

Phase Separation in Nearly Symmetric Polymer Mixtures

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(Received 26 March 1996)

Through computer simulations we demonstrate that even small structural or energetic asymmetries can cause polymer blends characterized by bare Flory χ values of 0 to phase separate. We show that this result is a consequence of the coupling between packing effects and attractive interactions, an aspect that is ignored by most popular theories of polymer thermodynamics. [S0031-9007(96)00957-X]

PACS numbers: 61.41.+e, 64.75.+g

Polymeric mixtures are predicted to be much less miscible than their small molecule analogs since the entropy of mixing is much smaller in the case of these catenated systems. This essential idea in describing the limited miscibility of macromolecular systems is embodied in the Flory-Huggins model [1], which predicts that the free energy of mixing per lattice site ΔG_{mix} for a binary mixture of polymers is

$$\beta \Delta G_{\text{mix}} = \frac{\phi}{N_1} \ln \phi + \frac{(1-\phi)}{N_2} \ln(1-\phi) + \chi \phi(1-\phi), \quad (1)$$

where ϕ is the volume fraction of one of the polymers, and N_i is the chain length of component i . $\chi \propto 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$ is the interchange energy parameter, where ϵ_{ij} is the energy of interaction between two nearest neighbor segments of type i and j . Note that this lattice model, which has assumed that the systems are incompressible and randomly mixed, reduces to regular solution theory in the limit $N = 1$. In the framework of this model, systems comprising equal chain length polymers which satisfy the criterion $\chi N < 2$ will be phase mixed under all conditions, thus suggesting that phase demixing can be caused only by mismatches in energetic interactions. Sanchez [2] has relaxed the incompressibility constraint in the Flory model by including holes. In addition to phase separation behavior that can be caused by a positive χ , this model shows that demixing can be triggered by differences in equation of state properties [2,3]. However, this will occur only above the boiling point of the more volatile component and will be associated with a lower critical solution temperature, in contrast to the energetically driven upper critical solution behavior.

In this work we have considered two free space binary polymer mixtures which would be expected to be energetically athermal, i.e., $\chi = 0$, if they followed the Flory assumptions of incompressibility and randomly mixed chain segments. One system, which has been proposed as a descriptor for commercially important hydrocarbon polymer mixtures [4–7], comprises chains of different stiffness where all monomers interact with identical Lennard-Jones potentials. The second system contains chains of identical architecture but with dis-

parate pure component Lennard-Jones interactions (i.e., $\epsilon_{11} \neq \epsilon_{22}$). However, we have selected $2\epsilon_{12} = \epsilon_{11} + \epsilon_{22}$ so that the bare $\chi = 0$ in this case as well. Since these free space mixtures are compressible, the model developed by Sanchez [2] predicts the blends to be miscible over much of the parameter space, except possibly at temperatures higher than the boiling point of the more volatile component [2] where they could phase separate due to mismatches in equation of state behavior. Instead we find, through the aid of computer simulation, that both of these systems undergo liquid-liquid phase separation with well defined upper critical solution temperatures. These results serve to stress that the coupling between packing (or entropic) effects and energetics, which are ignored in many common theories describing the thermodynamics of polymer systems [1,2], play an important role in determining their miscibility. We conclude by verifying the utility of a relatively straightforward extension of Flory-Huggins theory [4,5] which provides reliable estimates of phase diagrams in these cases.

The two polymeric species in each system were modeled as strings of beads of equal length and had monomers of identical size. Interactions between any pair of nonbonded beads were modeled through standard 6-12 Lennard-Jones potentials [8] which were truncated at 2.5σ . Long range corrections were utilized to correct for the truncation [8]. In the system termed the “energetic” blend the polymer chains were modeled as beads connected by stiff springs as in Ref. [9]. The Lennard-Jones energetic parameters characterizing 11 and 22 interactions followed the relationship $\epsilon_{22}/\epsilon_{11} = 0.8$, while the 12 interaction parameter was an arithmetic mean of the pure component values. In the “stiffness” blend all nonbonded interactions are described by the same Lennard-Jones ϵ parameter and the polymers were modeled as a series of tangent spheres [10]. The stiffness was controlled through a bond bending potential [10]: $\beta U_b = \frac{1}{2} k_\theta (1 + \cos \theta)^2$, where θ is the included angle between any two adjacent bonds. The adjustable parameter k_θ was set to 3.0 and 0.0 for the stiff and flexible components, respectively. All simulations were conducted at constant temperature and pressure ($P^* = P\sigma^3/\epsilon_{11} = 0$) so as to mimic

typical experimental conditions. Phase equilibria in these systems were monitored through the semigrand ensemble method [11,12]: Since the location of the phase boundary was unknown we treated $\Delta\mu$, the exchange chemical potential between the two species, as a parameter and located the phase boundary at each temperature through trial and error methods as outlined in Ref. [11]. Typical cells contained 20–40 chains (i.e., between 2000 and 6000 monomers), and periodic boundary conditions were utilized in all three directions.

