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A molecular simulations study of the miscibility in binary mixtures of polymers and low molecular weight molecules[☆]

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Abstract

The miscibility behavior of binary mixtures of polymeric and low molecular weight molecules was studied using a combination of modified Flory–Huggins theory and molecular simulation techniques. Three different atomistic approaches were used to investigate the phase behavior and χ parameters of binary mixtures consisting of polymethyl methacrylate (PMMA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB). Binary mixtures of methyl methacrylate monomer/5CB and methyl methacrylate oligomer/5CB were also studied. As a first approach, a fast method that calculates the local interaction between a fragment of the polymer and the organic molecule and then extends it to determine the energy of mixing using an estimated coordination number was used. By using modified coordination numbers, we were able to extend this method to include cases where the polymer segment and the small molecules are slightly dissimilar in size. More detailed studies which take into account bulk effects were also carried out where the cohesive energies of the pure compounds were derived from molecular dynamics simulations and the interaction parameters were determined from the differences in the cohesive energies. The concentration and temperature dependence of the χ parameters was evaluated by calculating the energy of mixing from the differences in the cohesive energy densities of the mixed and demixed systems. The present study provides a detailed understanding of the miscibility of PMMA and 5CB as PMMA polymerizes from its monomer, and the results indicate that although methyl methacrylate and 5CB are completely miscible, 5CB is not miscible in PMMA even in small quantities.

Keywords: Miscibility; Binary mixtures; Molecular simulation

1. Introduction

The miscibility behavior of binary mixtures of polymers and low molecular weight molecules is of interest both from theoretical and practical considerations. Important technological applications, such as the selection of solvent for a solute, control of polymer dissolution, diffusion and swelling processes, the use of plasticizers and modifiers in polymers, and the study of phase diagrams of molecular and polymeric alloys, all require information regarding miscibility. A theoretical prediction of the thermodynamics of binary systems is difficult due to the lack of availability of relevant parameterization, and the problem is even more complicated when one of the components is polymeric as additional factors such as molecular packing, chain-flexibility and molecular weight need to be considered [1–3]. Recently, with advances in the area of atomistic simulations and availability of accurate force fields some studies have used molecular simulations to provide useful insight into the thermodynamic phase behavior of binary systems [4–7]. These studies have found that although molecular simulations cannot yet be routinely used to predict complete phase behavior, they can certainly be used to provide a better fundamental understanding of atomic level interactions responsible for miscibility.

In the present work, we have focused on binary mixtures of poly(methyl methacrylate) (PMMA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB, a low molar mass liquid crystal). Binary mixtures of polymer and low molar mass liquid crystals (LC) are of interest to us due to their use as the starting components for polymer dispersed liquid crystals (PDLC)[8]. These PDLCs are fabricated from initial homogeneous mixtures of monomers and LCs by using polymerization induced phase separation (PIPS) to separate the LC from the polymer. PIPS is a non-linear dynamic process that is controlled both by the reaction kinetics as well as the thermodynamic phase equilibrium of the monomer/LC mixture before cure and the polymer/LC mixture during

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and after cure [9]. Recently, several experimental studies have been devoted to the study of the phase diagrams of the starting LC/monomer mixtures [9,10] and it was found that the morphology of the composite is very different depending on whether the polymerization is initiated in the isotropic region or in the two-phase region [9]. Since the performance of the material depends mainly on the morphology, understanding the thermodynamic phase equilibria of the monomer/LC and that of the polymer/LC mixture is important. In the present paper, the miscibility and the phase behavior of PMMA/5CB, methyl methacrylate ologomer/5CB, and methyl methacrylate monomer/5CB mixtures are investigated using molecular simulation techniques. The purpose of the study is to understand the phase behavior of the particular mixtures of interest and also to investigate the effectiveness of using different simulation methods to study the miscibility of binary mixtures of polymers and low molecular weight molecules. Although the final morphology of the PDLC is controlled not only by the thermodynamics of the mixture but also by the reaction kinetics, we believe that a study of the thermodynamic phase behavior is a first step towards predicting miscibility.

A necessary condition for the miscibility of a mixture is a negative free energy of mixing, where

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\,\Delta S_{\text{mix}} = \Delta E_{\text{mix}} + P\,\Delta V_{\text{mix}} - T\,\Delta S_{\text{mix}}. \tag{1}$$

The complete miscibility behavior can therefore be described by calculating the free energy of mixing (ΔG_{mix}) as a function of composition at different temperatures. In the case of mixing of a polymer and a liquid crystal, there are two main contributions to the free energy, one from isotropic mixing and another from anisotropic ordering. One way of describing the phase behavior for mixtures of polymer and LC is therefore by combining Flory–Huggins free energy for isotropic mixing and Maier–Saupe free energy of nematic ordering [11]. At any particular temperature, the free energy contribution from nematic ordering is significant only for very high concentrations of the liquid crystal and for most cases the isotropic contribution dominates. Studies [11] show that the free energy contribution from nematic ordering is significant only for high concentrations (ϕ) of the liquid crystal such that $\phi_{\text{NI}} \le \phi \le 1$. Here, $\phi_{\text{NI}} = (T/T_{\text{NI}})$, and T_{NI} is the nematic–isotropic ordering temperature. For 5CB, whose T_{NI} is at 308 K, ϕ_{NI} is within $0.92 \le \phi_{\text{NI}} \le 0.974$ for a temperature range of 284–300 K. Therefore, for most concentrations, contributions from anisotropic ordering can be neglected and in this paper, we focus mainly on isotropic mixing.

