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Distribution of Interactions in Binary Polymer Mixtures: A Monte Carlo Simulation Study

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ABSTRACT: Phase transitions from miscibility to immiscibility were observed in simulations of binary polymer mixtures on a planar square lattice using reptation sampling techniques. The relationship between the phenomenological interaction parameter, χ, and the true molecular interaction energy was followed, and the dependence of the number and distribution of heterocontacts in the mixture on the applied heterosegment interaction energy was determined. Deviations from the results of mean-field treatments, which overestimate the number of heterocontacts, were observed even for athermal mixtures. Kinetically driven hysteresis governed by a temperature equilibration time scale was examined for the phase transitions. An important prediction of expansion of the polymer chains in the miscibility region can be made on the basis of the results of chain end-to-end distance calculations.

Introduction

The subject of polymer blends has been studied extensively[1] mainly as a result of the potential applications of polymer blends as new materials. For each particular blend the question of miscibility and immiscibility arises. In general, miscibility is unusual for blends of high molecular weight polymers. The Gibbs free energy of mixing, which governs phase behavior, consists of three contributions: an exchange interaction term, the combinatorial entropy of mixing, and a free volume term. The basic term is considered to be the exchange interaction term. A prerequisite for miscibility is that the energy of mixing be endothermic. The combinatorial entropy of mixing is very small due to the large size of polymeric molecules. The free volume term, which is unfavorable to mixing, also has a relatively small effect at low or moderate temperatures in polymer–polymer systems since differences in the sizes of the molecules, and hence differences in the free volumes are small, unlike polymer–solvent systems. It is highly desirable to follow in detail the number of favorable/unfavorable heterocontacts in the mixture and also to determine the distribution of unlike contacts. It should be

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remembered, however, that the entropic and free volume contributions must not be underrated. The phase boundary is governed by a delicate balance and is determined not by the absolute values of the contributions to the free energy but by higher derivatives of ΔG_{mix} as a function of composition. Thus small contributions in absolute value can play an important role in phase behavior.

With the aim of following the number of segment–segment interactions between polymer A and polymer B in an AB mixture, a Monte-Carlo (MC) simulation study is presented as an alternative to a mean-field approach such as the Flory–Huggins theory (FH). It should be mentioned that the interaction term described above has not changed appreciably with more modern treatments, except that volume fractions have been changed to effective site fractions and segment size differences in the mixture have been accounted for.[2,3] The interaction term seems to be the weakest link in all thermodynamic models of mixtures. A MC simulation of multichain polymer mixtures, on the other hand, does not suffer from the mean-field approximation of random mixing, since unlike the FH theory, it takes into account the connectivity of segments within the chain. This treatment provides mean thermodynamic values and, more important, also provides the corresponding local microstructure of the mixture in the form of snapshot pictures. These dual results are important especially in phase separation phenomena, since phase separation can be visually observed in the form of distinct A(B) domains.

Simulation Technique

Multichain configurations were generated on a planar square 22 × 22 lattice. The system was formed by 22 chains each comprising 20 segments, and periodic boundary conditions were imposed on the lattice. To rule out undesirable interferences, the lattice with periodic boundary conditions should be larger than the correlation length within one chain, i.e., its end-to-end distance. This was satisfied when the end-to-end distance of the chains was essentially less than 10 lattice sites for all the systems investigated. A system of self-avoiding chains was treated as a binary mixture. A fraction of the chains was designated as type A and the remainder as B depending on the mixture composition. The composition was changed over the whole composition range when necessary. In addition to simple volume exclusion interactions within and between the chains, an interaction energy, ϵ, was applied between segments A and B and was taken into account whenever A and B segments occupied adjacent lattice sites. If the reduced interaction energy, $\epsilon' = \epsilon/k_B T$, was equal to zero, the system represented an athermal homopolymer melt. With a negative (positive) value of ϵ' miscible (immiscible) blends could be simulated. Void lattice sites occupying 9.09% of the system permitted the use of the usual reptation sampling technique.[4] As an initial arbitrary configuration, the parallel extended, "all-trans" chains in register was used. All runs began with an initial intermixing and equilibration period with the condition $\epsilon' = 0$ imposed. Each thermodynamic state was then obtained after equilibration by 10^6 reptation trial moves for each value of ϵ'. In special cases, to observe hysteresis, the number of moves was lower, 3×10^5. Trial moves were accepted or rejected according to the Metropolis rules,[5] i.e., a move was unconditionally accepted if the energy change, ΔE, was negative and accepted with probability $p = \exp(-\Delta E/k_B T)$ if the energy change was positive. When the move was rejected, the original configuration was counted once more in the averaging. The energy change was given by $\Delta E = (N_{AB}^{new} - N_{AB}^{old})\epsilon$, where N_{AB}^{new} and