Figures 1(a) and 1(b) represent the phase diagrams obtained for the two systems from our simulations. We begin by discussing the energetic blend. The results shown in Fig. 1(a) for this blend correspond to a chain length $N_1 = N_2 = 100$. We have also considered systems where $N_1 = N_2 = 25$ but found that they were miscible to very low temperatures (i.e., $T^* = k_B T / \epsilon_{11} = 0.8$) [13]. Consequently, the phase separation behavior reported in Fig. 1(a) represents truly polymeric behavior. The line drawn through the points is a best fit to the Ising model prediction: $(\phi - \phi_c) \propto (T - T_c)^\beta$, where T_c is the critical temperature, ϕ_c is the critical composition, and $\beta = 1/3$ [14,15]. Since the uncertainties in the compo-

sitions of the two phases are relatively large, we cannot determine the critical composition accurately. Therefore, we assigned $\phi_c = 0.5$ to reduce the number of fitting parameters. The stiffness blend phase diagram, Fig. 1(b), was determined at a chain length $N_1 = N_2 = 150$. Note that this phase diagram is not symmetric about $\phi = 0.5$ and that the critical composition obtained from the fitting procedure is $\phi_c = 0.45$, i.e., richer in the more flexible component. This conclusion is in near quantitative agreement with the predictions of Schweizer [5]. Clearly the region of immiscibility in the case of the stiffness blend is much narrower than in the energetic blend. This difference in behavior is an interesting unresolved question, which we are currently examining in more detail.

The important common conclusion we obtain from these results is that blends characterized by bare χ values of 0 in an incompressible lattice sense need not be miscible at low temperatures, and in fact can undergo liquid-liquid phase separation with an upper critical solution temperature. This fact cannot be captured by the standard Flory lattice model [1,2]. Since this model ignores the compressibility of the blend and assumes that chain segments mix randomly, the immiscibility of these systems reflects the failure of one or both of these approximations. We can rule out compressibility effects alone as being the cause since the model of Sanchez [2] incorporates this aspect but cannot reproduce the simulation results. Further support for this idea comes from our simulations, which suggest that in the single phase region the specific volume of each blend is essentially an arithmetic average of the molar volumes of the pure components, i.e., that the excess volume changes on mixing are effectively equal to zero within simulation uncertainties. Consequently, these blends may be treated as being incompressible. We also note that chain dimensions for the two species in each system do not change on blending [10]. Hence, conformational changes on mixing cannot be the cause for the observed demixing.

We therefore propose that the phase separation for these nearly symmetric systems arise primarily from packing disparity inherent at the level of the pure components. To illustrate this point in Fig. 2(a) we plot the *intermolecular* pair distribution function for the two pure materials which comprise the energetic blend. Consistent with Fig. 1(a) we set $N = 100$ and $T^* = 2$. Clearly the segments of type 1 pack much better than the segments of type 2, a result which can be rationalized by the more favorable intermolecular interactions in pure component 1. This packing disparity in the pure components manifests itself as nonrandom mixing of chain segments in the blends, as shown in Fig. 2(b) for the case $\phi_1 = 0.15$. It is clear that the energetically stronger 11 interactions are favored over 22 and 12 pair interactions in the blend as well. Note that there are quantitative differences between the intermolecular 11 and 22 $g(r)$'s obtained from the blends and pure melts, suggesting that this connection is

