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Anomalous mixing behavior of polyisobutylene/polypropylene blends: Molecular dynamics simulation study

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The unusual mixing behavior of polyisobutylene (PIB) with head-to-head (hhPP) and head-to-tail polypropylene (PP) is studied using large-scale molecular dynamics (MD). The heats of mixing and Flory χ parameters were computed from MD simulations of both blends using a united atom model. The χ parameters from the simulations were estimated from the structure factors using the random phase approximation in analogy with neutron scattering (SANS) experiments. MD simulations for syndiotactic hhPP/PIB predicted a lower critical solution temperature with a χ parameter in very good agreement with SANS experiments on the atactic hhPP/PIB blend. MD simulations also predicted that the isotactic PP/PIB blend was immiscible at high molecular weight in qualitative agreement with cloud point measurements on atactic PP/PIB. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1742761]

Unlike small molecule mixtures, most polymers are immiscible when blended. This is attributable to the much smaller favorable entropy of mixing in polymer versus small molecule mixtures arising from the chain connectivity of the macromolecules. In most blends displaying miscibility, the heat of mixing is negative due to specific interactions[1] such as hydrogen bonding between the components. By contrast, in polyolefin blends the interactions are non-specific, van der Waals interactions where it can be demonstrated that the Flory χ parameter should be positive.[1] Despite this fact a number of miscible polyolefin blends have been found to exist.[2–5] A striking illustration of the subtlety of polyolefin mixing is provided by blends of polyisobutylene (PIB) with polypropylene. From small angle neutron scattering (SANS) experiments, Krishnamoorti *et al.*[2] found that PIB is miscible with atactic head-to-head polypropylene (*a*-hhPP) having a lower critical solution temperature (LCST) of 463 K. Conversely, based on cloud point measurements PIB is immiscible[2] with atactic head-to-tail polypropylene (*a*-PP). Thus minor changes in the polypropylene architecture have major consequences on the phase diagram. The primary purpose of the present investigation is to determine if subtle effects of this type can be predicted and understood from large-scale, molecular dynamics (MD) simulations.

The prediction of the phase diagram of a polymer blend from computer simulation is exceedingly difficult and Gibbs Monte Carlo simulation techniques[6] would seem to be the method of choice. However, the probability of successful polymer swaps between systems is very low for polymers at melt densities, particularly when the two components have different molecular architectures. A different approach by Heine *et al.*[7] was taken in a recent study of the iPP/

polyethylene blends. They estimated the χ parameter by analyzing the MD generated structure factor from miscible short chain blends using the random phase approximation (RPA) in a manner completely analogous to the way experimentalists analyze SANS data. Here we test the validity of this approach by comparing our MD predictions for χ directly to SANS results for hhPP/PIB blends.

In the experimental study of Krishnamoorti *et al.*[2] the head-to-head polypropylene was obtained by hydrogenation of polydienes and, consequently, is an atactic polymer. The simulation of atactic polymers, however, presents complications related to the quenched randomness of the chains, hence we chose to study stereoregular polypropylenes instead. We carried out MD simulations of syndiotactic head-to-head (*s*-hhPP), isotactic head-to-tail (iPP) polypropylene and PIB melts and blends for N=48 and 96 CH$_n$ groups (sites) per chain. For these chain lengths the blends are miscible though at higher molecular weight they may not be. Simulations for the melts were carried out at a constant temperature of 453 K, which is high enough to avoid crystallization of the iPP. Constant densities corresponding to the experimental polymer values were imposed for the pure component simulations (0.033 60 sites/A^3 for hhPP, 0.032 82 sites/A^3 for iPP, and 0.035 68 sites/A^3 for PIB). Simulations on equimolar hhPP/PIB and iPP/PIB blends were also carried out at constant density assuming zero volume change on mixing. The heats of mixing, pair correlation functions, and RPA derived χ parameters were then obtained. Since the RPA analysis for χ requires an extrapolation to zero wave vector, we studied large systems consisting of 1600 chains of 96 sites and 3200 chains of 48 chains for a total of 153 600 united atoms. The simulations were carried out using the
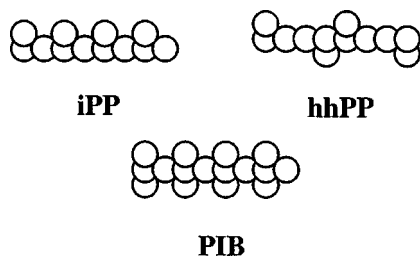
FIG. 1. Schematic representation of the UA models for iPP, hhPP and PIB. Each spherical site corresponds to a C, CH, CH_2 or CH_3 moiety.

