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Computation of surface energy and surface segregation phenomena of perfluorinated copolymers and blends – A molecular modeling approach[☆]

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Abstract

In this paper, we studied the surface properties and surface segregation phenomena of perflourinated copolymers and blends using molecular mechanics (MM) and molecular dynamics (MD) simulation in the NVT ensemble. The importance of functional group, 1H, 1H-dihydroperfluorohendecyl methacrylate (F10MA) and their surface preference over polymer backbone segments viz., methyl methacrylate (MMA) has been investigated. We have shown that degree of blockiness and change in chain architecture have significant effects on surface energy values. Surface energy differences between MMA and F10MA segments have been asserted by introducing a surface critical parameter, χ_s. Computations have been carried out to obtain bulk properties like cohesive energy density (CED) and solubility parameter (δ) by performing MM and MD simulations. Surface energies of MMA/F10MA blends have been computed by bulk pressure–volume–temperature (*PVT*) properties. Molecular dynamics simulation using NPT ensemble has been used to obtain specific volume as a function of temperature for different compositions of MMA/F10MA blends. From these results and using the equation of state approaches, thermal expansion coefficient has been obtained to calculate *PVT* parameters. These surface energy values compare well with the surface energy data calculated by the Zisman equation. Finally, the surface-enrichment behavior of F10MA components in the blend has been examined.

Keywords: Perfluorinated polymer; *PVT* parameter; Surface energy

1. Introduction

Molecular modeling strategies to investigate polymer surfaces and polymer surface modifications are important in several technological areas such as paints, coatings, adhesives, lubricants and polymer blends. Achieving the desired surface properties of a polymer depends upon the ability to locate particular functional group at the polymer surface. However, a common approach to surface modification is the inclusion of low-energy fluorocarbon components that lowers the surface energy. Wettability, low adhesion to surface, and friction resistance of polymeric coatings are the most important material properties that are controlled by the composition of the outermost surface layer. The physics of polymer surface interactions and polymer adsorption phenomena has been widely studied both experimentally and theoretically over the past decades [1–5]. However, in recent times, particular attention has been devoted to the study of surface properties of multicomponent polymer systems. Surface coatings may contain several constituents, one or a few of which may adsorb preferentially at the surface.

Evaluating the surface energy of binary polymer blends is very important when surface composition differs from the

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bulk composition. In general, this behavior observed in polymer blends [6,7] is called 'surface segregation' or 'surface enrichment'. Surface segregation of polymer blends is caused by the difference in surface energy between pure components and the lower surface energy components enriched on the surface of the blend systems has been studied extensively in the literature [8–10]. Surface segregation phenomena have also been observed in block copolymers [11,12] and polymer solutions [13]. A successful treatment for the surface tension of melts and blends involves the use of Cahn–Hilliard model as suggested by Poser and Sanchez [14]. Later, Theodorou [15,16] applied the mean-field consistent lattice theory of Scheutjens and Fleer [17] to the case of copolymers with arbitrary architecture in order to study the behavior of a polymer chain with an "attractive" end group. Thus, surface enrichment can be useful to design an "ideal" coating system that combines the bulk properties with surface properties.

In small-molecule systems such as metallic alloys [18] and liquid mixtures [19] it is well known that the surface composition differs from that of the bulk due to preferential surface adsorption of one of the constituents. This process driven in part, by the differences in surface energies, can be expressed by the classical Gibbs adsorption isotherm [20] given by:

$$d\gamma = -\Gamma_1 d\mu_1^\sigma - \Gamma_2 d\mu_2^\sigma \tag{1}$$

where Γ is surface excess in moles per unit surface area, σ and μ^σ is surface chemical potential. The subscripts 1 and 2 refer to two different chemical species. It is thus apparent that a surface concentration gradient exists in multicomponent systems where surface is enriched with the component of lower surface energy, i.e., surface energy, γ. Rearrangement of Gibbs adsorption equation leads to an expression relating surface excess, Γ_1 and surface energy, γ as,

$$\Gamma_1 = -\frac{1}{RT}\frac{d\gamma}{d\ln C} \tag{2}$$

where C is concentration of species 1, R is ideal molar gas constant and T is temperature in K. The condition $d\gamma/d\ln C < 0$ indicates the surface excess of species 1. On the other hand, if species 1 has a lower surface energy than species 2, there will be an enthalpic driving force for surface segregation of species 1 to air/polymer interface. Characteristically, surface is enriched with a component that has the lowest surface energy. Achieving the desired surface properties is usually dependent upon the ability to locate particular functional groups at the surface. Fluorinated polymers provide low surface energy materials that are widely used in industrial applications such as coatings and non-wetting biological systems [21–24].

