ments. We also thank Professor L. Mandelkern for assistance with X-ray diffraction measurements.

References and Notes

(1) Lenz, R. W.; Antoun, S.; Jin, J.-I. *Br. Polym. J.* **1980,** *12,* 132.

(2) Economy, J. *J. Macromol. Sci., Chem.* **1984,** *A21,* 1705.

(3) Lenz, R. W. *J. Polym. Sci., Polym. Symp.* **1985,** *72,* 1.

(4) Gray, G. In *Polymer Liquid Crystals*; Ciferri, A., Ed.; Academic Press: New York, 1982; p 13.

(5) Osman, M. A. *Macromolecules* **1986,** *19,* 1924.

(6) Kwolek, S. L.; Luise, R. R. *Macromolecules* **1986,** *19,* 1789.

(7) Schaefgen, F. R. US Patent 4 118 373, 1978.

(8) Bhaskar, C.; Kops, J.; Marcher, B.; Spanggaard, H. In *Recent Advances in Liquid Crystalline Polymers*; Chapoy, L. L., Ed.; Elsevier: London, 1985; p 79.

(9) Polk, M.; Bota, K.; Akubiro, E.; Phingbodhipakkiya, M. *Macromolecules* **1981,** *14,* 1626.

(10) Braun, D.; Schulke, U. *Makromol. Chem.* **1986,** *187,* 1145.

(11) Clausen, K.; Kops, J.; Rasmussen, K.; Rasmussen, K. H.; Sonne, J. *Macromolecules* **1987,** *20,* 2660.

(12) Pedersen, C. J. *J. Am. Chem. Soc.* **1967,** *89,* 7017.

(13) Jedlinski, Z.; Franek, J.; Kuziw, P. *Makromol. Chem.* **1986,** *187,* 2317.

(14) Galli, G.; Chiellini, E.; Ober, C. K.; Lenz, R. W. *Makromol. Chem.* **1982,** *183,* 2693.

(15) Lenz, R. W.; Furukawa, A.; Wu, C. N.; Atkins, E. D. T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.* **1988,** *29* (1), 480.

(16) Demus, D.; Richter, L. In *Textures of Liquid Crystals*; Verlag Chemie: New York 1978; p 203, plate 196.

(17) Blumstein, A. *Polym. J.* **1985,** *17,* 277.

(18) Bosio, L.; Foyolle, B.; Friederich, C.; Laupetre, F.; Meurisse, R.; Noel, C.; Virlet, J. In *Liquid Crystals and Ordered Fluids*; Griffin, A. C.; Johnson, J. F., Eds.; Plenum Press: New York, 1983; Vol. IV, pp 401-427.

(19) Domszy, R. C. Unpublished results.

(20) Stewart, J. J. P. *QCPE* **1983,** *No. 455.*

Registry No. 2a (copolymer), 126035-73-2; **2a** (SRU), 126035-82-3; **2b** (copolymer), 126035-74-3; **2b** (SRU), 126035-83-4; **2c** (copolymer), 126035-75-4; **2c** (SRU), 126035-84-5; **2d** (copolymer), 126035-77-6; **2d** (SRU), 126035-85-6; **3a**, 126035-78-7; **3b**, 126035-79-8; **4a** (copolymer), 105709-24-8; **4a** (SRU), 84329-77-1; **4b** (copolymer), 126035-80-1; **4b** (SRU), 84329-76-0; **4c** (copolymer), 126035-81-2; **4c** (SRU), 116695-92-2.

Monte Carlo Simulations of Ultrathin Polymer Blend Films: Influence of Interaction Strength on Segregation and Shape of Coils

J. H. van Vliet and G. ten Brinke*

Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received August 28, 1989; Revised Manuscript Received December 6, 1989

ABSTRACT: The influence of the interaction strength on segregation and anisotropy of individual polymer coils is studied by Monte Carlo simulations of chains on a square lattice for a homopolymer blend, a random copolymer/homopolymer blend, and a pure random-copolymer melt. These simulations show that in a two-dimensional blend an increase in interaction strength causes anisotropic swelling of polymer coils. The anisotropic swelling is less pronounced for the random copolymer/homopolymer blend where intramolecular repulsion also induces internal reorganization of the polymer coils. For realistic values of the interaction parameter segregation of individual coils remains a dominant feature. Therefore, in ultrathin polymer blend films a characteristic microdomain morphology may be present even if both components are *miscible.*