TABLE I. The contributions to the heat of mixing ($\times 10^5$) computed from MD simulations on 1600 chains of $N=96$ united atoms.

	hhPP/PIB	iPP/PIB
$\Delta E_{\mathrm{mix}}/nk_BT$	-131 ± 54	31 ± 54
bond	52 ± 16	24 ± 16
angle	107 ± 13	82 ± 13
torsion	25 ± 35	98 ± 35
improper	10 ± 16	5 ± 16
intra vdW	-133 ± 35	-82 ± 35
inter vdW	-193 ± 35	-96 ± 35

parallel MD code LAMMPS[8] on 64 DEC alpha processors. The simulations took approximately 24 h of cpu time for 1 ns and represent some of the largest polymer systems that are practical to model with MD at the present time. The MD simulation of the 1600 chain, 96-site blend was repeated a second time with a new starting configuration; essentially identical results were obtained suggesting that the samples had equilibrated.

We used the united atom TraPPE model of Martin and Siepmann,[9] originally obtained by fitting to short alkane phase behavior. In this model each CH_n site is treated as a single united atom (UA) as depicted in Fig. 1. The parameters for the UA potential can be found in Ref. 9. To preserve the stereochemistry of the *s*-hhPP and iPP a harmonic *improper* potential[10] involving the CH site, its two adjacent CH_2 sites, and the pendant CH_3 group is also included. Inter and intramolecular pairs of sites separated by more than three bonds interact through a Lennard-Jones potential with a cutoff at 12 Å. The simulations used a multiple time step second order symplectic integrator[11] (RESPA) to solve the equations of motion. A 1.25 fs time step was used for the bonding interaction, a 2.5 fs time step for the angular, torsional and improper interactions, and a 5 fs time step for the van der Waals forces. The temperature was kept constant at 453 K by employing the Nose-Hoover extended ensemble method[12] with a coupling frequency of 0.02 fs^{-1}. Self-consistent PRISM theory coupled with a pivot algorithm[10] was used to generate polymer chains with approximately the correct end-to-end distance. These chains were randomly placed in the simulation cell and a soft core potential was used to eliminate the resulting monomer overlap.[10] After the chains no longer overlapped, the full Lennard-Jones potential was switched on and each system was run a minimum of 30 ns of which at least the first 10 ns were always discarded from the analysis. This 10 ns was more than sufficient for a chain to diffuse its radius of gyration. The individual contributions to the total energy were calculated, as well as the contributions from each melt to the energy of the blend. For these system sizes the length of the simulation cell is approximately 162–168 Å, which means that the smallest *k*-vector for the partial structure factors is approximately 0.04 $\mathrm{Å}^{-1}$.

