Available online at www.sciencedirect.com
ScienceDirect
polymer
Polymer 47 (2006) 6914–6924
www.elsevier.com/locate/polymer

Molecular modeling and atomistic simulation strategies to determine surface properties of perfluorinated homopolymers and their random copolymers☆

B. Prathab [a], Tejraj M. Aminabhavi [a,*], R. Parthasarathi [b], P. Manikandan [b], V. Subramanian [b,*]

[a] *Molecular Modeling Division, Center of Excellence in Polymer Science, Pavate Nagar, Karnatak University, Dharwad 580 003, Karnataka, India*
[b] *Chemical Laboratory, Central Leather Research Institute, Adyar, Chennai 600 020, Tamil Nadu, India*

Received 14 March 2006; received in revised form 10 July 2006; accepted 17 July 2006
Available online 14 August 2006

Abstract

Molecular mechanics (MM) and molecular dynamics (MD) simulations on ten perfluoroalkyl methacrylates and four copolymers derived from methyl methacrylate (MMA) and 1,1-dihydroperfluorohendecyl methacrylate (F10MA) in different ratios have been performed to predict surface properties. 1,1-Dihydroperfluorohendecyl methacrylate, which contained highest number of fluorine atoms, exhibited lowest surface energy, a trend that is in accordance with experimental observations. Density calculations on selected perfluoroalkyl methacrylates have been performed using NPT dynamics, for which no experimental data are available. Computations were performed to obtain bulk properties like cohesive energy density and solubility parameter through MM and MD simulations in the NVT ensemble under periodic boundary conditions. From the equilibrated structures, surface energies were computed, which compared well with the experimental data reported in the literature. Surface energies of copolymers decreased with increasing number of perfluoroalkyl groups. Various components of energetic interactions have been examined in detail in order to gain a better insight into interactions between bulk structure and the film. The dominant contributions are from van der Waals and Coulombic energy terms. The computed mass density profile for thin films gave an indication whether the film is of sufficient thickness so that the interior of the film is indistinguishable from the bulk structure. The total pair correlation and bond correlation functions have been analyzed to confirm the amorphous nature of the simulated structures.

Keywords: Perfluoroalkyl methacrylates; Molecular dynamics; Thin films

1. Introduction

Surface properties of polymers are important for understanding adhesion and wettability [1]. The prediction of polymer surface properties is important in designing high performance materials for various applications such as coatings, adhesives and biomaterials [2–4]. However, an in-depth understanding of polymer surfaces at molecular level offers a tremendous capability to tailor the surfaces for specific applications. In the earlier literature, several theories have been advanced to predict surface properties of polymers of which Cahn–Hilliard theory [5] in conjunction with Flory, Orwoll and Vrij (FOV) equation of state [6] has been successful to provide a unified picture of surface tensions of oligomers as well as polymer single component liquids. Subsequently, the lattice model approaches developed by Helfand [7,8], Dill and Flory [9,10], and Scheutjens and Fleer [11] have been useful in studying the surface properties of polymers. Later, Theodorou [12] examined the bulk homopolymers at interfaces using the site lattice model approach of Scheutjens and Fleer [11] for polymer solutions. In recent years, molecular mechanics (MM) and molecular dynamics (MD) simulations as well as Monte Carlo (MC) techniques are considered to be the most powerful tools in predicting many important properties of polymers [13–22]. Eichinger et al. [23] computed cohesive energy density and solubility parameter values

---

☆ This paper is Center of Excellence in Polymer Science communication # 105.

* Corresponding authors. Fax: +91 836 2771575.

E-mail addresses: aminabhavi@yahoo.com (T.M. Aminabhavi), subuchem@hotmail.com (V. Subramanian).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.07.034

of polyetherimide (Ultem) to demonstrate the usefulness of MM and MD simulation protocols to predict the bulk properties of polymers for which experimental data are neither available nor such investigations would be inherently difficult. Further, these studies have shown that calculated cohesive energy densities and solubility parameters are in reasonable agreement with the experimental data.

Realizing these aspects and as a part of our continuing efforts to understand the dynamics of polymer chains, we have selected series ($n = 1-10$) of perfluoroalkyl methacrylates as model compounds to compute their surface properties. These fluoromonomers, either alone or mixed with other monomers, could help to extend higher flexibility while designing new polymers. Fluorocarbon polymers have been widely studied as materials having low surface energy coatings and hence, are useful in non-wetting biological applications [3]. Particularly, polymers containing atomic fluorine along the backbone or in the side chain possess many desirable properties [24] such as low surface energy, resistance to corrosive chemicals and organic solvents, high thermal stability, water repellency, low refractive index and low coefficient of friction. These characteristics are due to low polarizability and strong electronegativity of the fluorine atom; moreover, electronegativity induces a strong dipole in the C–F bond [25,26], which would make fluorocompounds simultaneously oleophobic and hydrophobic [27]. Taking advantage of these physical properties, fluoropolymers have been used as oil and water repellent agents, moisture proof coatings and cladding materials in polymeric optical fibers for medical diagnosis [28]. Moreover, fluoroalkyl compounds exhibit surface characteristics that are particularly important because they affect the structure and functions of the products, and surface characteristics of these polymers depend upon the characteristics of perfluoroalkyl group side chains [29]. There are other studies in literature [30] on acryl-based polymers having side chains of perfluoroalkyl group, wherein the influence of chain length and crystallinity of polymers has been investigated. Fluoropolymers have the propensity to migrate to the surface when dissolved or dispersed in other media, which would allow the perfluoroalkyl group to concentrate on the surface. The high concentration of perfluoroalkyl groups at the surface lowers the surface energy, thus creating very repellent surfaces, even at a very low concentration of perfluoroalkyl group, which could dramatically impart this effect. Such inherent characteristics of fluoropolymers can be successfully exploited to develop new polymers and materials with desired properties by blending or copolymerization with other polymers.

The commercial application of any fluorine-containing acrylate polymer system depends upon the effective and efficient use of fluorine i.e., the increasing amount of fluorine would lower the surface tension relative to the parent material. Efficiency refers to the minimum concentration of fluorine necessary to reach the minimum surface tension. The origin of these effects can be seen from the famous Gibbs adsorption equation [31] given in the form:

$$\gamma = A - \sum_i \Gamma_i \mu_i^\sigma \quad (1)$$

where γ is surface tension, Γ is surface excess of i in moles per unit area of surface σ, μ_i^σ is surface chemical potential of the ith species and A is Helmholtz free energy per unit area of surface, σ. Due to their low surface tensions, the application of perfluoroalkyl containing polymers as thermally stable materials for coating applications has attracted the attention of many investigators [32,33]. However, one of the drawbacks of perfluorinated polymers is their poor solubility in common organic solvents, which renders them intractable materials. This problem can be overcome by copolymerization of perfluorinated compounds with non-fluorine-containing monomers such as acrylates, methacrylates or styrene [34–39]. Fluoroalkyl acrylate and methacrylate homopolymers as well as their copolymers are being increasingly used in plastics' formulations. However, the synthesis and characterization of these new polymeric materials are time-consuming and hence, molecular modeling approaches would be an alternative solution to precisely predict the structural and functional properties of polymer surfaces. The principle objective of this investigation is to predict the surface properties of perfluorinated polymers by performing MM and MD simulations. The issues addressed here are: (i) how an increase in CF_2 units could influence the surface properties of polymers? and (ii) how does copolymerization of perfluoroalkyl methacrylates with other polymers would modify their surface properties? In order to further support these computations, density calculations, total pair correlation, bond correlation functions and mass density profiles have been calculated and analyzed. The general structure of perfluoroalkyl methacrylates used in this study is given in Fig. 1 and model perfluorinated homopolymers selected in this study are compiled in Table 1.