Also, polymers with fluorinated functional groups at the surface can be envisioned to convey other properties like resistance to corrosive chemicals and organic solvents, flame retardancy, water repellency, and low coefficient of friction. In this regard, recently we have shown [25,26] that perfluorinated methacrylates when incorporated with CF_2 units in succession exhibited a lowest surface energy for 1H,1H-dihydroperfluorohendecyl methacrylate (F10MA), which has a surface energy of 6.71 mJ/m^2. The principle objective of this paper is to predict surface properties and surface segregation of F10MA when it is co-polymerized or blended with methyl methacrylate. It may be noted that synthesis and experimental characterization of these new types of polymers are time-consuming and hence, molecular modeling and simulation approaches can be powerful tools and are inexpensive to predict structural and functional properties of fluoropolymer surfaces.

2. Block copolymers

2.1. Simulation of block copolymers

Studies on copolymer melt surface tensions have been reported [27–31] illustrating strong surface segregation of one of the blocks. A functional group that has lower surface energy than its polymer backbone will segregate to the surface in order to reduce the overall surface energy of the system. Polymers with highly fluorinated side chains in one block of a block copolymer are likely to be useful in a number of applications, driven by the low surface energy fluorinated block. Such a block copolymer is interface active and falls under the category of interface-active polymers, since such polymers are commonly known in the literature. However, a small amount of such an interface-active polymer can dramatically alter the interfacial energy of a polymer/polymer or a polymer/non-polymer system. Block copolymers with fluorinated components in one of the blocks are not only hydrophobic, but also lipophobic. They are likely to be useful in applications such as in compatibilizing hydrocarbon–fluorocarbon blends, mold-releasing agents, and in the modification of polymer surface properties in a simple non-corrosive and non-destructive manner. In order to probe the effect of blockiness, typical fluorinated block copolymers that have been investigated are those with the fluorinated alkyl chains attached as side groups, and they are termed "block-graft" copolymers that essentially differ from the linear diblock copolymers. These perfluorinated polymers with fluoroalkyl side groups are expected to cover the surface with CF_3 groups having lower surface energy than those of hydrocarbons and CF_2 groups. It has been observed that surface structures of such "block-graft" copolymers are strongly influenced by the structure of fluoroalkyl side groups [32–39].

Early on, the surface energy measurements on block and graft copolymers prepared from two monomers of different surface energies provide clear evidence that the distribution of various functional groups along the polymer chain has a marked influence on their surface properties [40]. An important goal of our ongoing research is to gain a molecular simulation-based understanding of how the distribution and nature of functional groups attached along a polymer chain can be used to design the surface properties of a functional polymer. In this contribution, copolymers of methyl methacrylate (MMA) and F10MA have been chosen as model compounds to study their surface properties. An extension of

Theodorou's formalism [15] is applied to theoretically probe how the location, number, and type of functional groups placed along a polymer chain influence the composition and distribution of functional groups at the surface. In this context, the questions that we need to address are: (i) how does the inclusion of perfluoroalkyl methacrylate modify the surface properties of block copolymer (ii) how does an increase in the block size of a polymer chain influence the surface properties of the copolymer and (iii) investigation on surface properties of copolymers upon changing the chain architecture from random to block copolymer. The information obtained through such simulation studies would provide a framework for molecular designing of functional polymer surfaces with the properties that are optimized for a particular application.

2.2. Modeling details

Simulation of polymers was performed using a MS modeling 3.1 software [41] from Accelrys, San Diego, CA, USA. MM and MD simulations have been performed using the Discover package by employing the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [42,43]. Minimization has been performed using the steepest descent approach followed by the conjugate gradient method. The temperature in all the simulations was equilibrated with the Andersen algorithm [44]. The velocity Verlet algorithm [45] has been used for the integration of equations of motion. The non-bonded interactions have been calculated using the group-based method with explicit atom sums being calculated to 9.5 Å.