N_{AB}^{old} are the total numbers of heterocontacts present in the mixture before and after the move, respectively. The number of heterocontacts in the system per chain, $\bar{N}_{AB}$, was accumulated during sampling as the key descriptor of the state of the system. After a sufficiently large number of moves was performed, the properties of the system reached an equilibrium established by the balance of the entropy and the applied interaction energy ϵ'. All configuration-dependent properties, such as the end-to-end distance, were calculated by using the usual techniques and collected in thermodynamic averages according to the Metropolis rules.

The generation of multichain configurations in dense systems is a difficult problem. Until now the reptation technique was mainly employed to solve this problem. Recently Mansfield's method[6] of bond breaking and reforming has been used[7] for a totally occupied lattice of chains. This method, however, introduces a molecular weight distribution into the system. Reptation moves have also been criticized, and moves where local kink jumps are performed are considered to be more representative of the system from the point of view of chain dynamics. However, we are interested in equilibrium properties and have used reptation moves only to generate different configurations. Nevertheless, this method still remains the only appropriate method for examining dense multichain systems.

Recently the MC reptation technique was used for the first time to simulate the kinetics of spinodal decomposition of a two-dimensional polymer mixture.[8] For the present system this regime was traversed by using long equilibration times to obtain the equilibrium properties and also to include both immiscibility and miscibility regions.

Results and Discussion

To ensure that the algorithm used in this analysis is correct, we first calculated the mean-square end-to-end distance of the chains in a homopolymer melt by using $\epsilon' = 0$. Our result, $\langle R^2 \rangle = 39.2 \pm 0.8$, is in good agreement with the value, $\langle R^2 \rangle = 40.4$ (in lattice spacing units), obtained by Wall et al.[9] for a square lattice of chains comprising 21 segments at a concentration (volume fraction) equal to 0.9.

Distribution of Interactions: Comparison with Mean-Field Results. The number of unlike contacts per chain, $\bar{N}_{AB}$, in the blend as a function of the applied A–B interaction energy ϵ', is shown in Figure 1 for the composition A/B = 1/1 in the blend. A diffuse transition of sigmoidal, second-order shape can be observed. In the miscibility region, where $\epsilon' < 0$, the mixture is characterized by a large number of A–B contacts, while in the immiscibility region, where $\epsilon' > 0$, unlike contacts are rare and the components phase separate. The microstructures of mixtures that correspond to three representative states on the transition curve are shown in Figure 2. It is immediately obvious that the mixing is nonrandom even in an athermal mixture where $\epsilon' = 0$ and depends on the applied interaction energy.