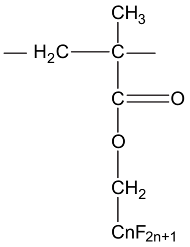

Fig. 1. Structure of perfluoroalkyl methacrylate ($n = 1-10$).

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

2. Computational strategies

2.1. Modeling details

MM and MD simulations were performed using MS modeling 3.1 software [40] purchased from Accelrys Inc. (San Diego, CA, USA) on a Discover package by employing the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [41,42]. Minimization was performed using the steepest descent approach followed by the conjugate gradient method. The temperature in all simulations was equilibrated with the Andersen algorithm [43]. The velocity Verlet algorithm [44] was used to integrate the equations of motion. The cutoffs [45] commonly encountered are atom-based and group-based. In the former case, when atoms with large partial or formal charges are present, significant errors have been 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, evaluation of electrostatic interactions by means of standard lattice summation methods (e.g., the Ewald method) was considered. However, one disadvantage is that such methods are computationally expensive and are thus 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 1000–2000 atoms. However, the group-based approach is very efficient and well-suited to conditions in which the system consists of molecules composed of essentially neutral fragments with dipoles and performs substantially accurate calculations in an efficient manner. Thus, non-bonded interactions have been calculated using the group-based method with explicit atom sums being calculated with the distance of 9.5 Å.

2.2. Density calculation on perfluoroalkyl methacrylates

Polymer density can be readily computed with greater accuracy using MM and MD simulations that rival experimental observations. Experimental density data on many perfluoroalkyl methacrylates are not available in the literature. Thus, density calculation was attempted using the method of constant pressure simulation (NPT dynamics), where N is number of particles, P is pressure and T is temperature. The overall methodology and the calculation of density of perfluoroalkyl methacrylates (F1MA–F10MA) were described in the earlier paper [46].

The polymer chain for the amorphous cell construction was generated by considering its isotactic stereochemical structure. The method used in the amorphous cell module of Material Studio is the combined use of an algorithm developed by Theodorou and Suter [47] and scanning method of Meirovitch [48]. Initially, the proposed structure was generated by using rotational isomeric state (RIS) theory of Flory [49] that describes conformations of the unperturbed chains. In order to avoid excessive overlaps between chains, modified conditional probabilities were used to account for non-bonded interactions between atoms to be placed and rest of the system. In the scanning method, all possible continuations of the growing chain were considered while calculating conditional probabilities. However, in practice, it was not possible to examine all continuations of the chain and look ahead is normally restricted to a few backbone bonds. The number of look ahead bonds represents the number of forward bonds that is considered during the construction, which was subsequently refined to provide the input for further calculations.

Then, by using MD protocol, systems were equilibrated in 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 density of the simulated system. The procedure was adopted for different oligomers ($N = 5$, 10, 20, 30, 40 and 50) to obtain the best average density value in each case. The average density of different perfluoroalkyl methacrylates are F1MA = 1.235 ± 0.021, F2MA = 1.3003 ± 0.025, F3MA = 1.3609 ± 0.027, F4MA = 1.4535 ± 0.028, F5MA = 1.4843 ± 0.032, F6MA = 1.533 ± 0.018, F7MA = 1.5518 ± 0.019, F8MA = 1.5612 ± 0.013, F9MA = 1.5873 ± 0.025 and F10MA = 1.6030 ± 0.033.

2.3. Amorphous cells

Polymer chains were generated with 50 monomer units. The chain was minimized and amorphous cells were constructed for series of perfluoroalkyl methacrylates, using the methodology described in Section 2.2. The edge lengths of bulk cells vary from 22.4409 to 31.7579 Å and cubic bulk cells were constructed by packing a single chain into the box with periodic boundary conditions. An amorphous model of the polymer is shown in Fig. 2 (CPK model structure).

The NVT ensemble (the constant volume refers to cell volume, but not the effective volume occupied by atoms in the periodic box) molecular dynamics simulation was employed

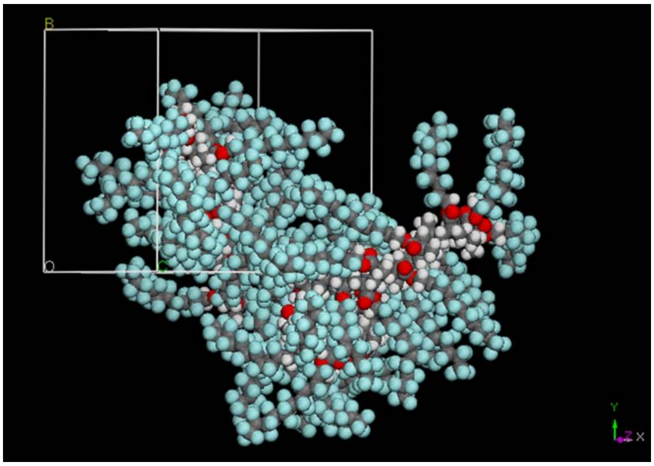

Fig. 2. The amorphous model of perfluoroalkyl methacrylate – F10MA (carbon atoms – grey, hydrogen – white, oxygen – red and fluorine – pale blue color) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

to relax the bulk cells. Initial structures have very high potential energy and relaxation of these high-energy structures followed a three-step strategy. Potential energy of the structure was minimized using an algorithm described above; high temperature molecular dynamic run was performed at 500–1000 K for 10 ps to shake the cell out of the unfavorable local minima that had high energies. Subsequently, systems were subjected to 50 ps of dynamics at 300 K with snapshots being saved every 0.1 ps during the last half of the run, and the conformer with a minimum potential energy was selected and minimized to a convergence of 0.01 kcal/mol/Å. The size and shape of cubic cells were kept unchanged during the MD runs. The cells having acceptable potential energies were selected and relaxation molecular dynamics simulation was performed at 300 K on short listed samples for 300 ps. The final energy minimized samples were used for all property calculations. These amorphous cells were subsequently used to generate thin films.

2.4. Thin films (free surfaces)

Polymer thin films are important in various technologies including adhesion, coatings, paints and microelectronics. Thin films experience a directional asymmetry during interaction with their surroundings. The properties and structures of films are thus different than those of the bulk states. Compared to several experimental methods to study film properties, MM and MD simulations can offer very detailed atomistic information using only the chemical constitution and inter-atomic force parameters.

