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Increase in the Chemical Potential of Syndiotactic Polypropylene upon Mixing with Atactic or Isotactic Polypropylene in the Melt

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Introduction

The miscibility of amorphous melts can depend strongly on the stereochemical composition of the two components.[1−4] As a prototypical example, short chain blends of atactic polypropylene (*a*PP) and isotactic polypropylene (*i*PP) are miscible in the melt,[1] but syndiotactic polypropylene (*s*PP) demixes from either *a*PP or *i*PP.[2−4] The demixing is stronger for the *i*PP/*s*PP blend than for the *a*PP/*s*PP blend. Clancy et al.[5] used a coarse-grained lattice simulation procedure and PRISM calculations to study these melts. Their analysis employed the pair distribution functions, $g(r)$, and the energy changes on mixing, ΔE_{mix}. The qualitative behavior of the binary PP melts was reproduced in the simulation. Intermolecular contributions were primarily responsible for the positive values of ΔE_{mix} for the 50:50 blends containing *s*PP.

A molecular mechanism for the behavior of *s*PP in these mixing processes was deduced from these simulations.[5] The crucial role is played by the attractive intermolecular interaction of pairs of short, aligned segments of two *s*PP chains in which the C−C bonds all adopt trans states. These attractive intermolecular interactions are less readily accessible to either *a*PP or *i*PP because the short-range intramolecular interactions cause these two chains to be less likely than *s*PP to adopt conformations with runs of C−C bonds in trans states. This mechanism implies an increase in the internal energy of an *s*PP chain when it is transferred from its own melt into another melt rich in either *a*PP or *i*PP. Clancy et al.[5] showed that the intermolecular contribution to ΔE_{mix} drove the immiscibility of the 50:50 *a*PP/*s*PP blend and the 50:50 *i*PP/*s*PP blend at 473 K, but they could not separate ΔE_{mix} into individual contributions from *a*PP, *i*PP, and *s*PP. That separation is achieved here, where we calculate and analyze the contribution of the change in chemical potential, $\Delta\mu$, for each of these three chains to the *free energy* of mixing, ΔG_{mix}, of the equimolar binary melts.

In addition to providing independent confirmation of prior conclusions about the behavior of PP melts, the present study also constitutes a test of the range of application of the chain increment method for the estimation of μ. Previous tests of this method have used amorphous one-component systems. Interfaces may develop in an immiscible two-component system, and the chain ends may have a preference for the interfacial region. Since the present method for estimating μ probes the chain ends, one might wonder whether it correctly estimates the chemical potential of the entire chain when a two-component system is immiscible. The method is found to be satisfactory in the weakly immiscible, constant density systems studied here.

Calculations

Method for Calculating the Change in Chemical Potential. The chain increment method is used for the calculation of the chemical potential.[6] This method is a modification of the Widom test-particle method[7] that has been widely used for this type of calculation, especially for simulations of small, nearly spherical molecules. The calculation evaluates the energy, U_t, of interaction of a test particle inserted randomly into a previously equilibrated fluid of N particles in the canonical ensemble. The amount, μ_r, by which μ exceeds the chemical potential of the molecule in the ideal-gas state at the same density and temperature, T, as the fluid is

$$-\beta\mu_r = \ln \langle \exp(-\beta U_t) \rangle_N \qquad (1)$$

Here $\beta = 1/k_BT$, k_B is Boltzmann's constant, and the angle brackets denote the ensemble average. The extension of this idea to the case of dense melts of long chain molecules is difficult, since most attempted insertions of a long test chain into a dense melt result in a configuration with overlap which results in $U_t = \infty$.

Two means have been proposed to overcome this difficulty. Frenkel[8,9] and de Pablo[10] used variations of the configurational bias Monte Carlo method, proposed originally by Rosenbluth and Rosenbluth,[11] to enhance the insertion probability of test chains without overlap. While this method is successful, it nevertheless fails for chains longer than 10 repeat units in a dense melt. The chain increment method of Kumar et al.[6] involves growing an arbitrary chain in the system by a single monomer as a test bead. Application of the Widom test particle method, eq 1, then yields the free energy to grow the chain in the system by a single monomer. Further, for long chains in a melt, it has been found that the chain chemical potential closely approximates the product of the incremental chemical potential and the chain length of the polymer in question.[8,12] The validity of this approach was demonstrated by simulation of a system composed of bead−spring chains.[8] Subsequently, this work has been extended to the more complicated architecture of a united atom model for polyethylene,[10,13] suggesting that inclusion of bond angle and torsion angle potentials do not cause additional difficulties in this enumeration.