Interaction and Temperature Dependence. According to the FH theory, the free energy of mixing per unit volume of binary polymer system is given as

$$\Delta G_{mix}/RT = (\phi_A/N_A) \ln \phi_A + (\phi_B/N_B) \ln \phi_B + \chi \phi_A \phi_B \tag{1}$$

where ϕ_i is the site fraction of the components and N_i is the degree of polymerization. The simplest interpretation of the Flory interaction parameter, χ, is as an interaction interchange energy, $\Delta\epsilon_{AB} = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$, since $\chi =$
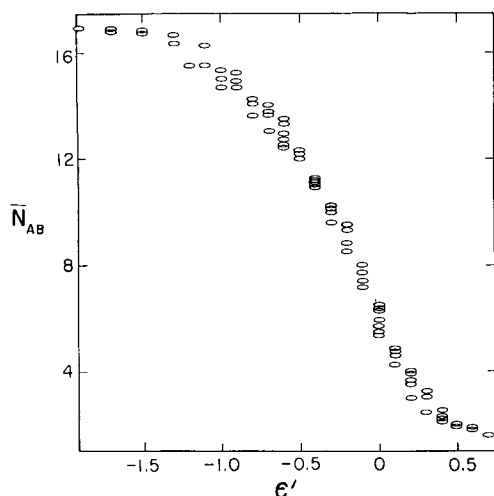
Figure 1. Transition curve constructed from the dependence of the number of unlike contacts present in the system per chain, $\bar{N}_{AB}$, on the reduced interaction energy ϵ'.
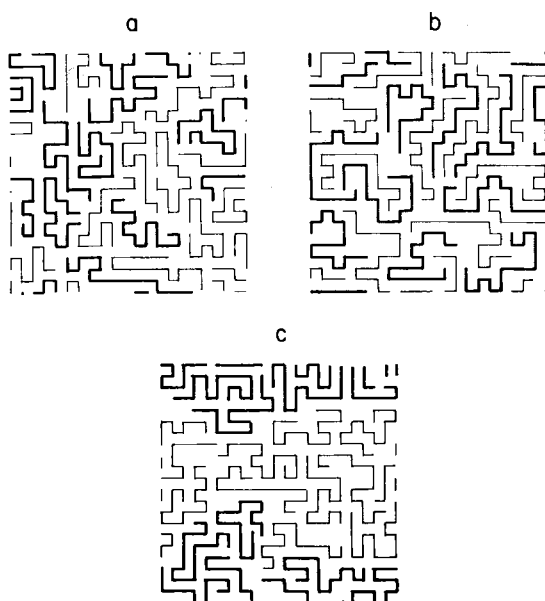

Figure 2. Snapshot picture of the mixture corresponding to three states on the transition curve shown in Figure 1: a, $\epsilon' = 0$; b, $\epsilon' = -0.5$; c, $\epsilon' = 0.5$, representing athermal, miscible, and immiscible regimes and taken after a long equilibration time.

Figure 3. Dependence of calculated χ parameter (text, eq 3) on the actual molecular constant ϵ', representing the strength of a heterosegmental A–B interaction.

$\Delta\epsilon_{AB}$ $z/2kT$, where z is the coordination number of the lattice. Experimental data suggest, however, that χ should be interpreted as the free energy

$$\chi(T) = \alpha + \beta/T \qquad (2)$$

where α and β are constants. This was the first evidence that χ is not a real molecular parameter but rather is an effective phenomenological parameter. Obviously a molecular interpretation of such a parameter is complex. Since the MC simulation used in this study is a numerical experiment performed on the molecular level, the phenomenological interaction free energy from eq 1 can be compared to the corresponding interaction term based on the true molecular parameter, ϵ'

$$\Delta G_{int}/RT = \chi\phi_A\phi_B = 22\epsilon'\bar{N}_{AB}(\epsilon')/N \qquad (3)$$