Flory–Huggins theory [1] for calculating the free energy of isotropic mixing was originally derived for small molecular systems, and has subsequently been extended to study binary mixtures of polymer and small molecules under the assumption that the polymer can be described to be made of a series of connected segments, each occupying a regular lattice site. The polymer segment can be chosen so that its volume is comparable to that of the low molecular weight molecule thereby making it possible for each lattice site to be occupied either by a polymer segment or a small molecule. Assuming that the volume change upon mixing is negligible, the free energy of mixing (ΔG) per mole of lattice sites for a mixture of solvent molecules A and polymer B is given by

$$\frac{\Delta G}{RT} = \phi_{\text{A}} \ln \phi_{\text{A}} + \left(\frac{\phi_{\text{B}}}{X_{\text{B}}}\right) \ln \phi_{\text{B}} + \chi_{\text{FH}} \phi_{\text{A}} \phi_{\text{B}}. \tag{2}$$

In Eq. (2), ϕ_{A} and ϕ_{B} are volume fractions of the solvent and the polymer, X_{B} is the degree of polymerization (or the number of segments of the same size as the solvent molecule in the polymer) of polymer B, and χ_{FH} is the Flory–Huggins interaction parameter. The first two terms in Eq. (2) represent the combinatorial contribution to the entropy of mixing and the third term is due to the enthalpic contribution. Therefore, once χ_{FH} is known, the entire phase behavior of the system can be calculated. In the original formulations of Flory–Huggins theory, χ_{FH} is strictly proportional to $1/T$ (has no concentration dependence) and can only give rise to phase diagrams with upper critical solution temperatures. Modification of the interaction parameter in Eq. (2) by replacing χ_{FH} with a more general function $\chi(T,\varphi,P)$ (so that χ depends on temperature, pressure, and concentration), allows for qualitative representation of different kinds of phase diagrams [3]. The free energy of mixing can now be represented by Eq. (3), in which the third term also includes contribution from non-combinatorial entropy (free volume and packing effects).

$$\frac{\Delta G}{RT} = \phi_{\text{A}} \ln \phi_{\text{A}} + \left(\frac{\phi_{\text{B}}}{X_{\text{B}}}\right) \ln \phi_{\text{B}} + \chi \phi_{\text{A}} \phi_{\text{B}}. \tag{3}$$

2. Results and discussion

In the present work, we have derived the interaction parameters of 5CB with methyl methacrylate monomer, with methyl methacrylate oligomers, and with PMMA. The interaction parameter in Eqs. (2) and (3) can be derived using different simulation methods, most of which are based on the assumption that the molecules interact through pair interaction energies. We have evaluated three such methods for calculating the interaction parameter (all of which differ significantly in their computational requirement) and will describe them in this section.

By ignoring any concentration dependence of the interaction parameter, the enthalpic term in Eq. (2) can be simply developed in terms of the differential energy of interaction Δe_{AB} such that

$$\frac{\Delta E_{\text{mix}}}{RT} = \chi_{\text{FH}} \phi_{\text{A}} \phi_{\text{B}} = \frac{(Nz\,\Delta e_{\text{AB}})}{RT} \phi_{\text{A}} \phi_{\text{B}}. \tag{4}$$

In Eq. (4), N is the Avogadro number, z is a coordination number, e_{AB} is the interaction energy between molecular pair AB such that

$$\Delta e_{AB} = e_{AB} - \frac{1}{2}(e_{AA} + e_{BB}).$$

The first method used, which is called the two-segment method [4–6], estimates interaction parameters from studies of interactions between isolated pairs of molecules. The differential energy of interaction Δe_{AB} in Eq. (4) is calculated directly using molecular simulation techniques. The interaction energy of pairs of molecules or that between a polymer segment and a small molecule (as in this case) is calculated and then modified Flory–Huggins models are used to estimate the free energy of mixing. The major advantage of this method is that it allows for a quick evaluation of miscibility and includes specific interactions that might arise between dissimilar molecules in a mixture. Its primary limitation however is the fact that simulations are carried out on isolated molecular pairs or chains and the interaction energies might not represent those present in bulk. Also, non-combinatorial entropic contributions are not included.

Simulations to calculate the interaction energies and the free energy of mixing were carried out using the Blends module in the CERIUS^2 molecular modeling software[1] and the COMPASS force-field [12]. COMPASS force-field is derived from ab-initio calculations and enables accurate prediction of conformational and thermophysical properties for a broad range of molecules in isolation and in condensed phases. Blends uses a modified Flory–Huggins method, the two important modifications being that the molecules are no longer required to be on a regular lattice and an explicit temperature dependence of χ is incorporated. In the case where the two segments are of the same size, χ is defined as

$$\chi = \frac{Nz\,\Delta e_{AB}}{RT}, \tag{5}$$

where

$$\Delta e_{AB} = \frac{1}{2}(e_{AB} + e_{BA}) - \frac{1}{2}(e_{AA} + e_{BB}).$$

The interaction energy was calculated using a Monte-Carlo approach that includes constraints arising from excluded volume [4]. This method allows for the generation of a large number of relative orientations of the two molecules thereby allowing for a more reliable estimate of the average interaction energy in binary mixtures. The pairwise interaction was calculated for a specified number of times (in our case for 50,000 pairs) and a probability distribution $P(E_{ij})$ was generated. An explicit temperature dependence of E_{ij} was incorporated by temperature averaging the pair energies using a Boltzmann method:

$$\langle E_{ij}(T)\rangle = \frac{\int \mathrm{d}E_{ij} P(E_{ij}) E_{ij} \exp\left(\frac{-E_{ij}}{kT}\right)}{\int \mathrm{d}E_{ij} P(E_{ij}) \exp\left(\frac{-E_{ij}}{kT}\right)}. \tag{6}$$

The coordination number z was explicitly calculated by measuring the number of molecules of type j that can be packed around a single molecule of type i. The technique involves generating clusters in which the nearest neighbors are packed around the central molecule until no more will fit [4]. Van der Waals surfaces were used to represent the shape of the molecule. Each nearest neighbor was added such that it touches the central molecule without overlapping the other nearest neighbor. The orientation of the surrounding molecules was determined randomly, i.e. packing was considered to be isotropic. To allow for the connectivity of the polymer molecule, the end atoms of the polymer segment were made inaccessible to other molecules thus excluding them from coming into contact with other atoms during packing. 500 clusters were generated and for each set of interactions an average z (for binary systems four coordination numbers Z_{AA}, Z_{BB}, Z_{AB}, Z_{BA} are possible) was calculated.