In this research, thin films were constructed from amorphous cells by elongating one of the boundary conditions until the parent chain no longer interacts with its image along the coordinate. This coordinate is considered to be z coordinate, which represents the coordinate that is normal to planes of all surfaces and interfaces. Thin films were constructed by employing the methodology used in literature [50–52] for other polymers and by extending z dimension of the 3D bulk periodic cell to 100 Å. This cell extension resulted in two free surfaces per thin film. Relaxation of the initial structures formed by conversion from bulk to film was achieved by subjecting thin films to MM energy minimization followed by high temperature MD stage (500–1000 K) using the NVT ensemble. The choice of a relatively higher temperature was essential to remove packing inefficiencies generated by the initial cell extension process. This was followed by 300 ps of MD simulation at 300 K. Snapshots of the trajectory were taken at every 0.01 ps. The lowest energy snapshot among the later half of the trajectories were chosen and minimized with the convergence of 0.01 kcal/mol/Å. No additional thermodynamic constraints on atoms or cell were employed other than those posed by the MD method as described in 3D bulk cell relaxation. Sufficient relaxation of the structures and acceptable fluctuations were observed for potential energy in order to ascertain whether samples were suitable for the purpose of estimating surface properties.

Surface energy was calculated from the difference in energy between thin film ($E_{\text{thin film}}$) and energy of the corresponding 3D bulk amorphous cell ($E_{\text{amorphous cell}}$) divided by the surface area created upon formation of thin film which is given by:

$$\gamma = \left(E_{\text{thin film}} - E_{\text{amorphous cell}}\right)/2A \tag{2}$$

here, the surface area is $2A$, as two surfaces of area A, was formed due to the creation of thin film. Total potential energy decomposition for the formation of thin films includes bond length (stretch) and bond angles (bend), torsional potential (torsion), energy deviations due to out of plane inversion (oop) and cross-terms to account for bond or angle distortions caused by the nearby atoms. The non-bonded interactions involve van der Waals (vdW) and electrostatic (Coulomb) energy terms. The contributions of these terms will be discussed later in Sections 3.3 and 3.4.

2.5. Simulation of random copolymers

The construction strategy as implemented in MS Accelrys was followed for building random copolymers of methyl methacrylate (MMA) and 1,1-dihydroperfluorohendecyl methacrylate (F10MA). An illustration of the structure of random copolymers of MMA and F10MA is shown in Fig. 3. The distribution of repeat units in random copolymers counts on the conditional probabilities. The conditional probability for chain growth was entered as an $n \times n$ matrix. A single parent chain of 50 monomer units with different compositions of MMA and F10MA has been simulated to study the influence of incorporation of perfluorinated methacrylate monomers on surface properties of copolymers. The sequence along MMA and F10MA copolymers was assembled based on the probability of composition: (MMA-*co*-F10MA – 0.99/0.01); (MMA-*co*-F10MA – 0.95/0.05); (MMA-*co*-F10MA – 0.90/0.10) and (MMA-*co*-F10MA – 0.75/0.25). A simulated structure of the random copolymer is shown in Fig. 4 (CPK model). The surfaces of homopolymers and random copolymers were treated with equal success using the same technique [53], but relaxation was adequately robust such that different monomer units of the random copolymer were assigned correctly between anisotropic surface and isotropic interior of the

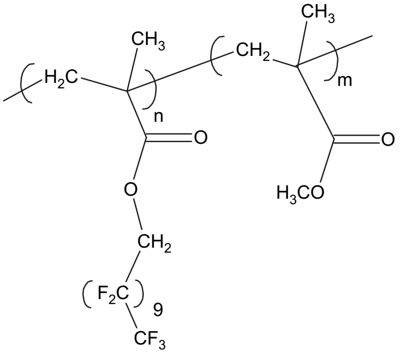

Fig. 3. Structure of copolymer of MMA and F10MA.

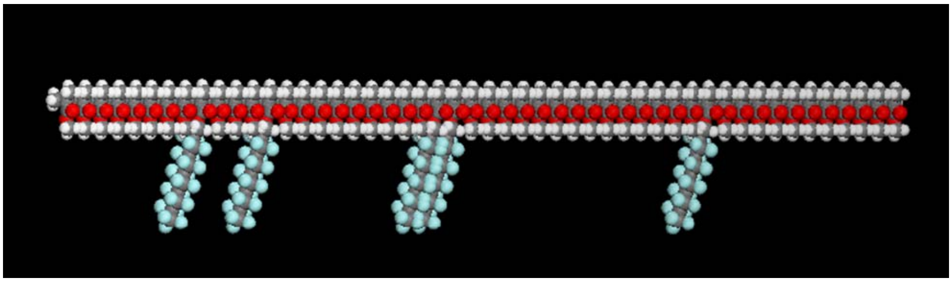

Fig. 4. Simulated structure of the random copolymer of MMA and F10MA.

film. Amorphous cells of three-dimensional periodicity and films were constructed and relaxed using the methodology discussed before. Edge lengths were varied depending upon the cell size, which in turn, depends upon the density of the system. Density of the chosen systems are, $\rho_{(\mathrm{MMA})} = 1.188\ \mathrm{g/cm^3}$ and $\rho_{(\mathrm{F10MA})} = 1.603\ \mathrm{g/cm^3}$. Densities of copolymer systems [51] were calculated based on different compositions of weight fractions of MMA and F10MA. Surface property calculations followed the same trends as discussed before for perfluorinated methacrylates.

3. Results and discussion

3.1. Cohesive energy density and Hildebrand solubility parameter

The cohesive energy properties of perfluoroalkyl methacrylates are difficult to determine experimentally because the chosen polymers are insoluble, have high glass transitions and are sometimes poorly characterized. Therefore, we thought of using MD simulations, which could provide useful information of higher quality than can be obtained by other methods. We have performed simulations in order to evaluate the cohesive energy density of the polymers. The cohesive energy, E_{coh} is defined as an increase in energy per mole of a polymer if all intermolecular forces are eliminated. On the other hand, cohesive energy density (CED) corresponds to cohesive energy per unit volume. If V_{mol} is molar volume of the polymer, then CED is defined as:

$$\mathrm{CED} = (E_{\mathrm{coh}}/V_{\mathrm{mol}}) \tag{3}$$

The Hildebrand solubility parameter, δ is given as:

$$\delta = (E_{\mathrm{coh}}/V_{\mathrm{mol}})^{1/2} \tag{4}$$

Calculated values of CED and δ from MD simulation performed on perfluorinated homopolymers and copolymers are given in Tables 3 and 5. However, in order to validate the simulation protocol, we found it worthwhile to compare the solubility parameter values of poly(methyl methacrylate) (PMMA) and polystyrene (PS) (see data presented in Table 2 and compared with the literature data [54]). The δ values agreed well within the limits of experimental errors. For instance, the computed δ value of 9.62 $(\mathrm{cal/cm^3})^{1/2}$ for PMMA agreed well with the literature value of 9.45 $(\mathrm{cal/cm^3})^{1/2}$; similarly, the computed δ value of 8.40 $(\mathrm{cal/cm^3})^{1/2}$ for PS agreed well with the experimental value of 9.0 $(\mathrm{cal/cm^3})^{1/2}$.

