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1991

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Short-Range Order in Miscible Polymer Blends: A Monte Carlo Study

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SYNOPSIS

Local ordering in miscible binary polymer blends with strong attractive interactions between the two types of chains was investigated by computer simulation of allowable conformations on an incompressible cubic lattice. A tendency toward maximum ordering (in which chains pack in alternate parallel rows) is shown by the calculation of pair correlations and in "snapshots" of the mixtures. A specific directional interaction is not necessarily required for ordering. A comparison of these results with those recently obtained using mean-field theory is presented. The heat capacity of mixing was also calculated and found to be positive, with a value close to that reported experimentally.

INTRODUCTION

Miscible polymer blends with composition-dependent "tunable" properties have attracted great interest in basic as well as in applied materials research. Many miscible or partially miscible polymer pairs have been found in the last decade. In fact, it should be noted that mixing is also important for all compatible (but not miscible) blends since intermixing at the interface to a large extent determines the final properties of a complex material. Miscible blends appear to be macroscopically homogeneous; however, on a microscopic scale, one might expect local "nonrandomness" or ordering if strong or specific interactions are present. A strong attractive interaction between the blend components is expected to induce both conformational changes in individual chains on mixing, and also ordering in the chain packing. Thus an alignment of dissimilar chains is expected where the respective chains parallel each other in an alternating order. A local extension of the chains is also conceivable. Theoretical¹⁻³ and experimental⁴ indications of such ordering have been reported. In our previous work⁵

we observed ordering in chain packing as well as an expansion of polymer chains in a two-dimensional (2D) mixture when strong, favorable interactions were present. In later work⁶ we observed that in 3D systems, the overall expansion of the chains in the same interactional energy range is not as pronounced as was found in 2D systems; however, we did not examine the case of strong interactions nor of possible ordering.

In the present contribution we investigate miscible systems in which the strength of the attractive interactions between dissimilar components is varied. A 3D system consisting of an incompressible cubic lattice is used in which the extent of ordering and the spatial arrangement of the chains is investigated by "cutting" cross sections of the system and thereby observing typical "profiles" of the mixture, as well as by calculating the pair correlation function in the system. The Monte Carlo method used here is a very suitable method for studying ordering since in comparison to the mean-field method it does not rely on the random mixing rule.

COMPUTATIONAL METHODOLOGY

To evaluate the thermodynamic averages we used the Monte Carlo method described previously.⁶ A periodic box of $22 \times 22 \times 22$ sites was filled with

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 29, 1389-1395 (1991)
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484 chains each comprising 20 segments (monomers) while a fraction of 0.0909 sites remained unoccupied. The mixture studied contained a 1 : 1 A : B composition of homopolymeric A and B chains. The chains obeyed intramolecular and intermolecular excluded volume constraints based on occupancy of lattice sites and the reduced interaction energy ϵ'_{AB} between A and B segments ($\epsilon'_{AB} = \epsilon_{AB}/kT$) contributed to the total energy of the system whenever A and B segments occupied adjacent lattice sites; ϵ_{AB} is the actual interaction energy between A and B segments. The equilibration of each state began at the configuration of an athermal mixture: $\epsilon'_{AB} = 0$. After introducing an appropriate interaction energy, the chains were permitted to move by reptation, each move being considered by Metropolis rules to contribute to the final thermodynamic average. The acceptance of trial moves in averaging was done using transition probability $\exp(-\Delta E/kT)$ where $\Delta E = E_{\text{new}} - E_{\text{old}}$ and instantaneous total multichain energy E was expressed by total number of nearest neighbor interactions $E = n_{AB}e_{AB}$. Up to 6.7×10^8 trial moves were used for equilibration depending on the statistics. In addition to the equilibrium number of heterocontacts per chain, N_{AB} , which represents the nearest neighbor situation of each segment, we also investigated the more distant environments for each polymer segment. After an equilibrium state was reached, the complete mixture was analyzed in the following way: the more distant environment of each polymer segment of the mixture was investigated in the six characteristic directions of the cubic lattice. The number of homo- or heteropairs encountered (one central segment of all pairs being the same for each investigation) was averaged for each distance r from the site in question over all sites of the mixture and over 20 configurations separated from each other by 10^6 reptation moves during the simulation, all occurring after equilibrium was reached. The sum of both homo- and heteropairs for each distance was slightly less than 6 by the factor representing the presence of voids in the system (0.0909). Thus defined, the correlation function is closely related to the general pair correlation function $g(r)$ and to the structure factor $S(q)$ given by

