Expansion of Polymer Coils in Miscible Polymer Blends of Asymmetric Composition

P. Cifra,[†] **F. E. Karasz,*** **and W. J. MacKnight**

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received September 5, 1991

ABSTRACT: Monte Carlo three-dimensional lattice simulations of the expansion behavior of homopolymer chains in a miscible blend have been performed for asymmetric blend compositions. Chain expansion coefficients were calculated as a function of segmental interaction energy and composition. Substantial expansions of the minority chains were found as the compositional asymmetry increased, a result in accord with recent experimental observations. The calculations also are in good agreement with predictions of chain expansions as a function of interaction energy.

Introduction

There is ongoing interest and discussion regarding the dimensions of polymer coils in dense polymer systems. It has been generally accepted that coils in a liquid polymer assume ideal Gaussian behavior. This model was first suggested by Flory[1] and later confirmed by Monte Carlo (MC) simulations[2] and small-angle neutron scattering (SANS) measurements[3] and, more recently, by a new theoretical analysis[4] involving the screening of the excluded volume by entanglements. In recent years deviations from this behavior have been found in polymer blends in which the differing chains in a dense entangled medium interact, producing effects in addition to those associated with simple volume exclusion between and within chains. For example, in a polymer blend with an unfavorable interaction between the respective components and with an asymmetric composition, the dispersed minority chains have a tendency to collapse, as suggested by the MC calculations of Sariban and Binder.[5] This behavior was recently experimentally reported in blends of partially compatible polymers.[6] In other studies, chain dimensions were found to be unchanged, probably because of the limited interaction between the respective components.[7] We reported earlier MC results on the expansion of polymer chains in miscible blends relative to those in an athermal mixture[8,9] in a system of symmetric (1:1) composition. The calculated expansion was relatively slight in the three-dimensional study[9] but higher in the two-dimensional computation.[8] In light of the new experimental results on coil collapse in partially compatible blends of asymmetric composition, it may be expected that the dimensional changes of minority chains in such miscible blends would be more pronounced than in the case of systems of symmetric composition.

Results and Discussion

The MC simulation techniques used follow earlier results and consist of two steps. First, 484 athermal, noninteracting polymer chains, each composed of 20 segments (i.e., polymer beads), were equilibrated on a periodic cubic lattice with 22 lattice sites per side. The fraction of void sites was 0.0909. This array represents a canonical system in which the number of particles, the volume, and the temperature are held constant. In this system, chains were allowed to reptate, the only constraint being intrachain and interchain excluded volume based on site occupancy. This athermal system was equilibrated to remove the bias of an initial arbitrary starting configuration. Second, the homogenized system was subdivided into a blend of A and B chains, each chain being randomly designated A or B according to the desired composition of x_B chains (x_B being the fraction of B chains in the overall system). In this study this parameter was varied in the range 0.0–0.5. Because the A and B chains were of equal length, it follows that this computation also covered the range 0.5–1.0. Segmental interactions were then introduced into the system in which each nearest-neighbor lattice contact of A and B beads contributed to the total energy of the system with an energy ϵ_{AB}. Studies were undertaken for a range of the reduced intersegmental energy $\epsilon_{AB}/kT \equiv \epsilon'_{AB}$ from 0.0 to −0.5, corresponding to an interaction parameter χ_{AB} of 0.0 to −2.0 and calculated according to $\chi_{AB} = \epsilon_{AB}(Z - 2)/kT$ with the usual cubic lattice coordination number $Z = 6$. The accounting of accepted and rejected reptation trial moves was based on Metropolis sampling rules, as previously described.[9] Trial moves were applied randomly to the total array of chains in the system. The number of trial moves used for equilibration of each state ranged up to 2×10^8, depending on the statistics. Equilibration was stopped when the observed thermodynamic averages started to fluctuate about their equilibrium values. We found that asymmetric compositions required longer equilibration and that the average acceptance ratio of a trial move was around 0.1. The mean-square end to end distances $\langle R^2 \rangle$ for both the minority and the majority component chains were calculated as usual; chains crossing the periodic boundary were "unwrapped" before inclusion in the statistical averages. For the reference state $\langle R^2 \rangle_0$ in the calculation of the expansion coefficient $\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0$, we used the value 28.90. We obtained this value for the majority chains (i.e., type A) at $x_B = 0.1136$, under the condition of zero-reduced intersegmental interaction, $\epsilon'_{AB} = 0$, a condition that approximates the homopolymer melt. This value is also similar to the classical result (28.50) obtained for the single unperturbed polymer chain with fixed valence angle φ (if we assume the average valence angle $\langle \cos \varphi \rangle = -0.2$ appropriate to the five-choice lattice used) and to earlier MC results (30.04) obtained for this system.[9]

Figure 1 shows the chain dimensions $\langle R^2 \rangle_A$ and $\langle R^2 \rangle_B$ in terms of their respective expansion coefficients for the system with a fixed reduced interaction energy, $\epsilon'_{AB} = -0.5$, as a function of blend composition. For the symmetric composition $x_B = 0.5$, both A and B chains clearly have

---

* To whom correspondence should be addressed.