Block copolymers of MMA/F10MA have been generated with the construction strategy as implemented in MS Accelrys. An illustration of the structure of block copolymers of MMA and F10MA is shown in Fig. 1. A single parent chain of 55 monomer units of MMA (50 units) and F10MA (5 units) was simulated to study the influence of incorporation of perfluorinated methacrylate monomers on the surface properties of the copolymer. In addition, the polymer chain of 110 monomer units of MMA (100 units) and F10MA (10 units) copolymer was constructed to probe the effect of block size (blockiness). The sequence of block copolymer is represented as b-$(MMA)_n(F10MA)_m$, where n and m specify the number of units of the respective monomers. In order to explore the difference in surface energy upon changing the chain architecture from random to block copolymers, the construction strategy of random copolymer has been detailed. The random copolymer with a degree of polymerization of 55 monomer units (50 MMA and 5 F10MA) has been constructed using the conditional probability method as employed in MS Accelrys. In order to account for the influence of chain architecture on surface energy, the composition (MMA-*co*-F10MA – 0.90/0.10) along the MMA and F10MA copolymer chain has been examined.

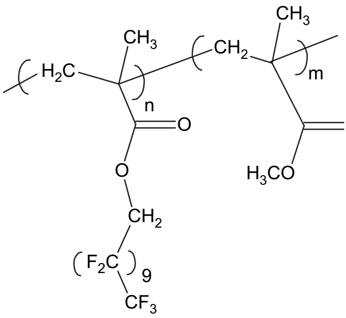

Fig. 1. Structure of block copolymers of MMA–F10MA.

The polymer chain was minimized and cubic bulk cells were constructed by packing a single chain into a cubic box with the periodic boundary conditions. The edge length varies depending upon the cell size, which in turn, depends upon the density of the system. Densities of the copolymer systems were calculated based on the composition of weight fractions of MMA and F10MA. Density of the chosen systems: $\rho_{(MMA)} = 1.188\ g/cm^3$ and $\rho_{(F10MA)} = 1.603\ g/cm^3$ (taken from Ref. [25]) has been considered for the computations. Density remains the same for all block copolymer systems, since copolymers studied here vary by compositions only. Hence, the edge length of the cubic cell is 22.2210 Å (55 units) and 27.9954 Å (110 units) based on the density value of $1.225\ g/cm^3$. For the random copolymer, edge length is 21.7285 Å based on a density value of $1.2295\ g/cm^3$.

The method used in the amorphous cell module of Material studio is the combined use of an algorithm developed by Theodorou and Suter [46] and the scanning method of Meirovitch [47]. Initially, the proposed structure is generated using rotational isomeric state (RIS) theory [48] that describes the conformations of unperturbed chains. However, to avoid excessive overlaps between chains, the modified conditional probabilities are used to account for non-bonded interactions between the atom to be placed and the rest of the system. In the scanning method, all possible continuations of the growing chain are taken into account while calculating the conditional probabilities. In practice, it is not possible to examine all continuations of the chain, but the lookahead is normally restricted to a few backbone bonds. The number of lookahead bonds represents the number of forward bonds that is considered during the construction. The constructs have been subsequently refined to provide the input for further calculations.

Amorphous model of the polymer is shown in Fig. 2 (CPK model). The initial structures have very high potential energy, and relaxation of these high-energy structures followed a three-step strategy. The potential energy of the structure was minimized using the algorithm described above; high temperature molecular dynamics 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 100 ps of dynamics calculations at 300 K with snapshots being saved at every 0.1 ps during the last half of the run, and the conformer with a minimum potential energy is selected and minimized to a convergence of 0.01 kcal/mol/Å. Size and shape of the cubic cells were kept unchanged during the MD runs. The cells that had acceptable potential energies were selected and relaxation molecular dynamics