Introduction

Two-dimensional polymer blends were investigated as a starting point for a more detailed study of the influence of the strength and type of interactions on polymer conformations and phase behavior in thin polymer films. Although truly two-dimensional polymer systems probably do not exist, the present study is directed to those properties that are believed to be of relevance for real polymer monolayers as well. Support for the existence of two-dimensionally coiled conformations was given by M. Watanabe et al.[1] They produced Langmuir-Blodgett films of poly(vinyl alkylals) consisting of hydrophilic main chains spread over the air/water interface with the hydrophobic side chains approximately normal to the interface. All observations indicated that the main chains had two-dimensional coiled conformations. From the limiting area results they concluded that the two-dimensional coiled main chains were packed very closely. Monolayers of mixtures of polymers at the water/air interface were already considered by Gabrielli and co-workers.[2,3] A typical example is given by mixtures of poly(methyl methacrylate) and poly(propyl methacrylate). These polymers were shown to be miscible, and the miscibility was ascribed to the interaction between the hydrophobic chains that were almost parallel to the air/water interface.

In the common bulk situation the driving forces for polymer miscibility can be divided into two principal classes: intramolecular repulsion and specific interactions. The intramolecular repulsion effect is characteristic for many blends involving random copolymers[4,5] but is also suggested to be of importance for blends of homopolymers such as poly(vinyl chloride) with aliphatic polyesters[6] or polyamide blends.[7] A clear example of specific intermolecular interactions is sulfonated polystyrene with poly(4-vinylpyridine).[8] Both classes will be considered and compared in the present study.

0024-9297/90/2223-2797$02.50/0

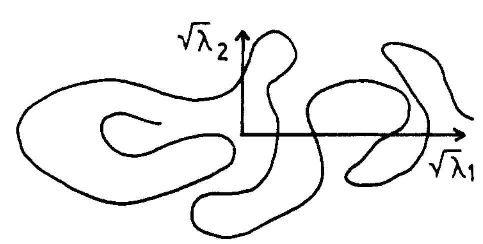

Figure 1. Principal radii of gyration $\lambda_1^{1/2}$ and $\lambda_2^{1/2}$ for a two-dimensional coil.

As predicted by de Gennes[9] and verified by Monte Carlo simulations,[10] the individual excluded-volume chains in athermal two-dimensional systems are highly segregated from each other. In a two-dimensional Monte Carlo simulation a substantial increase of the radii of gyration of chains was observed, probably accompanied by considerable chain interpenetration, for homopolymer blends with an attractive interaction between the two components.[11] Previous Monte Carlo simulations for random copolymer/homopolymer blends with intramolecular repulsion for the copolymer component indicated the importance of other factors like intermolecular and intramolecular ordering.[12] Before a more definite statement about chain interpenetration can be made, a careful look at the influence of the interaction strength on the shape of the polymer coils is necessary.

In concentrated polymer systems the excluded-volume interaction is largely screened out and the shape of a polymer coil is well described by random-walk statistics. That the shape of a random walk is not a spherical one was noticed half a century ago by Kuhn.[13] Anisotropy is a characteristic property of all kinds of nonexcluded-volume and excluded-volume chains,[14,15] and a three-dimensional coil can best be described as a "cake of soap".[16] The shape of a polymer chain can be characterized by the eigenvalues of the radius of gyration matrix, the sum of which equals the square radius of gyration.

$$R_g^2 = \lambda_1 + ... + \lambda_d \tag{1}$$

The square roots of the eigenvalues, called the principal radii of gyration, can be pictured (Figure 1) in three- and two-dimensional space as the length of the principal axes of an ellipsoid or an ellipse, respectively. The eigenvalues are usually indexed in descending order i.e. from λ_1 to λ_d, λ_1 being the largest and λ_d being the smallest eigenvalue for the matrix in d-dimensional space. They can be computed quite easily for any spatial dimension. For the two-dimensional systems dealt with here, the ratio of the two principal components is used to characterize the shape of a coil

$$\gamma = \langle\lambda_1\rangle/\langle\lambda_2\rangle \tag{2}$$

In the limit of infinitely long random-walk chains γ = 5.13.[17] Assuming that the average shape of a polymer coil resembles an ellipse with axes $2\langle\lambda_1\rangle^{1/2}$ and $2\langle\lambda_2\rangle^{1/2}$, a measure of the volume of the domain occupied by a polymer coil is

$$V = \langle\lambda_1\rangle^{1/2}\langle\lambda_2\rangle^{1/2} \tag{3}$$

The $\langle\ \rangle$ indicates an average over all polymer coils. If an increase of V coincides with an increase of γ, this is referred to as anisotropic swelling.

