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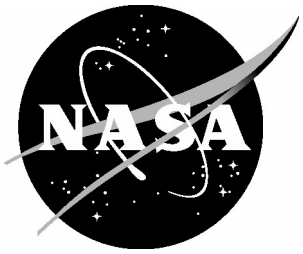

Coarse-Grained and Atomistic Modeling of Polyimides

Thomas C. Clancy
National Research Council
Langley Research Center, Hampton, Virginia

Jeffrey A. Hinkley
Langley Research Center, Hampton, Virginia

July 2004

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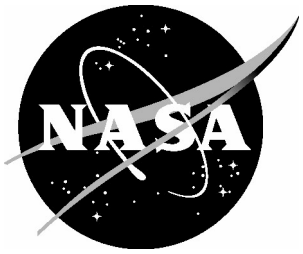

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National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23681-2199

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Abstract: A coarse-grained model for a set of three polyimide isomers is developed. Each polyimide is comprised of BPDA (3,3,4,4'-biphenyltetracarboxylic dianhydride) and one of three APB isomers: 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene or 1,3-bis(3-aminophenoxy)benzene. The coarse-grained model is constructed as a series of linked vectors following the contour of the polymer backbone. Beads located at the midpoint of each vector define centers for long range interaction energy between monomer subunits. A bulk simulation of each coarse-grained polyimide model is performed with a dynamic Monte Carlo procedure. These coarse-grained models are then reverse-mapped to fully atomistic models. The coarse-grained models show the expected trends in decreasing chain dimensions with increasing meta linkage in the APB section of the repeat unit, although these differences were minor due to the relatively short chains simulated here. Considerable differences are seen among the dynamic Monte Carlo properties of the three polyimide isomers. Decreasing relaxation times are seen with increasing meta linkage in the APB section of the repeat unit.

1. Introduction

Atomistic simulations of polymer glasses can shed light on such phenomena as solubility [1], gas permeation [2], and plastic yielding [3]. Particularly for polymers containing rigid aromatic rings, it can be difficult to produce glassy structures at realistic densities. Often hybrid methods are adopted, since for example, straightforward energy minimization often leads to structures trapped in local minima whereas molecular dynamics is difficult to carry out over a long enough time to allow relaxation of chain motion. To correctly capture the physics of macromolecules over a full range of relevant length and time scales, multi-scale modeling techniques have been devised [4-8]. These attempt to map the molecular structure and long-range motion onto a simplified chain model. Such simplified chain models are expected to have utility in a number of areas, for example, exploring the effects of nanoscale fillers on structure and dynamics of polymers [9,10].

Especially interesting are methods that allow a relaxed bulk structure to be reverse-mapped back to a realistic model with atomistic detail. As shown in Figure 1, this provides a route to circumvent a slow molecular dynamics (MD) equilibration. In

one example of such a method, computational efficiency has been enhanced by placing beads representing the coarse-grained chain onto a high coordination lattice [11]. The 2nnd lattice method provides a precise mapping between atomistic and coarse-grained models for vinyl polymers [12-16] and poly(ethylene oxide) [17], but does not seem so easily applicable to aromatic polymers.

In this paper, an off-lattice coarse-grained polymer model is developed. It solves the problem of retaining enough information to distinguish among the isomers of three structurally similar polyimides. Suitable pre-averaged expressions for the long range interaction energies (LRE) are applied in a consistent manner to all three isomers, and a lattice discretization is used to efficiently calculate inter-unit energies. Finally, structures are successfully reverse-mapped to atomistic models at the correct density.

2. Polyimide Materials

A vast number of aromatic polyimides has been synthesized [18]. For the purposes of illustrating the simulation method, a series of three isomeric polyimides was chosen. All were built from BPDA (3,3,4,4'-biphenyltetracarboxylic dianhydride); the diamine portions had varying degrees of flexibility. As shown in Figure 2, the repeat units differed only in the positions of the linkages about the rings in the bis(aminophenoxy)benzene (APB) diamine section. The BPDA 1,4,4-APB monomer has three para linkages, but the others contain meta linkages which impart a greater range of conformations. Figure 3 illustrates this effect. Vectors are sketched across the backbone contours of segments of the BPDA 1,3,4-APB and 1,4,4-APB isomers. Rotation about the carbon-oxygen bond (shown as a dotted line) substantially changes the angle between the two vectors in the 1,3,4-APB, but not in the 1,4,4-APB segment.

3. Multi-scale Simulation Method

There are four separate procedures involved in the methodology for this multi-scale simulation: 1) mapping of the atomistic polymer chain onto a coarse-grained model, 2) applying Monte Carlo (MC) simulation to the coarse-grained model, 3) reverse-mapping of the coarse-grained model to a fully atomistic representation, and 4)

equilibration of the atomistic model through standard molecular dynamics (MD) and molecular mechanics (MM) energy minimization techniques.

3.1 A coarse-grained model for polyimides

This section outlines a coarse-grained model of the polyimides shown in Figure 2. The coarse-graining is developed using a linked vector model with long range interaction energy (LRE) beads placed at the midpoints of each vector.