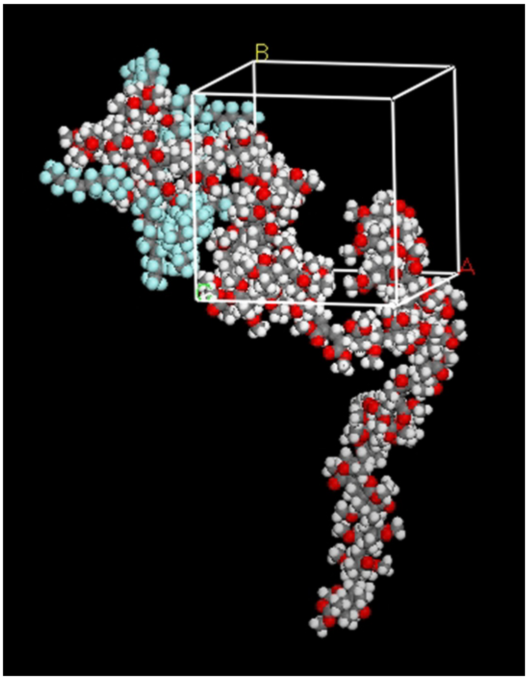

Fig. 2. Amorphous model of block copolymer, *b*-$(\mathrm{MMA})_{100}(\mathrm{F10MA})_{10}$ (Colors: carbon atoms – grey, hydrogen – white, oxygen – red and fluorine – pale blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

simulation was performed at 300 K on the short listed samples for 300 ps. The final energy minimized samples have been used for all property calculations. These amorphous cells were subsequently used to generate thin films.

2.3. Thin films (free surfaces)

Thin films have been constructed from the 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 regarded as z coordinate and represents the coordinate that is normal to the planes of all surfaces and interfaces. Thin films have been constructed by employing the methodology used in the literature [49–51] 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. The relaxation of initial structures formed by conversion from bulk to film has been achieved by subjecting thin films to MM energy minimization followed by a high temperature MD stage (500–1000 K). The choice of a relatively higher temperature was essential to remove the packing inefficiencies generated by the initial cell extension process. This was followed by 300 ps of MD simulation at 300 K. The lowest energy snapshot among the later half of the trajectories has been chosen and minimized with the convergence of 0.01 kcal/mol/Å. The relaxation procedure employed in this work is similar to the method described before for bulk polymers. However, no additional thermodynamic constraint on atoms or cell was employed other than those posed by the MD method as described in 3D bulk cell relaxation. Sufficient relaxation of the structures and acceptable fluctuations are observed for the potential energy in order to ascertain whether samples were suitable for the purpose of estimating surface properties. Surface energy has been 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 due to the formation of thin film and is given by:

$$\gamma = \left(E_{\text{thin film}} - E_{\text{amorphous cell}}\right)/2A \qquad (3)$$

Here, the surface area is $2A$, since two surfaces of area, A are formed upon the creation of the thin film.

3. Polymer blends

3.1. Simulation details

Many studies on polymer blend surface tension [52,53] and related surface studies using other techniques [54,55] have emphasized the classic miscible system, viz., polystyrene (PS) and poly(vinyl methyl ether) (PVME). Surface energy and other studies indicate a strong surface excess of the lower surface energy component. The modification of surface energy, γ of the polymer mixture or blend is important in many fundamental areas such as compatibilization, wetting, foaming, and lubrication. Upon blending a fluorinated polymer with another miscible component, surface composition of the mixture is dominated by fluorinated groups due to their low surface energy leading to highly hydro- and oleophobic surfaces [56–58]. In order to assess how blending influences the surface properties, the blends of perfluorinated polymers have been considered. However, to understand the basis for these and related phenomena, it would be useful to predict the properties of such blend systems at the molecular level, to a reasonable degree of accuracy and success, using the computer-based MD simulations.