We have modified Eq. (5) to also include segments that are slightly dissimilar in size (volume or surface area). The change in energy (ΔE_{mix}) on mixing N_A (number of A molecules) and N_B (number of B molecules) into a binary mixture AB with ϕ_A and ϕ_B volume fraction of A and B molecules is described in Appendix A. ΔE_{mix} per mole of lattice sites is given as

$$\Delta E_{mix} = \frac{1}{2}\phi_A\phi_B N\left[\left(\frac{v_{av}}{v_a}\right)Z_{AA}\varepsilon_{AA} + \left(\frac{v_{av}}{v_b}\right)Z_{BB}\varepsilon_{BB} - \left(\left(\frac{v_{av}}{v_a}\right)Z_{AB}\varepsilon_{AB} + \left(\frac{v_{av}}{v_b}\right)Z_{BA}\varepsilon_{BA}\right)\right].$$

Here v_{av} is the average volume element such that $V = Nv_{av}$. The interaction parameter can therefore be expressed as

$$\chi = \frac{N}{2RT}\left[\left(\frac{v_{av}}{v_a}\right)Z_{AA}\varepsilon_{AA} + \left(\frac{v_{av}}{v_b}\right)Z_{BB}\varepsilon_{BB} - \left(\left(\frac{v_{av}}{v_a}\right)Z_{AB}\varepsilon_{AB} + \left(\frac{v_{av}}{v_b}\right)Z_{BA}\varepsilon_{BA}\right)\right]. \tag{7}$$

Thus, by replacing the coordination number in Eq. (5) by effective coordination numbers (as shown in Eq. (7)), slight dissimilarity in molecular volumes can be taken into account. The effective coordination numbers are weighted averages of the calculated coordination numbers and depend both on the relative size of the segments and the concentration of the mixture.

The molecular volume (based on van der Waals radii) of 5CB is 263.55 Å^3. Since the volume of a single methacrylate segment is 108.88 Å^3, three different methacrylate

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[1] CERIUS^2 molecular modeling system is provided by Molecular Simulations Inc., San Diego, 1999.

Table 1
Coordination numbers

Component A	Component B	Z_{AA}	Z_{AB}	Z_{BA}	Z_{BB}
MMA1	5CB	7.176	5.31	10.892	8.112
MMA2	5CB	7.318	6.734	8.73	8.112
MMA3	5CB	7.42	7.652	7.81	8.112

Table 2
Effective coordination numbers

A	B	Mixture	Z_{AA}	Z_{AB}	Z_{BA}	Z_{BB}
MMA2	5CB	25% A + 75% B	8.815	8.111	8.26	7.674
MMA2	5CB	50% A + 50% B	8.312	7.649	7.788	7.237
MMA2	5CB	75% A + 25% B	7.81	7.187	7.334	6.80
MMA3	5CB	25% A + 75% B	6.676	6.872	8.09	8.425
MMA3	5CB	50% A + 50% B	6.924	7.14	8.412	8.738
MMA3	5CB	75% A + 25% B	7.172	7.396	8.714	9.051

oligomers with volumes close to that of 5CB were considered. Case 1: molecule with one methacrylate unit (MMA1, volume = 108.88 Å^3); case 2: molecule with two methacrylate units (MMA2, volume = 206.69 Å^3); case 3: molecule with three methacrylate units (MMA3, volume = 304.23 Å^3). The coordination numbers calculated using the Blends module are summarized in Table 1 and the effective coordination numbers in Table 2.

The calculated interaction energies and those normalized at 270 and 400 K (using Eq. (6)) for case 3 (three methacrylate units) are given in Table 3. The corresponding tables for cases 1 and 2 are given in Appendix B. The various contributions to the total energy for MMA3-5CB pairwise interactions are shown in Fig. 1. For all the pairwise interactions, it is noted that the main contribution is from van der Waals interactions. Fig. 2 shows the different pairwise interaction energies present in MMA3-5CB mixtures. Corresponding figures for MMA2 and MMA1 show similar trends. The interaction energies at each temperature were then fitted to a function with the form $A + BT + C/T$. For the MMA3-5CB mixture with 50/50 concentration, the fitted values were as follows: $A = -226.5$, $B = 0.347$ and $C = 27340$. The χ parameters were calculated (using Eq. (7)) for the temperature range of 270–400 K and the binary mixtures were found miscible in all cases (5CB & MMA1, 5CB & MMA2, 5CB & MMA3).

The two-segment method allows for an estimation of the interaction parameter between a polymer and a small molecule by extrapolating that between a shorter polymeric segment and the small molecule. This is meaningful only when the conformation of the shorter polymeric segment is representative of the polymer. In our case, we found that when using the same χ values for 5CB and PMMA as those for 5CB and MMA3, the calculated free energy of mixing of 5CB and PMMA results in a negative value indicating the mixture to be miscible. However, we know from experimental results that this is incorrect, and may result from the fact that the conformation of the short polymeric segment (in isolation) is not representative of PMMA. This was indeed confirmed by further analysis. Fig. 3 illustrates the probability distribution of the backbone torsional angles in PMMA and MMA3. These torsional angles were extracted from MD simulations with periodic boundary conditions. The results suggest that although for both cases *trans* and *gauche* (which includes both *gauche*− and *gauche*+) states are favored, the ratio of the two probabilities varies significantly. For PMMA the computed *trans* and *gauche* probabilities are 0.65 and 0.34, whereas for MMA3 they are 0.4 and 0.6, respectively. The higher *trans* probability in PMMA is not surprising owing to the extended nature of the chain compared to MMA3.

Therefore, although the two-segment method was reasonably successful in determining the miscibility of methyl methacrylate monomer/5CB, it was not so for PMMA/5CB and subsequently a different method that allows for bulk effects to be included was considered. In this second method, the cohesive energy densities (CED) of compounds were compared to verify their miscibility.