Two-dimensional polymer melts consist of segregated coils interacting mainly by surface contacts. In two-dimensional polymer blends the effective intermolecular interaction may introduce chain interpenetration characterized by swelling and an increasing number of intermolecular contacts. To what extent is investigated for two different systems: a blend of a random copolymer and a homopolymer with intramolecular repulsive interaction and a blend of two homopolymers with intermolecular attraction. In addition to these systems the influence of intramolecular repulsion on a random-copolymer melt is considered. In the limit of vanishing interaction strength all three correspond to an athermal homopolymer melt.

Model and Simulation Method

The systems simulated are modeled as chains on a 22 × 22 or 33 × 33 square lattice. Of all the lattice sites an 82.64% fraction is occupied, which, for the chain lengths of N = 20 or N = 30 segments considered, corresponds to 20 or 30 chains. Blends are equimolar mixtures of the two polymer components.

Configuration space is sampled according to the Metropolis importance sampling scheme together with the reptation algorithm.[18-20] To speed up equilibration, chain growth and reptation take place simultaneously.[21]

In this text $\tilde{\epsilon}_{AB} = \epsilon_{AB}/k_BT$. The systems studied are a random copolymer/homopolymer blend, P(A-*co*-B)/P(C), with $\tilde{\epsilon}_{AB} \geq 0$, a homopolymer blend, P(A)/P(B), with $\tilde{\epsilon}_{AB} \leq 0$, and a pure random-copolymer melt, P(A-*co*-B), with $\tilde{\epsilon}_{AB} \geq 0$. All other segmental interaction parameters are equal to zero. All systems are studied for the chain length N = 20. Some systems are also studied for the chain length N = 30. The random copolymer is composed of A and B segments according to a binomial distribution with the probability of taking a segment of either type, p = 0.5. In this paper the Flory/Huggins χ parameter for the homopolymer blend is defined by

$$\chi = (z - 2)\tilde{\epsilon}_{AB} \tag{4}$$

whereas for the random copolymer/homopolymer blend χ is given by[4,5]

$$\chi = -(z - 2)x_Ax_B\tilde{\epsilon}_{AB} \tag{5}$$

where z is the coordination number of the lattice, i.e. z = 4 and x_A and x_B are the molar fractions of A and B segments of the random copolymer, i.e. $x_A + x_B = 1$.

The values of $\tilde{\epsilon}_{AB}$ vary between 0.0 and 4.0 for the random copolymer/homopolymer blend and between 0.0 and −1.0 for the homopolymer blend. According to eqs 4 and 5 this ensures that the χ parameter varies between 0 and −2.0 for both systems. The pure random-copolymer melt is simulated only for $\tilde{\epsilon}_{AB}$ = 1.0. For N = 30 the athermal melt case and the blends with χ = −0.25 are simulated.

To have a definite point from where to start sampling after all chains have reached their final length, correlation coefficients for the square radius of gyration, and the square end-to-end point distance, were calculated. Each correlation coefficient is calculated by averaging over two independent runs. The definition of the correlation coefficient is the same as before.[12] In general the correlation coefficient is required to fluctuate around zero before sampling starts. Here "fluctuating around zero" implies that the correlation coefficient has decreased as a function of the number of attempted moves from its initial value of 1 to less than 0.2 and that for a period of at least 1 × 10⁶ attempted moves after this point is reached, the correlation coefficient does not drift away from an average of zero.

The correlation coefficients have been calculated for two special cases, the random copolymer/homopolymer blend with N = 20 and $\tilde{\epsilon}_{AB}$ = 4.0 and with N = 30 and

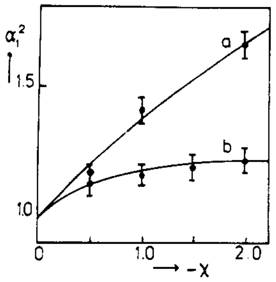

Figure 2. α_1^2 as a function of χ ($N = 20$; $\langle\lambda_1\rangle_0 = 5.5$): a, P(A)/P(B); b, P(A-*co*-B)/P(C).