where $\bar{N}_{AB}(\epsilon')$ is the mean number of A–B contacts per chain in the mixture at the applied energy, ϵ', and N is the total number of lattice sites in the system. The principal differences in the description of the interactions by the two corresponding expressions in eq 3 are obvious. The clas-
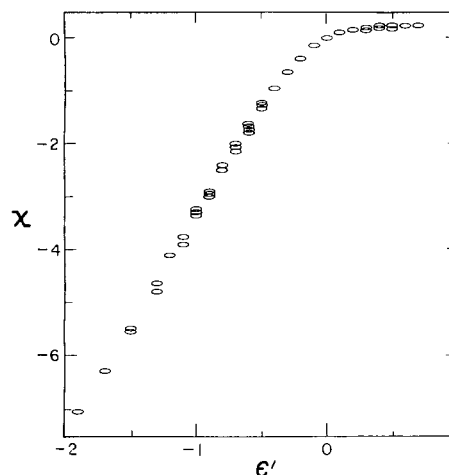
sical treatment assumes random mixing of the components, and thus the number of contacts is constant and is not dependent on the strength of the interactions. The χ parameter accounts for changes of ΔG_{int} coming from changes in interaction strength. In contrast, MC simulations which match the interaction on a molecular level better reflect the behavior of the system by changes in $\bar{N}_{AB}(\epsilon')$ as a function of the true molecular constant ϵ'. A molecular interpretation of χ in terms of our results is described in Figure 3, where χ is plotted as a function of ϵ'. It can be seen that in the region of miscibility χ is a linear function of the interaction energy ϵ' because the polymers are well intermixed. On the other hand, an increase in the A–B repulsion in the immiscibility region to higher positive values of ϵ' has little effect on χ since the polymers are segregated in their own domains. The value of χ would increase with increasing ϵ' only if the polymers were also intermixed in this region. This is reflected in the fact that different immiscible blends have small positive values of χ with only small differences. According to our results for this planar system, it seems that there exists a limiting positive value, χ_{max}, beyond which χ cannot increase.

$$\chi_{max} \simeq 0.3 \qquad (4)$$

A transition curve (Figure 1) can also be regarded in terms of an inverse temperature dependence at a fixed value of ϵ. It is obvious from Figure 1 that increasing temperature tends to minimize the effect of the interactions (either favorable or unfavorable), and at $T \rightarrow \infty$, systems with different interaction energies behave as athermal systems, $\epsilon' = 0$. This inverse temperature dependence, phenomenologically observed as eq 2, has its origin in the Boltzmann factors which weigh each particular multichain configuration. It should be noted also that this transition can be described as UCST behavior preceeded by a spinodal decomposition mechanism. It arises from a combination of the mixing entropy and the free energy of interaction (the free volume term is absent) and proceeds from a homogeneous mixture where small concentration fluctuations are enlarged by uphill diffusion characteristic of spinodal decomposition.

The exact position of the transition is in the vicinity of $\epsilon' = 0.05$. The shape is asymmetrical. In order to reach the phase separation regime from the transition point, a $\Delta\epsilon'$ of ~0.5 is needed; whereas to homogenize the system from the transition, a change of $\Delta\epsilon'$ of ~1.5 is required. This reflects the known tendency toward coil segregation
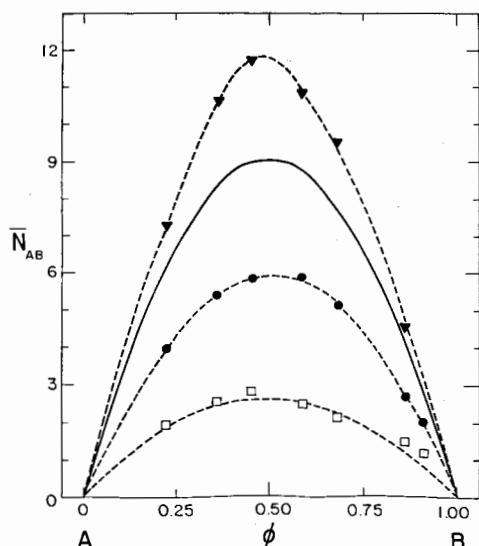
Figure 4. Number of unlike contacts in the mixture, per chain, $\bar{N}_{AB}$, as a function of blend composition ϕ for three different interactions: ($\blacktriangledown$), $\epsilon' = -0.5$; ($\bullet$), $\epsilon' = 0.0$; ($\square$), $\epsilon' = 0.5$. The solid curve represents results obtained by using the FH theory.

in planar dense systems[10,11] that has to be overcome during intermixing.