3.2. Validation of modeling strategy for surface energy calculations

In order to validate the theoretical simulation protocol used for the calculation of surface energies, we have taken PMMA and PS as model polymers for which experimental data [54] of surface energy are available to compare with the simulated results. Calculated surface energy for PMMA and PS (see Table 2) is agreeable within the limits of experimental errors, suggesting that molecular simulation strategies provide the reliable estimates of surface properties. For PMMA, the calculated surface energy value of 38.40 $\mathrm{mJ/m^2}$ matched well with the experimental value of 39.0 $\mathrm{mJ/m^2}$. Similarly, in case of PS, the surface energy value of 32.01 $\mathrm{mJ/m^2}$ agreed closely with the experimental value of 33.0 $\mathrm{mJ/m^2}$. Hence, molecular modeling simulation strategies are useful in predicting the surface properties of polymers for which experimental data are either not available or difficult to obtain.

3.3. Fluorinated polymers

Surface properties of ten perfluorinated methacrylates have been predicted by the MD simulation approach such that any synthetic effort can be minimized for selecting a suitable candidate to develop new polymers that exhibit water and oil repellent properties [55]. Surface properties of the chosen

Table 2
Comparison of calculated surface energy for model polymer systems

Polymers	Density ($\mathrm{g/cm^3}$)	Dimensions (Å)	CED ($\mathrm{cal/cm^3}$)	δ $(\mathrm{cal/cm^3})^{1/2}$	Surface energy ($\mathrm{mJ/m^2}$)	
					Simulation	Literature [54]
Poly(methyl methacrylate)	1.188	19.1271	92.61	9.62 ± 0.12 (9.45)	38.40 ± 3.95	39.0
Polystyrene	1.040	20.2594	70.63	8.40 ± 0.04 (9.0)	32.01 ± 2.49	33.0

Values in the parentheses represent literature data [54].

Table 3
Calculated CED, solubility parameter and surface energy of perfluoroalkyl methacrylates

Perfluoroalkyl systems	Density (g/cm^3)	Dimensions (Å)	CED (cal/cm^3)	δ (cal/cm^3)$^{1/2}$	Surface energy (mJ/m^2)	
					Free surface[a]	Zisman[b]
F1MA	1.2350	22.4409	39.88	6.32 ± 0.08	19.61 ± 4.1	21.98
F2MA	1.3003	24.0586	29.45	5.43 ± 0.05	15.60 ± 5.2	18.0
F3MA	1.3609	25.3830	25.59	5.06 ± 0.06	13.99 ± 1.2	16.40
F4MA	1.4535	26.2891	19.30	4.39 ± 0.12	11.96 ± 4.6	13.62
F5MA	1.4843	27.4077	15.10	3.89 ± 0.10	11.01 ± 2.9	11.58
F6MA	1.5330	28.2902	13.57	3.68 ± 0.06	10.27 ± 2.0	10.79
F7MA	1.5518	29.2566	11.44	3.38 ± 0.05	9.04 ± 3.7	9.64
F8MA	1.5612	30.2023	10.12	3.18 ± 0.09	8.36 ± 5.4	8.89
F9MA	1.5873	30.9725	8.85	2.97 ± 0.14	7.51 ± 4.0	8.14
F10MA	1.6030	31.7579	7.35	2.71 ± 0.04	6.71 ± 3.3	7.20

[a] See Eq. (2).
[b] See Eq. (5).

perfluorinated methacrylates are summarized in Table 3 along with the results of solubility parameter and cohesive energy density. It is observed that CED and surface energy values decreased continuously with increasing number of perfluorinated methacrylate in the PMMA side chain. Details of internal energy components in the bulk and the film for the chosen homopolymers are given in Table 4. Notice that van der Waals and Coulombic electrostatic interaction energy terms contribute considerably to the formation of free surface of the films. Also, with increasing fluorine content of the side chain of PMMA, there is a noticeable decrease in van der Waals energy with a systematic increase in Columbic energy. However, torsional, bending and bond stretching energies of the films are lower than the amorphous cells. Of particular interest in this research is the prediction of surface energy, which decreased from 19.61 to 6.71 mJ/m^2, respectively, for F1MA–F10MA homopolymers. This trend is in accordance with the experimental observation that with increasing fluorination, the surface energy decreases [56–59].

Alternatively, surface energy was also calculated from the solubility parameter values using the empirical equation of Zisman [60].

$$\gamma = 0.75(E_{\mathrm{coh}})^{2/3} \tag{5}$$

The surface energies calculated from Eq. (5) along with the CED values obtained from bulk simulations are included in Table 3. These values compare very well with surface energies obtained directly from simulations according to Eq. (2). Furthermore, surface energy values of perfluorinated homopolymers, F1MA, F6MA and F7MA calculated from Eqs. (2) and (5) are comparable with literature [56,57] available experimental values of 20.7, 9.8 and 9.0 mJ/m^2. This demonstrates a good agreement between calculated and experimental surface energy values, suggesting that simulation strategy adopted here is quite reliable to compute the surface energy values of the polymers.

Table 4
Components of the contribution of internal energy to surface energy of perfluorinated homopolymers

	F1MA	F2MA	F3MA	F4MA	F5MA
Bond	−2.24 ± 2.3	−2.11 ± 3.4	−1.69 ± 2.0	−5.55 ± 3.1	−4.90 ± 1.0
Angle	−10.81 ± 1.4	−13.10 ± 2.6	−10.79 ± 3.9	−9.56 ± 2.3	−5.88 ± 1.8
Torsion	−1.67 ± 4.5	−1.80 ± 3.2	−2.08 ± 7.1	−1.03 ± 3.7	−4.52 ± 6.2
Oop	−0.65 ± 0.9	−1.16 ± 1.8	−0.41 ± 0.3	−0.39 ± 0.6	−0.66 ± 1.7
Cross	−2.62 ± 2.1	−3.60 ± 0.7	−6.3 ± 1.5	−5.33 ± 0.9	−6.85 ± 2.4
vdW	32.62 ± 11.8	31.40 ± 12.4	29.24 ± 13.5	27.33 ± 9.8	26.67 ± 13.0
Coulomb	4.98 ± 3.5	5.97 ± 4.5	6.02 ± 2.5	6.49 ± 5.4	7.15 ± 3.0
Surface energy (mJ/m^2)	19.61 ± 4.1	15.6 ± 5.2	13.99 ± 1.2	11.96 ± 4.6	11.01 ± 2.9
Surface area (A)^2	503.59	578.81	644.30	691.12	751.18
	F6MA	F7MA	F8MA	F9MA	F10MA
Bond	−3.60 ± 3.1	−2.33 ± 1.9	−4.48 ± 3.1	−1.08 ± 4.0	−4.93 ± 2.4
Angle	−2.73 ± 3.3	−4.30 ± 3.2	−1.02 ± 1.2	−1.09 ± 4.1	−2.84 ± 3.5
Torsion	−11.8 ± 2.7	−9.04 ± 1.1	−10.77 ± 2.4	−8.89 ± 2.5	−9.62 ± 2.6
Oop	−0.50 ± 1.3	−0.26 ± 0.45	−0.37 ± 1.2	−0.14 ± 0.9	−0.53 ± 0.2
Cross	−3.21 ± 1.6	−5.55 ± 5.2	−4.09 ± 2.5	−9.75 ± 3.0	−2.49 ± 1.1
vdW	24.4 ± 10.3	21.84 ± 11.3	19.88 ± 12.8	18.57 ± 15.7	16.65 ± 9.3
Coulomb	7.71 ± 3.7	8.68 ± 4.2	9.21 ± 3.0	9.89 ± 2.8	10.47 ± 3.8
Surface energy (mJ/m^2)	10.27 ± 2.0	9.04 ± 3.7	8.36 ± 5.4	7.51 ± 4.0	6.71 ± 3.3
Surface area (A)^2	800.34	855.95	912.18	959.30	1008.56