[†] Permanent address: Polymer Institute, Slovak Academy of Sciences, Dubravska cesta, 842 36 Bratislava, Czechoslovakia.

0024-9297/92/2225-0192$03.00/0

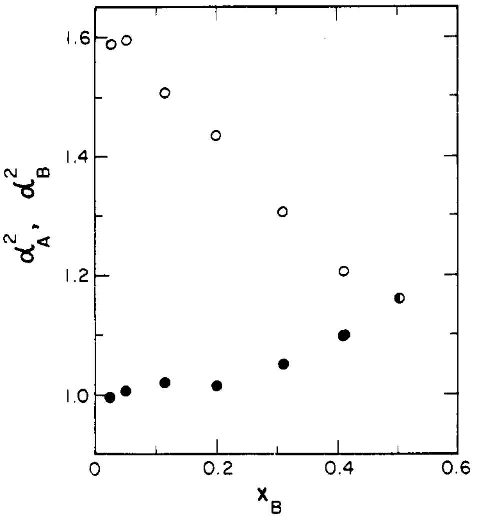

Figure 1. Variation of the expansion coefficient α^2 of minority B chains (○) and majority A chains (●) with chain composition x_B in the blend (constant reduced intersegmental interaction coefficient, $\epsilon'_{AB} = -0.5$).

Table I
Expansion Coefficients of Minority B and Majority A Chains Defined in the Text and Average Number of A-B Nearest-Neighbor Interactions per Chain (N_{AB}) as a Function of Blend Composition x_B at Constant Reduced Energy $\epsilon'_{AB} = -0.5$

x_B	α_A^2	α_B^2	N_{AB}
0.027	0.995	1.588	1.95
0.052	1.006	1.596	3.74
0.114	1.021	1.506	8.02
0.198	1.015	1.435	13.37
0.308	1.048	1.306	18.89
0.409	1.102	1.205	22.15
0.502	1.154	1.160	23.12

the same dimensions. (This fact was used in our previous simulations[8,9] for symmetric blend composition systems; the dimensions of both A and B chains could be sampled to yield a given thermodynamic average.) As the compositions become more asymmetric, the majority chains increasingly experience the environment of their own species and thus asymptotically approach the dimensions found in a homopolymer melt. Conversely, the minority chains dispersed in a polymeric "good" solvent (such as is provided by the majority chains in the case of a favorable interaction with the minority component) expand, and this expansion is enhanced as composition asymmetry increases. As anticipated, the expansion coefficient $\alpha_B^2 = 1.6$ is found for $x_B = 0.027$, a value significantly larger than that obtained in the symmetric composition: $\alpha_B^2 = 1.16$ for $x_B = 0.502$ (Table I).

Figure 2 illustrates a situation in which the composition x_B of the chains is fixed at the asymmetric value of 0.1136, and the favorable intersegmental interaction between A and B, ϵ'_{AB}, increases from 0 to −0.5. The majority chains are almost unaffected with respect to their dimensions because at this composition they experience largely their own environment. The dimensions of the minority B chains, however, undergo a pronounced increase as the favorable interaction increases.

To describe the extent of coil expansion, we can also use expressions developed for a single chain with excluded volume. In the "temperature blob" theory[10] of polymer chain statistics, a coil is modeled in terms of a sequence of N monomers in a succession of "blobs", each containing N_τ monomers. The sequence obeys Gaussian statistics appropriately within each blob; however, the necklace of N/N_τ blobs has an expanded structure. The expansion coefficient α^2 is then related to the ratio $X = N_\tau/N$. In the good solvent limit, $X \leq N^{-1}$, an expansion for the end to end distance is obtained

$$\alpha = 0.931N^{0.1} \tag{1}$$

which yields a value of $\alpha = 1.245$ for $N = 20$. In the present study, the minority chains at $x_B = 0.1136$ and $\epsilon'_{AB} = -0.5$ have a calculated expansion coefficient $\alpha = 1.24$ and on this basis can be considered as coils with well-developed excluded volume properties (Table II).