For mixtures in which no specific interactions are formed or destroyed, e_{AB} can be expressed as the geometric mean of

Table 3
Interaction energies for MMA3 and 5CB

Molecule A	Molecule B	Temperature (K)	Lowest energy (kcal/mol)	Highest energy (kcal/mol)	Average energy (kcal/mol)
MMA3	MMA3	Std	−6.72	3.02	−1.56
MMA3	MMA3	270	−6.72	3.02	−1.56
MMA3	MMA3	400	−6.72	3.02	−1.56
MMA3	5CB	Std	−11.3	7.84	−1.74
MMA3	5CB	270	−11.3	7.84	−10.5
MMA3	5CB	400	−11.3	7.84	−8.28
5CB	MMA3	Std	−11.4	9.4	−1.74
5CB	MMA3	270	−11.4	9.4	−10.9
5CB	MMA3	400	−11.4	9.40	−9.43
5CB	5CB	Std	−8.94	4.65	−1.91
5CB	5CB	270	−8.94	4.65	−6.56
5CB	5CB	400	−8.94	4.65	−4.92

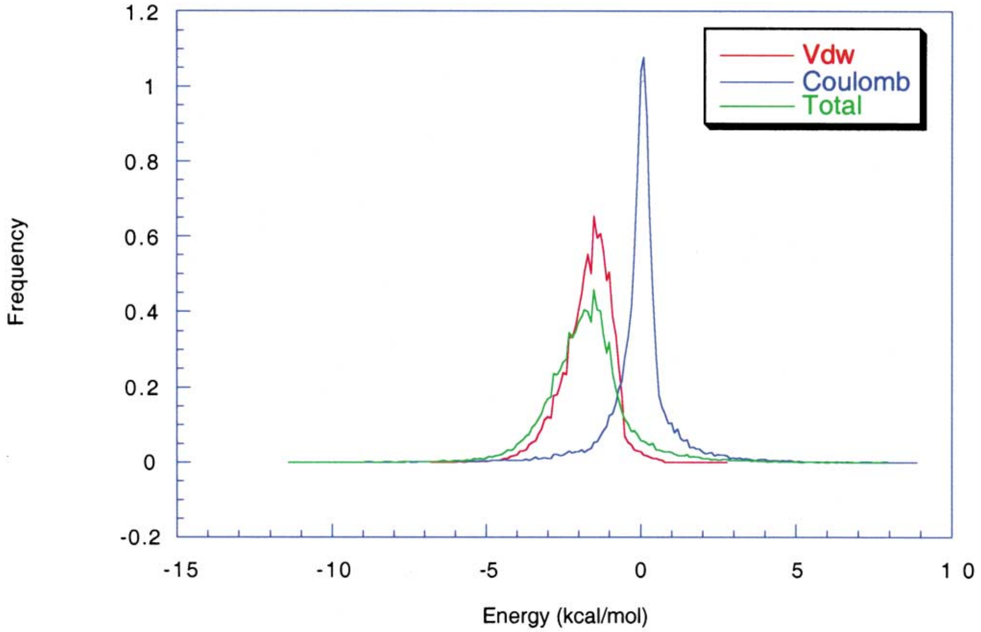

Fig. 1. Energy distribution analysis for MMA3-5CB. The plot shows the contributions from van der Waals and coulomb interactions to the total energy.

e_{AA} and e_{BB} such that

$$\Delta e_{AB} = \frac{1}{2}(e_{AA}^{1/2} - e_{BB}^{1/2})^2.$$

For many systems with non-polar or slightly polar molecules, this assumption is appropriate. Using Hildebrand's argument [2], $z\,\Delta e_{AB}$ in Eq. (4) can then be replaced by

$$V_A((E_c)_{AA}^{1/2} - (E_c)_{BB}^{1/2})^2.$$

Here, $(E_c)_{AA}$ and $(E_c)_{BB}$ are the CED of compounds A and B, respectively, and V_A is the volume of the small molecule. CED is defined as the energy required to break all intermolecular links in a unit volume of the material and it quantifies the relative strength of the interactions between like and unlike atoms. The Flory–Huggins interaction parameter in Eq. (4) then becomes

$$\chi_{FH} = \frac{NV_A}{RT}((E_c)_{AA}^{1/2} - (E_c)_{BB}^{1/2})^2. \tag{8}$$

Cohesive energies at different temperatures can be

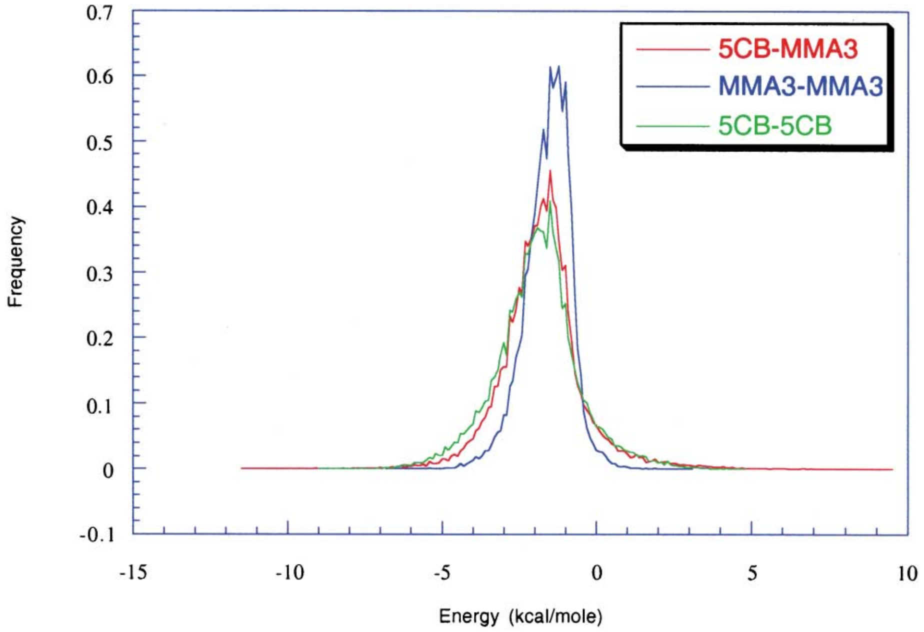

Fig. 2. Energy distribution analysis for MMA3-5CB. The plot shows total interaction energies for all the different intermolecular interactions.

