These tests showed that the results are fundamentally "stable"; i.e., the shape of the patterns turns out to be essentially the same as for the disk case. This confirms that the key point in the model is *the choice of the dipolar interaction.*

7. Conclusions

It has been shown that a simple model of two-body interactions between disclinations can account well for the experimental scattering patterns from LCP films. The presence of scattering maxima in the patterns can be predicted without using the concept of interference, which would be difficult to associate to a random orientation of the dipoles. The only parameter of the model (length L) is sufficient to explain the time evolution of the patterns. Further work on the V_V pattern is in progress.

Acknowledgment. I am most grateful to Professor G. Marrucci (University of Naples) for always being willing to let me have the benefit of his opinions. My thanks go to Dr. L. Abbondanza and Dr. L. Caccianotti, my friends and colleagues at Donegani, for many stimulating discussions and personal cooperation. Specifically, I wish to express my warmest thanks to Dr. L. Caccianotti for putting his computing experience at my disposal.

References and Notes

(1) de Gennes, P.-G. *The physics of liquid crystals*; Clarendon Press: Oxford, 1974.
(2) Hashimoto, T.; Nakai, A.; Shiwaku, T.; Hasegawa, H.; Rojstaczer, S.; Stein, R. S. *Macromolecules* **1989**, *22*, 422.
(3) Demus, D.; Richter, L. *Textures of liquid crystals*; Verlag Chemie: Weinheim, New York, 1978.
(4) Kleman, M.; Liebert, L.; Strzelecki, L. *Polymer* **1983**, *24*, 295.
(5) Rojstaczer, S.; Stein, R. S. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 293.
(6) Kerker, M. *The scattering of light and other electromagnetic radiation*; Academic Press: New York, London, 1969.
(7) Clough, S.; Van Aartsen, J. J.; Stein, R. S. *J. Appl. Phys.* **1965**, *36*, 3072.
(8) Leslie, F. M. *A.R.M.A.* **1968**, *28*, 265.
(9) Frank, F. C. *Discuss. Faraday Soc.* **1958**, *25*, 19.
(10) Dzyaloshinskij, I. E. *Sov. Phys.-JETP* **1970**, *31*, 773.
(11) Wood, B. A.; Thomas, E. L. *Nature* **1986**, *324*, 655.
(12) Hudson, S. D.; Thomas, E. L.; Lenz, R. W. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 63.
(13) Rojstaczer, S.; Hsiao, B. H.; Stein, R. S. *Polym. Prepr.* **1988**, *29*(1), 486.

Monte Carlo Simulation and Mean Field Analysis of Two-Dimensional Random Copolymer/Homopolymer Blends

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

Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands. *Received November 14, 1988; Revised Manuscript Received March 13, 1989*

ABSTRACT: A two-dimensional system consisting of a mixture of a random copolymer and a homopolymer is investigated in some detail. Segregation and chain interpenetration are discussed as a function of the strength of the intramolecular repulsion effect. Equations to deal with these phenomena are derived and compared with Monte Carlo simulations. The possibility that polymers which are immiscible in three dimensions become miscible in two dimensions is discussed. The Monte Carlo calculations show that, besides intermolecular chain ordering and slight chain interpenetration, the intramolecular repulsion effect induces an internal reorganization of the random copolymers. Arguments that this will be true for many blends of homopolymers as well are given.

Introduction

Some years ago,[1] Monte Carlo simulations were used to verify de Gennes's[2] prediction about polymer segregation in two-dimensional systems. A more recent paper[3] dealt with a mixture of two polymers with an attractive exchange interaction between the different segments involved. In this case interpenetration of the chains occurred. Spinodal decomposition was studied for a two-dimensional binary polymer mixture with a repulsive exchange interaction between the different segments.[4,5] A comprehensive review of Monte Carlo simulations of lattice models for macromolecules is given by Kremer and Binder.[6]

From experiments as well as mean field arguments, it is well-known that stable blends of a random copolymer and a homopolymer can exist, although mixtures of a homopolymer, comprising either kind of the monomers of the random copolymer, with the homopolymer phase separate.[7-9] This is due to the so-called intramolecular repulsion effect, a phrase which is used to indicate that the interaction between the different monomers of the random copolymer is relatively unfavorable. Closely related to this is the observation that relatively strong endothermic interactions between structural groups of the pure components are important factors in the formation of miscible homopolymer blends. One of the best known examples is the miscibility of poly(vinyl chloride) with a series of aliphatic polyesters.[10] Very recently this was also demonstrated for a large class of different polyamide blends.[11] From these and other studies, a picture of the intramolecular repulsion effect, being the real driving force for polymer–polymer miscibility in many systems, emerges.

