

Microsecond Atomic-Scale Molecular Dynamics Simulations of Polyimides

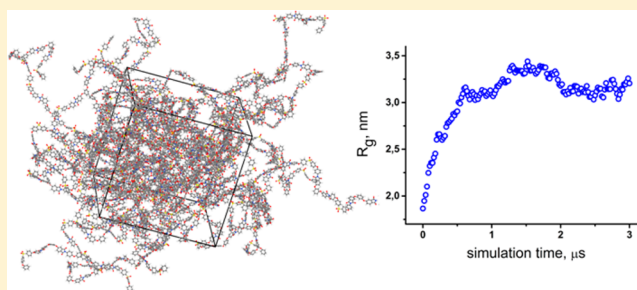
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ABSTRACT: We employ microsecond atomic-scale molecular dynamics simulations to get insight into the structural and thermal properties of heat-resistant bulk polyimides. As electrostatic interactions are essential for the polyimides considered, we propose a two-step equilibration protocol that includes long (microsecond-scale) MD simulations of polymer melt with partial atomic charges switched off, followed by relatively short runs (100 ns) of the polymer system with full electrostatics. We demonstrate that macroscopic characteristics of a polyimide sample (such as the glass transition temperature and density) are not particularly sensitive to the degree of equilibration. However, great caution should be paid when local structural characteristics are considered: proper equilibration of the local polymer structure (monitored through the radius of gyration and the end-to-end distance of individual chains) is found to require simulations on a microsecond time scale. Finally, we found a dramatic impact of electrostatic interactions on the properties of the bulk polyimides considered: when intra- and intermolecular dipole–dipole interactions come into play we witness compaction of individual polymer coils and eventually an increase in the glass transition temperature and polymer density.



1. INTRODUCTION

Computer modeling has become a standard tool for studying complex polymer systems, polymer-based nanocomposite materials being one of the numerous examples.^{1–4} Nowadays computers are widely employed to predict the properties of polymer materials, which could be regarded as a step toward virtual design of new materials with predefined characteristics. Such *in silico* design is closely related to the fundamental problem of the relationship between the details of the molecular structure of a polymer and the physical properties of a resulting polymer sample. For polymers, even a small modification of the chemical structure of the monomer unit can result in dramatic changes of the macroscopic characteristics of the bulk polymer.^{5,6} This implies that molecular design of new polymer materials with improved performance properties should rely largely on theoretical models of atomistic resolution.

Among polymer-based nanocomposites heat-resistant ones represent a very promising class of materials due to their potential to substitute traditional materials (such as metals) in many important industrial applications, thereby providing better performance and durability. In particular, aircraft, automobile, and shipbuilding industries demonstrate considerable demand for such novel polymer materials. In this paper we employ the state-of-the-art computer simulations to study

polyimides (PI), typical representatives of thermoplastic polymer matrices for heat-resistant nanocomposites.^{7–16}

Most of the existing simulation studies of polyimides have focused on diffusion of small solutes through polyimide-based membranes.^{4,6,17–34} As far as the thermal properties of polyimides are concerned, there exist only few related studies.^{32,35–39} The reason for that is 2-fold. First, the quality of computer simulations is largely defined by proper equilibration of the polymer sample. This problem exists for virtually all dense polymer systems as pointed out in the studies by Theodorou et al.^{40–42} and many others.^{4,17–19,43–45} Several methods for preparing well-equilibrated polymer samples have been reported; they include various Monte Carlo schemes, coarse-graining approaches with subsequent reverse-mapping procedures, and direct simulations of polymerization reactions.^{42,46–48} Second, the atoms of heat-resistant heterocyclic bulk polymers often have noticeable partial charges that cannot be neglected as this is normally done for polymers with simpler chemical structures (e.g., polyethylene or polystyrene).^{49–51} These two factors imply that atomistic computer simulations of bulk polyimides require extensive computational resources.