$$g(r) = (1/N) \sum_{i=1}^N \eta(r_i) \eta(r_i + r)$$

$$S(q) = \sum_r \exp(iqr) G(r) \quad (1)$$

where N is the total number of polymer segments in the mixture and the product of occupation vari-

ables η at the positions r_i and $r_i + r$ is unity if it is a homopair formed by identical segments at r_i and r_{i+r} and zero otherwise when homocorrelations are considered. While in the general case correlations are investigated spherically, we restrict ourselves here to the 6 principal directions of cubic lattice and denote the correlation function as $G(r)$. Nearest neighbor interactions in our system are formed along these directions and thus this search is representative for a cubic lattice. The lattice used here exceeds the typical dimension of the polymer coils in the system and the periodic boundary conditions suppress finite size effects in this homogeneous system. Calculations were performed for a few representative values of ϵ'_{AB} chosen according to our previous studies on the same system.⁶ The values, +0.3, +0.05, 0.0, -0.5, -1.5, represent a demixed system, the center of the mixing/demixing transition, an athermal system, a slightly favorable interaction and a strong interaction, respectively.

RESULTS AND DISCUSSION

Figure 1 depicts pair correlations of two types for the athermal system, $\epsilon'_{AB} = 0$. The open circles represent homocorrelations where both the given segment and that at a distance r are of the same type; the crosses represent heterocorrelations where the respective segments differ. A preference for homopairs over heteropairs at distances less than about five lattice units can be observed. When the nearest neighboring sites of a given segment are considered, the connectivity of the chains should be taken into account. Then, of 6 neighboring sites only 4 are free for possible occupation; two sites are of course filled by first neighbor segments along the chain (chain end effects can be neglected). In this way Figure 1 shows that there are 1.55 nearest neighbors ($r = 1$) which form heteropairs and there are $3.94 - 2 = 1.94$ homopairs (excluding the two nearest neighbors along the chain) for the average polymer segment in the mixture. The residual difference in the sum of homo- and heteropairs from the 4 net available sites is accounted for by the presence of voids in the mixture. A small preference for homo- over heteropairs in the next and further lattice sites can also be explained by the connectivity of the chains. A polymer segment is necessarily surrounded by further segments of the same chain and the only free space will be filled by other chains according to the overall composition of the mixture, which is 1 : 1 in the present case, and thus a preference can be expected. Figure 1 in fact represents a pure polymer

melt, since $\epsilon'_{AB} = 0$, and the correlations shown represent clearly what is understood by the concept of "correlation hole."⁷ Of course, for non-zero interaction energies an additional preference exists. The observed pair correlation function is characteristic of polymeric liquid mixtures; for low molecular weight liquids, correlations due to connectivity cannot exist and neighbors are chosen randomly in the athermal case $\epsilon'_{AB} = 0$. In the latter case $G(r)$ is constant at the random value, attained for polymers at $r = \infty$.

The correlations which can be observed in Figure 1 correspond to the size of individual polymer coils. If as usual, $R_G \equiv (\langle R^2 \rangle / 6)^{1/2}$, then using the previously obtained⁶ value of $\langle R^2 \rangle$ for the same system, we obtain $R_G = 2.24$ in lattice spacing units. If we calculate the average second moment Y^2 of a fluctuation distance of the homopairs from the random value ($r = \infty$) defined as

$$Y^2 = \frac{\sum_i r_i^2 [G(r_i) - G(\infty)]}{\sum_i [G(r_i) - G(\infty)]}$$

we obtain $Y = 1.93$. This represents the radius of gyration of the relative excess of similar segments around a given chain segment in a mixture. There is good agreement in this value with the R_G value above even though there are major differences in the method of calculation. As stated the present value for Y was obtained by averaging over the 6 directions of the cubic lattice, while R_G is obtained by integration over all directions; contributions from other chains of the same kind are possible and we did not investigate the correlations from the center of the mass of coils.