Concentration Dependence. Figure 4 shows the concentration dependence of the number of unlike contacts in the system for different values of the interaction energy, $\epsilon' = -0.5, 0.0,$ and 0.5. It can be seen that not even the curve corresponding to an athermal mixture fits the predictions of the FH theory according to which the number of unlike contacts in the system is $(Nz/2)\phi_A\phi_B$. As already mentioned, the FH theory assumes the same number of contacts for mixtures with different interactions. Deviations from the FH description of the concentration dependence of the interaction term are often treated by introducing an empirical concentration dependence:

$$\chi = \chi_0 + \chi_1\phi + \chi_2\phi^2 + ... \qquad (5)$$

If the deviations are known to arise from differences in the sizes of the A,B segments, then the concentration dependence of χ is given by[12]

$$\chi = \mu/(1 - \gamma\phi) \qquad \gamma = 1 - \sigma_2/\sigma_1 \qquad (6)$$

where μ is related to the interchange energy and σ_i is the interacting surface area of segment i. If $\sigma_1 = \sigma_2$, the simple FH relation is recovered. Deviations from the mean-field results observed here are evidence of nonrandom mixing in the polymer mixtures. This "nonrandomness" is obvious from the snapshot pictures (Figure 2). Instead of the mean concentration, given simply by the site fractions of the components, a local concentration different from the mean value applies. This local concentration arises from two effects: the effect of the interactions, $\epsilon' \neq 0$, and the effect of the connectivity of the segments into chains. Recently Howe and Coleman[13] made calculations on the distribution of unlike contacts in miscible polymer blends. They found positive deviations from the FH prediction for attractive A–B interactions and negative deviations for repulsive interactions, similar to our observation (Figure 4). However, for an athermal mixture, $\epsilon' = 0$, Howe and Coleman obtained the FH result since their treatment is mean-field in nature using a random mixing rule. As can be seen in the figure, for athermal mixtures the FH mean-field theory overestimates the number of unlike contacts. In reality of screening of the interactions arising from the connectivity of the segments into chains takes place. Our ob-
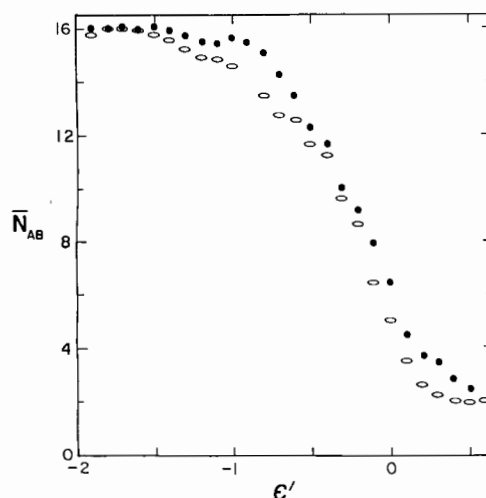

Figure 5. Effect of hysteresis on transition behavior observed after nonasymptotic thermal equilibration times in each state: ($\bullet$) corresponds to the transition from miscibility to immiscibility and (O) corresponds to the transition from immiscibility to miscibility.
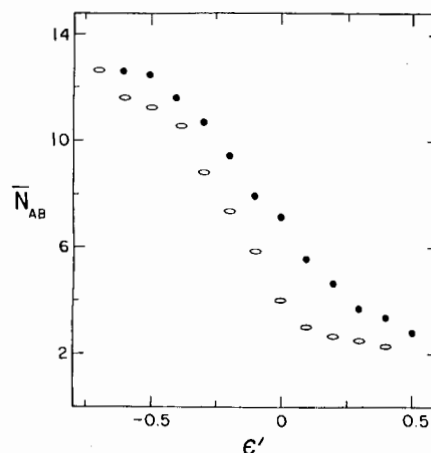

Figure 6. Hysteresis in the transitional region. Symbols of ($\bullet$) and (O) are the same as for Figure 5.

servation is in accordance with the reported effect of segregation of polymer chains in two-dimensional dense systems[10,11] since it implies that interchain contacts are decreased in favor of intrachain contacts.