Received: June 5, 2013

Revised: July 6, 2013

Published: July 22, 2013

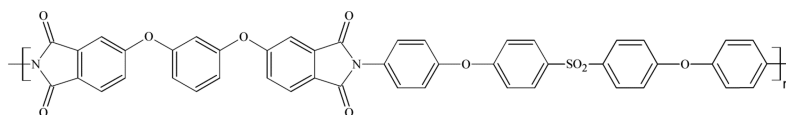


Figure 1. Chemical structure of an R-BAPS monomer unit.

Despite the fact that the proper equilibration of dense polymer samples is always a slow process, most of the existing atomistic simulations of bulk polymers are relatively short and in most cases do not exceed 50 ns.^{5,6,18–20,22–32,34–38,44,45,49–58} This is in great contrast to atomistic simulations of biomolecular systems where the state of the art has approached microsecond scales^{59–61} and millisecond simulations were reported recently.⁶² Such long simulations are crucial for studying slow relaxation processes in dense molecular systems and for performing critical tests of theoretical models (force-fields) available. It is therefore rather surprising that—to the best of our knowledge—polyimides have never been studied through atomistic computer simulations on a microsecond time scale.

To fill this gap here, we employ microsecond atomic-scale molecular dynamics (MD) simulations to get insight into the structural and thermal properties of heat-resistant bulk polyimides. We demonstrate that proper equilibration of polyimide melt requires several hundreds of microseconds due to strong dipole–dipole interactions between polyimide chains. To overcome this we chose to equilibrate the system with the use of a simplified force-field in which all the partial charges of the polyimide are set to zero. With this simplification at hand we show that polyimide melt can now be fully equilibrated during 1.5 μ s. After the equilibration has been achieved, the partial charges were switched back on, and a second, relatively short equilibration run (100 ns) was carried out. It turns out that local structural characteristics (the radius of gyration of a polymer chain and the end-to-end chain vector length) depend dramatically on whether the equilibrium state has been reached. In contrast, macroscopic characteristics such as the density and glass transition temperature are not particularly sensitive to the degree of sample equilibration.

2. MODEL AND SIMULATION METHODOLOGY

Model and Simulation Details. Amorphous heat-resistant polyimide R-BAPS (based on R dianhydride 1,3-bis(3',4'-dicarboxyphenoxy)benzene and diamine BAPS, 4,4'-bis(4''-aminophenoxy)biphenyl sulfone) was chosen for the present study; see Figure 1 for the chemical structure of a R-BAPS monomer unit. The system consists of 27 polymer chains of 8 monomer units each. The particular length of polyimide chains was dictated by two factors. First, the R-BAPS chains were chosen to be long enough to eliminate sensitivity of polyimide's thermal properties from the molecular weight of polymer chains. According to experimental data the glass transition temperature of the R-BAPS polyimide becomes almost insensitive to the molecular weight starting from the number-average molecular weight of 6 kg/mol (the corresponding chain length is estimated to be around 8 polyimide monomer units^{63,64}). Second, the polymer chains should be short enough to speed the equilibration process up. The total number of atoms in the polymer sample was ~ 18400 . The GROMOS96 force-field⁶⁵ was employed for the description of the R-BAPS polyimide. Partial charges of the R-BAPS polyimide were evaluated from the Hartree–Fock (HF) calculations on a R-BAPS

monomer unit at the 6-31G* level, the geometry optimization was followed by the Mulliken method to assign charges as it is implemented in the Firefly package.⁶⁶ It should be emphasized that the presence of a sulfone group in the R-BAPS monomer unit (see Figure 1) leads to relatively large partial charges which cannot be neglected. The largest partial charges were found for the SO₂ groups. In addition to the large partial charges, the diphenylsulfone part of the R-BAPS monomer unit is characterized by a substantial dipole moment. The value of this dipole moment can be used for verification of the atomic charges: It turns out that the calculated dipole moment of the diphenylsulfone part of the R-BAPS monomer unit ($\mu = 6.1$ D) agrees rather well with experimental values of the dipole moment of diphenylsulfone molecules ($\mu \sim 5.1$ D).^{67–70}