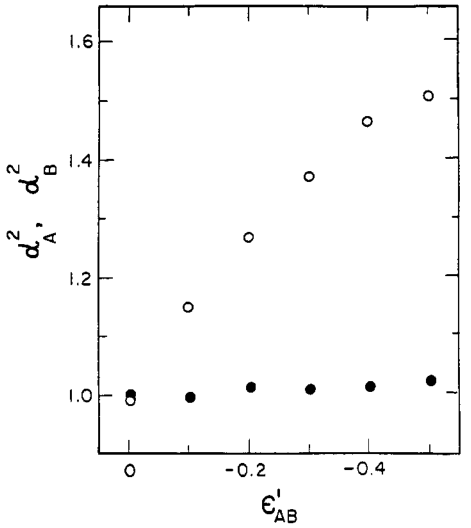

Figure 2. Variation of chain expansion with reduced interaction energy ϵ'_{AB} for the fixed asymmetric chain composition $x_B = 0.1136$: (○) minority B chains; (●) majority A chains.

Table II
Expansion of Minority and Majority Chains and Number of Heterocontacts per Chain (N_{AB}) in a Blend as a Function of ϵ'_{AB} for Constant Asymmetric Chain Composition $x_B = 0.1136$

ϵ'_{AB}	α_A^2	α_B^2	N_{AB}
0.0	1.000	0.987	6.21
−0.1	0.996	1.148	6.88
−0.2	1.008	1.266	7.29
−0.3	1.007	1.367	7.62
−0.4	1.008	1.461	7.86
−0.5	1.021	1.506	8.02

It is also possible to express the expansion of the minority chains in terms of the original Flory equations[11] for coil expansion, namely, $\alpha^5 - \alpha^3 \approx (^1/_2 - \chi)N^{1/2}$. If the interaction of the polymer chain with the solvent is formulated in terms of an interaction coefficient χ_{AB}, with the majority chains behaving like a polymeric good solvent, then the expected variation of ln α^2 with ln $(^1/_2 - \chi_{AB})$ is depicted in Figure 3. The present data are in satisfactory agreement with the prediction. The slope of 0.135 yields a proportionality $\alpha \approx (^1/_2 - \chi_{AB})^{0.135}$. The exponent obtained in the present study is not far from that of $^1/_8$ predicted by Muthukumar[12] in his relation

$$\alpha^2 = 0.932(^1/_2 - \chi)^{1/4}\phi^{-1/4} \tag{2}$$

for the expansion of coils in a good solvent at moderate concentrations, where ϕ is the volume fraction of chains. Equation 2, however, predicts larger values of α than those observed here, probably because it was derived for infinitely long chains. It is necessary to be careful, however, in making direct comparisons with the calculated exponent for single-coil expansion in a homopolymer solution. The reference state for coil expansion for a high chain concentration is $\chi = 0$, whereas for a single chain the reference

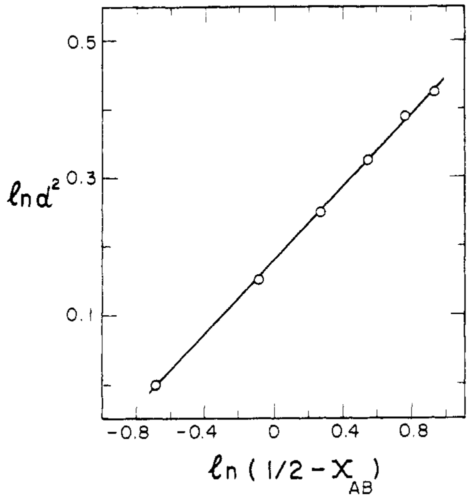

Figure 3. Expansion of minority chains at asymmetric chain composition $x_B = 0.1136$ in the range of ϵ'_{AB} from 0 to -0.5, shown as a double logarithmic plot of α^2 versus $(^1/_2 - \chi_{AB})$ (see text for details).

θ state is for $\chi = {}^1/_2$. It is also noted again that the present calculations are for oligomeric chain lengths only.

The dimensions of coils in polymer liquid mixtures are determined by two factors, namely, the concentration of the respective chains and their interactions in the mixture. Increasing the chain concentration increases the number of entanglements in the system that effectively screen out excluded volume effects in the chains. For high chain concentrations, ideal Gaussian behavior of unperturbed chains is expected. As can be seen from these results, the second effect (i.e., interaction between A and B chains) can overwhelm the concentration effect and the coil can expand considerably even in dense entangled media; but it expands most effectively in systems of asymmetric composition. A theoretical description of these systems could possibly be obtained by combining "temperature blob" theory[10] for expanding minority chains and "concentration blob" theory[4] to account for the screening of excluded volume interactions by high chain concentration.