Energies and Equilibrated Configurations. The simulations of Clancy et al.[5] employ coarse-grained PP chains in which each monomer unit is represented by a single bead, placed at the position of the backbone atom to which the methyl side group is bonded. The coarse-grained chains are placed on a high coordination lattice, with $10i^2 + 2$ sites in shell i.[14] The lattice has a step length of 2.5 Å. Beads with the mass of C_3H_6 must

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occupy 12% of the sites to obtain the experimental density, 0.75 g/cm^3, of a PP melt at the temperature of the simulation, 473 K.[15]

The chains were equilibrated with a Metropolis Monte Carlo simulation, using an energy expression composed of two types of terms: one type being short-range and intramolecular and the other type combining the intermolecular and long-range intramolecular interactions. The short-range intramolecular interactions are described by a three-state RIS model for PP,[16] the first- and second-order interaction energies of which are mapped exactly onto the coarse-grained chains.[17] The remaining intramolecular interactions and the intermolecular interactions are described by a discretized version of a continuous potential energy function, $u(r)$.[18] The discretization starts from the expression for the second virial coefficient of a nonideal gas, B_2, using the Mayer f function, $\exp[-\beta u(r)] - 1$.

$$B_2 = -{}^1/_2 \int f \, \mathrm{d}\mathbf{r} \tag{2}$$

The continuous integral over all space is reexpressed as the sum of contributions from successive shells on the high-coordination lattice with coordination number z_i.

$$B_2 = (V_{\text{cell}}/2)(1 - \sum z_i \langle f \rangle_{i\text{th}}) \tag{3}$$

Here $\langle f \rangle_{i\text{th}}$ denotes the average of the Mayer f function over the z_i cells in shell i, V_{cell} is the volume of one cell, and the summation extends over all shells. This average Mayer f function is then converted to a discrete energy, u_i.

$$\exp(-\beta u_i) - 1 = \langle f \rangle_{i\text{th}} \tag{4}$$

The procedure converts a continuous potential energy function, $u(r)$, into a set of discrete energies, u_i, such that both $u(r)$ and the u_i specify exactly the same value of B_2. The discrete u_i are used for the simulations on the high coordination lattice. The simulations of Clancy et al.[5] take $u(r)$ in eq 2 to be a Lennard-Jones (LJ) potential with the parameters tabulated by Reid et al.[19] for propane, $\epsilon/k_B = 237.1$ K and $\sigma = 5.118$ Å. This discrete potential was truncated at the third shell in the simulations.

A slight refinement of the input parameters, such as a small reduction in the value of ϵ in the LJ potential used as an input to eq 2, would be required if the simulation is to reproduce quantitatively as well as qualitatively the immiscibility of *s*PP with either *a*PP or *i*PP. A slight reduction in ϵ can be justified, because Hirschfelder et al.[20] tabulated the slightly different LJ parameters of $\epsilon/k_B = 206$ K and $\sigma = 5.240$ Å for propane. Our objective here is to illuminate the molecular mechanism responsible for the differences in the compatibility of the *a*PP/*i*PP, *a*PP/*s*PP, and *i*PP/*s*PP melts, and the present assignments of ϵ and σ are adequate for this purpose. Therefore, refinement of the numerical values of ϵ and σ has not been attempted.

When one of the coarse-grained chains in an equilibrated replica of a melt is extended from N beads to $N + 1$ beads, the energy of the test bead is calculated as

$$U_{\text{t}} = U_{\text{RIS},N+1} - U_{\text{RIS},N} + U_{\text{LJ}} \tag{5}$$

The first two terms on the right-hand side of eq 5 are the RIS energies of the newly extended chain of $N + 1$ beads and the N beads that were present in this chain before extension, evaluated using the RIS model of Suter et al.[16] This difference depends on the conformation at the new chain end and on the arbitrary assignment of the zeros of energy in the RIS model. The influence of this arbitrary assignment of the zero of RIS energy is transmitted into μ_{r} via eq 1, but it is eliminated when we calculate $\Delta\mu$. The last term, U_{LJ}, is the sum of the discretized LJ interactions of the newly inserted bead with all beads previously in the system, except for its nearest- and next-nearest-neighbor beads on the same chain. The interaction of directly bonded beads is a constant throughout the simulation and is therefore ignored. The intramolecular interaction of the newly inserted bead with its next-nearest-neighbor bead is incorporated in $U_{\text{RIS},N+1}$, using the short-range interactions in the RIS model, and is not counted again in U_{LJ}.

