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. © 2001 Published by Elsevier Science B.V.

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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 ($\simeq 200$ 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

Table 1
Energy functions

Bond lengths	Fixed
Bond angles	$E(\theta) = 1/2k_\theta(\theta - \theta_0)^2$
Torsional angles	$E(\phi) = 1/2k_\phi(1 - \cos 3\phi)$
Non-bonded interactions (Local: 1–4)	$E_{ij}(d) = \alpha_{ij}/d^{12} - b_{ij}/d^6$
Non-bonded interactions (Non-local)	$E_{ij}(d) = Ae^{-r_{ij}/\rho} - C/r_{ij}^6$

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

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[1] The MD runs were performed using **DL_POLY**, the molecular dynamics package developed at Daresbury laboratory (See Ref. [22]).

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:

$$\langle P_2(\hat{h}(t) \cdot \hat{h}(0)) \rangle = \frac{1}{2}[3\langle \cos^2 \vartheta(t) \rangle - 1] \quad (1)$$

(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)

$$S(q,t) = \left\langle \sum_{i=1}^{N} \frac{\sin(q\Delta r_i(t))}{q\Delta r_i(t)} \right\rangle \quad (2)$$

was used for a direct connection to neutron scattering experiments. In Eq. (2) q is the magnitude of the scattering vector and $\Delta r_i(t) = \| \vec{r}_i(0) - \vec{r}_i(t) \|$ 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

Table 2
Geometry and energy parameters

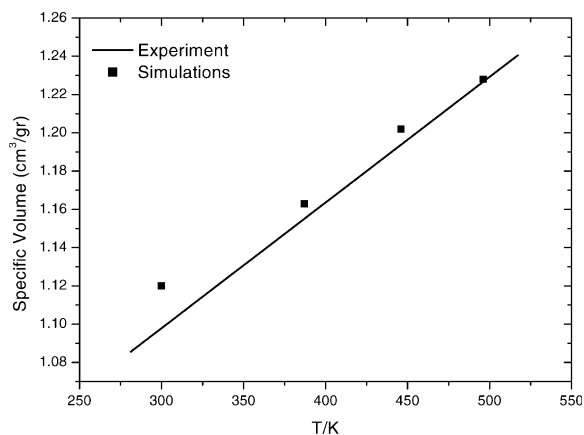| Bond type	Bond length (Å)		Torsional barrier (kcal/mol)
C–C	1.53		2.8 (overall)
C–H	1.10		
Bond Angle	$10^3 k_\theta/(kcal/rad^2/mol)$		θ_0/deg
C–C–C	115.3		111
C–C–H	87.8		109.5
H–C–H	73.2		107.9
Interacting pair (local)	$10^{-3}\alpha_{ij}/(kcal/Å^{12}/mol)$		$b_{ij}/(kcal\ Å^6/mol)$
C, C	398.3		366.0
C, H	56.8		127.9
H, H	7.3		47.1
Interacting pair (non-local)	$A/(kcal/mol)$	$\rho/Å$	$C/(kcal\ Å^6/mol)$
C, C	61861.09	0.277	504.68
C, H	10986.91	0.272	128.02
H, H	2627.30	0.267	32.24

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.

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 (τ_1) for bulk PIB extracted from fits to the DLM model [7] are shown for comparison. Alth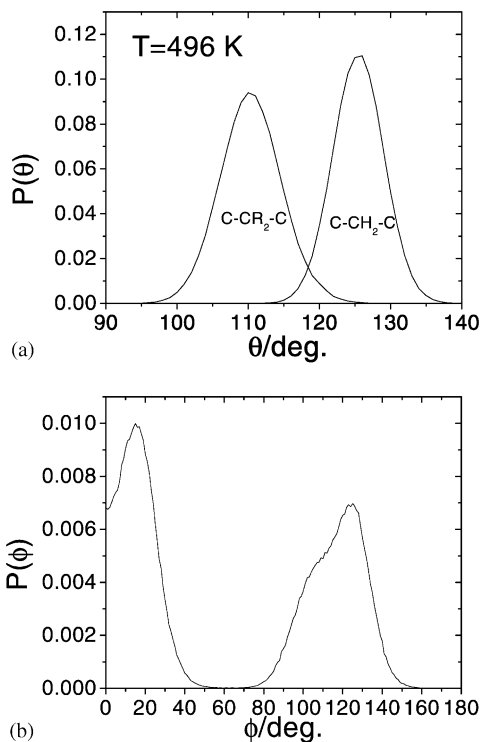ough simulation transition rates appear slower than the τ_1 data, they seem to follow a similar temperature dependence implying a common underlying motional mechanism. The barrier height E^* for the trans–
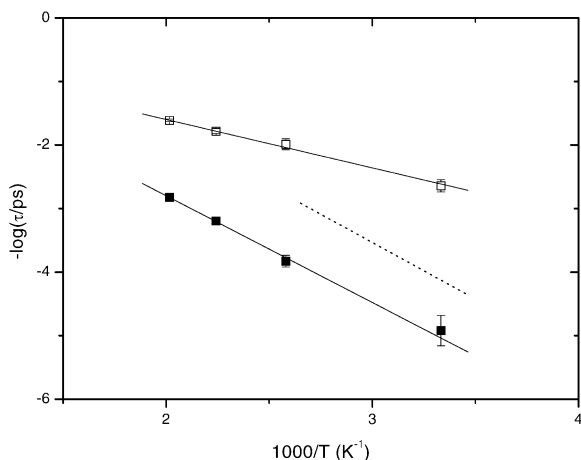
Fig. 3. Inverse transition rates for methyl (□) and backbone (■) trans to gauche jumps. The lines through the points are linear fits. The dotted line represents τ_1 relaxation times from NMR measurements.