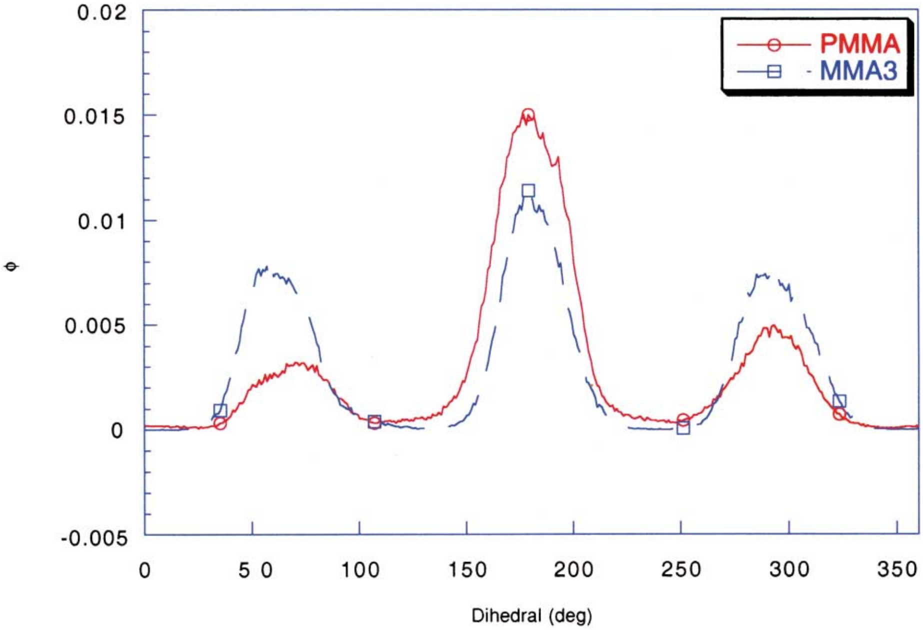

Fig. 3. Normalized probability distribution of the backbone dihedral angles.

derived from molecular dynamics (MD) simulations and the χ_{FH} parameter is thus determined. The major limitation of this approach is that non-combinatorial entropy is still ignored and one assumes that no specific interactions are formed or destroyed in the mixture. The concentration dependence of χ cannot be predicted and it can only give rise to phase diagrams with upper critical solution temperatures.

Another way of expressing Eq. (8) is by using the Hildebrand relationship [2] $\delta = E_c^{1/2}$. E_c can be expressed in terms of δ (solubility parameter) and χ_{FH} can be expressed as

$$\chi_{FH} = \frac{NV_A}{RT}(\delta_A - \delta_B)^2. \quad (9)$$

Due to the availability of solubility parameter data of small molecules (from experiments) and of polymers (using traditional group additivity approaches), this method of determining the interaction parameter has gained wide applicability.

In the present study, we have calculated the CED from MD simulations. MD simulations were carried out with the

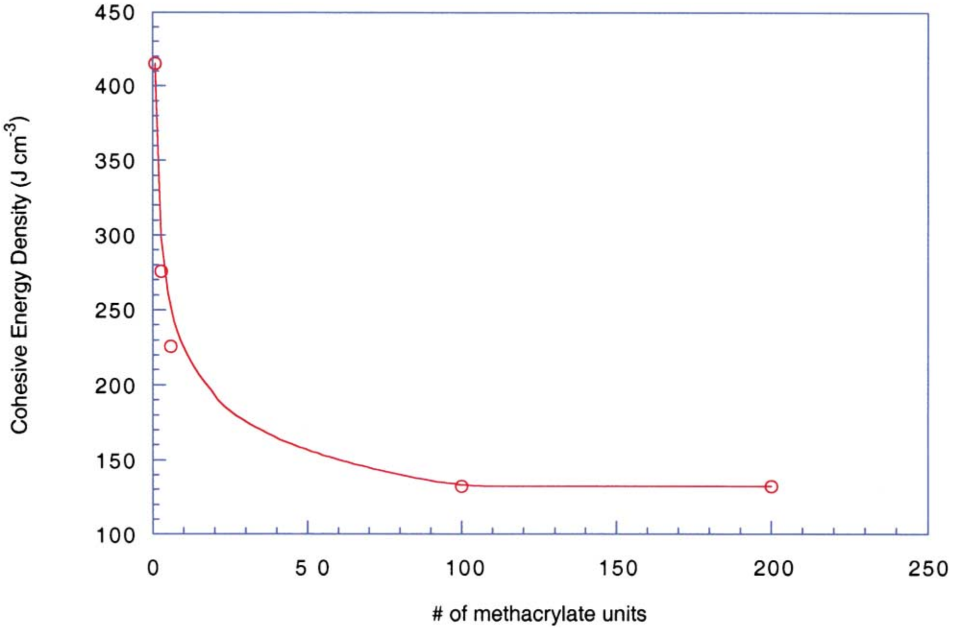

Fig. 4. Calculated cohesive energy.

DISCOVER® program[2] using the COMPASS force field on samples consisting of about 1000–1500 atoms. At typical densities, such a large number of atoms have been found to be sufficient to model bulk properties. Three-dimensional periodic boundary conditions along with minimum image convention were used. The initial structures were generated using a protocol described in our earlier work [8].

Thirty cyano-biphenyl molecules were arranged in a simulation box with a starting density of 1.008 g/cm^3. Constant pressure MD simulation was carried out at temperature of 300 K and pressure of 1 bar for 110 ps to derive equilibrium density, and a final density of 0.9782 g/cm^3 was achieved. Based on this density, 10 sets of simulation cells were constructed and MD simulations were carried out at 300 K under NVT conditions. The temperature was controlled using Anderson's method and the equations of motion were integrated using the Verlet velocity integrator. A time step of 1 fs was used. Equilibration was carried out for 60 ps followed by a data collection period of 40 ps. This protocol was followed for all 10 starting structures and then the properties were averaged. The average CED was calculated to be 396.0 ± 3.7 J/cm^3.