We now discuss the situation in the presence of finite A-B interactions which bring additional correlations into the system, i.e., in addition to the connectivity of segments which was present in the athermal system discussed above. Figure 2 shows the same function as in Figure 1 when such interactions are included, $\epsilon'_{AB} = -0.5$ (curves 1); $+0.3$ (curves 2). Thus when the A-B attraction is favorable we obtain a picture far different from that obtained for the athermal case (Fig. 1). The situation for the first neighbors is changed. From four possible contacts for an average polymer segment, 2.33 form heteropairs and only $3.17 - 2 = 1.17$ form a homopair. Thus the preference seen in Figure 1 is reversed in favor of heterocontacts. The situation in the more distant neighborhoods is characterized by almost ideal behavior. It seems that relatively small A-B attractions in the mixture eradicate correlations due to the chain connectivity and the correlation func-

Figure 1. Correlation function $G(r)$ in terms of the average number of A-A(B-B) (○) or A-B (+) pairs in the 6 principal directions of a cubic lattice as a function of distance from a given site. The data were averaged over all occupied sites of the mixture and for different configurations; see text. The reduced interaction energy, $\epsilon'_{AB} = 0$. The arrow indicates the radius of gyration of the coil R_G .

tion resembles that of low-molecular weight random mixtures. However, it should be noted that this approach to ideal behavior actually is a result of the compensation of the preference based on chain connectivity and that introduced by attractive A-B interactions.

The correlation function of an immiscible system with $\epsilon'_{AB} = +0.3$ is also illustrated in Figure 2. In a demixed system most of the polymer segments necessarily experience surroundings characteristic of homopolymer domains, thus homopairs prevail for distances less than the domain size. At very great distances both correlations converge since there is an equal probability of finding both kinds of domains at these remote sites.

With weak attractions the nearest neighbors can be seen to be interchanged in comparison to the athermal mixture, for strong A-B attractions the changes become more pronounced. Thus for $\epsilon'_{AB} = -1.5$, 2.99 of the nearest neighbors are heteropairs while there are just $2.68 - 2 = 0.68$ homopairs (see Fig. 3). We note that the next nearest neighbor sites are also relatively more populated by heterosegments. This preference is smaller: 2.92 compared

Figure 2. $G(r)$ for (1) $\epsilon'_{AB} = -0.5$; (2) $\epsilon'_{AB} = 0.3$. Symbols are the same as for Figure 1.

with 2.67. Possibly if A and B segments are brought together by a strong interaction, other parts of the chains are also brought into closer proximity and thus give rise to an increased heterosegment population in the next nearest neighboring sites. The fact that both correlation functions (Fig. 3) exhibit periodicity is more interesting; there is a complementary character in both periodicities: at the distances where heteropairs prevail, homopairs are less abundant and vice versa. This indicates an A/B alternating ordering in the mixture, i.e., a layered structure with an oscillatory concentration profile. This ordering apparently depends on the strength of the interaction (compare Fig. 2 curve 1 and Fig. 3). Figure 3 shows that this correlation survives distances larger than the size of the polymer coils which are slightly expanded⁶ in miscible polymer blends but generally remain close to the dimensions found in polymer melts.

The correlation function for strong interactions (Fig. 3) except its periodic effect, is close to that of ideal random situation, $r = \infty$, even for small r . In low-molecular weight mixtures (one molecule per site in our system) strong interactions would produce an alternation of values close to six and zero. In fact

it is the connectivity of segments which eradicates the much sharper periodicity which occurs in low molecular weight mixtures. This is consistent with similar observation of layering of chain segments in confined polymer melts near walls.⁸ While low-molecular weight mixtures can also give structured concentration profiles near the wall, the layering of polymer segments is much less structured.

Figure 4 shows "snapshot pictures" in which the profile of a typical cross section of the mixture is depicted. To visualize the situation in the mixture only one planar layer is shown. Only portions of a given chain can be seen; most of the chain ends are above or below the plane of the diagram. Some of the chains cross the plane orthogonally at just one lattice site and thus are represented by a single point. The type of chain (A, B) is differentiated in Fig. 4 by the thickness of the line or point. Typical profiles are shown for the athermal system ($\epsilon'_{AB} = 0$) and for the system with strong A-B attractions. In the case of the athermal system, we can recognize a random arrangement of chains. The chains do not experience any preferred surrounding and thus even random clusters of chains of the same kind occur. The situation changes when strong A-B attractions are introduced, $\epsilon'_{AB} = -1.5$. An examination reveals the tendency of A and B chains to parallel each other and to alternate in the mixture. Strong ordering is also shown in Figure 4c which represents a cross

Figure 3. $G(r)$ showing ordering in a miscible blend with strong favorable interactions, $\epsilon'_{AB} = -1.5$. Points are connected by lines for illustration only.