The Lennard-Jones interactions were cut off at 1 nm. The same cutoff radius was also used for the electrostatic interactions, beyond which the particle–mesh Ewald method was used.^{71,72} All bonds were constrained with the LINCS algorithm;⁷³ this allowed us to use the time step of 2 fs. The simulations were performed in the NpT ensemble. The Berendsen scheme was used for controlling both temperature and pressure;⁷⁴ the time constants were set to 0.1 and 0.5 ps for temperature and pressure coupling, respectively. The GRO-MACS suite was used for all simulations.^{75,76}

Polymer Sample Preparation. The preparation of a polymer sample was performed at $T = 600$ K. This temperature is ~ 100 K higher than the experimentally measured glass-transition temperature but lower than the temperature of the R-BAPS thermal destruction.⁷⁷ All the partial charges were switched off. Building up the polymer melt includes the following three steps, see Figure 2:⁶³

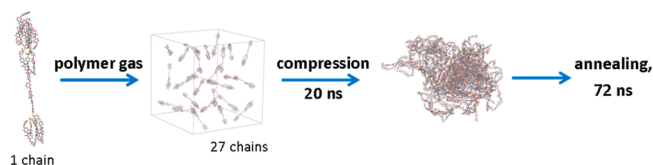


Figure 2. Preparation of a polyimide sample. Generation of a single polyimide chain, building up “polymer gas”, initial compression of the sample (20 ns), followed by three annealing cycles (72 ns).

- (1) Generation of a single polyimide chain in a semifolded dumbbell-like conformation. Such a conformation was used to avoid formation of crystal-like structures upon compression in step 3.
- (2) Building up “polymer gas”. A total of 27 copies of the polyimide chain were placed in a cubic box with the use of the Gromacs routine *genconf*; each chain was rotated by a random angle. The box volume was chosen large enough in order to avoid overlapping of chains.
- (3) Compression of the “polymer gas”. The system was compressed through applying high pressure. The compressive pressure was gradually elevated from 50 to 300 bar during 10 ns simulation run. The pressure was reduced then to 150 bar and the system was simulated

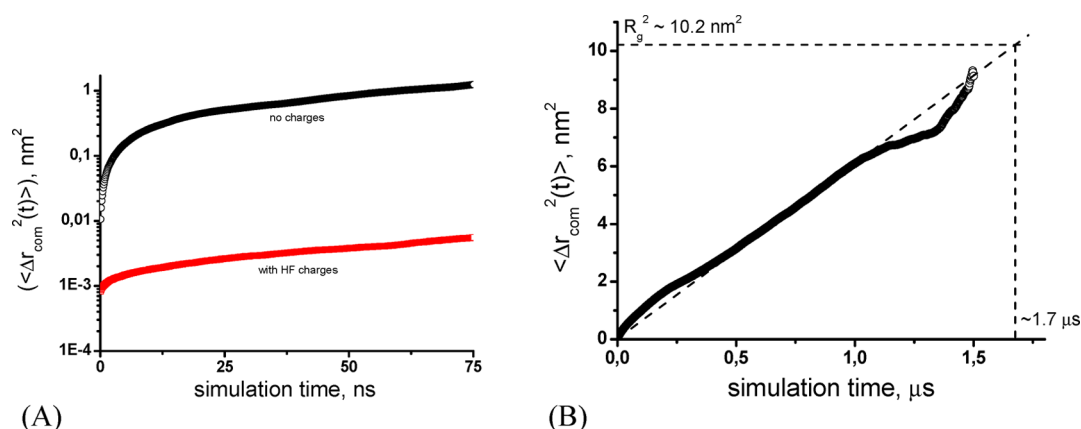


Figure 3. Mean-square displacement of the center of mass (COM) of a polyimide chain $\langle \Delta r_{\text{com}}^2(t) \rangle$ as a function of time ($T = 600$ K, averaging over all chains in the systems). (A) Two 100 ns simulation runs of a polyimide sample with and without partial atomic charges. (B) A 1.5 μs -long simulation run for a polyimide sample with partial charges switched off. Linear extrapolation gives $\sim 1.7 \mu\text{s}$ as a time required for the displacement of the chain COM on a distance equal to the mean radius of gyration.