Kinetically Driven Hysteresis. In general, a decrease in the number of samples thermodynamically averaged in the MC method leads to a larger scatter in the obtained results. If the number of reptation moves performed for one state is decreased, but not enough to increase the scatter in the data, some systematic deviations can be seen. Figure 5 shows the results of a run for which the thermodynamic states are changed stepwise, each calculated from 3×10^5 trial moves only. It can be seen that the system proceeds from the miscible to the immiscible region and vice versa by different thermodynamic pathways from those used previously. Figure 6 depicts another run under the same conditions close to the transition.

We now consider how the system undergoes a transition from either of the regimes by thermally induced movement of the chains, each properly weighted by the probability given by the Boltzmann factor with an interaction energy and a gradual change in the A–B interaction. If the system lies within the immiscibility region and the domains are already formed, it is difficult to change the morphology. Namely, if repulsion between the phases is decreased slightly, thermal movement of the chains is still more likely

to occur within a given domain and is not likely to cross the interface between the domains which would lead to an increase in unfavorable contact energy. Thus the majority of the moves occur within a domain, which has no effect on the transformation of the blend morphology into that of a homogeneous miscible blend. In the overall region, $\epsilon' > 0$, intradomain moves are more likely to occur than moves crossing the domain boundary. It is only after the attractive energy region, $\epsilon' < 0$, is entered that interdomain moves become more probable than intradomain moves and the morphology can be changed more rapidly. Thus if the thermodynamic parameters of the blend are changed and the system is allowed to equilibrate at given conditions for a short time, we can in this way proceed from state to state and finally reach the miscible region. However, the morphology cannot reflect fast changes in the thermodynamic parameters; it lags behind the true equilibrium thermodynamic state, and we proceed to the miscibility region in a path which depends on the thermal equilibration time scale.

On leaving the miscibility region and decreasing the attractive A–B energy, A(B) domains should be formed. The moving chains, however, avoid forming domains since domain formation leads to a decrease in the favorable mixing energy. Only a small fraction of moves is spent in transforming the morphology in the direction of phase separation. This situation changes again when ϵ' changes sign and the interaction becomes unfavorable. The fraction of moves resulting in a change in morphology becomes larger than that of moves which retain the morphology. Of course, domain formation and breakup occur simultaneously leading to diffuse transitions. These obvious rules, well matched by the MC routine used here, lead to hysteresis in phase separation behavior (Figures 5 and 6). This hysteresis is kinetically driven and is characteristic of phenomena which are generally reported as a dependence on "thermal history" of the polymer sample. However, it is important to differentiate this case from observations of thermal history caused by T_g viscosity behavior. In the present case all mixtures are liquids of flexible chains.

To ensure that well defined thermodynamic states were obtained, calculations corresponding to two successive complete cycles of the hysteresis loop (Figure 6) were performed. The two cycles produced equivalent results; thus the thermodynamic states produced correspond to well-defined local free energy minima even though they do not correspond to a true thermodynamic equilibrium.

In a recent report on MC simulation of spinodal decomposition in polymer films, Baumgärtner[8] suggested that in the late stages of decomposition a mechanism of evaporation and condensation of small "droplets" may apply. According to the above arguments this is not very probable. Instead we suggest the following mechanism: at late stages of decomposition, domains are large and contain several chains. It is highly improbable that single chains or small droplets evaporate, cross the unfavorable region, and finally condense to another domain of the same kind. However, there must be other types of motion in the mixture for which the reptation of a single chain cannot account, and this is a thermally activated translation of entire domains. This type of motion is assumed to be slower but does not require as large an activation energy. Whenever slowly moving domains of the same kind come into contact, it is probable that they irreversibly fuse into one larger domain, thus decreasing the unfavorable A–B boundary. This mechanism probably prevails in the latter stages of decomposition and accounts for the fusion of microdomains into definite macrophases.
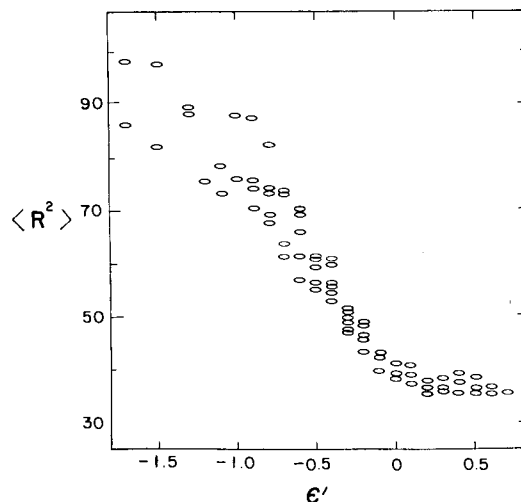