This conclusion prompted us to investigate in some detail the behavior of a two-dimensional system consisting of a homopolymer and a random copolymer. But there are additional important advantages associated with the involvement of random copolymers. If only homopolymers are considered, the interactions are cooperative in the sense that a perfect fit between the two different polymers is possible. In real systems this is for instance observed between isotactic and syndiotactic poly(methyl methacrylate)[12] or in various polyelectrolyte mixtures, like sodium polystyrene with poly(vinylbenzyltrimethylammonium chloride).[13] Such phenomena are referred to as complexation rather than mixing.

Finally there is a third aspect, which is also not present in numerical studies on homopolymer mixtures, but which may turn out to be of primary importance. Random copolymers may rearrange their individual conformations in such a way as to minimize the intramolecular contacts between the different segments. Besides for real random copolymers, this may also happen for homopolymer mixtures involving homopolymers with different structural groups, like the aliphatic polyesters mentioned before. Microdomain formation for random copolymers has recently been observed experimentally for styrene–imidazole copolymers. Sutton et al.[14] showed that in these hydrophobic/hydrophilic random copolymers, styrene and imidazole microdomains were formed for thin (0.1 μm) solid film samples cast on water from a good organic solvent.

In summary we see three important reasons why in numerical studies the use of random copolymers is of interest: the intramolecular repulsion effect, a reduced tendency for complexation, and the possibility of micellelike microdomains.

Model and Simulation Method

The system simulated is a one to one molar ratio mixture of a homopolymer and a random copolymer comprising two different types of segments in an approximately one to one ratio. The model is a square 22 × 22 lattice model. Of all the lattice sites, a 9.09% fraction is empty, which for the chain length of 20 segments considered corresponds to 22 chains. The random copolymers contain different segments, corresponding to a binomial distribution with each type of segment taken with a probability $p = 0.5$.

Configuration space is sampled according to the Metropolis importance sampling scheme together with the reptation algorithm.[15-17] To speed up equilibration, chain growth and reptation take place simultaneously.[18] The chains are modeled as self-avoiding walks. Interactions of nonconnected segments i and j one lattice distance apart are given by the energy parameter ϵ_{ij}/k_BT. Only nearest-neighbor interactions are considered. In our simulation studies the random copolymer consists of segments A and B with $\epsilon_{AB}/k_BT \geq 0$. All the other interactions, including those with segments C of the homopolymer, are athermic throughout the simulation. Therefore $\epsilon_{AB}/k_BT > 0$ corresponds to the well-known repulsion effect.

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, S^2, and the square end-to-end point distance, R^2, were calculated. Each correlation coefficient is found by averaging over two independent runs. Only the special case of $\epsilon_{AB}/k_BT = 1.0$ is considered. The correlation coefficient is defined by

$$\rho(A,t) = \sum_{i=1}^{n}(A(i,t) - \langle A(t)\rangle)(A(i,0) - \langle A(0)\rangle)/ \\ [\{\sum_{i=1}^{n}(A(i,t) - \langle A(t)\rangle)^2\}\{\sum_{i=1}^{n}(A(i,0) - \langle A(0)\rangle)^2\}]^{1/2} \quad (1)$$

where A equals S^2 or R^2, the summation is over all chains, and t is the number of attempted reptation steps after all chains have reached their final length. ⟨ ⟩ indicates an average over all chains involved.

The average number of attempted moves to get correlation coefficients fluctuating around zero turned out to be 4.4×10^6. To have a well-defined interval over which to sample, correlation coefficients for the same quantities were calculated starting from $t_0 = 4.4 \times 10^6$. In this case 6.6×10^6 attempted moves were necessary to get correlation coefficients fluctuating around zero. This interval of 6.6×10^6 attempts can be defined as a subblock. To calculate averages for the quantities of interest, each system studied was subjected to six independent runs. From each run 51 samples were drawn from the abovementioned subblock of 6.6×10^6 attempts, at equally spaced intervals. The sampling was stopped after this correlation time. Final averages were found by averaging over the subblock averages of six independent runs. Statistical errors were calculated by using these six subblock averages. Using the values of each sample is more complicated because of correlations between samples of a subblock.[19,20]