Krishnamoorti *et al.*[2] found that the χ parameter extracted from their SANS data could be represented in the standard form $\chi = a + b/T$. Their χ parameter was defined on a monomer basis where a hhPP or iPP monomer contains six CH_n sites and a PIB monomer four CH_n sites. The corre-

sponding *b* parameter (on an average monomer basis) is related to the heat of mixing ΔE_{mix} through

$$b = \frac{\mathrm{T}n_m}{\phi_A \phi_B}\left(\frac{\Delta E_{\mathrm{mix}}}{n_s k_B T}\right), \qquad (1)$$

where $n_m = n_A n_B/(\phi_A n_B + \phi_B n_A)$ is the average number of united atom sites per monomer (4.8 in our case), n_s is the total number of united atom sites, $\phi_A(\phi_B)$ is the fraction of sites of component $A(B)$, and $n_A(n_B)$ is the number of sites per $A(B)$ monomer. The heats of mixing from the MD simulations are shown in Table I for the largest ($N=96$) blends. It can be seen that MD predicts a negative heat of mixing for *s*-hhPP/PIB, implying LCST behavior in qualitative agreement with experiments[2] on *a*-hhPP/PIB. By contrast, the heat of mixing is positive for the iPP/PIB blend, which implies UCST behavior. The *b* parameters obtained from Eq. (1) are shown for both blends in Table II. Note the close agreement between the MD prediction for *s*-hhPP/PIB with the experimental value[2] for the *a*-hhPP/PIB mixture shown in parentheses.

It is commonly assumed that the heat of mixing is dominated by intermolecular contributions reflecting changes in local molecular packing when comparing the blend to the pure component liquids. The various contributions for the total heat of mixing are shown in Table I. As can be seen the intermolecular contributions of both blends are negative. Unexpectedly, the intramolecular components also contribute significantly to the total heat of mixing in both blends, and are the reason that the total heats of mixing are of opposite signs. Apparently the macromolecules undergo energetically unfavorable changes in their local intramolecular structure in part to gain favorable van der Waals interactions. These local structural changes have only a minor effect on the end-to-end distances of hhPP and PIB chains in the blend, which differ by only 0.53% and 0.30% from their pure component values. Changes in the chain dimensions are also small in the iPP/PIB blend where the end-to-end distances of iPP and PIB change by -0.91% and -0.04%, respectively. This illus-

TABLE II. The χ_m parameter ($\chi_m = a + b/T$) computed from MD simulations on 1600 chains of $N=96$ united atoms. Results from SANS experiments[2] are shown in parentheses. Note the MD simulations were carried out on *s*-hhPP whereas the experiments involved *a*-hhPP.

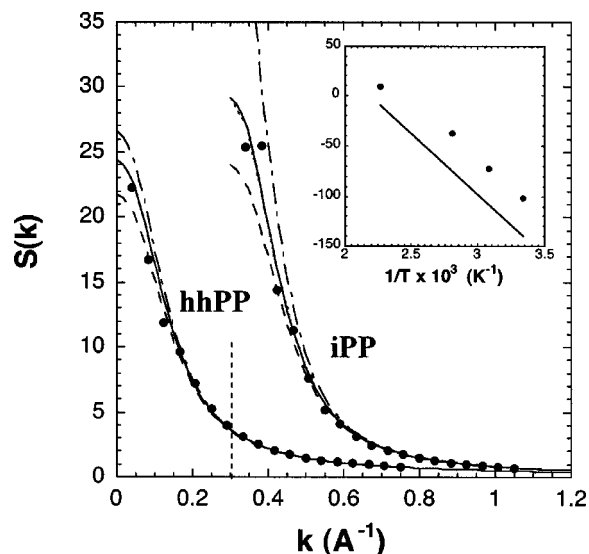|	hhPP/PIB	iPP/PIB
a	0.027 ± 0.003 (0.0246)	0.017 ± 0.002
b (°K)	-11.4 ± 0.6 (-10.34)	5.6 ± 1.3

FIG. 2. Average partial structure factor $S(k)$ for the s-hhPP/PIB and iPP/PIB blends as a function of wave vector k. The points are from MD simulations and the curves are RPA fits with various values of the monomeric χ parameter. s-hhPP/PIB: $\chi = -0.01$ (dashed), 0.0017 (solid), 0.01 (long/short dashed); iPP/PIB: $\chi = 0.0$ (dashed), 0.01776 (solid), 0.048 (long/short dashed). The iPP/PIB curves are shifted along the x-axis for clarity. The inset is a comparison between $\chi_m \times 10^4$ measured experimentally[2] on a-hhPP/PIB (points) and from MD simulations on s-hhPP/PIB.

trates that the mixing of polyolefin blends is nonuniversal and depends on the net effect of many small contributions as seen in Table I.

