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Molecular dynamics simulation of miscibility in several polymer blends

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ABSTRACT

The miscibility in several polymer blend mixtures (polymethylmethacrylate/polystyrene, (1,4-cis) polyisoprene/polystyrene, and polymethylmethacrylate/polyoxyethylene) has been investigated by using Molecular Dynamics simulations performed for fully atomistic representations of short chains. The trajectories obtained from simulation boxes representing the mixtures have been analyzed in terms of the collective scattering structure function. The Flory-Huggins parameter is determined from fits of the simulation results for this function to the random phase approximation expression. The numerical values of this parameter and its variation with temperature obtained with this procedure show a general qualitative and semi-quantitative agreement with existing experimental data for the different systems, though with significant error bars. These results together with those previously obtained for the polyvinylmethylether/polystyrene blends with the same method are compared with data yielded by other computational simpler approaches, which are considerably more sensitive to different parameter choices.

1. Introduction

The prediction of miscibility in mixtures is interesting both from the theoretical and technological points of view [1]. Usually, this property is characterized by the Flory-Huggins parameter, χ [2]. This parameter gives a theoretical description of the phase separation curves for polymers of different chain lengths and compositions. Parameter χ can be experimentally measured from thermodynamic properties [3]. Actually, experimental data of χ for different systems show variations with composition, and sometimes with chain length, what underline some deficiencies of the Flory-Huggins theory. Even if these problems are considered, a quantitative measurement of parameter χ for a given system is generally considered the best indication of its miscibility performance from the macroscopic point of view. Experimental values of χ can be obtained from data of the neutron scattering structure function. Usually, χ is numerically fitted to give the best reproduction of the structure function to a theoretical expression given by the random phase approximation (RPA) [4].

A similar approach can be used to obtain theoretical predictions of χ with numerical data extracted from numerical simulations. Atomistic representations of the mixtures can be built in a simulation box, including periodic boundary conditions. Molecular Dynamics (MD) constitutes the most convenient method of simulation for systems composed by molecules of relatively complex chemical structure [5]. These simulations should use appropriate forcefields to describe the interactions between different atoms. The MD simulations yield numerical trajectories of polymer blends. From these coordinates, "collective scattering" functions can be easily evaluated and the χ parameter can be evaluated by comparison with RPA predictions, following a procedure similar to the method used to analyze the experimental structure functions. This approach has been followed in some recent investigations for polymers with relatively simple molecular chemical structures as polypropylene/polyethylene [6] and polyisobutylene/polypropylene [7], represented by simplified united atom models. The procedure involves an important computational effort, which may constitute a shortcoming for its general application.

In a previous work [8], we reported results obtained for the structurally more complex polyvinylmethylether/polystyrene blend, *PVME/PS*, which has been broadly studied form the experimental point of view, detailing the choice of different simulation options, parameters and macroscopic variables useful to perform a reasonable prediction of χ with a fully atomistic model. These results were obtained using a moderate amount of computational resources through the consideration of short chains and a decreased density. In spite of these significant simplifications, the final data were in general agreement with the experimental data [3,9], showing compatible mixtures and a lower critical solution temperature.

In the present work, we report calculations for three other different blends: polymethylmethacrylate/polystyrene, *PMMA/PS*, (1,4-cis) polyisoprene/polystyrene, *PI/PS*, and polymethylmethacrylate/polyoxyethylene, *PMMA/POE*, using similar prescriptions. Our aim is to explore the shortcomings and benefits of this type of simplified computations, giving an indication on whether they can

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provide reasonable predictions of the Flory-Huggins parameter for all these cases. Since we investigate the use of this method in a general context, we are not adopting any specific simplification in the atomistic representations of the chains.

Precise values of the Flory-Huggins parameter χ for all these mixtures have been documented from neutron scattering data [3]. *PMMA*/*PS* blends show slightly positive and temperature decreasing χ values [10]. Therefore, long molecular weight *PMMA*/*PS* blends should show immiscibility and an upper critical solution temperature. *PI*/*PS* systems behave similarly, but they exhibit considerable higher values of χ [11]. Although the long molecular weight *PI*/*PS* blends are known to be immiscible, this system constitutes an important reference, since detailed simulations for atomistic [12] or structurally coarse-grained models [13] have been previously carried out. Finally, *PMMA*/*POE* blends are considered to be miscible [14] and, actually an upper critical solution temperature has been located for relatively high molecular weights [15]. Neutron scattering data of χ are partially consistent with this description, though the available results correspond to deuterated *PMMA* chains. These particular values are small and negative and do not show any noticeable variation with temperature [16].