3.1.1 Linked Vectors

The procedure begins by dividing the BPDA APB polyimide repeat unit into five sub-units (SU): two phthalimide SUs, followed by two phenoxy SUs and a benzene SU (SU1 = (-$N(CO)_2C_6H_3$-), SU2 = (-$C_6H_3(CO)_2N$-), SU3 = (-C_6H_4O-), SU4 = (-C_6H_4O-) and SU5 = (-C_6H_4-)). A coarse-grained model is constructed as a series of vectors linked at the termini of the bonds of the SUs as shown in Figure 4. The length, l, of each vector is assigned a probability, P_l. The angle, γ, between two succeeding vectors is assigned a probability P_γ. These probabilities are determined by sampling from MD simulations of connected pairs of SUs. MD was conducted at 650K using the PCFF forcefield [19]. The distribution of length probabilities, P_l, for an SU vector is sharply peaked and is effectively constant for these molecular constituents. The short range intramolecular energetic interaction between two successive SUs is determined by the angular distribution probability, P_γ.

3.1.2 The long range interaction energy (LRE)

For non-successive intramolecular SUs (and intermolecular SUs), a long range interaction energy is needed in order to maintain cohesion and excluded volume of the coarse-grained polymer model. This is done by placing a bead at the midpoint of each vector as shown in Figure 4.

Although bulk simulations are often run with only simple repulsive potentials, it is important to use reasonable LREs since it has also been shown that these functions can influence a variety of properties in coarse-grained polymer simulations [20]. Other coarse-grained models have used experimentally derived gas phase Lennard-Jones parameters to estimate the LRE between coarse-grained polymer beads [21]. That approach is not suitable in this case given the complexity of the species involved in the SUs of the coarse-grained model. Therefore, the following procedure was adopted.

First, a continuous spherically symmetric effective potential energy, $u_{effective}(r)$, is estimated for each pair of SUs. This effective potential is obtained by equation 3 as the reversible work function [22]

$$u_{effective}(r,T) = -k_B T \ln\left\langle e^{-\beta U'} \right\rangle, \tag{1}$$

where U' is the potential energy, $\beta=k_BT$, (where k_B is the Boltzmann constant and T is the temperature, and $\langle\cdots\rangle$, is the angular average for a fixed distance r between two SUs. The distance r is defined specifically as the distance between the midpoints of the SU vectors as shown in Figure 5. The temperature, T, is set at 650K.

The effective energy for two SUs is calculated by the following multi-step procedure. First, the two SUs are placed at a fixed distance from each other. One SU is then subjected to random rotations about the midpoint of the coarse-grained vector associated with it. Random rotations are also applied to the second SU and the inter-unit energies are stored. Finally, one of the SUs is translated towards the other along the line connecting the midpoints of the two SU vectors and the process is repeated. A Lennard-Jones 9-6 potential (equation 2) is used for each atom-atom potential.

$$E = \varepsilon[2(\sigma/r)^9 - 3(\sigma/r)^6]. \tag{2}$$

In this equation, r is the distance between two atoms and E is the energy. The Lennard-Jones parameters, ε and σ, are taken from the PCFF forcefield [19].

The quantity $\exp(-\beta U')$, is binned and averaged at each distance between the centers of the two SUs. These averages create the continuous effective potential energy in equation 1. This procedure will yield a different effective potential for a meta linked phenoxy SU than it will for an ortho linked phenoxy SU. Note that the two effective potentials would be identical if the SU center of mass rather than the midpoint of the vector were used. Figure 6 plots the estimated effective potential energy (in kJ/mol) for identical pairs of monomer SUs. Only five of the 15 possible combinations are shown for clarity.

A dynamic MC procedure employing Metropolis biasing [23] requires evaluation of the change in energy, ΔE, with each MC step. For an off lattice polymer model, the LRE contribution to ΔE would usually require evaluating the distances between any bead that has changed position and any other beads located within a defined cutoff distance. Although the linked vector model for polyimides developed here is not constrained to a lattice, for purposes of calculating the LRE, the periodic box is divided into cells of 1 Å cubed. A cell is occupied by a bead if the bead lies within the boundaries of this cell; the effective potentials between pairs of beads are discretized using a method derived from the method of Cho et al. [21]. A cell average Mayer *f* function, $\langle f \rangle$, is defined as

$$\langle f \rangle = \int_{cell} f d\vec{r} \,/\, \int_{cell} d\vec{r}\,, \tag{3}$$

where the Mayer *f* function is,

$$f = e^{-\beta u(r)} - 1 \tag{4}$$

and *u(r)* is the Lennard-Jones energy for the monomer of the coarse-grained model.

The effective interaction energy defined for each SU pair is used in equation 4. In reference 21, the effective interaction parameters were averaged over a 'shell' on a high coordination lattice. In the present paper, however, energy levels are grouped according to lattice cell vectors instead. This does not significantly increase the computational complexity.