A simulation cell was built consisting of atactic PMMA molecule with a degree of polymerization of 200 (case 1). A constant pressure MD simulation was carried out for 110 ps and a final density of 1.0189 g/cm^3 was achieved. Based on this density, 10 sets of cells were constructed and MD simulations were carried out at 300 K under constant NVT condition. Equilibration was carried out for 90 ps followed by a data collection period of 10 ps. The average cohesive energy density was calculated to be 144.82 ± 1.645 J/cm^3.

Recognizing that the equilibrium density determined in the present case was slightly lower than the experimental density of PMMA [13], MD simulations were also carried out at the experimental density of 1.1 g/cm^3 and the corresponding cohesive energy was calculated to be 226.74 J/cm^3. This corresponds to a solubility parameter of 15.058 (J/cm^{-3})$^{1/2}$ and is consistent with available literature data [14]. The discrepancy in the density values is not surprising because the experimental densities are for high molecular weight ($M_w = 12,000$) polymer of unspecified tacticity whereas the simulations were carried out for atactic PMMA with DP = 200. Since we are not interested in finding absolute values of densities and cohesive energies but instead in studying the miscibility of the binary mixtures and since the density would vary depending on the concentration of the mixture, we have used the earlier determined value of 144.82 J/cm^3 corresponding to a density of 1.0189 g/cm^3.

The cohesive energy densities are known to vary considerably with the molecular weight of the polymer. In order to evaluate how the cohesive energy changes with molecular weight, four shorter polymer segments were built. Case 2: molecule with 100 monomer units, case 3: molecule with six monomer units, case 4: molecule with three monomer units, and case 5: with just a single methacrylate segment. Simulations cell of the same size as for case 1 were built and the cohesive energies were calculated using the method described earlier. The cohesive energy for the 100 monomer case was calculated to be 150.0 ± 2.44 J/cm^3 (case 2). The cohesive energy for six monomer units was calculated to be 225.8 ± 2.75 J/cm^3 (case 3), three monomer units was calculated to be 276.8 ± 2.37 J/cm^3 (case 4) and that of the single methacrylate molecule was calculated to be 415.46 ± 4.32 J/cm^3 (case 5). Fig. 4 shows the variation in cohesive energy density with molecular weight. The decrease in cohesive energy with increasing molecular weight was found to be sharp for smaller segments. For a degree of polymerization beyond 100, the decrease was found to be very small with the cohesive energy leveling to an almost constant value.

The χ_{FH} parameter for 5CB and PMMA was calculated using Eq. (8). For PMMA (DP = 200), the χ_{FH} parameter was calculated to be 6.136, for PMMA (DP = 100), $\chi_{FH} = 5.80$, for the six monomer segment, $\chi_{FH} = 2.36$, for the three monomer segment, $\chi_{FH} = 1.07$ and for the single methacrylate segment, the χ_{FH} parameter was calculated to be 0.02285. χ_{FH} was considered to be strictly proportional to $1/T$ and the free energy of mixing was determined using Eq. (3). Once the free energy was evaluated the phase diagram was subsequently calculated.[3] The binodal curve was defined by compositions where the chemical potentials of the two components are equal and the spinodal curve was determined by taking the second derivative of the free energy. It was found that the binary mixture in case 5 was completely miscible. On increasing the molecular weight to three methacrylate units (case 4), a UCST type behavior was observed. The critical point was found at $T = 150$ K and $\phi_2 = 0.52$. The critical point moved to a higher temperature of $T = 447$ K and $\phi_2 = 0.62$ for case 3. At 300 K, the mixture was miscible for $\phi_2 < 0.12$ and $\phi_2 > 0.97$, in a metastable state for $0.12 > \phi_2 < 0.29$ and $0.85 > \phi_2 < 0.97$, and in an unstable phase for $0.29 > \phi_2 < 0.85$. No critical points were found for PMMA (DP = 100) and the mixture was completely immiscible. Similar results were found for PMMA (DP = 200).

Comparing the individual cohesive energies to estimate the miscibility of binary mixtures has a major shortcoming since it assumes that no specific interactions are formed in the mixture. In order to account for any specific interactions that might form, a more suitable method is to calculate the energy of mixing from the differences in the cohesive energy densities of the mixed and demixed systems. For a

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[2] Dynamics calculations were done with the DISCOVER® program within the Insight II molecular modeling system (4.0.0P) from Molecular Simulations Inc., San Diego, 1999.

[3] The phase diagrams were calculated using the Phase Diagram Module in InsightII. InsightII is a molecular modeling system provided by Molecular Simulations Inc., San Diego.

Table 4
Calculated cohesive energies

Compound	Cohesive energy ($J\ cm^{-3}$)	E_{AB} ($J\ cm^{-3}$)	ΔE_{mix} (50% PMMA + 50% solvent) ($J\ cm^{-3}$)
Dichloromethane	288.11 ± 3.3	368.4 ± 3.3	−149.3
Chlorobenzene	368.06 ± 2.8	300.00 ± 2.0	−41.0
Toluene	301.48 ± 2.8	232.00 ± 3.0	−6.26
PMMA (dp = 100)	150.00 ± 2.4		

binary mixture of A and B (Φ_A and Φ_B are the respective volume fractions) energy of mixing per unit volume (ΔE_{mix}) is

$$\Delta E_{mix} = -(E_c)_{AB} + \Phi_A(E_c)_A + \Phi_B(E_c)_B. \tag{10}$$

The χ parameter can then be determined by using Eq. (11) such that

$$\chi = ((V_{seg}\Delta E_{mix})/RT). \tag{11}$$

The cohesive energies can be derived at different temperatures and concentrations and both temperature and concentration dependence of χ can be studied. Also, by calculating the cohesive energies of mixtures with different concentrations, specific interactions that are formed in the mixtures are explicitly taken into account. However, this is a computationally extensive method and can be realistically done only for a few cases.

The cohesive energies were calculated using the earlier described protocol for a binary mixture consisting of equal proportion of 5CB and PMMA. The PMMA segment was considered to be of 100 monomer units long. The MD simulations were carried out at 300K. The cohesive energy for the binary mixture was found to be 173.00 ± 3.7 J/cm^3. Using the earlier calculated cohesive energies of the pure compounds, ΔE_{mix} was estimated to be 100 J/cm^3 indicating that the mixture is not miscible.