$\tilde{\epsilon}_{AB} = 1.0$. As will be argued, of all systems considered these are the ones for which equilibrating requires the highest number of attempted moves. The average number of attempted moves to get correlation coefficients fluctuating around zero for $N = 20$ and $\tilde{\epsilon}_{AB} = 4.0$ is 4.8×10^6, whereas for $N = 30$ and $\tilde{\epsilon}_{AB} = 1.0$ this number is 9.0×10^6. To have a well-defined interval over which to sample, correlation coefficients for the same quantities were calculated starting from, in units of attempted moves, $t_0 = 4.8 \times 10^6$ for $N = 20$ and from $t_0 = 9.0 \times 10^6$ for $N = 30$. Now 0.8×10^6 and 1.08×10^6 attempted moves were required to get correlation coefficients fluctuating around zero again. In the literature these intervals are defined as subblocks.[22,23] To calculate averages for the quantities of interest each system was subjected to at least four independent runs. For each run at least five samples were drawn at equally spaced intervals from one subblock and averaged. This procedure is preferred to the one that uses consecutive subblocks of the same run. Final averages and statistical errors in these averages were calculated by averaging over the subblock averages. For other systems considered the ratio of successful to attempted moves is always higher, with a corresponding shorter equilibration time.

The simulations described are believed to represent a polymer melt, i.e. a dense system. Support for this is found by comparing the present results for 17.36% empty lattice sites and previous results for 9.09% empty lattice sites.[12] Contacts between segments are divided in eight different classes based on two criteria: intramolecular or intermolecular contacts and type of contacts, i.e. AA + BB, AB, AC + BC, or CC. Each class is characterized by the number of contacts as a percentage of the total number of contacts. Numbers turn out to be the same within a maximum relative error of 0.1 for the P(A-*co*-B)/P(C) blends with $\tilde{\epsilon}_{AB} = 0.0$ and $\tilde{\epsilon}_{AB} = 1.0$. For a diluted system an influence of the fraction of empty sites on the distribution of the number of contacts would be expected.

Results and Discussion

To analyze the effect of the interaction strength on the occupied volume per coil, the shape of the coil, and the number of intermolecular and intramolecular contacts, various ratios of relevant quantities were computed for P(A)/P(B) and P(A-*co*-B)/P(C) blends, as a function of the χ parameter.

First, the principal radii of gyration $\lambda_1^{1/2}$ and $\lambda_2^{1/2}$ will be considered. Swelling is accompanied by an increase in one or both of the expansion factors $\alpha_1^2 = \langle\lambda_1\rangle/\langle\lambda_1\rangle_0$ and $\alpha_2^2 = \langle\lambda_2\rangle/\langle\lambda_2\rangle_0$, where the index 0 indicates the athermal melt. When one expansion factor decreases while the other one increases, the sign of the volume change is not obvious and should be calculated explicitly according to eq 3. The change in average shape of coils is reflected by a change in the ratio γ, defined by eq 2.

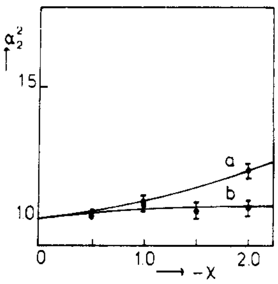

Figure 3. α_2^2 as a function of χ ($N = 20$; $\langle\lambda_2\rangle_0 = 1.15$): a, P(A)/P(B); b, P(A-*co*-B)/P(C).

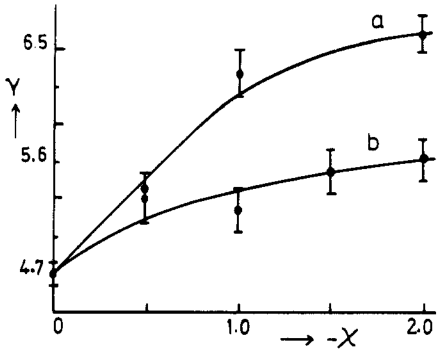

Figure 4. γ as a function of χ a, P(A)/P(B); b, P(A-*co*-B)/P(C).

