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REGULAR ARTICLE

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Computation of density of perfluoroalkyl methacrylates: a molecular modeling approach

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Abstract Molecular dynamics simulations have been carried out on different perfluoroalkyl methacrylates to predict their densities. Density calculations on selected perfluoroalkyl methacrylates have been performed using molecular dynamics in the NPT ensemble by employing COMPASS force field. The calculated density values compared quite well with the experimental data reported in the literature.

Keywords Perfluorinated methacrylates · COMPASS force field · NPT ensemble

Molecular modeling and simulation methodologies to predict bulk properties of polymers have advanced to a large extent due to advances in high performance computers and sophisticated algorithms. It is therefore possible to calculate the bulk properties of polymers reliably with better accuracy and comparison with experimental observations [1]. In designing new polymers and prediction of their bulk properties, density is an important parameter. Thus, there is a need to standardize molecular dynamics simulation protocols to compute densities of polymers. Sun and Rigby [2] used the NPT approach to predict the density of polysiloxanes using consistent force field (CFF) [3–5] method. Later, Fried et al. [6] attempted using condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field [1,7] to compute densities of polyphosphazenes and found a good agreement with experimental observations.

The objective of this communication is to standardize the molecular dynamics simulation strategies to predict densities of polymers. In addition, efforts have been made to probe how well the COMPASS force field predicts bulk density of perfluoropolymers for which experimental data are not available. The molecular dynamics method using the NPT ensemble, where N is the number of particles, P is pressure and T is temperature were used in the earlier literature to predict densities. In this study, molecular mechanics (MM) and molecular dynamics (MD) simulations were performed using the NPT ensemble to predict densities of series of perfluorinated methacrylates, and tested the validity of the COMPASS force field. In the case of COMPASS force field approach, total energy, $\mathrm{E_T}$ of the system is represented by the sum of bonding and non-bonding interactions given as,

$$\mathrm{E_T = E_b + E_o + E_\phi + E_{oop} + E_{vdw} + E_q} \tag{1}$$

Here, the first four terms represent the bonded interactions, which correspond to energies associated with bond stretch, $\mathrm{E_b}$, bond angle bending, $\mathrm{E_o}$, torsion angle rotations, $\mathrm{E_\phi}$ and out of loop, $\mathrm{E_{oop}}$. The last two terms represent non-bonded interactions, which consist of van der Waals term, $\mathrm{E_{vdw}}$ and electrostatic force, $\mathrm{E_q}$.

Fluoroalkyl methacrylates are known to exhibit interesting surface properties that make them useful as oil and water repellent agents [8] as well as in non-wetting biological applications [9]. Based on their low surface tension, the application of perfluoroalkyl containing polymers as thermally stable materials for coatings has attracted the attention of many researchers [10,11]. Prediction of surface properties of polymers is necessary to design new fluoropolymers and copolymers, which require the knowledge of densities. The general structure of perfluoroalkyl methacrylates used in this study is given in Fig. 1. The ten compounds used and their nomenclatures are given in Table 1.

The MM and MD simulations were carried out using the DISCOVER package employing the COMPASS force field. Minimization was performed using the methods of steepest descent followed by the conjugate gradient method. For dynamics, the pressure control developed by Berendsen et al. [12], and temperature control using the stochastic collision approach of Andersen [13] were used. The cut-offs [14]

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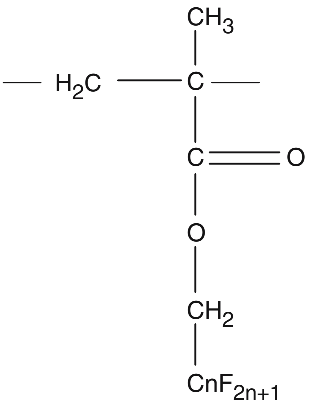

Fig. 1 Structure of perfluoroalkyl methacrylate (*n* = 1–10)

Table 1 Nomenclature of the perfluoroalkyl methacrylates chosen to study surface properties