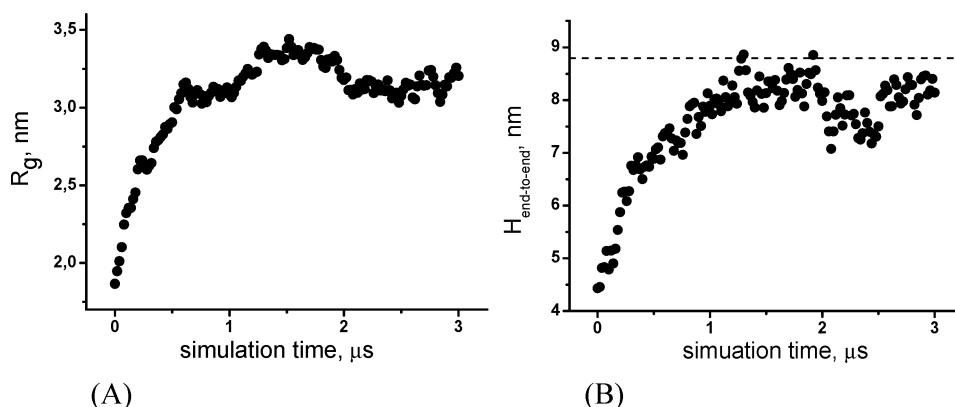


Figure 4. Radius of gyration (A) and the end-to-end distance (B) for R-BAPS chains in melt as a function of time for the polymer sample with partial charges switched off (averaged over all polyimide chains). The dashed horizontal line in part B corresponds the end-to-end distance predicted analytically,⁷⁸ $H_{\text{end-to-end}} = 8.8 \text{ nm}$;⁷⁸ see text for details.

for 5 ns. Finally, the system was equilibrated for another 5 ns at pressure 1 bar.

After the initial preparation of the polymer sample, we performed three annealing cycles, the annealing followed closely to the protocol described in refs 63, 78, and 79. The polyimide melt was stepwise cooled down from 600 to 290 K with a temperature step of 50 K and heated back to 600 K. At each temperature the polymer system was simulated for 2 ns. Overall, the total simulation time for the annealing procedure was 72 ns.

Calculation of the Glass Transition Temperature. The glass-transition temperature of a polyimide bulk sample was evaluated from a temperature-dependence of the polymer density.^{31,32,35–38} A polyimide sample was stepwise cooled down from 600 to 290 K. The glass-transition temperature was determined as a value on the temperature axis where the slopes of straight-line extrapolations of the density–temperature curve change. The cooling velocity of 1.5×10^{12} K/min was employed.

3. RESULTS AND DISCUSSION

Two-Step Equilibration Protocol for a Polymer Sample. Before equilibrating the prepared polyimide sample, it is instructive to get a rough estimate of the equilibration time

required. In simple terms, the equilibration of the polymer melt implies mixing up individual polymer coils. In order to achieve the proper chain mixing the polymer coils should be able to move on the distances comparable with their own size during the course of simulations. The time scales required for such chain displacements were estimated on the basis of a 100 ns simulation of the polyimide sample at elevated temperature of 600 K. To reveal the influence of electrostatic interactions on the equilibration rate we also repeated such a simulation for the same sample with partial atomic charges switched on. The mean-square displacement (MSD) of the center of mass of polyimide chains $\langle \Delta r_{\text{com}}^2(t) \rangle$ (averaged over all chains in the sample) is shown in Figure 3A for both considered situations. As is evident from the Figure electrostatic interactions dramatically slow down self-diffusion of a polymer chain in melt, which is a signature of strong intermolecular interactions of (most likely) dipole–dipole nature. From the estimate for the diffusion coefficient, $D \sim 10^{-8} \text{ cm}^2/\text{s}$, one can conclude that the displacement of a chain coil on the distances comparable with the mean radius of gyration of a chain ($R_g \sim 3.2 \text{ nm}$) occurs on a microsecond time scale for the system with partial charges switched off. If the electrostatic interactions are properly accounted for, this characteristic time is estimated to be 2 orders of magnitude longer. Taken together with the well-known slowing down of MD simulations due to computation-