Mixing of Polymers and Interpenetration of Chains

For Ising lattice films it is well-known that the ferromagnetic transition temperature decreases when the thickness decreases.[21] The interpretation deals mostly with the decrease of the average atomic coordination number.[31] For polymers there is an additional effect which probably is far more important. In a two-dimensional melt of pure polymers the polymers are strongly segregated; polymer–polymer interpenetration is hardly present. This is even more pronounced if a binary mixture of polymers is considered with a slightly positive interaction parameter. In the first part of this section we will restrict ourselves to that situation. Assuming that the polymer molecules interact primarily by surface contacts between the coils, the familiar mean field expression for the free energy of mixing per coil for a binary system reads

$$\Delta F/k_BT = \varphi_\alpha \ln \varphi_\alpha + \varphi_\beta \ln \varphi_\beta + \Gamma_{\alpha\beta}\varphi_\alpha\varphi_\beta \quad (2)$$

where φ_α and $\varphi_\beta = 1 - \varphi_\alpha$ are the "volume" fractions of polymer α and β, respectively. $\Gamma_{\alpha\beta}$ is the exchange interaction parameter related to the interaction between the coils $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$, and $\epsilon_{\alpha\beta}$ in the common way:

$$\Gamma_{\alpha\beta} = \frac{\bar{z}}{k_BT}\{\epsilon_{\alpha\beta} - \tfrac{1}{2}(\epsilon_{\alpha\alpha} + \epsilon_{\beta\beta})\} \quad (3)$$

where $\bar{z}$ is something like the average coordination number of a coil, i.e., a measure for the nearest-neighbor coils. Under the assumption of negligible coil interpretation, the interaction energy between two coils scales with the "surface" Σ per coil:

$$\epsilon \cong \Sigma \quad (4)$$

For coils in a two-dimensional melt Σ in turn scales with the chain length N according to

$$\Sigma \cong N^{1/2} \quad (5)$$

The interaction between two homopolymer coils α and β therefore depends on the interaction ϵ_{AB} between the segments A and B of these coils in the following way

$$\epsilon_{\alpha\beta} \cong N^{1/2}\epsilon_{AB} \quad (6)$$

For the special case considered by Cifra et al.[3,5] of homopolymers α and β with $\epsilon_{AA} = \epsilon_{BB} = 0$ this implies

$$\Gamma_{\alpha\beta} = \frac{\bar{z}_{eff}}{k_BT}N^{1/2}\epsilon_{AB} \quad (7)$$

where $\bar{z}_{eff}$ incorporates all kinds of front factors ignored so far because they cannot be determined unambiguously.

In this paper our main interest is the special case of a random copolymer α comprising A and B segments in a ratio $x_A{:}x_B = 1 - x_A$ and a homopolymer β comprising C segments. Furthermore only the simple case of $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{CC} = \epsilon_{AC} = \epsilon_{BC} = 0$ will be considered. In that case eq 7 is replaced by[8]

$$\Gamma_{\alpha\beta} = -\frac{\bar{z}_{eff}}{k_BT}x_Ax_BN^{1/2}\epsilon_{AB} \quad (8)$$

The critical value of the Γ parameter beyond which phase separation occurs is given by

$$\Gamma_{\alpha\beta} = 2 \tag{9}$$

Equations 7–9 imply that values of the segmental interaction energies of the order of $N^{-1/2}$ can be tolerated before phase separation occurs. Of course, phase separation requires $\epsilon_{AB} > 0$ for two homopolymers and $\epsilon_{AB} < 0$ for the random copolymer/homopolymer blend. In the usual three-dimensional situation the critical value of the segmental interaction energies are of the order N^{-1}. For high molecular mass polymers this value is very small and the general conclusion is that miscibility in three dimensions requires exothermic mixing, i.e., a negative enthalpy of mixing. This in turn implies that if finite compressibility effects are ignored, phase separation will not occur. In practice, it corresponds to the absence of an UCST (upper critical solution temperature) in polymer blends. For the two-dimensional case, the unfavorable values of the segmental interaction energy that can be tolerated are much higher ($\cong N^{-1/2}$). As a consequence, polymers that are not miscible in three dimensions can in principle be miscible in two dimensions. Moreover, UCST behavior, very rare in three dimensions, might be a far more common phenomenon in very thin films.[32]

So far mixing of polymer coils was considered, assuming chain interpretation can in a first approximation be ignored. This seems reasonable as long as the interaction between the coils is zero or slightly unfavorable. However, if an attractive interaction between the segments of the different polymers involved exists, or if the repulsion effect is present, chain interpenetration will occur. For the case of two homopolymers, this effect has already been observed by Cifra et al.[3] Interpenetration of coils implies a decrease in conformational entropy, which is compensated by a decrease in the energetic contribution to the free energy. By use of a Flory type argument,[22-24] a simple expression for the degree of interpenetration will be derived considering a 1:1 molar ratio mixture of polymer chains of equal length.