The set of vectors with lengths which are less than the applied cutoff is used to query the neighboring cells of a MC moved bead for occupancy information. Since most of the computer time is spent evaluating the energy of a trial move for acceptance according to the Metropolis biasing criteria, the discretization chosen is a significant factor in the computational workload of the calculation. When a cutoff of 10 Å is applied, and the periodic box is divided into 1 Å cubes, there are 4168 lattice points to check for occupancy by a bead; when a cutoff of 9Å is used and the periodic box is divided into 3Å cubes, there are only 122 lattice points to check for occupancy by a bead. Table 2

provides discretized energy values for the continuous effective potential energy between SU3 and SU3 of BPDA 1,3,4-APB and between SU4 and SU4 of BPDA 1,3,4-APB. Even though both SUs contain the same number and geometry of atoms, (-C_6H_4O-), different results are obtained because of the orientation of the atoms with respect to the coarse-grained backbone vector.

3.2 The Monte Carlo (MC) simulation

The second basic procedure in the multi-scale method is the MC simulation. This section describes the basic MC moves and the simulation procedure applied to the models for bulk simulation.

3.2.1 The Monte Carlo (MC) moves

The bulk polymer model is initially prepared as a set of random walks for the parent chains using the linked vectors with periodic boundary conditions. For the initial configuration, only the short range energies (enacted through the angle and length probabilities for successive vectors) are considered. The vectors comprising the coarse-grained chain are then moved by a MC procedure and tested for acceptance by the Metropolis biasing method. Figure 7 illustrates the MC moves. In Figure 7a the vectors *i* and *i+1* are rotated about the axis formed from the sum of these two vectors to generate the new vectors i' and $i+1'$. The angles γ_i (between vectors *i-1* and *i*) and γ_{i+2} (between vectors *i+1* and *i+2*) are changed during this rotation to the angles γ_i' and γ_{i+2}'. In addition, a MC move involving slight random repositioning of the vectors is illustrated in Figure 7b. This move changes the lengths of the vectors as well as the associated angles. Since the probabilities of these lengths are sharply peaked, this MC move does not effect much change, but is included in the procedure to ensure proper sampling of the narrow length distribution, P_l.

3.2.2 Monte Carlo (MC) simulation procedure

A MC simulation is performed with 7 chains of 10 repeats (50 SUs) in a periodic box of 36Åx36Åx36Å for a density of 1.37 g/cm^3. The computational requirements are reduced by using the 3Å lattice spacing with a cutoff of 9Å in the evaluation of the discretized LRE. The initial configuration is subjected to 8.5x10^6 MC steps at 650K, where one MC step is defined as an average of one MC trial move on all vectors comprising the system. Statistically independent samples are obtained from this MC

simulation and box conformations are selected for reverse-mapping. Prior to reverse-mapping, a finer grained lattice is used (1Å) with a cutoff of 10 Å and the MC simulation is run for an additional $8.5x10^4$ MC steps.

3.3 Reverse-mapping to an atomistic model

After the coarse-grained MC model is equilibrated, the model can be reverse-mapped back to a fully atomistic model by placing the atoms of the SUs along the vectors in the proper sequence. One piece of information that is lost in the coarse-graining process is the rotational angle of the monomer SU about the axis of the corresponding linked vector in the coarse-grained model. As a part of the reverse-mapping, a MC procedure is applied to optimize the molecular geometry. The SUs are subjected to random rotations about the vectors and then to a limited number of bead flips that correspond to the MC move in Figure 7a. The MC moves are accepted according to the Metropolis biasing procedure. A two step procedure is used to optimize the geometry of the reverse-mapped coordinates. In both steps, the bond angle energies are evaluated at the joints of the SUs (bond angles interior to a SU do not change with respect to each other). In the initial MC run, the continuous effective energy, $u_{effective}(r)$, of the monomer SUs is evaluated after each trial MC step. This procedure is quite effective in producing atomistic structures with very infrequent ring concatenation and spearing and is typically run for less than $1x10^4$ MC steps. To completely eliminate all possible cases of ring concatenation and spearing, a second short MC run is applied. In this final MC run, atomistic Lennard-Jones potentials are applied to each atom pair and a very short range repulsive phantom atom is placed in the center of each ring. This is typically applied for less than $1x10^3$ MC steps.

Following this short MC procedure, the atomistic coordinates are relaxed with conventional molecular mechanics and molecular dynamics techniques. The LAMMPS software as supplied from Sandia National Laboratories is used for the MD simulation [24,25]. An initial energy minimization is applied, followed by 400ps of constant pressure MD at 1atm and 300K.

4. Results

In this section, the validity of the LRE estimates is assessed by analysis of the density of thin films. Equilibrium conformational properties of the coarse-grained polyimide models are discussed, and the dynamical properties exhibited in the MC simulation are compared. Results for reverse-mapping are presented.

4.1 Validity of the LRE estimates

One criterion for the LREs for coarse-grained polymer models is that they produce a reasonable density in a thin film simulation [17]. Slight changes in the LRE parameters can cause significant density changes even for a repeat unit with few atoms such as polyethylene [26].