Figure 4. "Snapshot" pictures showing profiles of the three-dimensional mixtures. (a) Athermal system, $\epsilon'_{AB} = 0$; (b) ordered system with strong interactions, $\epsilon'_{AB} = -1.5$; and (c) a slice taken through a region containing large voids which in macroscopic systems would result in a negative volume of mixing due to strong interactions; the interaction energy is the same as in (b).

section of the system at a plane containing a large number of voids. The tendency to expel voids from the space between the chains was also observed in 2D systems.⁵ This is again a result of strong A-B attractions; it results in a closer packing of chains and macroscopically can result in a negative volume of mixing. Thus negative excess volumes of mixing can arise from strong interactions and do not necessarily stem from differences in the equation of state parameters.

Recently Sanchez and Balazs³ developed a generalization of the lattice-fluid to account for strong or specific interactions. They adopted as a basis the incompressible model of ten Brinke and Karasz² but also accounted for the observed compressibility. They argue that if two monomeric segments of two different polymers interact strongly, there exists a specific spatial constraint on the interaction. Thus an entropic cost is necessary to form specific interactions. The model is based on the concept of an A-B interaction that can be weak (nonspecific) with an energy ϵ_{AB} , or strong (specific) with energy $\epsilon_{AB} + \delta\epsilon$, and in which a corresponding fraction θ of all A-B interactions is strong and a fraction $1-\theta$ is weak. In addition to the energetic parameter $\delta\epsilon$, Sanchez

and Balazs also introduce an entropic parameter Q which expresses the ratio of degeneracies of non-specific and specific interactions and is related to the lattice coordination number z . The theory accounts for directional specific interactions, however, when the system includes strong interactions which do not require specific orientation the theory reduces to the original lattice fluid theory and does not exhibit ordering. The present Monte Carlo results show that a strong tendency towards ordering exists even without directional specific interactions; the ordering arises merely from strong A-B attractive interactions.

According to the Boltzmann distribution law, the number of A-B interactions N_{AB} should be proportional to $m \exp(-\epsilon_{AB}/kT)$, where m is the degeneracy of the state. Accordingly, for the athermal reference state, N_{AB}^0 should be proportional to m^0 . Thus we obtain

$$\ln(N_{AB}/N_{AB}^0) = \ln(m/m^0) - \epsilon_{AB}/kT \quad (2)$$

where the superscripts refer to the athermal state. Only if the statistical degeneracies do not depend on the interaction energy (or on temperature) when $\ln(N_{AB}/N_{AB}^0)$ is plotted versus ϵ'_{AB} , a straight line will be obtained. Figure 5 shows the present concave curve, which suggests that the entropic term related to the ratio of degeneracies in fact also depends on the interaction energy. Thus with increasing interaction strength ordering is increased and the number of possible arrangements m decreases. This plot shows that entropy changes in system due to order-

Figure 5. Plot of $\ln(N_{AB}/N_{AB}^0)$ versus $-\epsilon'_{AB}$ according to eq. (2). $\epsilon'_{AB} = 0.0, -0.1, -0.3, -0.5, -1.0, -1.5$.

ing are interaction energy dependent. The same trend is seen from Sanchez and Balazs,³ [eq. (12)] for interaction-free energy where entropy effect increases with interaction $\delta\epsilon$. (Note that m here is not equivalent to degeneracy q from Sanchez and Balazs' paper.)