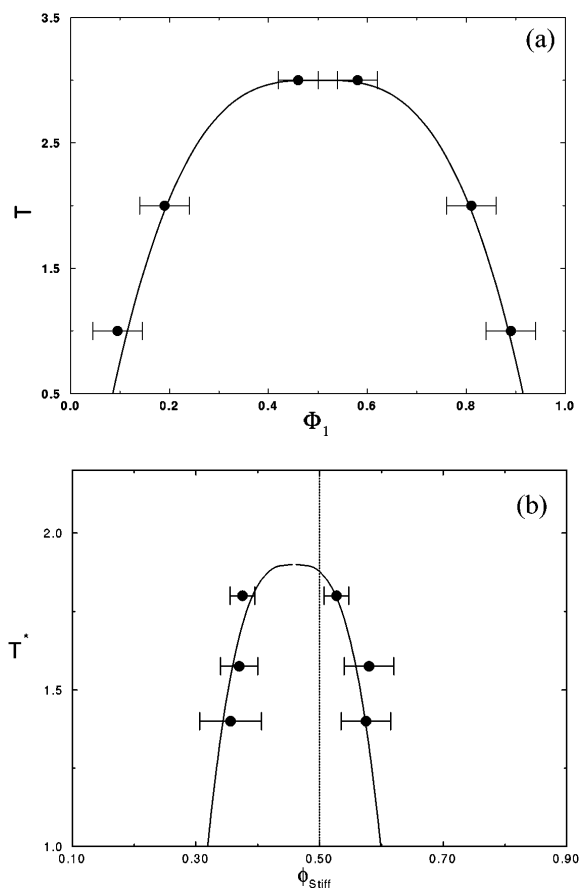


FIG. 1. Computed phase diagrams plotted as T^* as a function of composition ϕ . (a) Energetic Blend for $N_1 = N_2 = 100$. (b) Stiffness Blend for $N_1 = N_2 = 150$. Points are simulation data, while the line is the scaling prediction.

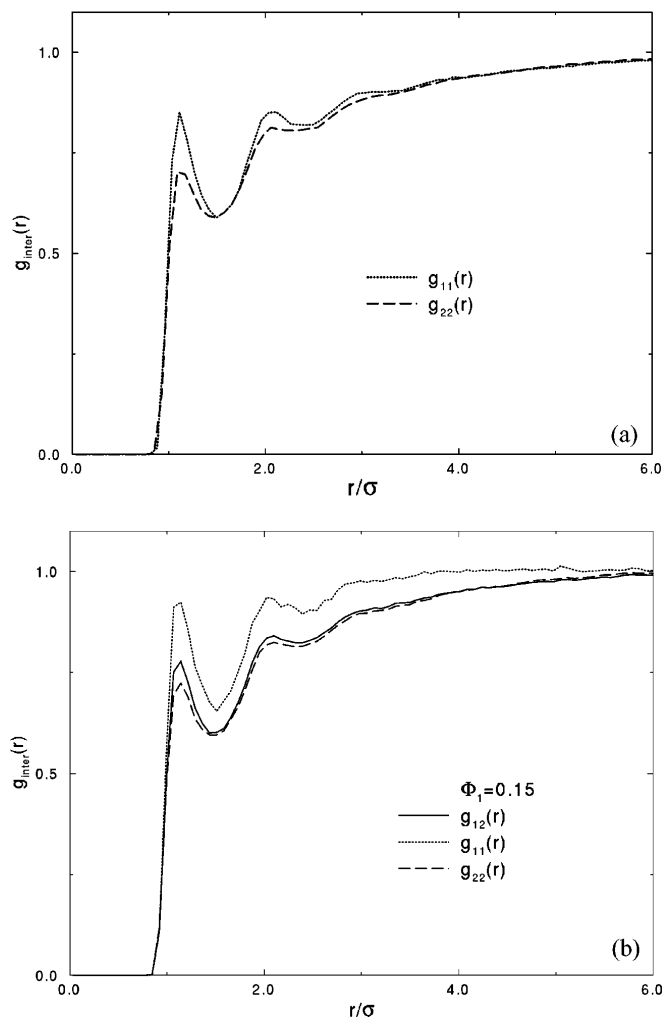


FIG. 2. Intermolecular radial distribution functions for the energetic blend comprising chains of length $N_1 = N_2 = 100$, at $T^* = 2$. (a) Results are for the two pure components. (b) Results from a blend with composition $\phi_1 = 0.15$.

only semiquantitative. Similar results were found near the first peak of $g(r)$ under all conditions in the one phase region for this system. These results are in accord with predictions of the PRISM model [5]. In the case of the stiffness blend the intermolecular stiff-stiff $g(r)$ is always significantly higher than the flexible-flexible pair distribution function [10], in both the pure materials and in all blends, demonstrating that this system also has packing asymmetry.