ally expensive algorithms for calculating long-range electrostatic interactions (e.g., through the particle–mesh Ewald method), we come to the conclusion that the proper equilibration of considered polyimide samples with nonzero partial atomic charges is not feasible with the state-of-the-art computational resources as it requires hundreds of microseconds.

To overcome this problem, we propose the following two-step protocol for the polyimide sample equilibration:

- (1) Microsecond-scale equilibration of a sample with partial charges switched off;
- (2) Switching on the partial charges, followed by a relatively short MD run (~ 100 ns).

Below we demonstrate that such a protocol indeed allows one to equilibrate properly the polyimide sample at temperatures higher than the glass transition temperature.

Microsecond-Scale Simulations of a Polymer Sample with Partial Charges Switched off. To follow closely the process of equilibration of a polymer sample, we carried out a 3 μ s atomistic molecular dynamics simulation of the system with partial charges switched off ($T = 600$ K). In Figure 4, we showed the time evolution of the radius of gyration and of the end-to-end distance of a polyimide chain in melt. It turns out that both the radius of gyration and of the end-to-end distance reach their equilibrium values at $t \sim 1.5$ μ s. This time scale almost coincides with the characteristic time required for the displacement of a chain coil on a distance equal to the chain's radius of gyration, see Figure 3B. Remarkably, the equilibrium value of the end-to-end distance, $H_{\text{end-to-end}} = 8.2$ nm, turns out to be rather close to the values predicted analytically: $H_{\text{end-to-end}} = 8.8$ nm for the model with freely rotated bonds and $H_{\text{end-to-end}} = 9.2$ nm for the model in which correlations for the rotations around neighboring bonds are taken into account.^{63,78}

It is important to emphasize that the reported equilibration time of 1.5 μ s is observed for a melt of polyimide chains of eight monomer units. It is relatively straightforward to get a rough estimate of as to how the required equilibration time depends on the chain length. The characteristic time of moving a polymer coil on the distances comparable with its own size is proportional to the squared radius of gyration and is inversely proportional to the diffusion coefficient. For ideal Gaussian chains, one has an increase in the equilibration time by a factor of 4 when the length of the chain is doubled. Therefore, the lower time-scale limit for the equilibration of a melt of polyimide chains of 16 monomer units is around 6 μ s.

In addition to the local structural characteristics, we also explored whether macroscopic properties are sensitive to the degree of equilibration. First, we calculated the total density of a polyimide sample at elevated temperature, $T = 600$ K. As is evident from Figure 5, the polymer density only slightly changes during the course of microsecond MD simulations, demonstrating small fluctuations around the average value $\rho = 1233$ kg/m³. Therefore, one can conclude that the slow mixing of polymer coils does not affect the total density of a polymer sample. In particular, this implies that reaching a constant value of the sample density cannot serve as an unambiguous criterion for the polymer sample equilibration as is often assumed in many simulation studies for polyimides.^{18,22,26,31,54}

As far as the glass transition temperature, T_g , is concerned, it is defined by the change in the slope of the density–temperature curve. It is therefore reasonable to expect that T_g —similar to the total density—will not be affected to a large extent by the degree of equilibration. Indeed, as one can see