Figure 7. Mean-square end-to-end distance of chains as a function of ϵ', calculated for the blend composition, A/B = 1/1.

Expansion of Coils in the Miscibility Region. It is well-understood that in dense systems long flexible chains can be described by Gaussian distributions with ideal behavior. This was first suggested by Flory[14] and later shown by MC simulations[15] and SANS measurements[16] as well as by other theoretical arguments.[10] In two-dimensional systems, however, peculiarities have been observed. While an ideal exponent, $\nu = 0.5$, for chain dimensions has been observed, the observed pre-exponential factor[11] is larger than that of ideal unperturbed chains, $\langle R^2 \rangle / \langle R^2 \rangle_0 = 2.1 \pm 0.1$. Another interesting feature is the segregation of polymer coils in polymer films. In this paper we present a new peculiarity in coil size related to the interchain interaction in blends.

The end-to-end distances of a chain in a binary polymer mixture of composition A/B = 1/1 for a range of values of ϵ' was calculated. Since the A,B chains are of the same length, at this composition all chains in the system can be included in a single thermodynamic average. The resulting dependence of $\langle R^2 \rangle$ on ϵ' is shown in Figure 7. For a homopolymer melt, as can be seen in the figure, the above larger preexponential factor is obtained

$$\langle R^2 \rangle / \langle R^2 \rangle_0 = 2.06 \pm 0.07 \qquad \epsilon' = 0 \qquad (7)$$

where the ideal dimension $\langle R^2 \rangle_0$ is 19. For the immiscibility region, $\epsilon' > 0$, the mean dimensions are basically the same as for the homopolymer melt. Most of the chains are within their own domains equivalent to a homopolymer melt. Changes in ϵ' have an effect only at the A/B interface. The chains are forced to return to their own phases at the boundary and this restriction leads to a slightly smaller mean dimension in the immiscible blend relative to the homopolymer melt.

In contrast, a pronounced change in dimensions can be seen in the miscibility regions, $\epsilon' < 0$. In this case A chains act as a good solvent for B chains and vice versa. This leads to an expansion of coils of both kinds. This excluded volume effect should really be defined as the effect of a good solvent, i.e., as an intermolecular effect since simple volume exclusion operates within the chains and the effect of ϵ' is the interchain effect. The approximate limiting expansion in miscible blends relative to the ideal unperturbed dimensions for the A,B chains is given by

$$\alpha_2 = \langle R^2 \rangle / \langle R^2 \rangle_0 = 4.84 \pm 0.32 \qquad \epsilon' \leq -1.5 \qquad (8)$$

Negative Volume of Mixing in the Miscibility Region. Miscible blends are known to exhibit negative volumes of mixing. This tendency toward contraction
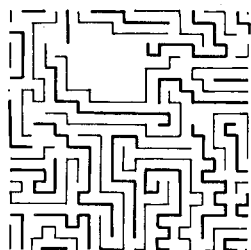
Figure 8. Morphology of system in the miscibility regime, $\epsilon' = -1.7$. Note large void caused by favorable A–B interaction and interpreted as contraction (i.e. negative mixing volume) of the blend.

prevails at high temperatures, or equivalently, low densities. Phenomena arising from differences in the equation of state parameters, such as LCST behavior, cannot be explained in terms of an incompressible lattice. However, even in such a lattice it can be shown that a negative volume of mixing in blends in caused by favorable interactions.