To simulate a thin film, periodic boundary conditions are removed in one of the three dimensions of a bulk model [27]. This was done for all three coarse-grained polyimides using the 3 Å lattice granularity at 650K. The resulting thin films had densities of 1.2-1.4 g/cm^3. Most polyimides seem to have a density in the range of 1.2-1.6 g/cm^3 [28]. LaRC^{TM}-SI, a polyimide similar to the ones studied here, is reported to have a density of 1.376 g/cm^3 [29]. This agreement imparts a degree of confidence in the estimated LRE values. Precise agreement with experimental densities could presumably be obtained by adjusting parameters, but this was not a goal of the present work. Rather, a consistent method was found which generates densities in a reasonable range.

4.2 Coarse-grained model

A variety of data can be obtained by post-processing the coarse-grained MC simulations of the three polyimides. These data can generally be categorized as: 1) equilibrium properties averaged over the MC steps, or 2) dynamic quantities considered as functions of the MC steps.

4.2.1 Equilibrium properties

Two of the most frequently calculated conformational properties of polymers are the average end to end distance, <ETE>, and the average radius of gyration squared, $\langle R_g^2 \rangle$ [30,31]. Table 2 contains the calculated values for the <ETE> and $\langle R_g^2 \rangle$ for the three different coarse-grained bulk simulations. The standard deviations were relatively large for these short chains. The trends were as expected, however, with decreasing

<ETE> and $\langle R_g^2 \rangle$ for the polyimide chains with increasing meta linkages in the APB part of the monomer.

4.2.2 Dynamic properties of the coarse-grained models

In a dynamic MC simulation, it is possible to calculate dynamic quantities as a function of MC step. Some dynamic MC coarse-grained simulations have even been compared directly with corresponding MD simulations equating MC step with 'time step' [32]. For the present purpose, it suffices to compare the three coarse-grained models.

There are two relaxation times relevant for the generation of statistically independent polymer conformations from dynamic MC algorithms. The first is the number of MC steps required for the decay of the normalized average autocorrelation function of the end-to-end vector to a value of 1/e. The second is the number of MC steps required for the mean squared displacement of the center of mass $\langle COMD^2 \rangle$ to achieve the value of the $\langle R_g^2 \rangle$.

The end vector autocorrelation functions for the three coarse-grained simulations are plotted in Figure 8. The two polyimides with para linkages in the APB part of the monomer (BPDA 1,3,4-APB and BPDA 1,4,4-APB) have similar decay profiles. The third polyimide (BPDA 1,3,3-APB), with all meta linkages in the APB part of the monomer, has a much faster decay. The times (in MC steps) at which these functions decay to 1/*e* are listed in Table 3.

The mean squared displacements of the centers of mass ($\langle COMD^2 \rangle$) for the three coarse-grained simulations are plotted in Figure 9. The results were derived from the same simulations as those of Figure 8. The BPDA 1,4,4-APB polyimide isomer had the slowest rate of movement, while the BPDA 1,3,3-APB polyimide isomer had the fastest rate of movement. The rates of these mean squared displacements are given in Table 3. Dividing the $\langle R_g^2 \rangle$ by the $\langle COMD^2 \rangle$ yields the relaxation time for this property. These results indicate that the MC procedure requires about 10^6 MC steps to achieve a statistically independent sample.

4.3 Reverse-mapped atomistic model

Three statistically independent samples of each coarse-grained polyimide model were reverse-mapped. These were selected at intervals in the MC simulation greater than the relaxation periods given in Table 3. The reverse-mapping procedure described in

section 3.3 produced cohesive bulk polymer simulations at the prescribed initial density of 1.37 g/cm^3 with no spearing or ring concatenation. The reverse-mapped atomistic structures were subjected to standard molecular mechanics energy minimization procedures.

These minimized structures, which had been subjected to 400 ps of constant pressure MD at 1 atm and 300 K, had equilibrium densities of about 1.3 g/cm^3. Specifically, the polymers with the 1,3,4-APB, 1,4,4-APB, and 1,3,3-APB isomers had densities of 1.270 ± 0.007, 1.283 ± 0.006, and 1.290 ± 0.004 g/cm^3 respectively. Each of these values is an average from three equilibrated atomistic samples which were reverse-mapped from statistically independent coarse-grained chains.

There is therefore no measureable variation in density as a function of the degree of meta linkage. This finding is consistent with the experimental fact that the overall packing of polymer segments (as reflected in the bulk density) is remarkably insensitive to the chain architecture [33,34].

On the other hand, the rigid benzene rings likely affect the packing on a very local scale [34,35]. Simulations could be very useful in predicting or interpreting the effects of this local structure (e.g. in gas sorption or diffusion). Figure 10 shows one measure of this structure, the intermolecular pair correlation function, g(r), for all atoms in the BDPA 1,3,4-APB reverse-mapped atomistic simulation.

5. Conclusions

Consistent procedures for mapping polyimides onto a coarse-grained Monte Carlo model were developed. Local chain structure is preserved in enough detail to allow reverse mapping back to the atomistic description, and a consistent set of long range interaction energies among the chain subunits results in chemically-plausible bulk structures and reasonable bulk and thin film densities. Although only minor differences in the equilibrium average long-range chain conformational variables were calculated, significant differences in the dynamic MC quantities were observed. A method for generating statistically independent equilibrium ensembles of atomistic structures has been established. The approach is expected to have utility in structure-property studies of high performance polymers and composites.

