbone) motion. Although detailed analysis was not performed at this stage, there were clear indications that the observed spectra were composed by multiple relaxation processes. Identification and analysis of these motional mechanisms, both in a qualitative and quantitative manner, is under progress. Independently though of any different temperature or $q$ dependence among the individual processes, the average dynamic behaviour (as can be represented by a shift of the spectra as a whole) is found to follow the temperature dependence of the rheological measurements rather, than the NMR extracted $\tau_1$ dependence.

In general lines, the level of agreement of our model with experimental findings is particularly encouraging, and motivates us to proceed with a thorough investigation of the motional mechanisms related to the intriguing behaviour of PIB.

Acknowledgements

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