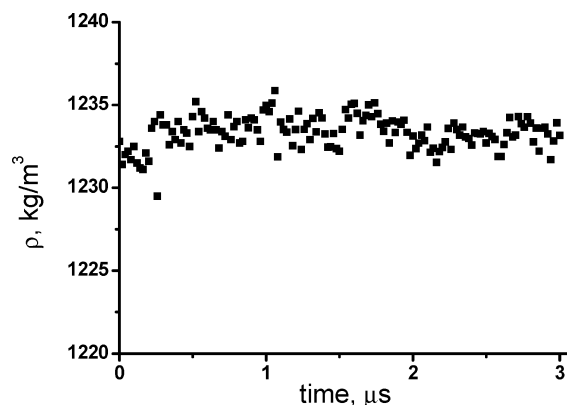


Figure 5. Total density of a polyimide sample as a function of time at elevated temperature $T = 600$ K (partial atomic charges are switched off).

from Figure 6 the values of the glass transition temperature at the beginning and at the end of a 3 μ s molecular dynamics simulation run are rather close. It is noteworthy that the calculated values of the glass transition temperature scatters considerably during the course of simulations. Such large fluctuations of the glass transition temperature are related to the inherent errors in the straight-line fitting used for the

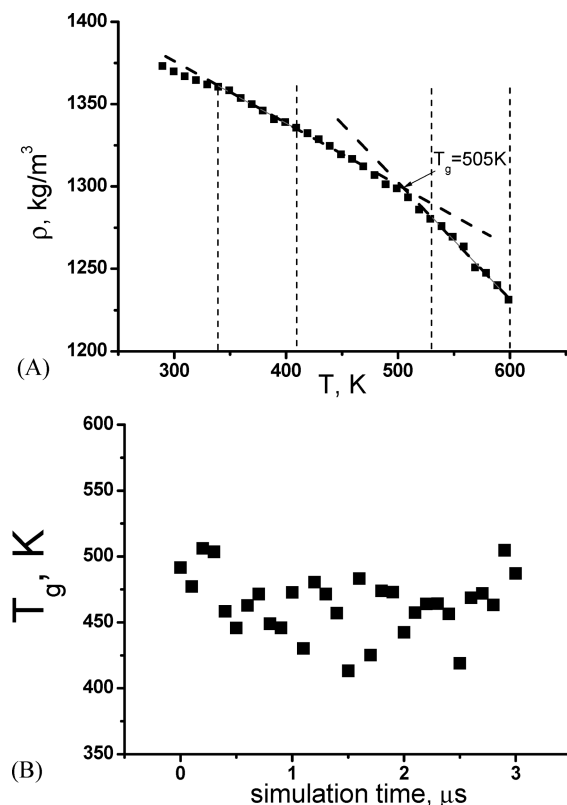


Figure 6. (A) Typical representative of the density–temperature curves. A polymer sample was taken after a 200 ns simulation run ($T = 600$ K, no partial charges) and stepwise cooled down to 290 K. To determine the glass transition temperature straight-line fitting (shown by dashed lines) of the density–temperature curve was performed in the ranges 340–410 K (below T_g) and 530 K – 600 K (above T_g). (B) Glass transition temperature of a polyimide sample as a function of simulation time at elevated temperature $T = 600$ K (partial atomic charges are switched off). The average value of T_g equals 464 ± 18 K.

determination of T_g , see Figure 6 and section 2. These errors have nothing to do with system equilibration and can be reduced through averaging over many statistically independent configurations of the same polymer sample.^{31,36–38,79} Overall, we conclude that the equilibration degree does not have noticeable influence on the glass transition temperature of a polyimide sample with no partial charges, which fluctuates around the average value of 464 K.

The Influence of Electrostatic Interactions. To explore the influence of electrostatic interactions on the structural and thermal properties of bulk polyimides we selected 16 different polymer samples from the second half of the 3 μ s equilibration run (every 100 ns during the 1.5 μ s run), i.e., from the part of the MD trajectory where the system is proved to be in equilibrium, see Figure 4. We switched the charges on in these samples and simulated them for 100 ns each.