The ability of our numerical results to reproduce experimental data for the different systems gives an idea of the usefulness of the method to yield simulation estimations of χ in comparison with other numerically simpler procedures also involving short chains. In particular, we consider in our discussion the results that we have previously obtained [17] from a direct calculation of interaction energies and coordination numbers between monomer units, proposed time ago [18]. Moreover, we also take into consideration values obtained from our simplified theoretical method based in the evaluation of binary interaction integrals between pairs of short chains [17]. Both methods have been shown to be especially sensitive to details in the description of the potential energy between atoms.

2. Numerical methods

Full details on the methods to build chains and construct the simulation box have been previously described [8]. We choose atactic configurations for the *PS* and *PMMA* chains. For *PS*, *PI* and *PMMA*, we build chains of 3 repeat units. For *POE*, the chains include 4 repeat units. The average radii of gyration of all these chains are in the range $R_g = 3.7 \pm 0.2$ Å, as it was also the case for the previously investigated *PVME* chains, composed of 5 repeat units.

We have been able to construct relaxed initial configurations of moderate total energy, i.e. without serious overlapping between chains, in simulation boxes of size L with periodic boundary conditions and a given mean density, ρ. We include 5 chains of each type in the box. This value is compatible with a reasonable use of our computational resources and may be sufficient to reproduce the realistic interactions between chains in the relatively small region of the space needed to explore most of the interactions represented by the mean-field parameter χ. The different box sizes are within the 17–20 Å interval. Previous simulations performed for *PI*–*PS* blends constituted with considerably longer oligomers (15 monomers per chain) [12] revealed that the corresponding radial distribution functions reach their asymptotic limits in the 10–15 Å distance range.

Using longer chains corresponding to moderately high molecular weight polymers would require setting high values of L. Moreover, longer chains have slower dynamics, reducing the mobility of the systems. All these factors would imply a significant increase of the computer time required to achieve equilibrated samples and to obtain sufficiently long production trajectories. Furthermore, short chains allow for the construction of homogeneous systems even in the case of blends with moderately positive values of χ. Our small sizes may take into account a significant part of the enthalpic interactions between the two components. However, some of the entropic effects, particularly those connected with the influence of long range distance correlations within the most rigid chains cannot be properly described.

MD simulations are carried out using the “compass” forcefield, valid for fully atomistic chain models [19]. “Compass” is based in ab initio quantum mechanical calculations, parameterized to be consistent with condensed phase properties. It was shown to give the fastest equilibration and best reproduction of experimental data for the *PVME*/*PS* blends in our previous study [8]. Partial charges are set according fixed bond increment rules assigned in the forcefield files and also with the “charge equilibration” method [20]. Differences between the charges obtained with these two methods are important for some atoms [8]. The simulations are performed at constant temperatures with the help of the Andersen thermostat [5], valid for static properties. We use time steps of 1.5 fs for the *PMMA*/*PS* and *PI*/*PS* systems. This time is higher than those usually employed to study dynamical properties, 0.5 or 1 fs, but we have verified that it is able to give stable trajectories. However, in the case of the *PMMA*/*POE* systems, we have only obtained stable trajectories if the time step is reduced to 1 fs.

It should be noted that experimental data for the tracer diffusion coefficient of PS are smaller than 10^{-11} cm^2 s^{-1}, or 10^{-4} Å^2 ns^{-1}, for *PS* samples of moderately small molecular weight, $M_w = 4500$–66,000 g/mol, at 150 °C [21,22]. Previous simulations for *PI*–*PS* oligomers [12] yielded center-of-masses squared displacements values about 10 Å^2 ns^{-1} at 450 K. Consistently to these data, we expect that the mobility of the interacting molecules in the present systems should be very small when we consider realistic melt densities close to $\rho = 10^3$ kg/m^3, even though we only include short chains in the simulation boxes. According with our previous exploratory results for the displacement of *PS* chains in a *PVME*/*PS* reported previously [8], we have to decrease density to the smaller value of $\rho \cong 0.7 \times 10^3$ kg/m^3 in order to give enough mobility to achieve an adequate equilibration of this type of systems and, specially, to provide fairly accurate average results for the scattering functions using a reasonable amount of computational time. More specifically, we have obtained [8] a mean-square displacement of about 2 Å^2 ns^{-1} and 33 Å^2 ns^{-1} at 350 K for *PS* in the *PVME*/*PS* blends with densities 10^3 kg/m^3 and 0.9×10^3 kg/m^3, closer to the experimental values. The displacement is increased to 300 Å^2 ns^{-1} for $\rho = 0.7 \times 10^3$ kg/m^3, value that is also adopted in the present work.