Table 1. The discretized energy values for the continuous effective potential energy, between monomer sub-unit 3 (SU3) and sub-unit 3 (SU3) of the BPDA 1,3,4-APB isomer and between monomer sub-unit 4 (SU4) and sub-unit 4 (SU4) of the BPDA 1,3,4-APB. The vector is representative of the set of symmetrically related vectors. The lattice size is 3 Å.

Lattice shell	Vector	Vector length (Å)	SU3-SU3 Energy (kJ/mol)	SU4-SU4 Energy (kJ/mol)
1	(1,0,0)	3.00	12.107	7.536
2	(2,0,0)	6.00	-0.797	-0.459
2	(1,1,0)	4.24	3.935	2.305
3	(3,0,0)	9.00	-0.536	-0.568
3	(2,1,0)	6.71	-1.270	-0.779
3	(1,1,1)	5.19	0.570	0.363
4	(4,0,0)	12.0	-0.072	-0.095
4	(3,1,0)	9.49	-0.375	-0.452
4	(2,2,0)	8.49	-0.755	-0.691
4	(2,1,1)	7.35	-1.239	-0.855
5	(5,0,0)	15.0	-0.004	-0.005
5	(4,1,0)	12.4	-0.059	-0.075
5	(3,2,0)	10.8	-0.149	-0.206
5	(3,1,1)	9.95	-0.268	-0.351
5	(2,2,1)	9.00	-0.535	-0.567

Table 2. The average end to end distances and the average radii of gyration for the three simulated coarse-grained polyimides.

	<ETE> (nm)	$\langle R_g^2 \rangle$ (nm^2)
BPDA 1,3,4-APB	6.7±0.3	8.9±0.8
BPDA 1,4,4-APB	6.8±0.8	9.3±1.6
BPDA 1,3,3-APB	6.1±0.4	6.9±0.6

Table 3. Dynamic conformational properties of the bulk coarse-grained polyimide isomer models. The number of Monte Carlo (MC) steps required for decay of the autocorrelation function of the end vector to a value of 1/e, the rate of the average squared displacement of the center of mass (<COMD^2>) of the coarse-grained polymer chains, and the number of MC steps required for the <COMD^2> to achieve the value of <R_g^2>.

	End vector ACF decay, 1/e value (MC steps)	<(COMD)^2> rate (nm^2/MC step)	<(COMD)^2> relaxation time (MC steps)
BPDA 1,3,4-APB	1.0×10^6	8.3×10^{-6}	1.0×10^6
BPDA 1,4,4-APB	1.1×10^6	5.4×10^{-6}	1.7×10^6
BPDA 1,3,3-APB	2.6×10^5	2.8×10^{-5}	2.4×10^5

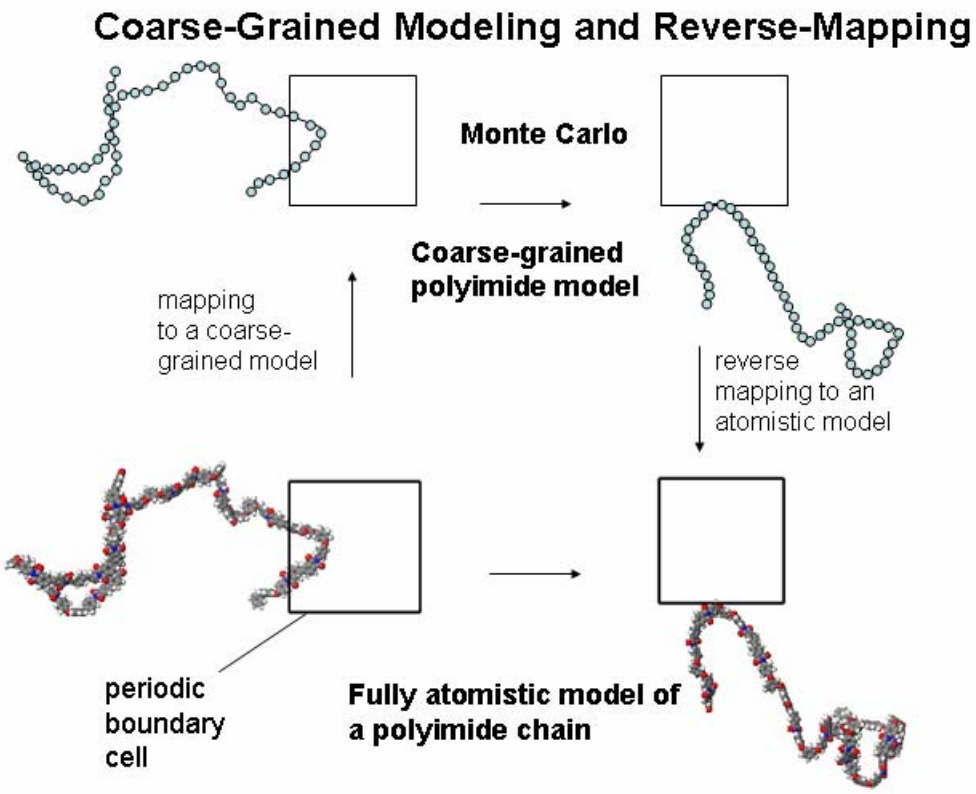

Figure 1. The procedure for coarse-graining and reverse-mapping. Chains shown are parent chains in a simulation with periodic boundary conditions (square box).