Table I
Data for Comparison of Various Blends

system[b]	$\tilde{\epsilon}_{AB}$	χ	η	α_1^2	α_2^2	γ
athermal melt; $N = 20$	0.0		1.54	1[a]	1[a]	4.7
random copolymer; $N = 20$	1.0		1.65	1.04	0.98	5.0
random co/homopolymer; $N = 20$	1.0	−0.5	1.95	1.13	1.01	5.3
homopolymer/homopolymer; $N = 20$	−0.25	−0.5	2.09	1.17	1.03	5.4
athermal melt; $N = 30$	0.0		1.18	1[a]	1[a]	5.0
random co/homopolymer; $N = 30$	1.0	−0.5	1.39	1.07	1.07	5.0
homopolymer/homopolymer; $N = 30$	−0.25	−0.5	1.63	1.17	1.13	5.2

[a] Value equals 1 by definition. [b] $N = 20$; $\langle\lambda_1\rangle_0 = 5.5$; $\langle\lambda_2\rangle_0 = 1.15$. $N = 30$; $\langle\lambda_1\rangle_0 = 9.1$; $\langle\lambda_2\rangle_0 = 1.81$

Figures 2 and 3 present α_1^2 and α_2^2 as a function of the interaction strength for the two classes of blends considered. For both blends an increase of the largest eigenvalue $\langle\lambda_1\rangle$ is observed. For $\langle\lambda_2\rangle$ there is only a slight increase for the P(A)/P(B) blend and hardly any increase at all for the P(A-*co*-B)/P(C) blend. In both cases the increase is more pronounced for the homopolymer blend. Figure 4 shows γ as a function of the interaction strength. From these results it is clear that swelling occurs and is accompanied by an increase in the anisotropy. The effects are stronger for the homopolymer blend than for the copolymer blend. The data presented are for molecules of chain length $N = 20$; similar data for $N = 30$ are given in Table I. Again the swelling is quite obvious, but the anisotropy is reduced compared to $N = 20$. For the pure random-copolymer melt the intramolecular repulsive interaction has only a very slight effect on the size and shape of the individual coils.

In the absence of any interaction $\gamma = 4.7$ and 5.0 for $N = 20$ and 30, respectively, which is slightly smaller than the limiting value of 5.13 for long random walks.[17] Bishop and Saltiel[24] found a value of approximately 4.3 for non-excluded-volume chains of length 24, so that a cautious conclusion is that chains of a finite length in a two-dimensional melt are slightly more anisotropic than ran-

Table II
Number[a] of Contacts between Segments of Random-Copolymer Chains

	$\bar{\epsilon}_{AB} = 0.0$		$\bar{\epsilon}_{AB} = 1.0$		$\bar{\epsilon}_{AB} = 4.0$	
system	AA + BB	AB	AA + BB	AB	AA + BB	AB
random co/homopolymer; $N = 20$						
intramolecular contacts	9.7	10.0	11.0	4.4	11.1	0.0
random co/homopolymer; $N = 30$						
intramolecular contacts	11.5	12.1	12.6	6.4		
pure random copolymer melt						
intramolecular contacts	19.6	19.9	27.3	10.6		
intermolecular contacts	30.3	30.3	45.1	17.1		

[a] Number of contacts as a percentage of the total number.

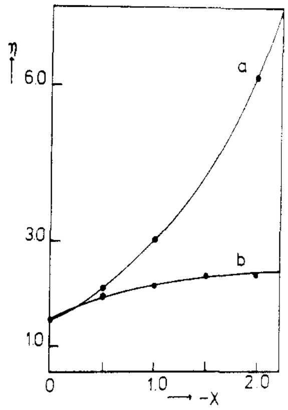

Figure 5. η as a function of χ (statistical errors equal to diameter of dots used): a, P(A)/P(B); b, P(A-*co*-B)/P(C).

dom walks. A related observation already noticed before[25,26] is that the average radius of gyration for the melt is about 10% higher than the analytic result for nonreversal random walks. As argued by Curro et al.[27] this may be due to local expansion of the chains.