The choice of small chain lengths and reduced densities may constitute an important simplification in the description of the real samples. However, we should consider that, at least from the theoretical point of view, parameter χ is independent of the chain length and density, though variations with both magnitudes have been experimentally observed for real systems. We have investigated this point performing some Monte Carlo simulations with blends of simplified models of generic polymer chains, represented by the widely used coarse-grained lattice Bond Fluctuation Model [23,24]. The variation of χ with chain length and density for this simplified model is small and comparable with the statistical uncertainties [8].

We have verified that, with these specifications, both total energy and temperature oscillate around stabilized mean values in the final trajectories used for the calculation of properties. Equilibration times of 4–8 ns are typically required for most systems. In each run, the system coordinates are saved and included in the statistical samples every 2000 steps. Our final statistics combine the results of the different runs. Typically, we have to perform several (4–7) MD runs, each one from a different equilibrated sample and covering 12 ns, in order to obtain a sufficient accuracy in the final scattering results. Each run takes 5–10 days in a standard PC CPU processor.

The collective scattering structure function is computed from the simulation trajectories as a configurational average [25],

$$S(q) = n_s^{-1}\left\langle \sum_i^{n_s}\sum_j^{n_s} f_i f_j \exp(i\mathbf{q}\cdot\mathbf{R}_{ij})\right\rangle \tag{1}$$

where n_s is the total number of scattering units. The terms f_k are scattering factors, taking into account the scattering contrast between different types of atoms. Adopting the simplest description, which is significantly different that the representations adequate for real experimental techniques, our scattering factors discern about the particular type of chain where each atom is located. We consider that all the non-hydrogen atoms contained in the A/B blend simulation box are identical scatters and we assume that they have opposite sign for atoms in A or B chains, with $S(q) = 0$ for $q = 0$. The latter condition is set so that no scattering is observed at a macroscopic wavelength. Therefore,

$$f_i = n_B/n_s \tag{2a}$$

if atom i belongs to an A chain, or

$$f_i = -n_A/n_s \tag{2b}$$

if atom i belongs to a B chain (n_A and n_B are the total number of scatters in A and B chains). $\mathbf{R}_{ij}$ is the vector joining centers i and j in a given configuration. Finally, $\mathbf{q}$ is the scattering vector whose components are conditioned by the box size,

$$q_k = (2\pi/L)n_k, \quad k \equiv x,y,z, \quad n_k = 1,2,3\ldots \tag{3}$$

The range of q values corresponding to our L values, $q \cong 0.3$–1.2 Å^{-1}, is one to two orders of magnitude higher than the typical intervals used in the neutron scattering experiments. Moreover, our lowest values are about six times higher than those considered in the previously mentioned extensive simulations performed for other structurally simpler blends [6,7]. However, they are small enough to avoid the close bonding intramolecular interactions. The selected range corresponds to typical distances for molecules in contact which may show some inhomogeneities difficult to detect with higher q values. It is interesting to discern if the contribution of this range of relatively short-distances to the χ parameter may decide the final miscibility of the blend at macroscopic level. The use of short chains ensures that our highest q values are less than 5 times higher than $1/R_g$. Therefore, we can observe systematically decreasing scattering functions. Consequently, specific interactions on the scattering curves are not shown in terms of sharp peaks, but in a smoother way, allowing for an easier comparison with the RPA, though some particular features of the different blends can be observed in the global behavior of these curves.