These results show that at least qualitatively, comparing the cohesive energies of the pure compounds was successful in predicting the miscibility of PMMA and 5CB. Further calculation of the cohesive energies of the mixed systems provided additional insight into the concentration dependence of the χ parameter. The more rigorous approach was not particularly advantageous in determining miscibility because no specific interactions are being formed between 5CB and PMMA molecules on mixing. In order to validate this, we chose three polar solvents that make PMMA soluble — dicholoromethane, chlorobenzene and toluene. They provide us with three test cases where specific interactions between the dissimilar molecules are being formed on mixing. The cohesive energies of pure solvents were calculated along with those of mixtures with 50% PMMA. The same protocol as described earlier was used. In each case, constant pressure MD was carried out to determine the equilibrium density and then NVT simulations were carried out to determine the cohesive energies. The calculated cohesive energies are tabulated in Table 4. The results show that a simple comparison of the cohesive energies indicates that PMMA is not soluble in any of the solvents, whereas calculating the cohesive energies for mixtures of 50% PMMA and 50% solvent clearly show that PMMA is soluble in the solvents. These results clearly indicate that comparing the cohesive energies of the pure compounds is appropriate for a limited number of cases while a more definitive study requires the derivation of the energy of mixing from the differences in the cohesive energy densities of the mixed and demixed systems.

3. Conclusion

The miscibility behavior of binary mixtures of PMMA/5CB, methyl methacrylate oligomer/5CB, and methyl methacrylate monomer/5CB was investigated using a combination of modified Flory–Huggins theory and molecular simulation techniques. Three different atomistic approaches were used.

As a first approach, the two-segment method was applied which allows for a quick evaluation of miscibility in which the local interaction between the polymer fragment and the organic molecule is calculated and the energy of mixing is estimated using a coordination number. By analyzing the local interaction energies, a better understanding of the different significant contributions to the interactions between the molecules was achieved. The difficulty in defining a single coordination number for binary mixtures limits the applicability of this method. In the present case, this was a serious limitation as the smallest polymeric fragment had to be a multiple of the monomer repeat unit. A method to calculate modified coordination numbers to take into account small dissimilarity in the molecular sizes was therefore developed. Use of a set of modified coordination numbers allows for the use of the two-segment method for studying miscibility in binary systems with molecules of dissimilar sizes. However, extra care has to be taken to check that the conformation of the polymer fragment (in case one of the components happens to be polymeric) is representative of the polymer. Although this is a computationally fast method, the final results were found to be very dependent on the choice of polymer fragment. Since the polymer fragment and the small molecule need to be somewhat comparable in size, this places a restriction on how long the polymer fragment can be. A short polymeric segment was found not to be representative of the PMMA conformation. Therefore, the interaction parameter derived for the polymeric fragment and 5CB could not be substituted for PMMA and 5CB and this method was found not to be suitable to study PMMA/5CB miscibility. The method was, however, found useful in studying miscibility of small molecules such as that between 5CB and methyl methacrylate.

In the second approach, cohesive energies of the pure compounds were derived from MD simulations. The interaction parameter was then derived from the differences in the cohesive energies. Although it does not take into account any concentration dependence of the χ parameter, this method was found to be fairly successful in studying the miscibility of 5CB and PMMA. In a more detailed study, the energy of mixing was calculated directly from bulk simulations of mixed and demixed systems. This method allows for studying concentration and temperature dependence of the χ parameter but is computationally very expensive. In the present case, it was found not to be advantageous as compared to the earlier method in determining qualitatively the miscibility because no significant interactions are being formed between the 5CB and the PMMA molecule on mixing. A combination of the two approaches indicated that 5CB is not miscible in PMMA even in small quantities. However, methacrylate monomer and 5CB are completely miscible. The miscibility decreases as the monomer polymerizes and even for segments with six methacrylate units the miscibility is significantly reduced.

The results indicate that with advances in the area of atomistic simulations and availability of accurate force fields, theoretical prediction of miscibility is now possible. Although full atomistic simulations provide the most reliable results, a combination of different simulation techniques is also very useful in providing in-depth insight into polymer miscibility. Use of atomistic simulations allowed us to derive the interaction parameters of 5CB and PMMA as a function of increasing molecular weight starting from very low molecular weight monomers. In the future, these parameters will be used in mesoscale models which take into account the dynamic nature of the system in studying the evolution of morphology in PDLC's as a function of polymerization time.

Appendix A

The change in energy (ΔE_{mix}) on mixing N_{A} number of A molecules and N_{B} number of B molecules into a binary mixture AB with ϕ_{A} and ϕ_{B} volume fraction of A and B molecules can be estimated as $\Delta E_{\mathrm{mix}} = E_{\mathrm{pure}} - E_{\mathrm{mix}}$, where E_{mix} is the energy of the binary mixture and E_{pure} that of the pure compounds. If V is the total volume of the mixture, V_{A} and V_{B} the volumes in pure state, and v_{a} and v_{b} the individual volumes of molecules A and B,

$$N_{\mathrm{A}} = \phi_{\mathrm{A}}\left(\frac{V}{v_{\mathrm{a}}}\right), \quad N_{\mathrm{B}} = \phi_{\mathrm{B}}\left(\frac{V}{v_{\mathrm{b}}}\right).$$

$$E_{\mathrm{pure}} = \frac{N_{\mathrm{A}} Z_{\mathrm{AA}} \varepsilon_{\mathrm{AA}}}{2} + \frac{N_{\mathrm{B}} Z_{\mathrm{BB}} \varepsilon_{\mathrm{BB}}}{2}$$

$$= \phi_{\mathrm{A}}\left(\frac{V}{v_{\mathrm{a}}}\right)\frac{Z_{\mathrm{AA}}\varepsilon_{\mathrm{AA}}}{2} + \phi_{\mathrm{B}}\left(\frac{V}{v_{\mathrm{b}}}\right)\frac{Z_{\mathrm{BB}}\varepsilon_{\mathrm{BB}}}{2}.$$