The amount of swelling is closely connected to the ratio η of intermolecular over intramolecular contacts. Figure 5 shows η as a function of the interaction strength for the homopolymer and the random-copolymer blend. For the former blend a strong increase in η is observed, whereas for the latter η seems to level off. Table II gives a more detailed account of the intramolecular interactions present in the P(A-*co*-B)/P(C) blends. For increasing values of $\bar{\epsilon}_{AB}$ the number of intramolecular AA and BB contacts increases while the number of intramolecular AB contacts decreases. The intramolecular AB contacts are partly replaced by intramolecular contacts and partly by intermolecular contacts. For the P(A-*co*-B)/P(C) blends with chain length 20 a limiting value of 11 for the number of intramolecular AA + BB contacts is found. For the pure random-copolymer melt the reduction in intramolecular AB contacts is approximately compensated by formation of intramolecular AA + BB contacts. Only 1.6% of the intramolecular contacts are replaced by intermolecular contacts going from $\bar{\epsilon}_{AB} = 0.0$ to $\bar{\epsilon}_{AB} = 1.0$. For the corresponding blend with P(C) this shift is 4.3%. The replacement of intramolecular AA + BB by intramolecular AB contacts within a random-copolymer coil results in typical intramolecular microdomains (Figure 6).

From snapshots it is clear that the centers of mass of the coils of all blends considered become ordered when χ becomes more negative. Examples of such snapshots were published before.[12] For all the systems, including the athermal melt, the long principal axes of neighboring polymer coils tend to arrange in parallel order. This effect is only local, and there is certainly not a kind of nematic order. Furthermore, this tendency to align locally seems not to depend on χ for the values used.

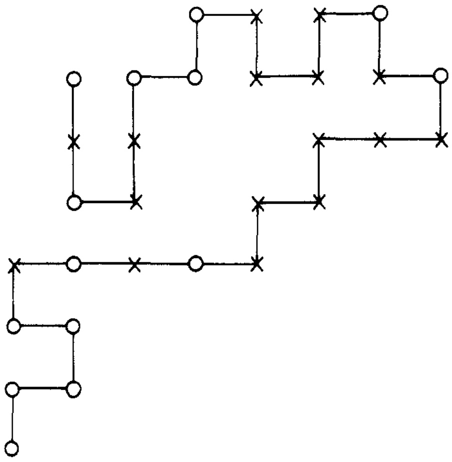

Figure 6. Snapshot picture of a random-copolymer coil from a random copolymer/homopolymer melt with $N = 30$, $\bar{\epsilon}_{AB} = 1.0$, and $\chi = -0.5$, where A and B are the segments of the random copolymer (situation obtained after 9.9 × 10^6 attempted reptation moves): ○, A; ×, B.

Depending on the type of system considered an increase in the interaction strength leads to an increase of favorable intermolecular contacts, P(A)/P(B), favorable intramolecular contacts, P(A-*co*-B), or both P(A-*co*-B)/P(C).

In case of the homopolymer blend the only possible way of reducing the number of relatively unfavorable AA and BB contacts is by replacing them with intermolecular AB contacts resulting in an anisotropic shape and external ordering of polymer coils. Swelling is clearly present because both expansion factors α_1^2 and α_2^2 are larger. Nevertheless, for values of the χ parameter which occur in most experimental cases i.e. $-\chi \leq 0.5$, segregation of individual coils, as indicated by the small values of α_1^2 and α_2^2, remains a dominant feature.

In case of the pure random-copolymer melt the number of unfavorable AB contacts can be reduced by replacing intra- and intermolecular AB contacts with intra- and intermolecular AA and BB contacts. Only a few intramolecular AB contacts are replaced with intermolecular AA and BB contacts. Since interpenetration of coils is not energetically favorable and swelling is entropically unfavorable, the anisotropic swelling is very small.

In the P(A-*co*-B)/P(C) blend the relatively unfavorable AB contacts are replaced by AC, BC, AA, and BB contacts. For this blend intramolecular as well as intermolecular reorganization diminished repulsion, so anisotropic swelling of polymer chains is, although more pronounced than for the random-copolymer melt, far less than that for the homopolymer blend. The limiting number of intramolecular AA + BB contacts as a function of the interaction strength is due to the fixed number of A and B segments per random-copolymer chain, thereby limiting the total number of AA + BB contacts possible.

Of course segregation is even more obvious than for the homopolymer blend.

Table I also shows that the ratio of intermolecular contacts over intramolecular contacts, η, is a decreasing function of N. The reason is quite obvious. In two dimensions polymer coils are highly segregated; hence the ratio η is expected to be proportional to the surface to volume ratio, which decreases as a function of N.