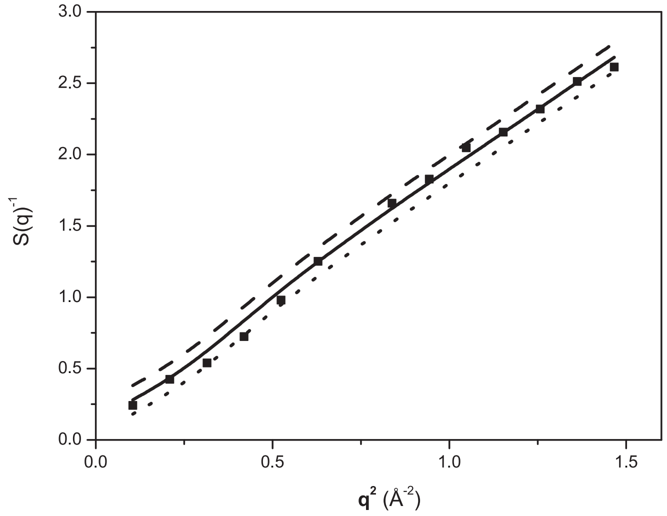

Fig. 1. $1/S(q)$ vs. q^2 from the MD simulation of a *PMMA/PS* mixture at 400 K. Partial charges are assigned by the forcefield. Symbols: simulation data; curves correspond to the RPA results from Eq. (4), from bottom to top: dotted line, $\chi/V_0 = 0.05$; solid line: $\chi/V_0 = 0$; dashed line, $\chi/V_0 = -0.05$.

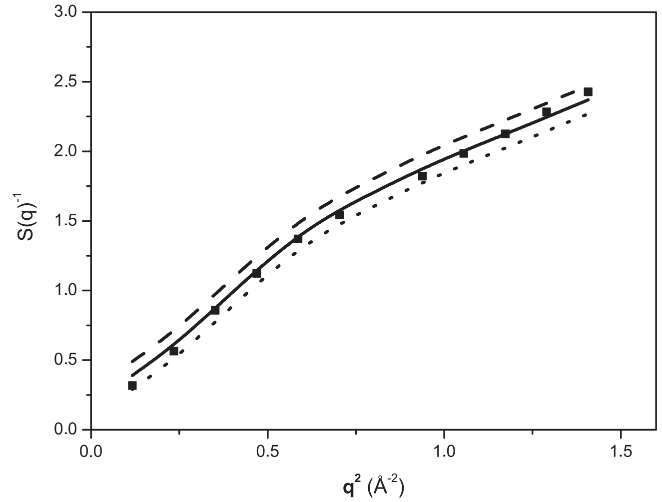

Fig. 2. $1/S(q)$ vs. q^2 from the MD simulation of a *PI/PS* mixture at 400 K. Partial charges are assigned by the forcefield. Symbols: simulation data; curves correspond to the RPA results from Eq. (4), from bottom to top: dotted line, $\chi/V_0 = 0.05$; solid line: $\chi/V_0 = 0$; dashed line, $\chi/V_0 = -0.05$.

3. Results and discussion

In Figs. 1–3 we show representations of $S(q)^{-1}$ vs. q^2 results obtained from the MD runs with $T = 400$ K with forcefield assigned partial charges for the three different types of blends. Also, two other temperatures, 350 and 450 K, have been considered to cover the realistic range of temperatures for which experimental data have been reported [3]. The simulation points always tend to a positive extrapolated ordinate at $q = 0$, confirming the systems homogeneity.

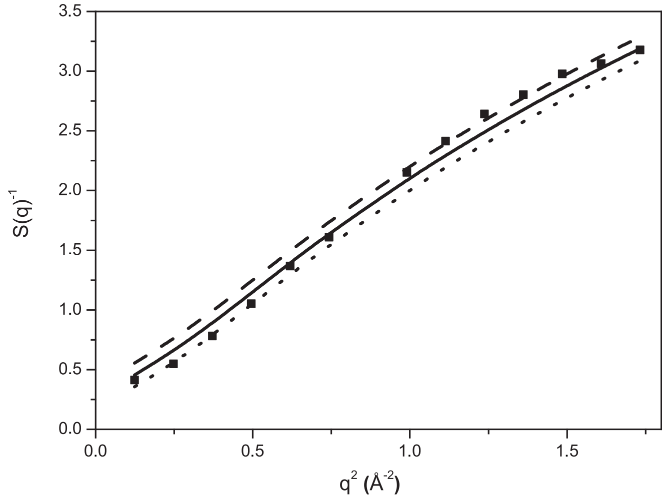

Fig. 3. $1/S(q)$ vs. q^2 from the MD simulation of a *PMMA/POE* mixture at 400 K. Partial charges are assigned by the forcefield. Symbols: simulation data; curves correspond to the RPA results from Eq. (4), from bottom to top: dotted line, $\chi/V_0 = 0.05$; solid line: $\chi/V_0 = 0$; dashed line, $\chi/V_0 = -0.05$.