No. of units (*n*)	Perfluorinated homopolymers	Code
1	2,2,2-trifluoroethyl methacrylate	F1MA
2	2,2,3,3,3-pentafluoropropyl methacrylate	F2MA
3	2,2,3,3,4,4,4-heptafluorobutyl methacrylate	F3MA
4	3,3,4,4,5,5,6,6,6-nonafluoropentyl methacrylate	F4MA
5	3,3,4,4,5,5,6,6,7,7,7-trioctafluorohexyl methacrylate	F5MA
6	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroheptyl methacrylate	F6MA
7	1H, 1H-dihydroperfluorooctyl methacrylate	F7MA
8	1H, 1H-dihydroperfluorononyl methacrylate	F8MA
9	1H, 1H-dihydroperfluorodecyl methacrylate	F9MA
10	1H, 1H-dihydroperfluorohendecyl methacrylate	F10MA

commonly encountered is atom-based and group-based. In the former case, when atoms with large partial or formal charges are present, significant errors were introduced if non-bonded interactions were computed using the atom-based cutoffs. In principle, it was possible to eliminate these artifacts by dispensing with the cutoffs for electrostatic interactions. In a periodic system, the evaluation of electrostatic interactions by means of standard lattice summation methods (e.g., Ewald method) was considered. However, one disadvantage is that such methods are computationally expensive and are not suited in generating long chain dynamics trajectories. The approximate computational cost of Ewald summation and charge group-based cutoff approach is in the ratio of 10–20:1 for systems with 1,000–2,000 atoms. However, the group-based approach is very efficient and performs substantially accurate calculations in an efficient manner [15]. Thus, non-bonded interactions were calculated using the group-based method with explicit atom sums being calculated with the distance of 9.5 Å . A tail correction was applied to non-bonded interactions during the dynamics.

In order to construct the amorphous cells, polymer chain was generated by considering its isotactic stereochemical structure. The polymer chain was minimized before constructing the cubic bulk cells by packing a single chain into a box with the periodic boundary conditions. All the simulations have been carried out using Material Studio modeling [16] software (version 3.1, Accelrys, Inc. San Diego, CA, USA) implemented in Pentium-based computers.

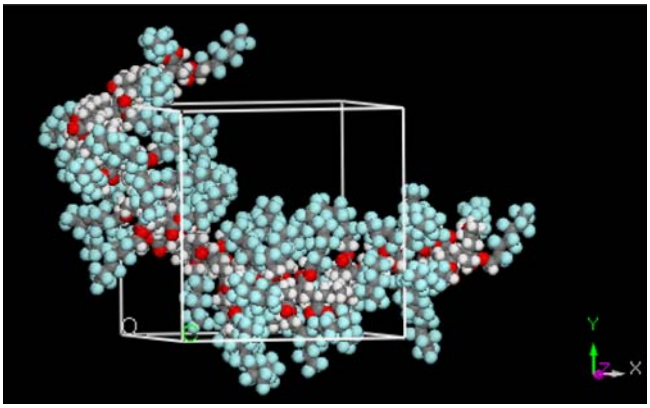

Fig. 2 The amorphous model of perfluoroalkyl methacrylate – F6MA (carbon atoms, *grey*; hydrogen, *white*, oxygen; *red* and fluorine; *pale blue* in color)

The procedure used to construct the amorphous cell module of Material studio involved the combined use of an algorithm developed by Theodorou and Suter [17] and the scanning method of Meirovitch [18]. The constructs were subsequently refined to provide an input for further calculations. A typical amorphous model of F6MA system with 50 monomer units (1,652 atoms) is shown in Fig. 2 (CPK model). The constructed amorphous cell was then minimized to a convergence value of 0.01 kcal/mol/Å . After minimization, the MD simulations were carried out using the NPT protocol, where simulations were run by keeping pressure and temperature constant using Berendsen's pressure control algorithm. The Berendsen method involves changing the pressure by altering the coordinates of the particles and the size of the unit cell in periodic boundary conditions. Furthermore, the Berendsen method couples the system to a pressure bath to maintain the pressure at a certain target. Then, by using the MD protocol, systems were equilibrated in the NPT ensemble at 298 K. The equilibration dynamics of 20 ps was performed prior to the production stage of duration 200 ps, which enabled us to find the density of the simulated system.