In the present investigation, binary blends of MMA and F10MA have been chosen to predict the effect of blending on surface properties. Oligomers with a degree of polymerization of 20 for MMA and 10 for F10MA have been selected for the blend simulation. Concentration of the blends during simulation was controlled by including different ratios of the number of chains of F10MA to the number of chains of MMA. Density of the blend system was estimated on the basis of pure component densities and by assuming the volume additivity relationship, MMA (1.188 g/cm^3) and F10MA (1.603 g/cm^3). At first, MD simulations of oligomers of the above systems have been performed at 300 K for a wide range of compositions. The amorphous cell construction strategy and minimization process followed the same methodology as discussed before. The construction of amorphous cell of three-dimensional periodicity follows the same tactic, but amorphous phases were checked for filling space regularly after the initial construction of the amorphous cell. If two component chains are not well "mixed" (sufficient intermolecular contacts) in the initial configuration, these are discarded and a new one is attempted. Minimization was carried out using the same algorithm with the convergence level of 0.1 kcal/mol/Å. As mentioned above, configurations have been generated individually for each system and relaxed to compute the cohesive energy density. MD simulations under constant temperature and density (NVT ensemble) are performed for each configuration using the Discover program. Systems built with 3D periodicity are equilibrated in the NVT ensemble at 300 K. Molecular dynamics run for 50 ps have been performed to remove the unfavorable local minima that had high energies. Subsequently, systems are subjected to 250 ps of dynamics at 300 K, with the trajectories being saved at every 0.1 ps during the last half of the run to calculate physical properties of interest.

In molecular simulations, if V_{mol} is molar volume of the polymer, then CED is defined as:

$$\mathrm{CED} = (E_{\mathrm{coh}}/V_{\mathrm{mol}}) \tag{4}$$

The Hildebrand solubility parameter, δ is given as:

$$\delta = (E_{\mathrm{coh}}/V_{\mathrm{mol}})^{1/2} \tag{5}$$

3.2. Surface energy estimation by bulk PVT properties

Kano and Akiyama [59] estimated surface energy of blends of poly(ethyl acrylate) and poly(vinylidene fluoride-*co*-hexafluoroacetone) experimentally, using the contact angle method [60] and bulk *PVT* properties [61]. In the past, there are no efforts to procure molecular simulation study on surface energy of polymer blends. However, theoretical simulations using molecular dynamics to probe the surface energy of polymer blends by *PVT* parameters are the first of its kind, investigated here. Surface energy of a polymer can be evaluated with the bulk *PVT* properties [60,61] using the relation:

$$\gamma = \gamma^* \tilde{\gamma} \tag{6}$$

where γ^* and $\tilde{\gamma}$ are characteristic and reduced surface energies, respectively. According to Patterson and Rastogi [61], γ^* is related to equation of state parameters given by:

$$\gamma^* = k^{1/3} P^{*2/3} T^{*1/3} \tag{7}$$

where k is Boltzmann constant, P^* and T^* are characteristic parameters for pressure and temperature, respectively. According to Prigogine and Saraga [62], the equation for reduced surface energy is,

$$\tilde{\gamma} = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3}-1}{\tilde{V}^{2}} \ln\left[\frac{\tilde{V}^{1/3}-0.5}{\tilde{V}^{1/3}-1}\right] \tag{8}$$

where $\tilde{\gamma}$ and $\tilde{V}$ are reduced values of surface energy and molar volume; M is fractional decrease in the nearest neighbors of a cell due to migration from bulk phase to surface phase and its value varies from 0.25 to 0.29 for a closely packed cubic lattice. In the present calculations, we have used $M = 0.29$ to compute *PVT* parameters using Flory equation of state [63,64]. Reduced volume is calculated from thermal expansion coefficient, α using the relationship:

$$\tilde{V} = \frac{[1+(4/3)\alpha T]}{[1+\alpha T]^{3}} \tag{9}$$

Characteristic pressure, P^* is defined as the ratio of ε^*/v^*, where ε^* is total interaction energy per mer and v^* is close-packed mer volume. Thus, P^* is a direct measure of the cohesiveness or strength of intermolecular interactions. Hence, P^* is equal to CED in the closely packed state [61,65,66] because, $\mathrm{CED} \equiv \Delta E_{\mathrm{vap}}/V = \varepsilon^*/v^* \equiv P^*$.

Characteristic temperature, T^* is evaluated as:

$$T^* = \frac{T\tilde{V}^{4/3}}{\tilde{V}^{1/3}-1} \tag{10}$$

Thermal expansion coefficient, α is obtained from the slope of specific volume, V_{SP} vs temperature plot. In order to compute the specific volume for bulk *PVT* parameters, MD simulations have been performed on MMA/F10MA blends of different compositions at various temperatures below 300 K. The procedure to calculate specific volume by means of constant pressure simulation (NPT ensemble) has been investigated earlier by Fried and Ren [67]. The NPT ensemble molecular dynamics simulation was preceded with the constructed and minimized structures of MMA/F10MA blends. In our initial approach, the systems have been equilibrated for 50 ps in the NPT ensemble at 300 K. Using the equilibrated systems as the starting structure for performing dynamics at the next temperature, the temperature of the cells are lowered stepwise (5 K) from 300 K down to 270 K. At each temperature, the amorphous cells are subjected to 150 ps NPT dynamics to determine the specific volume.