We compare the simulation data with the predictions from the RPA equation [4] that, for the present definition of scattering units, can be written as

$$S^{-1}(q) = \frac{1}{N_A \Phi_A P_A(q)} + \frac{1}{N_B \Phi_B P_B(q)} - 2\chi/V_0 \tag{4}$$

N_i is the total number of scatters in any i chain, V_0 is the volume of each scatter. Parameter χ corresponds to a given microscopic reference volume, V_R. Therefore,

$$V_0 = V_R/\left(L^3/n_s\right) \tag{5}$$

Volume fractions are obtained from the total number of scatters of each type, $\Phi_i = n_i/n_s$. We also evaluate the form factors of the two types of chains, according to the expression

$$P_i(q) = (N_i)^{-2}\left\langle \sum_i^{N_i}\sum_j^{N_i} \exp(i\mathbf{q}\cdot\mathbf{R}_{ij})\right\rangle \tag{6}$$

where the average extend over the different i chains in all the box configurations along the simulation trajectories. These functions reflect the intramolecular interactions included in the considered q range. It should be remarked that, in a strict application of the random phase approximation, form factors would be calculated from trajectories corresponding to single component boxes. Our form factors, however, may also include some effects on the interaction between components.

In Figs. 1–3, we also plot the RPA curves corresponding to the choices $\chi/V_0 = -0.05$, $\chi/V_0 = 0$ and $\chi/V_0 = 0.05$. It can be observed that the simulation data are always close to these predictions, showing the same general curvature features that are also exhibited by the RPA predictions. These features are similar for a given blend at all temperatures. The *PMMA/PS* blends (Fig. 1) show monotonous curves close to a linear behavior. However, the *PI/PS* systems (Fig. 2) show a strong curvature downwards, more marked than that observed previously for the *PVME/PS* results [8]. Finally, the *PMMA/POE* curves (Figs. 3 and 4) show a moderate curvature at higher values of q. The different curvatures appear at intermediate or high values of q and are related with the different chain intramolecular interactions, as described by the individual form factors and their combination in the RPA equation.

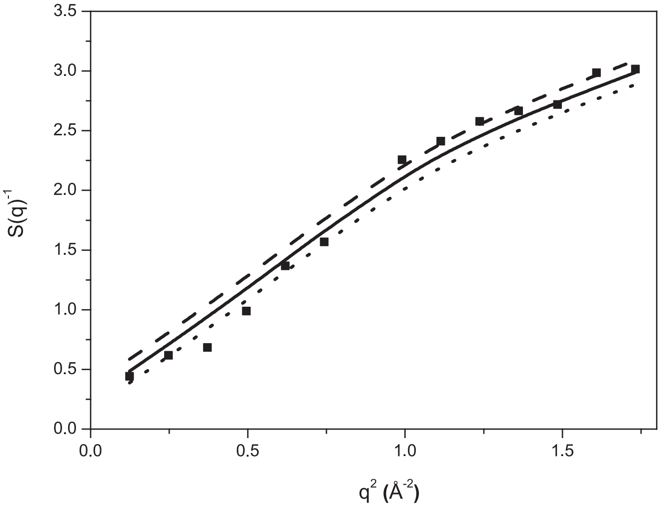

Fig. 4. $1/S(q)$ vs. q^2 from the MD simulation of a *PMMA/POE* mixture at 400 K. Partial charges are obtained according to the charge equilibration method [20]. Symbols: simulation data; curves correspond to the RPA results from Eq. (4), from bottom to top: dotted line, $\chi/V_0 = 0.05$; solid line: $\chi/V_0 = 0$; dashed line, $\chi/V_0 = -0.05$.