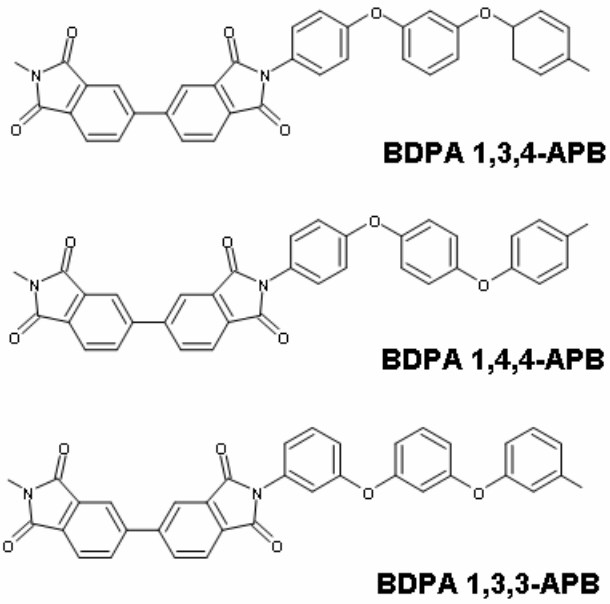

Figure 2. The repeat units for the three different polyimide isomers.

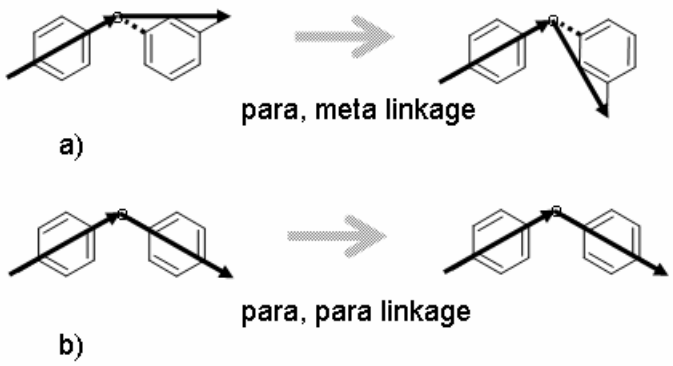

Figure 3. a) Rotation about the carbon-oxygen bond (possessing a meta-para linkage) can yield a substantial alteration in angle between the vectors along the polymer backbone. b) The angle is not substantially altered by this bond rotation with the para-para linkage.

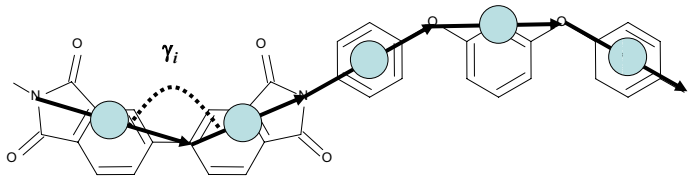

Figure 4. The atomistic polyimide model is mapped onto a coarse-grained representation. The linked vectors follow the contour of the polymer backbone. The angles, γ_i, between successive vectors are determined from molecular dynamics simulation. Beads (shown as shaded circles) are placed at the midpoint of each vector. These beads are the sites for the long range interaction energy (LRE) between two non-successive beads and for beads on different chains.

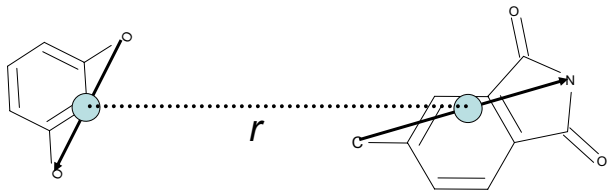

Figure 5. The continuous effective potential energy between two monomer sub-units (SUs) is estimated by averaging over the orientations of each SU and summing the atomistic Lennard-Jones potentials.