These calculations also have relevance for solid polymer microstructure. Recent insights derive from the application of scattering techniques. SANS, for example, can measure the dimension of polymer coils in a solid system. However, the analysis of the chain dimensions in mixtures that yields χ parameters uses the random-phase approximation (RPA), which treats the system as one composed of ideal Gaussian coils.[4,13] The method is limited to miscible blends with a not too negative polymer–polymer interaction coefficient. In addition to deriving χ—the basic aim of these studies—the apparent radius of gyration $\langle R_{app}{}^2\rangle$ can be extracted.[3,14] The problem is that $\langle R_{app}{}^2\rangle$ obtained from SANS studies probably does not properly reflect the chain dimensions in the polymer blend for two reasons: First, according to the basic hypothesis, as exemplified in eq 6 in ref 13, as χ changes from negative to positive values, $\langle R_{app}{}^2\rangle$ should increase—whereas it has been previously found,[8,9] and confirmed here, that there is a *decrease* in coil dimension under these conditions. Second, eq 6 in ref 13 predicts that the largest change in $\langle R_{app}{}^2\rangle$ will be found at a symmetric composition, whereas it is shown here for coil expansion, and elsewhere[5,6] for coil collapse, that the largest changes in coil dimension occur at strongly asymmetric compositions. We therefore suggest that there could be a potential problem in the use of SANS data for polymer mixtures in identifying $\langle R_{app}{}^2\rangle$ with true coil dimensions, for this variable may not properly reflect the noted changes.

In this context, we also refer to the SANS investigations of Jelenic et al.,[15] who studied strongly asymmetric miscible blends and for most systems found chain dimensions close to those of the corresponding homopolymer melt; in some cases, an expansion of the minority coils to what was qualified as being "not far from the unperturbed state" was observed. In other studies[7] no change of dimensions was observed. A possible explanation for the absence of expansion in these studies is, again, that the segmental interaction was insufficiently strong to induce coil expansion beyond the experimental error. We feel that some explanation will be forthcoming, because in the present study we have shown, by following the respective majority and minority chains dimensions over a wide composition range, that coil expansion in miscible blends is a general phenomenon.

Finally, it may be mentioned that the expansion of coils with chain lengths longer than those studied here is expected to be even stronger, analogous to excluded volume effects in single chains, and longer chains would intensify the effect shown here by the MC simulations. It would also be interesting to compare the expansion of minority chains in "very good" polymer solvents (majority chains) to that in a low molecular weight solvent with the same intersegmental interaction energy; i.e., $\epsilon'_{AB} = \epsilon'_{SB}$, where ϵ'_{SB} refers to the latter situation.

The pronounced increase in the dimensions of minority chains at asymmetric compositions in miscible blends that is shown here is systematic and represents a challenge to both theory and experiment. At the same time, it is a useful example of the role of MC simulations as a supplement to experiment and theory.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Grant No. 90-001.

References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1949,** *17,* 303.
(2) Olaf, O. F.; Lantschbauer, W. *Makromol. Chem. Rapid Commun.* **1982,** *3,* 847.
(3) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974,** *7,* 863.
(4) de Gennes, P.-G. *Scaling Concepts in Polymer Physics;* Cornell University Press: Ithaca, NY, 1979.
(5) Sariban, A.; Binder, K. *Macromolecules* **1988,** *21,* 711.
(6) Peterson, K. A.; Stein, A. D.; Fayer, M. D. *Macromolecules* **1990,** *23,* 111.
(7) (a) Maconnachie, A.; Fried, J. R.; Tomlins, P. E. *Macromolecules* **1989,** *22,* 4606. (b) Wignall, G. D.; Child, H. R.; Li-Aravena, F. *Polymer* **1980,** *21,* 131. (c) Kambour, R. P.; Bopp, R. C.; Maconnachie, A.; MacKnight, W. J. *Polymer* **1980,** *21,* 133.
(8) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1988,** *21,* 446.
(9) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Polym. Sci. Polym. Phys.* **1988,** *26,* 2379.
(10) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979,** *12,* 276.
(11) Flory, P. J. *Principles of Polymer Chemistry;* Cornell University Press: Ithaca, NY, 1953.
(12) Muthukumar, M. *J. Chem. Phys.* **1986,** *85,* 4722.
(13) Lapp, A.; Picot, C.; Benoit, H. *Macromolecules* **1985,** *18,* 2437.
(14) Ito, H.; Russell, T. P.; Wignall, G. D. *Macromolecules* **1987,** *20,* 2213.
(15) Jelenic, J.; Kirste, R. G.; Oberthur, R. C.; Schmitt-Strecker, S. *Makromol. Chem.* **1984,** *185,* 129.