Some peculiarities of the simulation points in the different blends should be commented. The most common feature is that the errors are not random but, generally, they have a tendency so that the results for χ decrease when q increases. Similar variations have been observed in some neutron scattering experiments [26]. Moreover, the *PI–PS* simulation data show further systematic deviations upwards respect to the RPA curves in the range of $q > 1$ Å^{-1}. The same behavior is observed at all temperatures and also when the charge equilibration method is employed to assign partial charges. In the case of the *PMMA/POE* blends, the simulation curves have a marked sigmoidal aspect. It should be mentioned that the *PMMA/POE* systems have been harder to equilibrate. The simulation results for the *PMMA/POE* systems obtained with the charge equilibration method show even more important deviations with respect to the RPA predictions and a higher statistical noise, see Fig. 4. Similar conclusions are obtained for this particular blend at other temperatures. Systematic deviations with respect to the RPA prediction are also observed in the *PMMA/PS* data, though the differences are smaller in this case. The greater amount of oxygen atoms with a relatively high partial charge and more prone to specific interactions may cause these deviations in the blends including *PMMA* and POE chains, as it will be discussed below.

χ can be calculated from the simulation results, $S_{\mathrm{sim}}(q)$, at a given value of q that have been evaluated according to Eq. (1)

$$\chi = \left[S^{-1}_{\mathrm{RPA}}(q, \chi = 0) - S^{-1}_{\mathrm{sim}}(q)\right]V_0/2 \tag{7}$$

where $S_{\mathrm{RPA}}(q,\chi = 0)$ is the prediction given by the RPA for $S(q)$ with $\chi = 0$, i.e. with the first two terms on the right hand of Eq. (4). We obtain χ as the arithmetic mean of the values calculated from Eq. (7) with the different values of q. The systematic deviations of the simulation points with respect to the RPA predictions are obviously associated with higher error bars in the *PMMA/POE* systems.

In Table 1 we report the numerical values of χ obtained following this procedure for the different systems at several temperatures, with partial charges assigned by the forcefield or calculated with the charge equilibration method. Differences between both methods to obtain charges are small for the *PMMA/PS* and the *PI–PS* blends. However, they are more important for the *PMMA/POE* systems, where the charge equilibration method yields even higher error bars. The differences between results for χ obtained with the two charge methods do not follow a systematic

Table 1
Simulation values of χ/V_0 for different blends, obtained with the two alternative methods to assign the partial charges, see text.

T(K)	Forcefield assigned	Charge equilibration method
PMMA/PS		
350	0.006 ± 0.005	0.007 ± 0.005
400	0.009 ± 0.007	0.002 ± 0.010
450	0.005 ± 0.004	0.001 ± 0.006
PS/PI[a]		
350	0.007 ± 0.010	0.002 ± 0.011
400	0.002 ± 0.006	−0.001 ± 0.007
450	−0.002 ± 0.010	−0.004 ± 0.011
PS/PI[b]		
350	0.022 ± 0.008	0.023 ± 0.005
400	0.018 ± 0.005	0.010 ± 0.004
450	0.015 ± 0.008	0.014 ± 0.006
PMMA/POE		
350	−0.004 ± 0.010	−0.015 ± 0.018
400	−0.008 ± 0.013	0.004 ± 0.018
450	0.006 ± 0.008	−0.006 ± 0.013

[a] All points considered.
[b] Neglecting the last three points, see text.

pattern for any of these three blends. In our previous work for *PVME*/*PS* system, however, we obtained moderately negative χ values with the charge equilibration method and slightly positive χ values, actually closer to the slightly negative experimental results, with forcefield assigned charges. It seems apparent that the forcefield details have more influence in the final estimation of χ for this particular mixture. Incidentally, the arithmetic means obtained with the data contained in these two sets gave results in good agreement with the experiments for *PVME*/*PS* blends.

In Fig. 5 we have plotted the arithmetic means obtained from the values of χ calculated with the two methods to assign charges for the different systems and temperatures. As discussed previously, differences between the results calculated with both methods are not systematic, except for the previously studied *PVME*/*PS* systems, whose mean values [8] are also included in Fig. 5 for the sake of comparison with the other blends. In the presently investigated systems, evaluating a mean value between both methods may be simply considered as a way to improve statistics and, therefore, we consider the results from both methods as independent samples. These mean values are compared with experimental data obtained from neutron scattering experiments for the different blends, summarized by fitting curves for the considered temperature range [3].