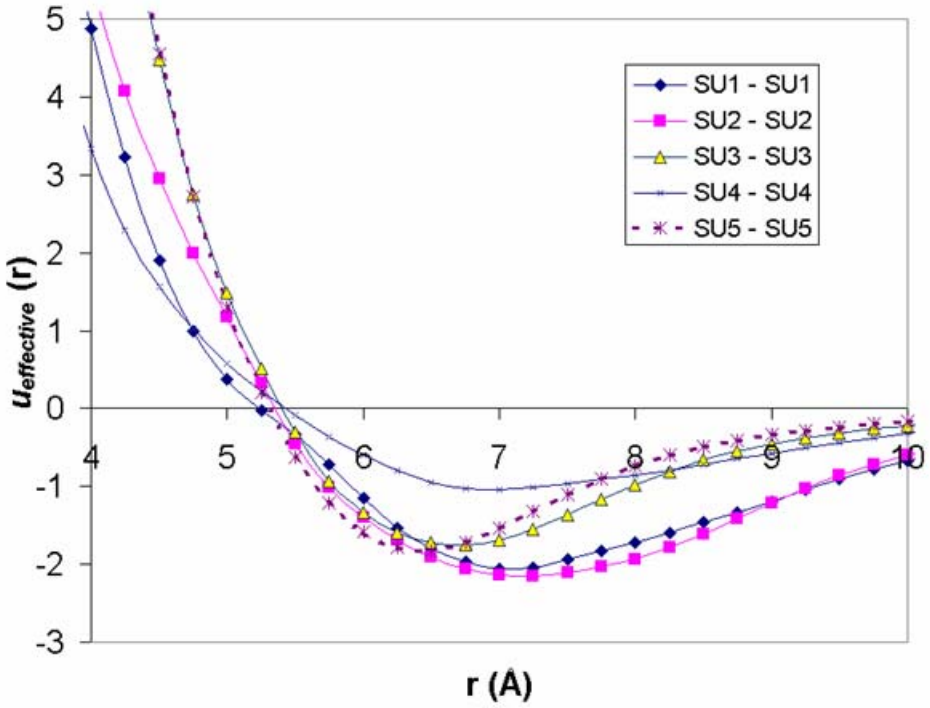

Figure 6. Plot of $u_{effective}(r)$ for five pairs of sub-units (SU1-SU5) for the BPDA 1,3,4-APB monomer. Only five of the fifteen possible combinations are shown for clarity. Energies are given in kJ/mol.

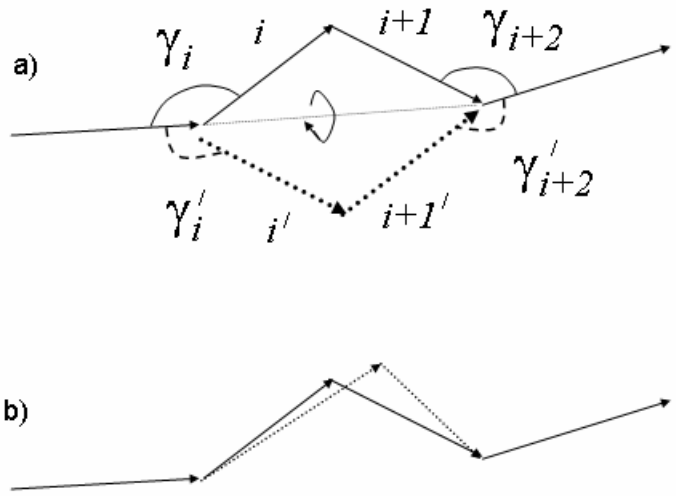

Figure 7. Monte Carlo moves used for the simulation. a) Rotation of two vectors (*i, i+1*) about the axis of the sum of the two vectors. b) A slight repositioning of two successive vectors. This move is relatively insignificant since the length probabilities for these vectors are sharply peaked.

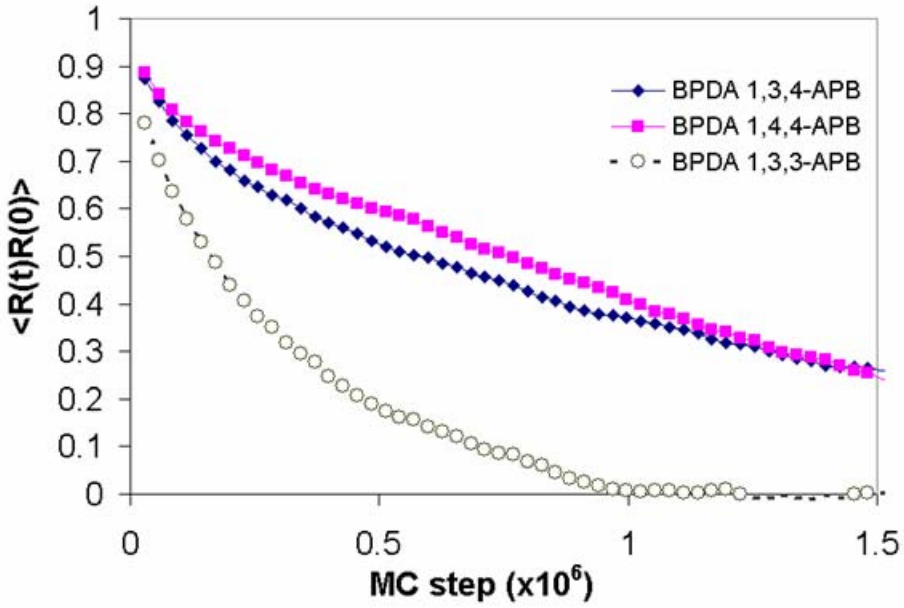

Figure 8. Autocorrelation functions for the end vectors for the three bulk coarse-grained simulations.