As it is seen from Figure 7, partial atomic charges lead to a slight decrease in the local structural characteristics such as the radius of gyration, R_g , and the end-to-end distance, $H_{\text{end-to-end}}$ of individual polymer chains. In other words, one can witness some compaction of polymer coils in melt although the characteristic ratio $((H_{\text{end-to-end}}^2)/(R_g^2)) = 6$ stays unchanged.^{80,81} We also observe a remarkable decrease in fluctuations of the local structural characteristics, which is again a sign of strong intra- and intermolecular interactions of dipole–dipole nature in the system. Such interactions arrest relaxation processes in the polymer sample, so that the system reaches the new equilibrium state relatively fast. Indeed, Figure 7 shows that it is a matter of several nanoseconds for the polymer melt to equilibrate after the partial charges are switched on, so that a relatively short MD run of ~ 100 ns is sufficient for the proper equilibration.

The observed electrostatics-induced compaction of individual polymer coils in melt should produce a cumulative impact on the total density of the sample. As seen from Figure 7C, an increase in the mass density of a sample is very pronounced: it rises by almost 10% over just a few nanoseconds. The fluctuations of the density are also notably smaller in the polymer sample with partial charges switched on.

Finally, we evaluated the effects of the electrostatics on the glass transition temperature T_g of polymer samples. It turns out that the value of T_g (averaged over all samples) increases from $T_g = 464$ K to $T_g = 482$ K upon switching partial atomic charges on. This can be understood in terms of dipole–dipole molecular interactions that partially freeze the internal mobility of polymer chains, thereby elevating the glass transition temperature. Experimental value of T_g for the R-BAPS polyimide sample with the same molecular weight is ~ 210 °C or 483 K,⁶⁴ i.e., almost coincides with the value measured in MD simulations. Thus, electrostatic interactions are shown to be essential for the correct description of the properties of heat-resistant polyimides with sulfone groups in the monomer unit. As a final remark, one has to note that the observed agreement between experimental and computational values of T_g should not be misleading due to a considerable difference in cooling rates in simulations and experiment. The glass transition temperature in MD simulations should drop with the decrease of the cooling rate so that the computational value of T_g should deviate more and more from the one measured in experiment. However, since such deviation cannot be determined due to enormous computational resources required for simulations with low cooling rates, one can regard the observed agreement between simulations and experiment as rather reasonable.