By analogy with analysis[13] of SANS data, we obtained an average structure factor $S(k)$ from our MD simulations according to

$$S(k) = \frac{(v_A v_B)^{-1/2} \Sigma_{i,j} \langle b_i b_j \exp(i\vec{k} \cdot \vec{r}_{ij}) \rangle}{(b_A/v_A - b_B/v_B)^2}, \quad (2)$$

where v_α is the site volume for site type α, and the site scattering lengths b_α were arbitrarily taken to be $+1$ (-1) for PP (PIB) to provide contrast between the two species. $S(k)$ was then fit to the RPA formula[13]

$$\frac{1}{S(k)} = \frac{1}{\phi_A v_A \hat{\omega}_A(k)} + \frac{1}{\phi_B v_B \hat{\omega}_B(k)} - 2\chi_s/\sqrt{v_A v_B}, \quad (3)$$

where χ_s is the SANS χ parameter on a site basis. Since all the UA sites have essentially the same volume, the site volumes effectively drop out of Eqs. (2) and (3). The $\hat{\omega}(k)$'s are the single chain structure factors obtained from MD simulations on the pure component liquids. Since χ is proportional to the free energy of mixing per site, the monomeric χ parameter (χ_m) can be expressed as $\chi_m = n_m \chi_s$.

The results from the RPA analysis are shown in Fig. 2 for both blends. To assess the sensitivity of the RPA fits to the χ parameter, three values of χ_m are shown for each blend. It can be observed that the RPA plots are fairly insensitive to χ_m. At 453 K, the temperature where the simulations were carried out, χ_m estimated from the experimental a and b parameters (see Table II) is 0.0017 for a-hhPP/PIB. The RPA plot for this value of χ_m is in very good agreement with our MD generated structure factor as can be seen in Fig. 2. An extrapolation of our three lowest wave vector points to

$k=0$ on an Ornstein-Zernike plot yields $\chi_m = 0.0022 \pm 0.0024$. Notwithstanding the insensitivity of our RPA analysis, with this χ_m value, together with the b parameter obtained from the heat of mixing, we estimated the "a" parameter given in Table II. It can be seen that both a and b parameters are in very good agreement with experiment for the a-hhPP/PIB blend. The inset of Fig. 2 compares the MD and experimental χ_m parameters. It should be emphasized that the experiments were performed on a-hhPP/PIB mixtures while our simulations were carried out for the stereoregular s-hhPP/PIB blend. It is known that tacticity can be an important factor in the miscibility of polypropylene blends so the apparent quantitative agreement of our simulations with experiment may be fortuitous. A similar procedure, based on our best fit of $\chi_m = 0.03 \pm 0.02$, yields our estimate of the "a" parameter in the iPP/PIB blend.

The major computational difficulty with using the RPA analysis approach with MD simulations is that very large system sizes are required to study the low wave vector regime. In Ref. 2 the SANS data on a-hhPP/PIB is reported in the approximate range $0.01 \text{ Å}^{-1} \leq k \leq 0.08 \text{ Å}^{-1}$, however, experimentalists are now able to explore wave vectors as low as 0.003 Å^{-1}. By contrast the lowest wave vector attainable from simulations of our largest system is $k \sim 0.04 \text{ Å}^{-1}$. Extraction of a χ parameter from simulation is facilitated somewhat by the fact that we know precisely the $k=0$ limit $\hat{\omega}(0) = N$ of the single chain structure factors in Eq. 3.