Concluding Remarks

From our simulations one conclusion emerges which is potentially of considerable practical interest. In bulk systems a characteristic microdomain morphology can be obtained in a number of ways. For instance a temperature jump of a homogeneous blend may lead to phase separation with a regular highly interconnected two phase morphology, characteristic for spinodal decomposition.[28,29] Another well known example is the occurrence of mesomorphic structures in certain block copolymer systems.[30] In both cases the microdomain morphology is the result of the immiscibility of the components involved. However, in ultra thin polymer blend films a microdomain morphology may be obtained by using *miscible* polymers due to segregation of individual coils.

A characteristic feature of the random copolymer/homopolymer blend with intramolecular repulsion is the formation of intramolecular micelle like domains. That this might be a far more common general phenomenon was shown quite recently by Shakhnovich and Gutin.[31] Theoretical considerations based on a mean field approximation showed that in a pure random-copolymer melt of A and B segments with a repulsive interaction between unlike segments, microphase separation occurs. In the three-dimensional case the microdomains will be predominantly intermolecular and not as for the two-dimensional systems studied here, intramolecular. The difference is due to the segregation of individual coils in two dimensions.

References and Notes

(1) Watanabe, M.; Kosaka, Y.; Oguchi, K.; Sanui, K.; Ogata, N. *Macromolecules* **1988**, *21*, 2997.
(2) Gabrielli, G.; Puggelli, M.; Baglioni, P. *J. Colloid Interface Sci.* **1982**, *86*, 485.
(3) Caminati, G.; Gabrielli, G.; Ferroni, E. *Colloids Surf.* **1989**, *41*, 189.
(4) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(5) Kambour, R. P.; Bendler, T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(6) Lai, C. H.; Paul, D. R.; Barlow, J. W. *Macromolecules* **1988**, *21*, 2492.
(7) Ellis, T. S. *Macromolecules* **1989**, *22*, 742.
(8) Nathason, A.; Murali, R.; Eisenberg, A. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 175.
(9) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(10) Baumgärtner, A. *Polymer* **1982**, *23*, 334.
(11) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Polym. Commun.* **1987**, *28*, 180.
(12) van Vliet, J. H.; ten Brinke, G. *Macromolecules* **1989**, *22*, 4627.
(13) Kuhn, W. *Kolloid-Z.* **1934**, *68*, 2.
(14) Šolc, K. *Polym. News* **1977**, *4*, 67.
(15) Rudnick, J.; Gaspari, G. *Science* **1987**, *237*, 384.
(16) Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756.
(17) Beldjenna, A., private communication.
(18) Kron, A. K. *Polym. Sci. USSR (Engl. Transl.)* **1965**, *7*, 1361. Kron, A. K.; Ptitsyn, O. B. *Polym. Sci. USSR (Engl. Transl.)* **1967**, *9*, 847. Kron, A. K.; Ptitsyn, O. B.; Skvortsov, A. K. *Mol. Biol.* **1967**, *1*, 487.
(19) Wall, F. T.; Mandel, F. *J. Chem. Phys.* **1975**, *63*, 4592. Mandel, F. *J. Chem. Phys.* **1979**, *70*, 3934.
(20) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(21) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *84*, 1922.
(22) Straatsma, T. P.; Berendsen, H. J. C.; Stam, A. J. *Mol. Phys.* **1986**, *57*, 89.
(23) Bishop, M.; Frinks, S. *J. Chem. Phys.* **1987**, *87*, 3675.
(24) Bishop, M.; Saltiel, C. J. *J. Chem. Phys.* **1986**, *85*, 6728.
(25) Sariban, A.; Binder, K. *Macromolecules* **1988**, *21*, 711.
(26) ten Brinke, G.; Ausserre, D.; Hadziioannou, G. *J. Chem. Phys.* **1988**, *89*, 4374.
(27) Curro, J. G.; Schweizer, K. S.; Grest, G. S.; Kremer, K. *Bull. Am. Phys. Soc.* **1989**, *34*, 951.
(28) McMaster, L. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1974**, *15*, 254.
(29) Berger, W.; Kammer, H. W. *Makromol. Chem., Macromol. Symp.* **1987**, *12*, 145.
(30) Molau, G. E. *Block Copolymers*; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970; p 79.
(31) Shakhnovich, E. I.; Gutin, A. M. *J. Phys. (Les Ulis, Fr.)* **1989**, *50*, 1843.