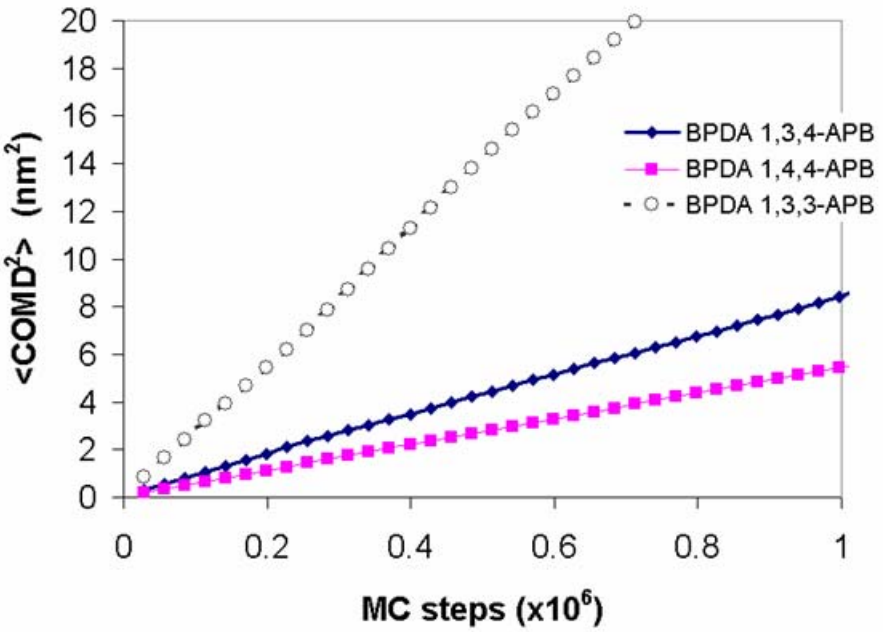

Figure 9. The mean square displacements of the oligomer centers of mass (<COMD^2>) for the three bulk coarse-grained simulations.

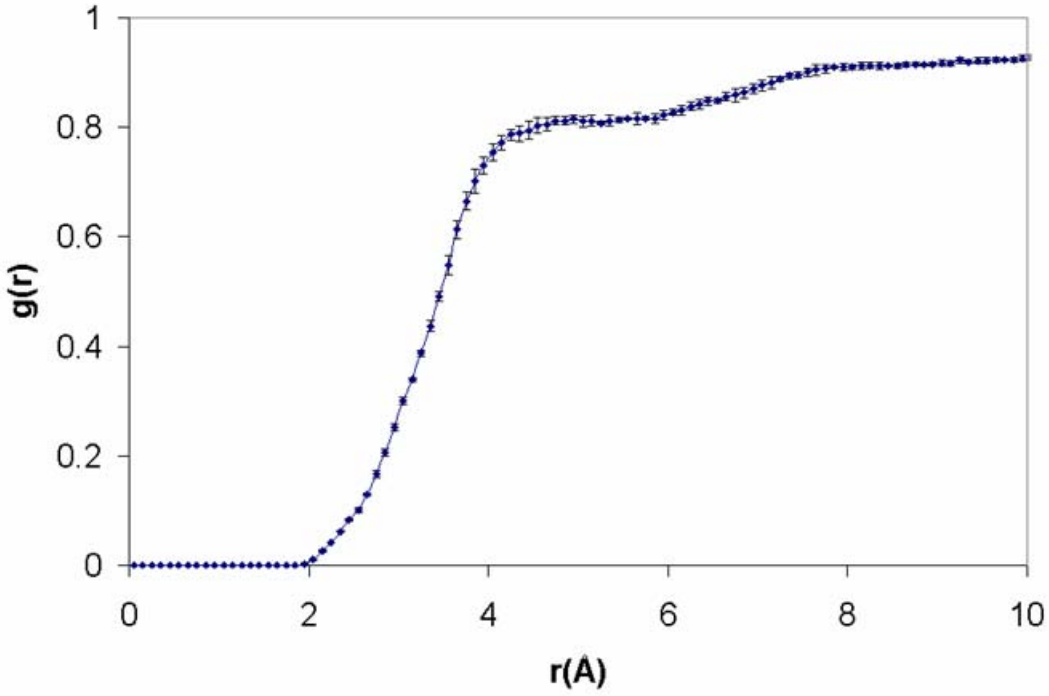

Figure 10. The intermolecular pair correlation function, g(r), for all atoms of the BPDA 1,3,4-APB bulk simulation. The function is averaged over three independent reverse-mapped atomistic simulations.

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14. ABSTRACT

A coarse-grained model for a set of three polyimide isomers is developed. Each polyimide is comprised of BPDA (3,3,4,4'-biphenyltetracarboxylic dianhydride) and one of three APB isomers: 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene or 1,3-bis(3-aminophenoxy)benzene. The coarse-grained model is constructed as a series of linked vectors following the contour of the polymer backbone. Beads located at the midpoint of each vector define centers for long range interaction energy between monomer subunits. A bulk simulation of each coarse-grained polyimide model is performed with a dynamic Monte Carlo procedure. These coarse-grained models are then reverse-mapped to fully atomistic models. The coarse-grained models show the expected trends in decreasing chain dimensions with increasing meta linkage in the APB section of the repeat unit, although these differences were minor due to the relatively short chains simulated here. Considerable differences are seen among the dynamic Monte Carlo properties of the three polyimide isomers. Decreasing relaxation times are seen with increasing meta linkage in the APB section of the repeat unit.

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