It can be observed that, even though the error bars are significant and sometimes larger than the means, the simulation results for χ are relatively close to the experimental values. Moreover, the data suggest a variation with temperature in qualitative agreement to the actual experimental behavior of the different systems, except in the case of the less accurate results for the *PMMA*/*POE* blends. (As pointed out in Introduction, the experimental temperature behavior of these particular blends has not been totally clarified.) In any case, we should summarize some previously commented methodological problems that have to be taken in consideration to judge the performance of the simulation results. As a general point, we should remark that the simulation data cover a range of values of q considerably higher than the experimental results and, moreover, they correspond to short chains and decreased densities. Incidentally, it is worthy to note that the lowest-q point gives a good estimation of χ for the three blends investigated in the present work, see Figs. 1–4. Furthermore, we should have in mind that the *PI*/*PS* data are calculated from means of the results calculated from Eq. (7) after subtracting the 3 highest q points (short distance range points), for which systematic upward deviations are obtained. Otherwise, we obtain very small absolute values of χ (also contained in Table 1) that do not agree with the experimental curve. The main problem with the *PMMA*/*POE* values is their higher error bars, associated with a sigmoidal curvature significantly more marked than that exhibited by the RPA results. This feature should be considered together with the significantly higher statistical noise associated with the charge equilibration method results. Finally, the previously obtained *PVME*/*PS* systems showed systematic differences between the results obtained with the two different methods to assign charges. In spite of these cautionary comments, Fig. 5 shows a pattern of semi-quantitative agreement between experimental and simulation data of χ, which seems to support the use of the present method at least for a preliminary evaluation of the miscibility in complex chain systems.

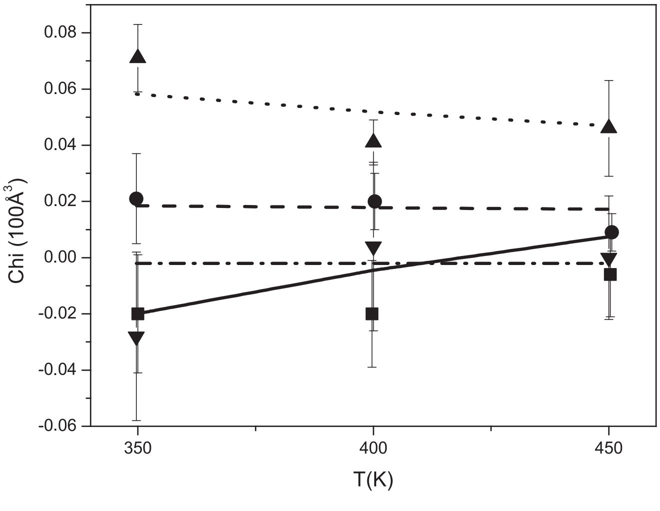

Fig. 5. Parameter χ (referred to a volume of 100 Å^3) vs. temperature. Mean values of the simulation results, obtained from Eq. (7) are denoted by symbols (with error bars). Squares: results obtained previously for the *PVME*/*PS* system [8]; circles: *PMMA*/*PS*; triangles: *PI*/*PS*, neglecting last thee points, see text; inverted triangles: *PMMA*/*POE*. Lines correspond to the reported fitted equation to neutron scattering experimental data [3]. Solid: *PVME*/*PS*; dashed: *PMMA*/*PS*; dotted: *PI*/*PS*; dashed–dotted: *PMMA*/*POE*.