Table 1. $\Delta\mu$, in kJ/mol Beads, for Coarse-Grained PP Chains in 50:50 Blends and in Their One-Component Melts at 473 K

type of PP	*a*PP/*i*PP blend	*a*PP/*s*PP blend	*i*PP/*s*PP blend
*a*PP	−0.21 ± 0.22	−0.17 ± 0.31	
*i*PP	−0.12 ± 0.23		−0.04 ± 0.23
*s*PP		2.17 ± 0.81	1.76 ± 0.78

Table 2. ΔG_{mix} and ΔE_{mix}, Both in kJ/mol Beads, for Mixing the 50:50 Blends at 473 K; ΔE_{Mix} Are from Table 4 of Clancy et al.[5]

blend	ΔG_{mix}	ΔE_{mix}
*a*PP/*i*PP	−0.16 ± 0.22	0.13 ± 0.17
*a*PP/*s*PP	1.00 ± 0.56	0.61 ± 0.36
*i*PP/*s*PP	0.86 ± 0.50	0.95 ± 0.34

The Monte Carlo simulations of Clancy et al.[5] for each equilibrated melt were divided into 10 nonoverlapping parts, each containing the same number of replicas, and $\langle \exp(-\beta U_t) \rangle$ was evaluated for each of these 10 parts. The value of μ and its uncertainty for each component are identified with the mean and standard deviation, respectively, of the 10 independently averaged $-\beta^{-1} \ln \langle \exp(-\beta U_t) \rangle$.

Results and Discussion

The values of $\Delta\mu$ for transferring a polypropylene chain from its pure melt to a 50:50 blend at 473 K are presented in Table 1. Uncertainties are as large, or larger, than $\Delta\mu$ for *a*PP and for *i*PP. Only for *s*PP does the average of $\Delta\mu$ exceed the uncertainty.

Table 2 reports the values of the excess Gibbs energy change on mixing for the three 50:50 blends, calculated from the data in Table 1 as

$$\Delta G_{\text{mix}} = {}^1/_2[\Delta\mu(\text{A in AB}) + \Delta\mu(\text{B in AB})] \tag{6}$$

For comparison, this table reproduces the ΔE_{mix} from Table 4 of Clancy et al.[5] They obtained ΔE_{mix} as the difference in the average LJ and RIS energies per bead in the 50:50 blends and in the pure components. When allowance is made for the standard deviation, the values of ΔG_{mix} in Table 2, based on the insertion energies, track the values of ΔE_{mix}, based on direct calculation of the averages of the LJ and RIS energies in the blends and in the pure components. If one attempts to estimate ΔS_{mix} from the simulation, the standard deviation is much larger than the mean; i.e., the entropy of mixing is not distinguishable from zero in the simulation.

Both sets of data suggest *a*PP/*i*PP should show little or no tendency for demixing, consistent with the experiments of Lohse.[1] The two sets of data also suggest that both *a*PP/*s*PP and *i*PP/*s*PP melts should demix, consistent with the experiments of Mülhaupt and coworkers.[2-4] Apparently, the environment sampled by the ends of the chains is representative of the environment felt by the entire chain, even in the immiscible mixtures that contain *s*PP.

Table 1 shows that *s*PP is more strongly affected than either *a*PP or *i*PP when it is transferred from its own melt to either of the blends. This result was inferred, but not specifically demonstrated, by Clancy et al.[5] on the basis of their calculations of the contributions of the RIS and LJ energies to ΔE_{mix}. They showed that the largest contributions to ΔE_{mix} were from the LJ interactions in the two blends containing *s*PP. However, they did not unambiguously decompose ΔE_{mix} for the melt into LJ contributions from the individual species. The present analysis via $\Delta\mu$ makes that decomposition. The positive values of $\Delta\mu$ for *s*PP in both of its blends point to a decrease in the intermolecular attraction, or cohesion, of *s*PP chains when they are transferred from their one-component melt to either of the blends.

The $\Delta\mu$ in Table 1 cannot be unambiguously decomposed into individual components from the RIS and LJ energies because this decomposition requires equating the average of a product, $\langle \exp(-\beta U_{\mathrm{RIS}}) \exp(-\beta U_{\mathrm{LJ}})\rangle$, to the product of the averages, $\langle \exp(-\beta U_{\mathrm{RIS}})\rangle \langle \exp(-\beta U_{\mathrm{LJ}})\rangle$.