Table 5
Calculated CED, solubility parameter and surface energy values of copolymers of MMA/F10MA

Copolymer composition	Mole fraction of F10MA units	Density (g/cm^3)	Dimensions (Å)	CED (cal/cm^3)	δ (cal/cm^3)$^{1/2}$	Surface energy (mJ/m^2)		
						Free surface[a]	Zisman[b]	Literature [56]
P(MMA-*co*-F10MA) 0.99/0.01	0.02	1.1921	19.7419	37.83	6.15 ± 0.08	24.3 ± 4.4	21.23	23.0
P(MMA-*co*-F10MA) 0.95/0.05	0.06	1.2088	20.8096	19.69	4.44 ± 0.06	12.95 ± 1.7	13.80	12.7
P(MMA-*co*-F10MA) 0.90/0.10	0.10	1.2295	21.7285	17.60	4.20 ± 0.05	10.4 ± 3.0	12.81	11.4
P(MMA-*co*-F10MA) 0.75/0.25	0.26	1.2918	24.7111	10.68	3.27 ± 0.10	9.58 ± 3.5	9.21	9.7

[a] See Eq. (2).
[b] See Eq. (5).

3.4. Random copolymers

In the present research, we have typically considered four different ratios of MMA and F10MA to calculate their surface energies. The chain proportion, density, dimensions and calculated surface energy values of the random copolymers of MMA and F10MA are given in Table 5. These data clearly indicate the noticeable changes in surface energies due to copolymerization. An increase in F10MA content of the random copolymer, produced a decrease in surface energy of the copolymer. Molecular contributions to surface energy of the random copolymers are presented in Table 6. As explained before for homopolymers, van der Waals and Coulombic energy contributions are the major part of the surface energy. For each copolymer composition, the calculated surface energy values of the random copolymers from Eqs. (2) and (5) are in excellent agreement with the published data [56]. A direct comparison of the simulated surface energy with van de Grampel experimental data [56] is listed in Table 5 and plotted in Fig. 5 as a function of mole percent of F10MA segments in the chain. The agreement is excellent, which implies that the simulated results could effectively predict the experimental surface energies. It is thus realized that one can vary the surface energy by altering the concentration of MMA and F10MA in the copolymer chain for different applications.

3.5. Radial pair distribution functions

Pair correlation (or radial distribution, RDF) functions have been calculated for various pairs of atoms of the molecules under consideration for mainly three types of contributions viz., total, intermolecular and intramolecular. RDF can provide an insight as to how the atoms pack in an amorphous structure. RDFs are usually designated by the symbol, $g_{AB}(r)$ and calculated from the average of the static relationship of every given pair of particles, AB as:

$$g_{\mathrm{AB}}(r) = \frac{\langle n_{\mathrm{AB}}(r)\rangle}{4\pi r^2 \Delta r \rho_{\mathrm{AB}}} \tag{6}$$

where $\langle n_{\mathrm{AB}}(r)\rangle$ is the average number of atom pairs between r and $r+\Delta r$ and ρ_{AB} is the density of atom pairs of type AB. The total pair distribution function, $g(r)$, which gives a measure of the spatial organization of atoms about the central atom, can be used to demonstrate long-range order in the structure. Therefore, the function $g(r)$ was utilized to distinguish between amorphous and crystalline structures. Fig. 6(a) and (b), respectively, displays the total pair distribution function as a function of r for both bulk and surface simulated structures of F10MA and the random copolymer of MMA-*co*-F10MA − 99/1.

However, the distributions of those atom pairs that present relevant information are discussed here: (i) prominent peak having relatively high intensity is observed for side chain C−F pairs in the vicinity of 1.35 Å, (ii) main chain C−CH$_3$ bond and the ester side chain O−CH$_3$ display distribution in the range 1.5−2 Å and (iii) skeletal carbons of different chains are kept apart by the substituents surrounding them, so that the

Table 6
Components of the contribution of internal energy to surface energy of random copolymers of MMA/F10MA

	R99/1	R95/5	R90/10	R75/25
Bond	−10.72 ± 1.9	−11.22 ± 2.0	−8.30 ± 1.6	−6.03 ± 2.3
Angle	−5.22 ± 2.0	−8.43 ± 5.9	−9.76 ± 4.2	−4.4 ± 1.4
Torsion	−4.05 ± 1.0	−3.30 ± 4.1	−5.1 ± 2.3	−6.64 ± 3.1
oop	−0.33 ± 0.3	−0.30 ± 0.2	−0.76 ± 0.75	−0.53 ± 0.41
Cross	−3.68 ± 2.2	−11.24 ± 3.5	−4.08 ± 3.0	−5.66 ± 3.6
vdW	40.65 ± 9.3	38.7 ± 13.3	26.86 ± 12.0	18.48 ± 11.2
Coulomb	7.36 ± 2.5	8.74 ± 4.1	11.54 ± 2.8	14.36 ± 3.1
Surface energy (mJ/m^2)	24.01 ± 4.4	12.95 ± 1.7	10.4 ± 3.0	9.58 ± 3.5
Surface area (*A*)^2	389.74	433.04	472.13	610.64

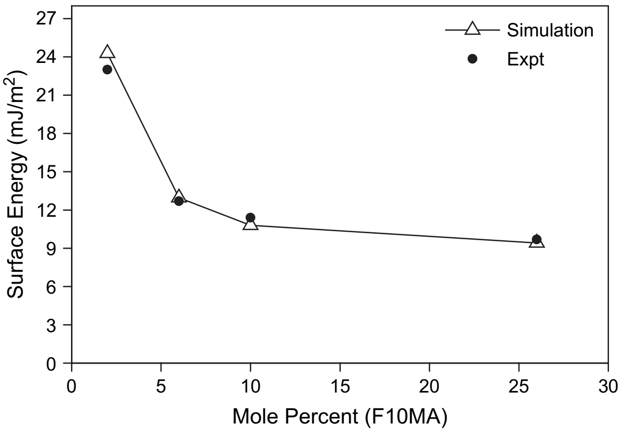

Fig. 5. Variation of surface energy with mole percent of F10MA in random copolymers of MMA-*co*-F10MA.