Fig. 4. P_2 autocorrelation functions for methyl and backbone C–H bonds, at the examined temperatures.

gauche conformational jumps as evaluated from the effective dihedral potential is 5.1 ± 0.1 kcal/mol in the examined temperature range. This value can be compared to $E^* \simeq 5$ kcal/mol estimated by NMR measurements of PIB in solution [7], as well as to theoretical predictions [15] yielding $E^* \simeq 4.5$ kcal/mol at $T = 400$ K, and to the rotational barrier of $E^* \simeq 4.4$ 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 ± 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].

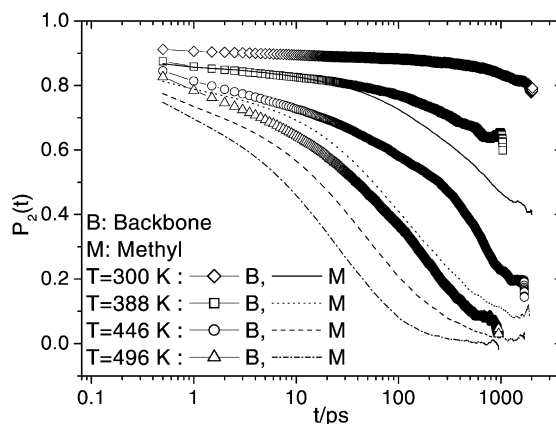Fig. 4 shows P_2 auto-correlation functions for the backbone (solid lines) and the methyl (dotted lines) C–H bonds. Comparison of average relaxation times defined as $\tau_{av} = \int_0^\infty P_2(t)\,dt$, between backbone and methyl dynamics at the higher temperatures where decorrelation has advanced more,[2] 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 τ_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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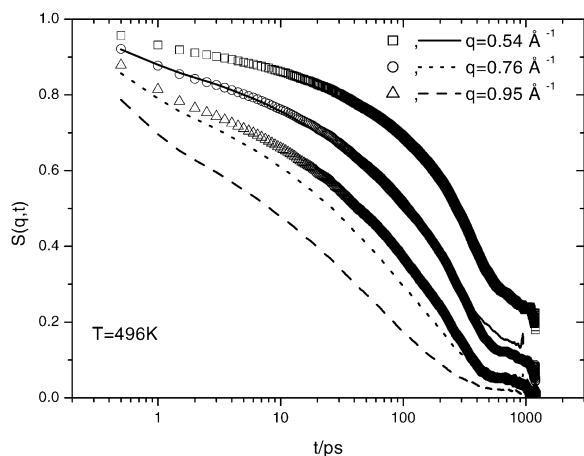[2] The long time tail was fitted by a single exponential.

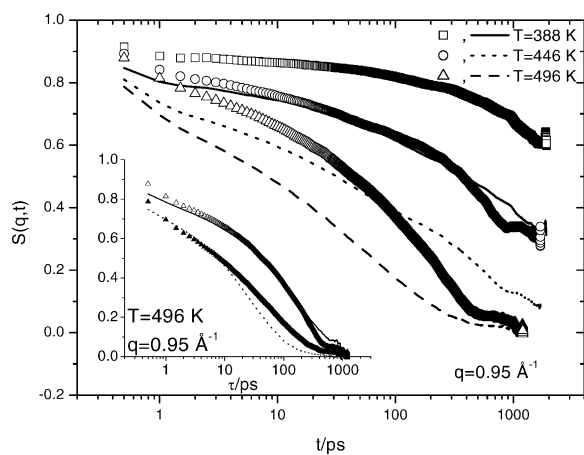Fig. 5. Incoherent structure factor for backbone and methyl dynamics at $T = 496$ K.

Fig. 6. Incoherent structure factor for methyl (lines) and backbone (symbols) dynamics for the three higher temperatures at $q = 0.95 \text{ Å}^{-1}$. Inset: comparison of $P_2(t)$ (solid line for backbone and dotted line for methyl reorientations) and $S(q,t)$ ($\triangle$ backbone, $\blacktriangle$ methyl) dynamics at $q = 0.95 \text{ Å}^{-1}$ and $T = 496$ K.

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 ($\sim 2\pi/q$) 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))

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

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 τ_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 τ_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.
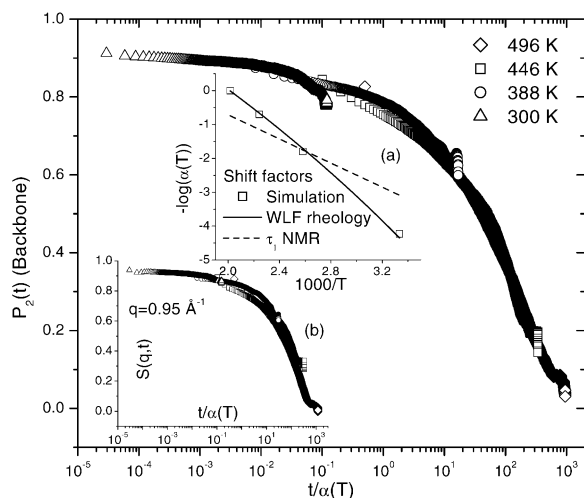
Fig. 7. Time temperature superposition for $P_2(t)$ and $S(q, t)$ of backbone hydrogens (inset b) at $q = 0.95$ Å^{-1}. Inset (a) shows the temperature dependence of the shift factors: extracted from the simulated $P_2(t)$ curves ($\square$), from rheological measurements (solid line), and from τ_1 NMR relaxation times (dashed line).

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 $q \simeq 1$ 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 τ_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.

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