Structure functions for melts of long molecular weight polymers have been previously obtained through neutron or X-ray scattering and they have also been simulated through MD [27–32]. These results reveal specific interactions at relatively long distances that may help to understand some of the peculiar features of the present blend curves. In our range of q values, peaks located at $q < 0.9$ Å^{-1} are generally associated to intermolecular interactions, while peaks located at $q > 1.2$ Å^{-1} can be assigned to intramolecular interactions. The structure function of *PS* melts shows a small intermolecular peak at about $q = 0.6$–0.8 Å^{-1} [27] that becomes prominent for fully deuterated samples [28]. This peak is partially overlapped with another sharp peak at 1.4 Å^{-1}, associated to strong phenyl–phenyl interactions. The structure function of *PI* melts, however, only shows a smoother first intramolecular peak at about 1.5 Å^{-1} [29]. The presence of intermolecular interactions between *PI* and *PS* in the blends may destruct part of the their intramolecular interactions, resulting in an apparent decrease of χ in the range of distances smaller than 6 Å that cannot be described by the RPA equation, though the results obtained for smaller q show a consistent RPA prediction of clearly positive χ values. The experimental structure factor of *PMMA*/*POE* blends [30] reveals a peak at $q \cong 0.9$ Å^{-1} associated to *PMMA* specific intermolecular correlations at about 7 Å. However, the peak decreases when the *POE* concentration increases, indicating effective interactions between the two types of chains at this distance. The experimental structure function of *POE* melts [31], however, only shows a first intramolecular peak at $q \cong 1.5$ Å^{-1}, region where there are not peaks in the case of the *PMMA* melts. Therefore, we expect to see a stronger segregation effect of the *PMMA* chains in the blends at lower q, and a destruction of intramolecular interactions between *POE* chains by the intermolecular interactions at higher q, explaining the sigmoidal aspect of our simulation data. Our data suggest a more effective destruction of the *PMMA*–*PMMA* correlations by the presence of *PS* chains in the *PMMA*/*PS* blends, where specific intermolecular interactions occur at similar distances for both polymer melts so that they can be mutually canceled in the blend. This blend also shows a weaker tendency to break the stronger intramolecular interactions at shorter distances than in the case of the *PMMA*/*POE* blends. Both effects tend to smooth the sigmoidal shape of the simulation data. Finally, the *PVME* structure function [32] shows peaks at $q \cong 1$ Å^{-1} and $q \cong 1.4$ Å^{-1} similar to those observed in the *PS* melts, which seems to favor a better performance of the RPA equation, though the destruction of intramolecular interactions explains the higher miscibility observed for highest q values [8].

In a previous work [17], we have reported calculations performed with direct calculation of interaction energies and coordination numbers between monomer units in contact, proposed time ago [18]. This procedure includes a Monte Carlo generation of differently oriented monomer conformations. The results from these calculations were in general qualitative agreement with the experimental behavior of the blends studied in the present work, though the absolute values of χ were clearly overestimated in all cases. Moreover, an abrupt increase of χ with temperature was predicted for the *PMMA*/*POE* blends. Furthermore, the performance of this method was especially poor in the case of *PVME*/*PS* blends, for which high positive and temperature decreasing values of χ were obtained.

We also considered an alternative computationally simple method, based in a basic theoretical treatment that has allowed us to relate a particular form of binary interaction integrals with parameter χ [17]. This method is also implemented by performing Monte Carlo orientational averages for pairs of our short chain conformations placed at different distances. The results are in general qualitative agreement with the experimental data for all systems, including the *PVME*/*PS* chains. Also, a fair semi-quantitative agreement is found in most systems, though the method yields too high values of χ for the *PMMA*/*PS* blends. However, it should be noted these satisfactory results have been obtained after performing some modifications of the forcefield parameters with respect to the default values recommended for condensed phase and used in the present MD simulations. These forcefield modifications were common for all the systems. Specifically, we chose a fixed shorter cut-off for both the Van der Waals and Coulombic interactions and we included a carefully fitted distance-dependent dielectric constant.

Taking into account the shortcomings of the most simplified Monte Carlo methods, also involving short chains, it can be argued that the present type of MD calculations constitute a more reliable and systematic method to estimate χ for different blend of molecules of relatively complex chemical structures through the use of a common forcefield. However, they require a greater computational effort, even if the results are provided with wide error bars and the calculations cannot meet the optimal technical specifications for chain lengths, densities and box sizes. These specifications need much larger systems and longer times [12] and, currently, they can only be approached through the use of individually designed models and extensive computational experiments [7].

In our previous report of MD simulations for the *PVME*/*PS* blend [8], we also discussed alternative calculations for χ obtained through the evaluation of a cohesive energy density or solubility parameter [33]. In comparison with the experimental data, these results also showed negative χ estimations, though with higher absolute values and a negative temperature variation. An important advantage of obtaining χ from scattering functions is that the calculations are performed using atom coordinates from the trajectories, therefore avoiding the direct involvement of energy values that are much more sensitive to the parameter choices. Consequently, the influence of the forcefield details is minimized.

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