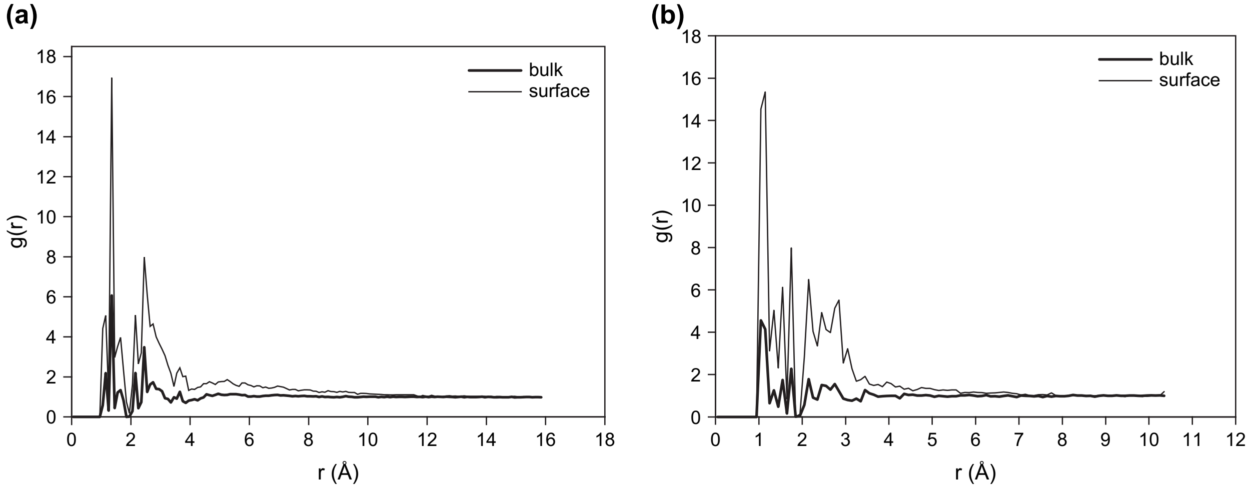

Fig. 6. Total pair distribution function, $g_{AB}(r)$ for (a) F10MA and (b) MMA-*co*-F10MA.

C–C distribution shows a broad hump at distances around 2.5–3 Å. Further, the absence of any peaks beyond 4 Å distance indicates that there is no long-range order in the systems. At long distances, $g_{AB}(r)$ approaches unity, which is quite probable for a purely amorphous system. A similar pattern was observed for other perfluorinated homopolymers and random copolymer, but not displayed here to avoid redundancy and to minimize the number of plots.

3.6. Bond directional correlation function

The bond order parameter has been used to characterize the orientation of bonds in a polymer chain. As a measure of orientation correlation between bonds and bond directional correlation function, S, is defined by the equation:

$$S(r) = \frac{3\langle \cos^2\theta \rangle - 1}{2} \tag{7}$$

where θ is the angle between two skeletal bond chords of the chain. The $S(r)$ was calculated as a function of number of carbon–carbon backbone bonds, indicating the correlations at given spatial distances. When the function, $S(r)$ becomes zero, then no correlation exists along the chain. Its positive value indicates the tendency of parallel alignment of bond chords, while negative values imply the tendency towards perpendicular arrangements. Of special interests are the intermolecular contributions to $S(r)$ for bulk of the simulated systems and only these are demonstrated here. Purely intermolecular part of $S_{\text{inter}}(r)$ obtained by considering C–C bond chords of perfluoroalkyl methacrylates and random copolymers is displayed in Fig. 7. The homopolymers, F6MA and F10MA have shown a positive correlation at approximately 7.65 Å and 8.65 Å. Similarly, random copolymers of MMA/F10MA at 99/1 and 95/5 compositions have shown the positive correlation between distances of 5 Å and 6 Å. Thus, there is a tendency towards parallel alignment in perfluorinated homopolymers and random copolymers. The fact that $S_{\text{inter}}(r)$ goes to zero at longer distances proves that there is no long-range correlation. These results imply that perfluorinated systems are in an amorphous state. A similar observation was found for other homopolymer and random copolymer systems. Also, a trend towards the perpendicular arrangement was observed. This could be possible due to the limited statistics on bond orientations contributing to the orientation function.

3.7. Mass density profiles

The mass density profile for a thin film gives an indication of whether the film is of sufficient thickness so that interior of the film is indistinguishable from the bulk. Density profiles in the films as a function of distance from the center of mass of the film are shown in Fig. 8. Density was calculated by slicing the z-axis (normal to surface) with a thickness of 2 Å. Density profile was described by a hyperbolic tangent function [61] of the type:

$$\rho(z) = (\rho_0/2)[1 - \tanh(z/x_i)] \tag{8}$$

where ρ_0 is bulk density and x_i is width of the surface region (2 Å). Profiles near the surface are sigmoidal, as expected. However, density in the interior of the films reached bulk values as shown in Tables 3 and 5 for perfluorinated homopolymers and random copolymers. The density drops rapidly at a distance between 5 Å and 10 Å from the surface for perfluorinated homopolymers and random copolymers. However, density profiles for both homopolymers and random copolymers showed an excellent agreement with the density values of the 3D bulk structures. The agreement of density of the interior film region with that of the bulk is consistent with the previous simulations [50,62].