$$E_{\mathrm{mix}} = N_{\mathrm{AA}}\varepsilon_{\mathrm{AA}} + N_{\mathrm{BB}}\varepsilon_{\mathrm{BB}} + \frac{1}{2}(N_{\mathrm{AB}}\varepsilon_{\mathrm{AB}} + N_{\mathrm{BA}}\varepsilon_{\mathrm{BA}}),$$

where N_{ij} is the number of ij interactions which are given as

$$N_{\mathrm{AA}} = \frac{N_{\mathrm{A}} Z_{\mathrm{AA}} \phi_{\mathrm{A}}}{2} = \phi_{\mathrm{A}}\left(\frac{V}{v_{\mathrm{a}}}\right)\frac{N_{\mathrm{A}} Z_{\mathrm{AA}} \phi_{\mathrm{A}}}{2},$$

$$N_{\mathrm{BB}} = \phi_{\mathrm{B}}\left(\frac{V}{v_{\mathrm{b}}}\right)\frac{N_{\mathrm{B}} Z_{\mathrm{BB}} \phi_{\mathrm{B}}}{2},$$

$$N_{\mathrm{AB}} = \phi_{\mathrm{A}}\left(\frac{V}{v_{\mathrm{a}}}\right)N_{\mathrm{A}} Z_{\mathrm{AB}} \phi_{\mathrm{B}},$$

$$N_{\mathrm{BA}} = \phi_{\mathrm{B}}\left(\frac{V}{v_{\mathrm{b}}}\right)N_{\mathrm{B}} Z_{\mathrm{BA}} \phi_{\mathrm{A}}.$$

Substituting N_{ij} in the earlier equations, we get

$$\Delta E_{\mathrm{mix}} = \frac{1}{2}\phi_{\mathrm{A}}\phi_{\mathrm{B}}\left[\left(\frac{V}{v_{\mathrm{a}}}\right)Z_{\mathrm{AA}}\varepsilon_{\mathrm{AA}} + \left(\frac{V}{v_{\mathrm{b}}}\right)Z_{\mathrm{BB}}\varepsilon_{\mathrm{BB}} - \left(\left(\frac{V}{v_{\mathrm{a}}}\right)Z_{\mathrm{AB}}\varepsilon_{\mathrm{AB}} + \left(\frac{V}{v_{\mathrm{b}}}\right)Z_{\mathrm{BA}}\varepsilon_{\mathrm{BA}}\right)\right].$$

The energy of mixing per mole of lattice sites can thus be estimated to be equal to

$$\Delta E_{\mathrm{mix}} = \frac{1}{2}\phi_{\mathrm{A}}\phi_{\mathrm{B}}N\left[\left(\frac{v_{\mathrm{av}}}{v_{\mathrm{a}}}\right)Z_{\mathrm{AA}}\varepsilon_{\mathrm{AA}} + \left(\frac{v_{\mathrm{av}}}{v_{\mathrm{b}}}\right)Z_{\mathrm{BB}}\varepsilon_{\mathrm{BB}} - \left(\left(\frac{v_{\mathrm{av}}}{v_{\mathrm{a}}}\right)Z_{\mathrm{AB}}\varepsilon_{\mathrm{AB}} + \left(\frac{v_{\mathrm{av}}}{v_{\mathrm{b}}}\right)Z_{\mathrm{BA}}\varepsilon_{\mathrm{BA}}\right)\right].$$

Since v_{av} is the average volume element and $V = Nv_{\mathrm{av}}$, the interaction parameter can be expressed as

$$\chi = \frac{N}{2RT}\left[\left(\frac{v_{\mathrm{av}}}{v_{\mathrm{a}}}\right)Z_{\mathrm{AA}}\varepsilon_{\mathrm{AA}} + \left(\frac{v_{\mathrm{av}}}{v_{\mathrm{b}}}\right)Z_{\mathrm{BB}}\varepsilon_{\mathrm{BB}} - \left(\left(\frac{v_{\mathrm{av}}}{v_{\mathrm{a}}}\right)Z_{\mathrm{AB}}\varepsilon_{\mathrm{AB}} + \left(\frac{v_{\mathrm{av}}}{v_{\mathrm{b}}}\right)Z_{\mathrm{BA}}\varepsilon_{\mathrm{BA}}\right)\right].$$

Appendix B

Interaction energies for MMA1 and 5CB

Molecule A	Molecule B	Temperature (K)	Lowest energy (kcal/mol)	Highest energy (kcal/mol)	Average energy (kcal/mol)
MMA1	MMA1	Std	−3.1	1.05	−0.881
MMA1	MMA1	270	−3.1	1.05	−1.26
MMA1	MMA1	400	−3.1	1.05	−1.12
MMA1	5CB	Std	−5.93	4.22	−1.33
MMA1	5CB	270	−5.93	4.22	−3.6
MMA1	5CB	400	−5.93	4.22	−2.36
5CB	MMA1	Std	−6.14	5.41	−1.33
5CB	MMA1	270	−6.14	5.41	−3.59
5CB	MMA1	400	−6.14	5.41	−2.4
5CB	5CB	Std	−8.94	4.65	−1.91
5CB	5CB	270	−8.94	4.65	−6.56
5CB	5CB	400	−8.94	4.65	−4.92

Interaction energies for 5CB and MMA2

Molecule A	Molecule B	Temperature (K)	Lowest energy (kcal/mol)	Highest energy (kcal/mol)	Average energy (kcal/mol)
MMA2	MMA2	Std	−4.2	.841	−1.29
MMA2	MMA2	270	−4.2	.841	−2.18
MMA2	MMA2	400	−4.2	.841	−1.83
MMA2	5CB	Std	−9.62	7.0	−1.59
MMA2	5CB	270	−5.93	4.22	−9.0
MMA2	5CB	400	−5.93	4.22	−6.51
5CB	MMA2	Std	−9.85	6.88	−1.6
5CB	MMA2	270	−9.85	6.88	−9.03
5CB	MMA2	400	−9.85	6.88	−6.11
5CB	5CB	Std	−8.94	4.65	−1.91
5CB	5CB	270	−8.94	4.65	−6.56
5CB	5CB	400	−8.94	4.65	−4.92

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