Figure 8 shows the equilibrium situation in a miscible blend having an attractive energy, $\epsilon' = -1.7$. From Figure 1 it can be seen that this value lies within the miscibility region. In the left region of Figure 8 there is a large void containing almost all empty lattice sites permitted in the system. For an athermal blend, the voids are randomly distributed in the lattice. In contrast, in a miscible blend the voids are expelled from the system and are collected into a single large void thus favoring the formation of A–B contacts. This behavior is not random and is observed systematically in the attractive energy regime. The void is not longer an integral part of the system and represents a negative volume of mixing. Since it is known that solid polymers can have substantial free volume, the negative volume of mixing accompanying the process of close packing of chains in a mixture of miscible polymers can be quite large. However, in this treatment we cannot account for the temperature dependence of the negative volume of mixing. As the temperature increases, the void space diminishes since increasing temperature tends to minimize the effect of the A–B interactions as expected, but the lattice does not expand with increasing temperature.

Conclusion

The results obtained in this study enable us to make the following conclusions.

The number of heterocontacts, which to a large extent determines the phase behavior in a polymer mixture, does not follow random mixing even for the athermal case. Depending on the heterosegment A–B interaction energy, chains can form morphologies in which the different chains are segregated in different domains. In the case of miscible blends, some ordering is observed in which the chains tend to lie along each other in an alternating A,B pattern and thereby maximize interactions.

The mean-field approximation underestimates the number of heterocontacts in the mixture by not taking the connectivity of segments within the chains into account.

The phenomenological χ parameter is linear with the heterosegment interaction energy ϵ' in the miscible region. In the immiscible region χ cannot change with ϵ' to higher positive values because of poor intermixing of the components; there appears to be an upper limiting value, $\chi_{max} \simeq 0.3$.

Kinetically driven hysteresis, related to the temperature equilibration time scale, may lead to phenomena often reported as a dependence on "thermal history".

An important prediction of chain expansion in miscible polymer blends based on calculations of mean square end-to-end distances may lead to further experimental investigations of this problem.

References and Notes

(1) Solc, K., Ed. *Polymer Compatibility and Incompatibility: Principles and Practices*; Harwood: New York, 1982; MMI Symp. Ser., Vol. 3. Olabishi, O.; Robeson, L. E.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979. Klentjens, L. A.; Lemstra, P. J. *Integration of Fundamental Polymer Science and Technology*; Elsevier: New York, 1985.
(2) Guggenheim, E. A. *Mixtures*; Clarendon: Oxford, 1952.
(3) Flory, P. J. *J. Am. Chem. Soc.* 1967, *89*, 6814.
(4) Wall, F. T.; Mandel, F. *J. Chem. Phys.* 1975, *63*, 4592.
(5) Metropolis, N.; Rosenbluth, A. N.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* 1953, *21*, 1087.
(6) Mansfield, M. L. *J. Chem. Phys.* 1982, *77*, 1554.
(7) Boyd, R. H. *Macromolecules* 1986, *19*, 1128.
(8) Baumgärtner, A.; Heermann, D. W. *Polymer* 1986, *27*, 1777.
(9) Wall, F. T.; Chain, J. C.; Mandel, F. *J. Chem. Phys.* 1977, *66*, 3143.
(10) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(11) Baumgärtner, A. *Polymer* 1982, *23*, 334.
(12) Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* 1937, *56*, 885.
(13) Howe, S. E.; Coleman, M. M. *Macromolecules* 1986, *19*, 72.
(14) Flory, P. J. *J. Chem. Phys.* 1949, *17*, 303.
(15) Olaj, O. F.; Lantschbauer, W. *Makromol. Chem., Rapid Commun.* 1982, *3*, 847.
(16) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* 1974, *7*, 863.