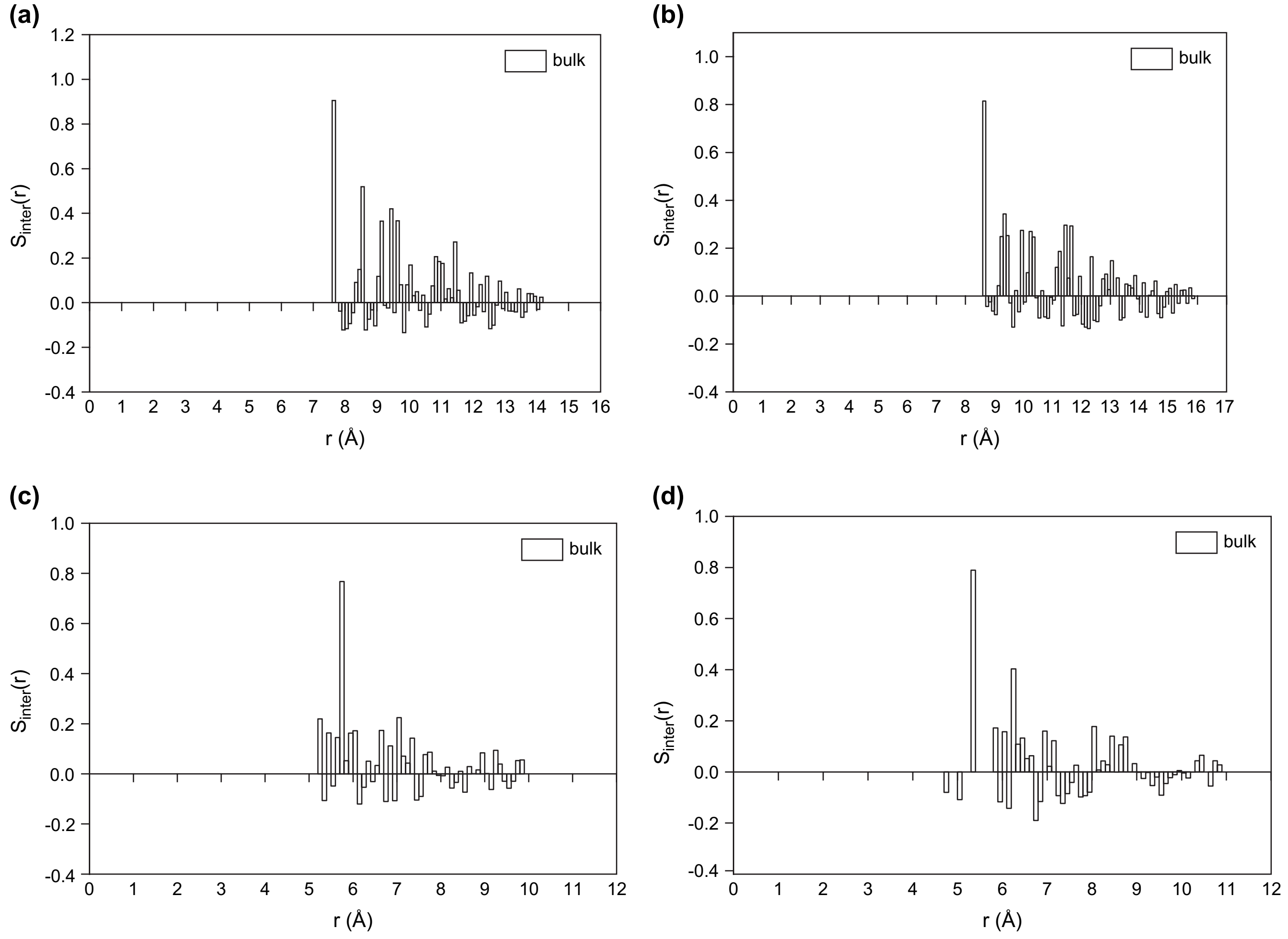

Fig. 7. Intermolecular bond directional correlation function of homopolymers for (a) F6MA, (b) F10MA and random copolymers, (c) MMA-*co*-F10MA (99/1) and (d) MMA-*co*-F10MA (95/5).

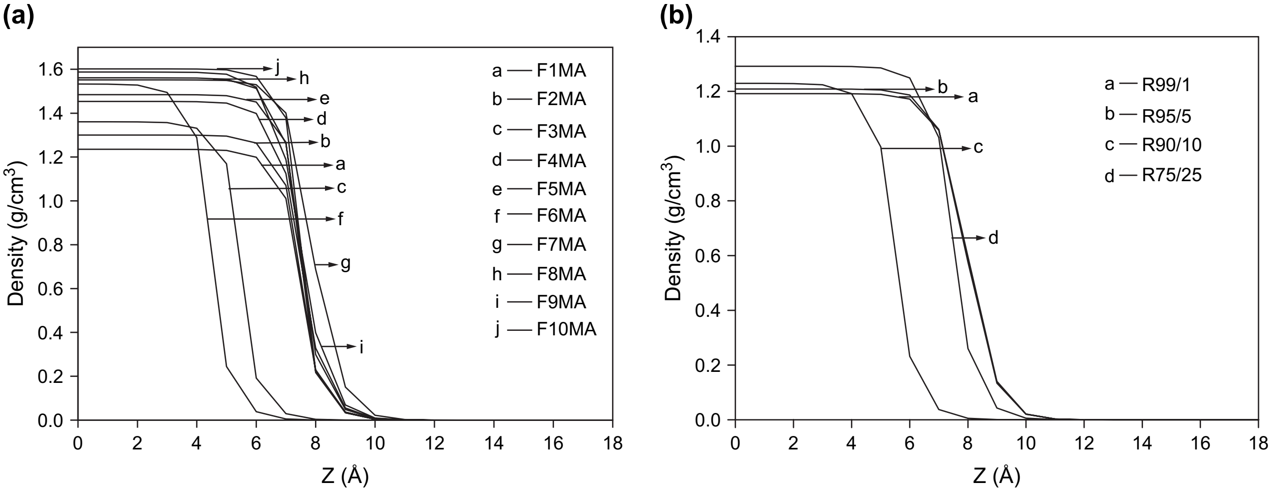

Fig. 8. Density profiles as a function of distance from the center of mass for (a) perfluorinated homopolymers and (b) random copolymers of MMA-*co*-F10MA.

4. Conclusions

Atomistic and molecular modeling approaches employing the molecular mechanics and molecular dynamics simulations in the NVT ensemble have been used to generate the bulk and thin film structures of ten model compounds of perfluoroalkyl methacrylates and four random copolymers of MMA and 1,1-dihydroperfluorohendecyl methacrylate (F10MA). Density values have been calculated using the NPT dynamics by employing the COMPASS force field. It was found that density data are reliable and agreed well with the available literature findings on few systems. The surface properties of perfluorinated polymers have been evaluated using various simulation strategies. The techniques employed in this study have reliably reproduced the surface properties of the well-known polymers like PMMA and PS. As expected, an increase in perfluorinated chain attached to MMA produced a decrease in surface energy of perfluorinated homopolymers. Also, surface energies of F1MA, F6MA and F7MA were in close agreement with the experimental observations. Surface energy values of the random copolymers computed by the simulation protocols are in close agreement with the existing experimental values. The results for MMA/F10MA copolymers also suggest that the sequence of monomers could influence the surface properties.

The total pair distribution function showed an absence of any peaks beyond 4 Å, signifying no long-range order in the systems. Similarly, bond directional correlation function reveals no correlation at longer distances in perfluorinated homopolymers and random copolymers. These results suggest that the simulated perfluorinated methacrylates are in an amorphous state. However, in the bulk region of perfluorinated homopolymers and random copolymer thin films, the density was uniform and attained the bulk value at the center of mass of the film. A good agreement between simulation results for geometry, density and surface energy calculations as well as experimental data indicated the validity of COMPASS force field approach. The ability of simulation methodology used to obtain structural and energetic informations on the chosen model compounds (amorphous phase in the bulk as well as at the free surface) was successful, which further showed the great promise to employ such protocols to other flexible polymers. The present study clearly reveals that molecular modeling and simulation tools are quite useful in selecting the possible polymeric systems with the desired surface properties, particularly while designing novel functionalized polymers for various coating applications.