In our comparison between MD simulation and SANS experiments, we used the TraPPE UA potential with improper torsions for all the components; no adjustable parameters were employed, though we carried out our simulations with zero volume change on mixing. From the pressure change upon mixing from the simulation, and the experimental compressibility[2] of PIB (8.8×10^{-4}/MPa), we estimated the volume change of mixing $\Delta V_{mix}/V$ to be approximately 0.002 and 0.001 for s-hhPP/PIB and iPP/PIB respectively had the simulations been carried out at constant pressure. This is close to the experimental volume change of mixing $\Delta V_{mix}/V \sim 0.001$ measured by Krishnamoorti[14] for a 50/50 a-hhPP/PIB blend. It is noteworthy that we obtained LCST behavior for the hhPP/PIB blend despite the fact that the volume change of mixing was taken to be zero. This demonstrates that so-called "equation-of-state effects" are not, at least in this case, a necessary condition for the LCST.

Can MD simulation give any insights to polyolefin miscibility despite the nonuniversal aspects of the problem? In the UA representation of the blends, there are 21 independent, intermolecular pair correlation functions between sites. As a measure of the average packing in the liquid, we examined the radial distribution functions $g(r)$ between methyl groups on different species in the blend. In Fig. 3 these $g(r)$'s are compared with what one would expect based on the average intermolecular CH_3/CH_3 correlations in the pure component liquids. From this comparison it can be seen that $g(r)$ for the hhPP/PIB mixture is slightly closer to the average melt packing than for the iPP/PIB blend, despite the fact that ΔV_{mix} was constrained to zero in the simulations. This implies that unlike components are, on the average, closer together in the hhPP/PIB mixture, contributing to its more
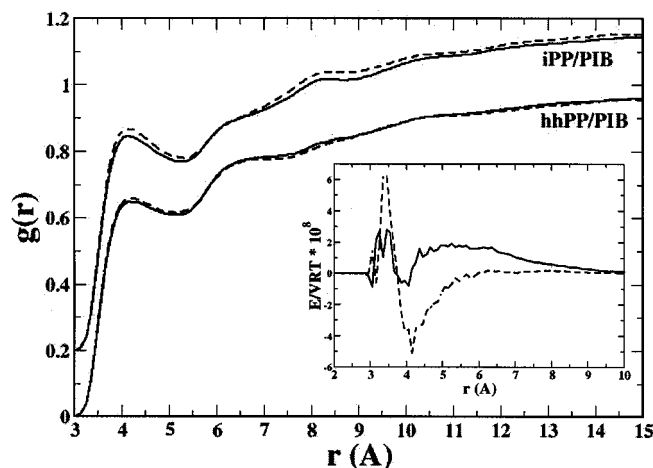
FIG. 3. Intermolecular distribution function $g(r)$ for pairs of CH_3 sites in the blend belonging to chains of different types (solid lines) and the average intermolecular distribution function $g_{av}(r)$ between CH_3 sites obtained from the melts (dashed lines) $g_{av}=(g_{PP}^0+g_{PIB}^0)/2$. The inset is the potential energy of mixing between a CH_3 on PIB and a CH_3 group on hhPP (dashed) and iPP (solid) as a function of separation.

favorable heat of mixing. This is confirmed in the inset of Fig. 3. It can be observed that the potential energy between CH_3 groups on different species is clearly lower at length scales beyond 3.8 A in the hhPP/PIB blend. Similar conclusions regarding the packing are reached by considering correlations between other pairs of sites. Thus PIB provides a favorable environment for hhPP macromolecules resulting in more efficient packing than for iPP chains. Since ΔV_{mix} is estimated to be about the same for both blends, a similar conclusion would probably hold if the simulations were carried out at constant pressure. While the closeness of the agreement observed between MD and experiment for the χ parameter is probably fortuitous, our results demonstrate that MD simulation can be used as a reliable tool for studying the miscibility of polyolefin blends.

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