In an attempt to understand the role of disparity in the packing of the pure components on the miscibility of these blends we consider a recent proposal by Krishnamoorti and Graessley [4] who found that the phase behavior of hydrocarbon systems could be predicted by Flory-Huggins theory if the χ parameter was estimated from the relationship [16]

$$\chi = \frac{V_m}{RT} (\delta_1 - \delta_2)^2. \quad (2)$$

Here V_m is the molar volume of the liquid and δ_i is the Hildebrand solubility parameter of pure component i [17]. δ_i is defined as [18]

$$\delta^2 \propto \int u(r) g_{\text{inter}}(r) r^2 dr, \quad (3)$$

where $u(r)$ is the pair potential. The rationale for utilizing this approach is that the solubility parameter defined in Eq. (3) couples packing and energetic interactions when estimating the cohesive energy of the system. Consequently, pure systems with stronger intermolecular interactions which pack better [see Fig. 2(a), for example] have larger solubility parameters than would be expected from models such as Flory's, which ignore this packing effect. Consequently [4,5], the χ parameter derived from this approach will provide a more reasonable estimate for the enthalpy change of mixing of this system. When utilized in conjunction with the Flory model, this approach should yield relatively accurate phase diagrams in these cases.

We consider first the energetic system and derive the pure component solubility parameters from our simulations [18]. Following Eq. (2) yields a $\chi \approx 0.036$ at $T^* = 2$, which suggests that chain mixtures longer than $N \approx 55$ would be immiscible at this temperature. This result is in reasonable agreement with our simulations. Similar agreement has been found at the two other temperatures considered, which suggests that the modification of Flory theory proposed by Graessley [4] yields relatively accurate estimates of the phase diagram. An identical procedure can be applied to the stiffness blends. The positive χ parameter estimated from Eq. (2), when utilized in the Flory model at $T^* = 1.8$, predicts that chains longer than $N \approx 190$ should be immiscible. This is in reasonable accord with the simulations.

These results emphasize that although the Lennard-Jones energetic parameters in these systems are matched so as to yield a bare $\chi = 0$, nevertheless, the most important disparity in these systems is caused by differences in intermolecular packing in the pure states. This aspect, which is anticipated by PRISM theory [5], serves to emphasize that the limited miscibility of polymer blends relative to their small molecule counterparts is not only due to the reduced entropy of mixing embodied in the Flory model, but also to packing effects which couple to energetics.

Our results on the energetic blends are qualitatively in agreement with the behavior of classical, immiscible blend systems such as polystyrene/polymethylmethacrylate which are characterized by large χ parameters (≈ 0.03). The simulations presented here are consistent with the notion that such blends can phase separate simply because of differences in packing behavior without having to evoke any specific unfavorable interactions.

Further, the results obtained from the stiffness blend are consistent with the observed immiscibility of mixtures

of hydrocarbon polymers. Previous work [4–7] has suggested that these commercially important blends could be modeled as mixtures of chains with different stiffness. We find this mapping to be reliable as long as one introduces attractive interactions between the monomers. Without these attractions, the consequences of packing asymmetry are insufficient to cause phase separation in blends with parameters relevant to the experiments [10]. However, the addition of uniform attractions does result in phase separation, stressing the importance of this coupling [5].

In conclusion, we have demonstrated that small energetic or structural asymmetries can cause polymer blends to phase separate even when the blends are characterized by bare χ values of 0. We suggest that this behavior is a consequence of two polymeric phenomena. The first factor is the reduced entropy of mixing for polymers, as embodied in the fifty year old Flory-Huggins model [1]. The second contribution arises from the coupling between packing (or entropic) effects and attractive interactions, which serves to destabilize these blends and cause phase separation. These findings prove that attaining miscibility in polymers is even more difficult than thought before and that strongly favorable interactions are generally necessary to achieve this goal.

Financial support from the National Science Foundation (Grant No. CTS-931195) is gratefully acknowledged. We thank Professor K. S. Schweizer for valuable discussions.

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- [18] The solubility parameters were actually calculated as follows: $\delta^* \equiv \delta \sigma^{3/2} / \epsilon^{1/2} \equiv \sqrt{(U_{\text{liq}}^* - U_{\text{gas}}^*) / V_{\text{liq}}^*}$, where each internal energy was evaluated through the relationship $U^* = 4\pi\rho \int r^2 g_{\text{total}}(r) u(r) dr$, where $g_{\text{total}}(r)$ is the total distribution function, including both intermolecular and intramolecular contacts. The two relevant states in this calculation are the saturated liquid and the equilibrium gas state, which we approximate by an isolated chain. It is commonly assumed that if the chain conformations do not change in going from gas to liquid, then the difference in internal energy between these two states can be described in terms of the intermolecular distribution function alone as in Eq. (3). Since chain dimensions do change in going from a gas to a liquid state Eq. (3) is only an approximate relationship.