The procedure was repeated for numerous time periods to obtain the good average for each N-mer. In addition, multiple runs were also carried out for each N-mer starting from

Table 2 Densities computed from NPT simulation on methyl methacrylate

N-mer	Methylmethacrylate
5	1.180
10	1.192
20	1.162
30	1.174
40	1.153
50	1.205
Average density (g/cm^3)	1.178 ± 0.019
Experimental density (g/cm^3)	1.188

Table 3 Densities computed from NPT simulation for perfluoroalkyl methacrylates

N-mers	F1MA	F2MA	F3MA	F4MA	F5MA	F6MA	F7MA	F8MA	F9MA	F10MA
5	1.1989	1.2871	1.3272	1.4496	1.5162	1.5284	1.5514	1.5810	1.5986	1.5817
10	1.2515	1.3164	1.3800	1.4395	1.5218	1.5432	1.5698	1.5572	1.6077	1.6609
20	1.2489	1.2548	1.3986	1.5101	1.4467	1.5258	1.5215	1.5628	1.5469	1.5748
30	1.2342	1.3184	1.3747	1.4356	1.4979	1.5533	1.5370	1.5435	1.6131	1.5818
40	1.2547	1.3152	1.3395	1.4439	1.4675	1.5020	1.5741	1.5538	1.5661	1.5939
50	1.2245	1.3100	1.3459	1.4425	1.4560	1.5442	1.5572	1.5691	1.5911	1.6240
Average density (g/cm^3)	1.235 ±0.021	1.3003 ±0.025	1.3609 ±0.027	1.4535 ±0.028	1.4843 ±0.032	1.533 ±0.018	1.5518 ±0.019	1.5612 ±0.013	1.5873 ±0.025	1.6030 ±0.033

different initial configurations created by the amorphous cell. This minimized the deviations from the calculated densities. The procedure was adopted for different oligomers (n = 5, 10, 20, 30, 40 and 50) to obtain the average density in each case. The edge length of the simulated systems are: F1MA = 22.4409 Å; F2MA = 24.0586 Å; F3MA = 25.3830 Å; F4MA = 26.2891 Å; F5MA = 27.4077 Å; F6MA = 28.2902 Å; F7MA = 29.2566 Å; F8MA = 30.2023 Å; F9MA = 30.9725 Å; F10MA = 31.7579 Å. Simulation was validated by performing computations on methyl methacrylate (MMA) containing different N-mers for which experimental data are available [19]. The calculated density values of MMA are given in Table 2. It is evident that there is a good agreement between calculated and experimental densities, suggesting that the NPT protocol adopted here will provide reliable estimates of densities.

Computed densities of perfluoroalkyl methacrylate oligomers are presented in Table 3. Comparing the densities of the monomers of F1MA, F2MA and F3MA systems would further test the validity of the simulation protocol used and the predictive power of the COMPASS force field. For instance, the computed densities are 1.1796, 1.2813 and 1.3450, respectively, for F1MA, F2MA and F3MA, which are in good agreement with the literature data [20] of 1.1810, 1.2770 and 1.3450. In the absence of direct experimental density data for higher series of perfluoroalkyl methacrylates, few structurally similar systems viz., 3,3,4,4,5,5,6,6,6-nonafluorohexyl methacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate were selected. The computed densities of 1.402 and 1.496 for these systems are in close agreement with the density values of 1.4535 and 1.533 for F4MA and F6MA systems. This suggests that the NPT ensemble-based simulation methodologies are a reliable test protocol to obtain densities of polymers. It is also demonstrated in this investigation that given the appropriate force field (such as COMPASS), it is possible to predict density values of the compounds for which experimental data are not available.

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