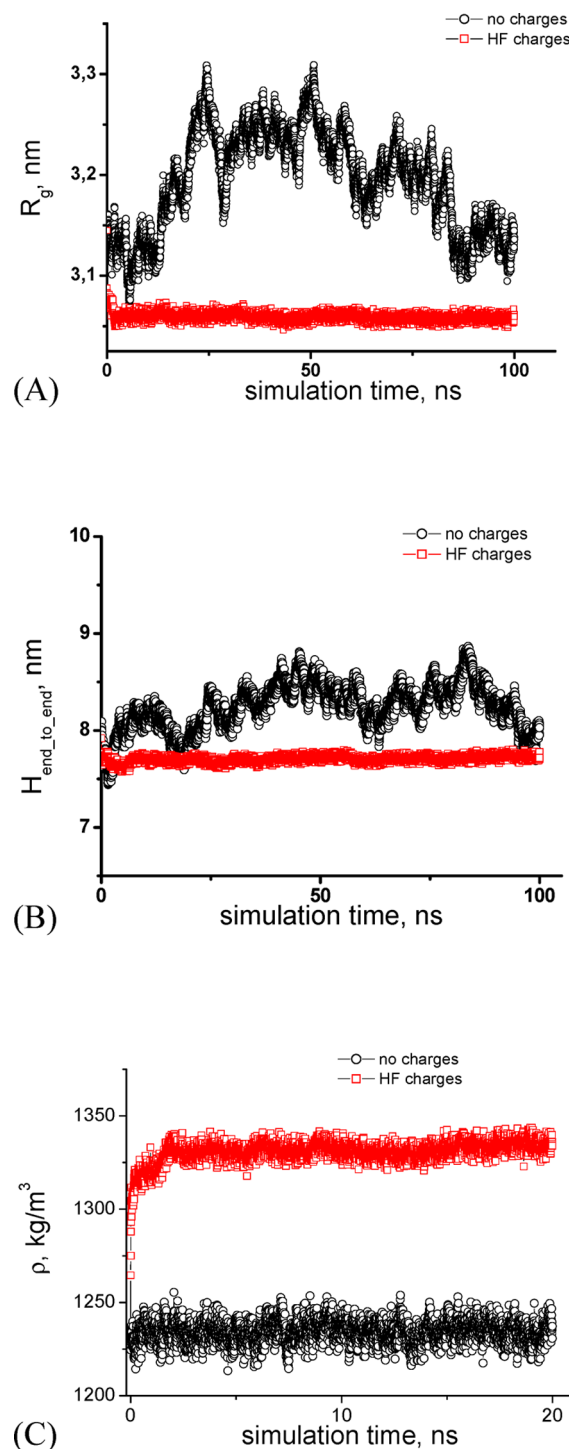


Figure 7. (A) Radius of gyration, (B) the end-to-end distance for individual polyimide chains, and (C) the mass density of the polymer sample as a function of time. Shown are the results for representative samples without partial charges (black lines) and with partial charges switched on (red lines).

CONCLUSIONS

In this paper, we employed extensive atomic-scale molecular dynamics simulations to probe the structure and thermal properties of heat-resistant polyimides in bulk. For this purpose we chose amorphous polyimide R-BAPS. From the point of view of computer modeling the study of the polyimide of this type is especially challenging as it has an oxidized sulfone group

in its monomer unit, see Figure 2, so that partial atomic charges of the polymer are noticeable and cannot be neglected. We show that proper equilibration of such polymers in bulk is not straightforward as it can take hundreds of microseconds even at elevated temperatures that are well above the glass transition temperature.

To address this issue we propose a two-step equilibration protocol that includes long (microsecond-scale) MD simulations of a polymer sample with partial atomic charges switched off, followed by relatively short runs of the bulk polymer with full electrostatics. The microsecond-scale simulations employed in this study provide an unprecedented insight into the process of equilibration of polymer melt. We demonstrate that macroscopic characteristics of a polyimide sample (such as the density and the glass transition temperature) are not particularly sensitive to the degree of equilibration, thereby justifying earlier computational studies in the field, which were normally limited by 100 ns simulations. However, studying local structural characteristics should be carried out with great caution as the proper equilibration of the local polymer structure (monitored through the radius of gyration and the end-to-end distance of individual chains) requires MD simulations on a microsecond time scale. This conclusion also holds for polymers with negligibly small partial charges such as polyethylene or polystyrene.

When the partial charges are switched on in the polyimide sample the strong intra- and intermolecular electrostatic interactions of dipole–dipole nature come into play. They result in compaction of individual polymer coils in melt and eventually lead to an increase of the sample density. The fluctuations in the systems become damped and the glass transition temperature increases, both phenomena being a signature of the partially frozen internal mobility of polymer chains due to strong dipole–dipole interactions. Remarkably, the glass transition temperature of a polyimide sample with full electrostatics provides a noticeably better agreement with experimental data as compared to the system with no partial charges. This implies that electrostatic interactions play an important role and cannot be neglected in MD simulations of bulk polyimides of the type considered in this study.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was carried out under the financial support of the Russian Ministry of Education and Science (State Agreement No. 8023 and State Contract No. 16.523.12.3001). The simulations were carried out with the use of the computational resources of the Institute of Macromolecular Compounds, Russian Academy of Sciences, and the Chebyshev and Lomonosov supercomputers at Moscow State University. AVL acknowledges the support from the Russian Ministry of Education and Science, activity 1.5 of the Federal Programme on “Scientific and scientific-educational personnel of innovative Russia” for 2009–2013 (State Agreement No. 8645).

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