The behavior of the $\Delta\mu$ evaluated here is compatible with the molecular mechanism identified by Clancy et al.[5] from analysis of the dynamics and local conformations of the chains in their simulations. They found that extended subchains of *s*PP can participate in attractive intermolecular interactions in the one-component melt when they are aligned, and these interactions are weakened upon dilution of *s*PP into a blend with either *a*PP or *i*PP. The RIS model causes the subchains in *a*PP and *i*PP to have less likelihood of being extended than is the case for subchains in *s*PP. Therefore, an *s*PP chain in its one-component melt can more easily find another chain in a conformation that will support this attractive interaction than can a similar *s*PP chain in a two-component melt rich in either *a*PP or *i*PP.

A mechanistically similar interaction occurs in simulations of poly(vinyl chloride) (PVC).[21] The interaction is stronger in PVC because the RIS model causes C−C bonds in syndiotactic PVC to have a higher probability for trans placements than the C−C bonds in *s*PP, and the polar nature of PVC, evident in a larger value of ϵ in the LJ potential for ethyl chloride than for propane,[20] causes a stronger attractive intermolecular interaction of two extended and aligned segments. The ability of this interaction of extended syndiotactic subchains to induce demixing depends on the probability of extension (governed by the short-range intramolecular interactions incorporated in the RIS model) and the strength of the attractive intermolecular interaction of aligned, extended segments (governed by the attractive part of the LJ potential[22]).

Conclusions

The values of the Gibbs free energy changes on mixing can be estimated by the chain increment method in the simulations of coarse-grained chains in which the short-range intramolecular interactions are evaluated using a rotational isomeric state model. The calculated free energy changes on mixing provide a strong basis for the experimental observations that the miscibility of polypropylene melts depends strongly on the stereochemical compositions of the two blended components. The *s*PP chains experience an increase in μ when they are transferred from their melt to a 50:50 blend of *s*PP with either *a*PP or *i*PP.

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References and Notes

(1) Lohse, D. J. *Polym. Eng. Sci.* **1986**, *26*, 1500.
(2) Thomann, R.; Kressler, J.; Setz, S.; Wang, C.; Mülhaupt, R. *Polymer* **1996**, *37*, 2627.
(3) Thomann, R.; Kressler, J.; Rudolf, B.; Mülhaupt, R. *Polymer* **1996**, *37*, 2635.
(4) Maier, R. D.; Thomann, R.; Kressler, J.; Mülhaupt, R.; Rudolf, B. *J. Polym. Sci., Part B* **1997**, *35*, 1135.
(5) Clancy, T. C.; Pütz, M.; Weinhold, J. D.; Curro, J. G.; Mattice, W. L. *Macromolecules* **2000**, *33*, 9452.
(6) Kumar, S. K.; Szleifer, I.; Panagiotopoulos, A. Z. *Phys. Rev. Lett.* **1991**, *66*, 2935.
(7) Widom, B. *J. Chem. Phys.* **1963**, *39*, 2808.
(8) Siepmann, J. I.; Frenkel, D. *Mol. Phys.* **1992**, *75*, 59.
(9) Frenkel, D.; Mooij, G. C. A. M.; Smit, B. *J. Phys.: Condens. Matter* **1992**, *4*, 3053.
(10) de Pablo, J. J.; Laso, M.; Suter, U. W. *J. Chem. Phys.* **1992**, *96*, 6157.
(11) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1956**, *23*, 356.
(12) Spyriouni, T.; Economou, I. G.; Theodorou, D. N. *Macromolecules* **1997**, *30*, 4744.
(13) Spyriouni, T.; Economou, I. G.; Theodorou, D. N. *Phys. Rev. Lett.* **1998**, *80*, 4466.
(14) Rapold, R. F.; Mattice, W. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2435.
(15) Orwoll, R. A. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; American Institute of Physics: Woodbury, NY, 1996; p 81.
(16) Suter, U. W.; Pucci, S.; Pino, P. *J. Am. Chem. Soc.* **1975**, *97*, 1018.
(17) Haliloglu, T.; Mattice, W. L. *J. Chem. Phys.* **1999**, *111*, 4327.
(18) Cho, J.; Mattice, W. L. *Macromolecules* **1997**, *30*, 637.
(19) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; MacGraw-Hill: New York, 1987; p 773.
(20) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1964; p 1111.
(21) Clancy, T. C.; Mattice, W. L. *Macromolecules* **2001**, *34*, 6482.
(22) Clancy, T. C.; Mattice, W. L. *J. Chem. Phys.* **2001**, *115*, 8221.

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