4. Results and discussion

4.1. Block copolymers of MMA/F10MA

Surface energy is much lower for block copolymers where lower energy repeat units are less constrained and free to adsorb preferentially at the air/polymer interface. It is thus pertinent to probe the influence of distribution of F10MA monomer in the copolymer. When F10MA is positioned at the end, i.e., *b*-$(\mathrm{MMA})_{50}(\mathrm{F10MA})_{5}$, the surface energy was calculated to be 10.25 ± 2.9 mJ/m^2. Furthermore, it is seen that increasing the block length of *b*-$(\mathrm{MMA})_{100}(\mathrm{F10MA})_{10}$ leads to a decrease in surface energy, 8.78 ± 1.2 mJ/m^2. Introduction of even a small block of F10MA segments within the polymeric chain results in a significant change in surface energy values. Similarly, the chain architecture is expected to have a significant influence on the surface properties of functional polymers. Hence, the change in chain architecture from block to random copolymer has led to an increase in surface energy, which is calculated to be 12.43 ± 3.5 mJ/m^2. Since F10MA segments are randomly distributed along the entire chain length, the chain cannot preferentially expose them to the surface. A comparison of surface properties of random and block copolymers has clearly demonstrated that the introduction of blockiness has a dramatic effect on surface energy. In addition, the surface energy trend for the copolymers exhibited concurrence with van de Grampel et al. [68] observation.

The observed surface property of F10MA is characterized by introducing a parameter called surface interaction parameter, which indicates the tendency of the functional group (F10MA) to adsorb preferentially over the repeat unit segment viz., MMA and it is calculated as:

$$\chi_s = (\gamma_1 - \gamma_2)a/k_B T \tag{11}$$

where γ_1 and γ_2 refer to surface energy of functional group and repeat unit segment, k_B is Boltzmann constant, T is temperature in K and $a = (v_{ref})^{2/3}$, where v_{ref} is reference volume, which is set equal to volume of the functional group. The surface interaction parameter is thus defined such that the functional group is "attractive" when it has a lower surface energy than that of the polymer backbone, i.e., ($\chi_s < 0$) and it adsorbs preferentially at the surface and becomes "repulsive" when it acquires a higher surface energy value than the chain backbone ($\chi_s > 0$); however, this is depleted from the surface. The χ_s value is calculated to be −4.91 with the surface energy values of 39.0 mJ/m^2 and 6.71 mJ/m^2 (taken from Ref. [26]), respectively for MMA and F10MA. As per the definition of surface interaction parameter, the functional group (F10MA) is attractive and is in accordance with the above findings. These calculations clearly ensure that the presence of F10MA segments in the chain architecture has a significant influence on surface properties.

4.2. Blends of MMA/F10MA

Density, CED and solubility parameter for different compositions of the blend, MMA/F10MA, are given in Table 1. The surface energy calculated using the bulk *PVT* parameters involves the computation of thermal expansion coefficient, which is determined from the plots of specific volume obtained from the NPT dynamics vs temperature over a range of temperature. The model plots of specific volume vs temperature for the composition of 3MMA/3F10MA are shown in Fig. 3. In each case, the least squares fit is used to draw a line through the data points. Then, the equation describing these lines has been used to calculate thermal expansion coefficient, α given as:

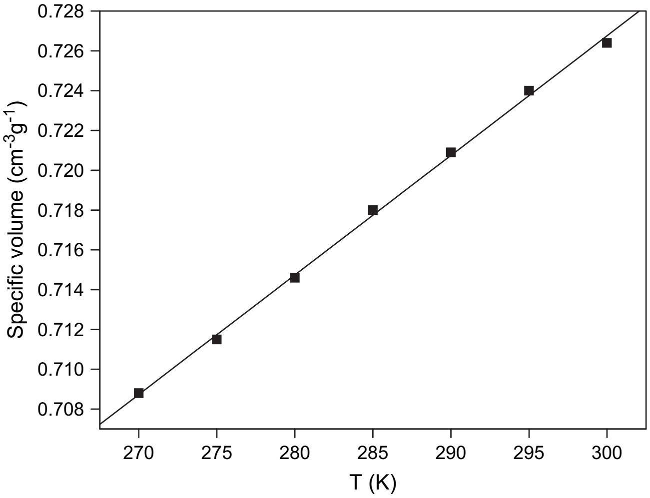

Fig. 3. Specific volume vs temperature for 3MMA/3F10MA blend.

$$\alpha = \frac{1}{v}\left[\frac{dv}{dT}\right]_P \tag{12}$$

Computed values of α and *PVT* parameters involved in the calculation of surface energy of the blends are given in Table 2. It is evident that an increase in concentration of F10MA monomers in the blend gave a decrease in surface energy values.

In order to establish the validity of data obtained using Eq. (6), surface energy is plotted as a function of volume fraction of F10MA in bulk in Fig. 4. Using the Origin 5.0 version software, the straight line obtained by the least squares approximation at 95% confidence limit with correlation coefficient, r^2 value of 0.9984 is given by the empirical equation:

$$\gamma = -6.79(\Phi_b) + 17.50 \tag{13}$$

where Φ_b is volume fraction of F10MA in bulk. Since γ is proportional to Φ_b, it is justifiable that γ calculated by Eq. (13) expresses mean γ in the bulk. Also, surface energy calculated by using Eq. (13) shows a concurrence with the surface energy data calculated using *PVT* parameters from Eq. (6) (see Table 2). On the other hand, surface energy (γ) of MMA/F10MA blends can also be estimated from the CED values using the empirical equation given by Zisman [69].

$$\gamma = 0.75(E_{coh})^{2/3} \tag{14}$$

Table 1
Calculated CED and solubility parameter (δ) of MMA/F10MA blends

Number of chains per unit cell	Composition (wt% F10MA)	Density (g/cm^3)	Dimensions (Å)	CED (cal/cm^3)	δ (cal/cm^3)$^{1/2}$
5MMA, 1F10MA	16.67	1.258	27.754	26.38	5.1 ± 0.05
4MMA, 2F10MA	33.33	1.325	29.452	21.64	4.7 ± 0.07
3MMA, 3F10MA	50.0	1.395	30.804	17.16	4.1 ± 0.10
2MMA, 4F10MA	66.67	1.465	31.933	13.82	3.7 ± 0.19

Table 2
Calculated thermal expansion coefficients (α), reduced values for volume ($\tilde{V}$) and surface energy ($\tilde{\gamma}$), characteristic surface energy (γ^*) and surface energy values of MMA/F10MA blends

Blend composition of MMA/F10MA	$\alpha \times 10^4$ (K^{-1})[a]	$\tilde{V}$	$\tilde{\gamma}$	γ^* (mJ/m^2)	Surface energy (mJ/m^2)		
					PVT[b]	Linear fit[c]	Zisman[d]
5:1	7.14 (0.995)	1.1843	0.1260	121.71	15.34	15.37	16.73
4:2	6.68 (0.992)	1.1776	0.1290	107.56	13.88	13.87	14.68
3:3	6.01 (0.999)	1.1609	0.1361	94.47	12.85	12.77	12.83
2:4	5.45 (0.999)	1.1477	0.1429	81.01	11.57	11.95	11.82

[a] Thermal expansion coefficient is calculated using Eq. (12), the correlation coefficient, r^2, for the line connecting specific volume data is given in parenthesis.
[b] see Eq. (6).
[c] see Eq. (13).
[d] see Eq. (14).