We can also use our data to calculate the heat capacity of the systems exhibiting ordering. As is generally known heat capacity is sensitive to phenomena such as association, ordering, clustering, and in general, all phenomena for which the number of degrees of freedom changes. If we assume that the energy per chain is $E = N_{AB}\epsilon_{AB}$ then the constant volume heat capacity per chain is given by

$$c_v = k \partial N_{AB} / \partial (1/\epsilon'_{AB}) \quad (3)$$

From the plot depicted in Figure 6 we observe that all systems investigated have a positive heat capacity of mixing (Δc_v) (note that c_v for the pure components is equal to zero in our simulation). Δc_v becomes more positive in the case of strong interactions. The parameter $\epsilon'_{AB} = -0.4$ is approximately -0.4 at the "onset" of ordering. According to the classic relation, $\chi_{AB} = (z - 2)\epsilon_{AB}/kT$, this value represents ordering starting for interactions as negative as $\chi_{AB} = -1.6$ in our system with a degree of polymerization of 20. For longer chains the negative entropy change during ordering becomes smaller and thus equilibrium requires a less negative χ_{AB} than the above value. (However, kinetic effects might also be important when approaching equilibrium ordering in long chain systems. We have observed a "slowing-down" in simulation calculations during equilibration of systems with strong A-B interactions and this should be more pronounced for longer chains.)

If we calculate the Δc_v of mixing immediately after the "onset" of ordering, we obtain the value $\Delta c_v = 0.026 \text{ J g}^{-1} \text{ K}^{-1}$ for the average molar mass 100 g of a segment. This value is well within the experimental range of values obtained by Sun et al.⁹ and Barnum et al.¹⁰ and is in good agreement with the ten Brinke and Karasz² results. We note that Sanchez and Balazs³ predict much smaller values, in the range $10^{-4} \text{ J g}^{-1} \text{ K}^{-1}$.

The excess heat capacity of our system can also be obtained directly for each state from the fluctuations of the total energy. According to statistical mechanics, the heat capacity per monomer segment is related to the fluctuation of the total energy E by the relation

$$c_v = (\langle E^2 \rangle - \langle E \rangle^2) / kT^2 N \quad (4)$$

Figure 6. Evaluation of Δc_v from the slope of a plot of N_{AB} versus $1/\epsilon'_{AB}$.

where N is the total number of polymer segments in the mixture. The averages in brackets were obtained from simulations for each state and the result is depicted in Figure 7 for an average segment molar mass equal to 100 g. The heat capacity of the pure components is zero due to the absence of A-B interactions. Thus the required excess heat capacity is identical to the value obtained for the mixture. The results are shown in Figure 7. Interpretation of the results for the approximate onset of ordering, $\epsilon'_{AB} = -0.4$, gives a value of excess heat capacity, $0.091 \text{ J g}^{-1} \text{ K}^{-1}$. This value is of the same order of magnitude as that obtained using eq. (3) and is in the range of experimentally reported values.^{9,10} Equations (3) and (4) express the same thermodynamic quantity, but experimentally can produce different results because one is obtained from temperature dependence of total energy and the other one from energy fluctuations at constant temperature. For more negative ϵ'_{AB} (but less realistic values since $\epsilon'_{AB} = -1.5$ already corresponds to $\chi_{AB} = -6$) the change in heat capacity is more pronounced. As argued above we use relatively short chains; for longer chains ordering has already begun at less negative interaction energies. Accordingly we may also expect smaller changes in the excess heat capacities for long chains.

CONCLUSIONS

Ordering in polymer mixtures with strong interactions between chains of different types has been studied by the Monte Carlo method and has yielded results independent of mean-field assumptions.

Figure 7. Excess heat capacity Δc_v calculated from fluctuations of the total energy of the system versus interaction energy ϵ'_{AB} based on a monomer molar mass of 100 g.

- A strong local ordering tendency (in which A and B chains tend to lie parallel and alternate configurations in the mixture) was observed without the presence of directional specific interactions.
- Local ordering extends throughout the mixture over a distance depending on the strength of the interactions; correlation lengths as large as polymer coil dimensions and larger are possible.
- The onset of ordering for the 20 segment chain system used in this study corresponds to $\chi_{AB} \sim -1.6$.

- The excess heat capacity due to ordering is positive; we found values in the region 10^{-2} J g⁻¹ K⁻¹ at the approximate onset of ordering which is close to values reported from experiment.

This work was supported by the Air Force Office of Scientific Research through grant # 89-001.

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Received May 23, 1990

Accepted February 21, 1991