Acknowledgments

Professor Tejraj M. Aminabhavi and Mr. B. Prathab thank University Grants Commission, New Delhi (Grant No. F1-41/2001/CPP-II) for a financial support to establish Center of Excellence in Polymer Science (CEPS). This research is a collaborative effort between CEPS and Central Leather Research Institute (CLRI), Chennai under the MoU.

References

[1] Stamm M. Adv Polym Sci 1992;100:357.
[2] Anton D. Adv Mater 1998;10:1198.
[3] Feast WJ, Munro HS. Polymer surfaces and interfaces. New York: Wiley; 1987.
[4] Price GJ, AshokKumar M, Grieser F. J Phys Chem B 2003;107:14124.
[5] Cahn JW, Hilliard JE. J Chem Phys 1958;28:258.
[6] Flory PJ, Orwoll RA, Vrij A. J Am Chem Soc 1964;86:3507.
[7] Helfand E. J Chem Phys 1975;63:2192.
[8] Helfand E. Macromolecules 1976;9:307; Weber TA, Helfand E. Macromolecules 1976;9:311.
[9] Dill KA, Flory PJ. Proc Natl Acad Sci USA 1980;77:3115.
[10] Dill KA, Flory PJ. Proc Natl Acad Sci USA 1981;78:676.
[11] Scheutjens JMHM, Fleer GJ. J Phys Chem 1979;83:1619.
[12] Theodorou DN. Macromolecules 1988;21:1400.
[13] Hutnik M, Gentile FT, Ludovice PL, Suter UW, Argon AS. Macromolecules 1991;24:5962.
[14] Fan CE, Hsu SL. Macromolecules 1991;24:6244.
[15] Lee KJ, Mattice WL. Comput Polym Sci 1992;2:55.
[16] Ludovice PL, Suter UW. Computational modeling of polymers. New York: Marcel Dekker; 1992.
[17] Kim EG, Misra S, Mattice WL. Macromolecules 1993;26:3424.
[18] Zhang R, Mattice WL. Macromolecules 1995;28:7454.
[19] Vasudevan VF, McGrath JE. Macromolecules 1996;29:637.
[20] Rapold RF, Suter UW, Theodorou DN. Macromol Chem 1994;3:19.
[21] Nick B, Suter UW. Comput Theor Polym Sci 2001;11:49.
[22] Allen MP, Tildesley DJ. Computer simulation of liquids. Oxford Science Publications: Clarendon Press; 1987.
[23] Eichinger BE, Rigby D, Stein J. Polymer 2002;43:599.
[24] Reisinger JJ, Hillmyer MA. Prog Polym Sci 2002;27:971.
[25] Pauling L. The nature of the chemical bond. Ithaca, New York: Cornell University Press; 1960.
[26] Banks RE, Smart BE, Tatlow JC. Organofluorine chemistry principles and applications. New York: Plenum Press; 1994.
[27] Scheirs J. Modern fluoropolymers. Chichester, England: Wiley; 2000.
[28] Kulkarni PV, Antich PP, Anderson JA, Fernando J, Aminabhavi TM, Harlapur SF, et al. Polym Plast Technol Eng 1997;36:1.
[29] Montonobu Kubo. Surface (Hyoumen) 1995;33:185.
[30] Pittman AG. Surface properties of fluorocarbon polymers. New York: Wiley; 1972.
[31] Defay R, Prigogine I, Bellemans A, Everett DH. Surface tension and adsorption. New York: Wiley; 1966.
[32] Chuvatkin NN, Panteleeva IY. Modern fluoropolymers. New York: Wiley; 1997.
[33] Anton DR. Adv Mater 1998;10:1197.
[34] Schmidt DL, Coburn CE, DeKoven BM, Potter GE, Meyers GF, Fischer DA. Nature 1994;368:39.
[35] DeSimone JM, Guan Z, Elsbernd CS. Science 1992;257:945.
[36] Ciardelli F, Aglietto M, Montagnini di Mirabello L, Passaglia E, Giancristoforo S, Castelvetro V, et al. Prog Org Coat 1997;32:43.
[37] Zhang YX, Da AH, Butler GB, Hogen-Esch TE. J Polym Sci Part A Polym Chem 1992;30:1383.
[38] Thomas RR, Anton DR, Graham WF, Darmon MJ, Sauer BB, Stika KM, et al. Macromolecules 1997;30:2883.
[39] Tirelli N, Ahumada O, Suter UW, Menzel H, Castelvetro V. Macromol Chem Phys 1998;199:2425.
[40] Accelrys Inc. MS modeling. San Diego, CA: Accelrys Inc; 2003.
[41] Sun H. J Phys Chem B 1998;102:7338.
[42] Rigby D, Sun H, Eichinger BE. Polym Int 1997;44:311.
[43] Andersen HC. J Chem Phys 1980;72:2384.
[44] Verlet L. Phys Rev 1967;159:98.
[45] Brooks CL, Pettitt B, Karplus M. J Chem Phys 1985;83:5897.
[46] Prathab B, Aminabhavi TM, Parthasarthi R, Subramanian V. Theor Chem Acc, in press.
[47] Theodorou DN, Suter UW. Macromolecules 1985;18:1467.
[48] Meirovitch HJ. Chem Phys 1983;79:502.
[49] Flory PJ. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; 1953.
[50] Misra S, Fleming PD, Mattice WL. J Comput Aided Mater Des 1995;2:101.
[51] Natarajan U, Tanaka G, Mattice WL. J Comput Aided Mater Des 1997;4:193.
[52] He D, Reneker DH, Mattice WL. Comput Theor Polym Sci 1997;7:19.

[53] Clancy TC, Mattice WL. Comput Theor Polym Sci 1999;9:261.
[54] Brandrup J, Immergut EH. Polymer handbook. 2nd ed. New York: Wiley Interscience; 1975.
[55] Grajeck EJ, Petersen WH. Text Res J 1962;32:320.
[56] van de Grampel RD. Surfaces of fluorinated polymer systems. Ph.D. thesis, Eindhoven University of Technology, The Netherlands; 2002.
[57] Luning J, Stohr J, Song KY, Hawker CJ, Iodice P, Nguyen CV, et al. Macromolecules 2001;34:1128.
[58] Luning J, Yoon DY, Stohr J. J Electron Spectrosc Relat Phenom 2001;121:265.
[59] Tsibouklis J, Graham P, Eaton PJ, Smith JR, Nevell TG, Smart JD, et al. Macromolecules 2000;33:8460.
[60] Zisman WA. Contact angle, wettability, and adhesion. In: Advances in Chemistry Series, vol. 43. Washington, DC: American Chemical Society; 1964.
[61] Kumar SK, Russell TP, Hariharan A. Chem Eng Sci 1994;49:2899.
[62] Mansfield KF, Theodorou DN. Macromolecules 1990;23:4430.