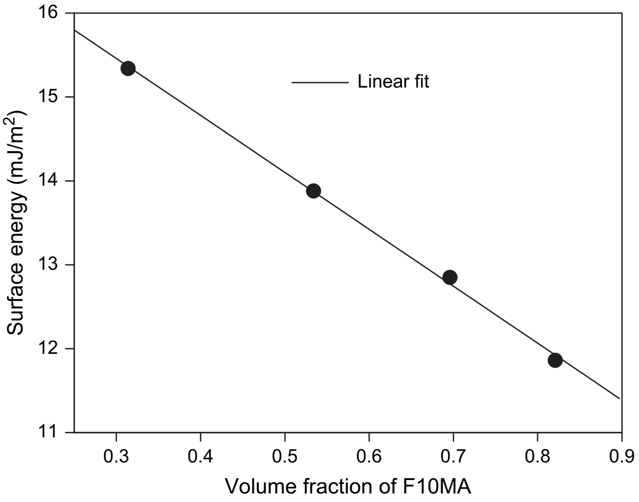

Fig. 4. Relationship between surface energy estimated by Eq. (6) and volume fraction of F10MA in MMA/F10MA blends.

The surface energies calculated from Eq. (14) are given in Table 2. These values compare very well with the surface energy data obtained from the *PVT* parameters according to Eq. (6).

Since the surface energy of blends decreases with increasing weight fraction of F10MA, it is necessary to probe the surface composition. If surface energy of the blend is assumed to be proportional to the fractional surface coverage of each constituent, then surface fraction of F10MA can be estimated [52] as:

$$f_{F10MA} = (\gamma_{blend} - \gamma_{MMA})/(\gamma_{F10MA} - \gamma_{MMA}) \quad (15)$$

It then follows that weight fraction of F10MA at the surface is given by:

$$\omega_{F10MA} = f_{F10MA} \times \rho_{F10MA}/[f_{F10MA} \times \rho_{F10MA} + (1 - f_{F10MA})\rho_{MMA}] \quad (16)$$

The relative enrichment can then be described through a distribution coefficient for F10MA defined as:

$$K_{F10MA} = (\omega_S/\omega_B)_{F10MA} \quad (17)$$

where ω_S and ω_B are surface and bulk weight fractions of F10MA, respectively. The results of these calculations are presented in Table 3, indicating an increase in the surface fraction of F10MA as the bulk composition of F10MA increases in the blend. Thus, it is clear that the surface enrichment varies with the blend composition of F10MA. In addition, the distribution coefficient explains the surface distribution of F10MA and shows a steady decrease with respect to increase of F10MA content in bulk. These results clearly suggest a segregation of F10MA at the surface of the blends. Therefore, the above calculations are a direct indication of strong adsorption of F10MA at the surface. However, the driving force for surface enrichment of F10MA is its lower surface energy (6.71 mJ/m^2) as compared to MMA (39.0 mJ/m^2).

5. Conclusion

Molecular modeling simulations employing molecular mechanics and NVT molecular dynamics have been used to generate bulk and thin film structures of different copolymer systems. Surface properties vary with the distribution of F10MA monomer in the block copolymer of MMA and F10MA. Furthermore, the change in chain length and chain architecture of the block copolymer has shown a significant variation in the surface energy values. The negative value of surface

Table 3
Surface compositions from surface energy data

Wt. fraction of F10MA in bulk	Wt. fraction of F10MA on surface	Volume fraction of F10MA in bulk	Surface fraction of F10MA (f_{F10MA})	Distribution coefficient (K_{F10MA})
0.3820	0.788	0.3143	0.733	2.06
0.6070	0.825	0.5340	0.778	1.36
0.7555	0.850	0.6962	0.808	1.12
0.8407	0.890	0.8173	0.861	1.05

interaction parameter, χ_s implies that the functional group, F10MA, is attractive and gets adsorbed preferentially at the surface. MD simulations have been performed on the blends of MMA/F10MA. Surface energy of different ratios of MMA/F10MA blends were calculated by the bulk *PVT* properties, through equation of state approach, which involves the determination of thermal expansion coefficient, obtained from the plots of specific volume vs temperature by performing NPT dynamics. As expected, an increase in F10MA component of the blend has decreased the surface energy values of MMA/F10MA blend. The relationship between γ obtained using Eq. (6) and volume fraction of F10MA in bulk exhibited a straight-line trend, which demonstrates the reliability of the method employed. Moreover, surface energy calculated from the *PVT* parameters compares very well with the surface energy data computed using the Zisman equation. In addition, surface fraction and distribution coefficient of F10MA were calculated to emphasize the surface-enrichment behavior of F10MA components of the blend.

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