First, several assumptions will be made. Consider a mixture of α and β polymers comprising A and B segments, respectively. If an attractive exchange interaction between A and B is present, i.e., $\chi < 0$, polymer α swells because segments B from polymer β will start to interpenetrate the outside layers of the α coil. Similarly, segments A interpenetrate the β coils. In order to be able to estimate the effect on the free energy, we assume isotropic swelling and a homogeneous distribution of the small amount of segments A and B within the domains of polymer β and α, respectively. Of course, in this way the contributions to the conformational entropy as well as to the energy are far from correct, but we expect that these errors will compensate each other to some extent, as in the case of Flory's calculation of the excluded-volume exponent.[2]

The squared expansion factor λ^2 is defined as the ratio between the unperturbed Gaussian value of the mean-square end-to-end point distance $\langle R^2 \rangle_0$ and the mean-square end-to-end point distance $\langle R^2 \rangle$ of the swollen coil:

$$\lambda^2 = \langle R^2 \rangle / \langle R^2 \rangle_0 \tag{10}$$

Apart from a trivial constant, the decrease in entropy ΔS per chain due to swelling is given by

$$\Delta S = \ln \lambda^2 - \lambda^2 \tag{11}$$

The corresponding decrease in energy is given by

$$\Delta U = {}^1\!/_2 N \chi (1 - 1/\lambda^2) \tag{12}$$

where N is the chain length and $1 - 1/\lambda^2$ corresponds to the fraction of polymer segments of polymer β within polymer α and vice versa. The factor $^1/_2$ in front of eq 12 takes into account the fact that the interaction energy has to be divided equally among the α and β coils. Of course, this expression is only meaningful for $1 \le \lambda^2 \le 2$. For $\lambda^2 = 2$ a homogeneous mixture is obtained; further swelling will only lead to an additional reduction in conformational entropy without compensating energetic contributions. The net change in the free energy per chain is therefore given by

Table I
Number of Interactions, Radii of Gyration, and End-to-End Point Distances

		no. of contacts					
ϵ_{AB}/k_BT	contacts	intra	inter	tot	chains	$\langle S^2 \rangle$	$\langle R^2 \rangle$
0.0	AA + BB	35	27	62	$\alpha + \beta$	6.6	38
	AB	37	26	63	α	6.4	37
	AC + BC		140	140			
	CC	69	55	124	β	6.7	39
0.5	AA + BB	39	25	64	$\alpha + \beta$	7.0	42
	AB	25	16	41	α	7.0	42
	AC + BC		171	171			
	CC	68	44	112	β	6.9	41
1.0	AA + BB	42	27	69	$\alpha + \beta$	7.1	41
	AB	17	10	27	α	7.3	42
	AC + BC		186	186			
	CC	66	40	106	β	7.0	41

$$\Delta F(\lambda) = \ln \lambda^2 - \lambda^2 + {}^1\!/_2 N \chi (1 - 1/\lambda^2) \tag{13}$$

Minimizing with respect to λ results in the final expression

$$\lambda^4 - \lambda^2 = -\frac{N}{2}\chi \tag{14}$$

This equation predicts that swelling is already complete, i.e., $\lambda^2 = 2$, for $\chi = -4/N$. Compared to our numerical results, to be discussed in the next section, and the results of Cifra et al.,[3] the degree of swelling is enormously overestimated. It turns out that intermolecular ordering combined with a change in average shape[30] is more favorable than chain interpretation. For systems involving random copolymers there is the additional effect of internal reorganization.

Numerical Results

In dense systems of self-avoiding walks the excluded-volume effects are largely screened out. The self-avoiding walk statistics is replaced by nonreversal random walk (NRRW) statistics.[25,26] An analytic expression for $\langle R^2 \rangle$ of NRRW's is given by Domb and Fisher.[27] From this an analytic expression for $\langle S^2 \rangle$ can be derived

$$\langle S^2 \rangle_{\mathrm{nrrw}} = \frac{1+q}{1-q}\,\frac{1}{6}\,\frac{N(N+2)}{N+1} - \frac{q}{(1-q)^2}\,\frac{N-2}{N+1} + \frac{2q^2}{(1-q)^3}\,\frac{N}{(N+1)^2} - \frac{2q^3}{(1-q)^4}\,\frac{1-q^N}{(N+1)^2} \tag{15}$$

where N is the number of links and $q^{-1} = z - 1$. In our case $N = 19$. This results in $\langle R^2 \rangle_{\mathrm{nrrw}} = 36.5$ and $\langle S^2 \rangle_{\mathrm{nrrw}} = 6.05$. In previous simulation studies the actual values turned out to be approximately 10% higher.[28,29] Our results are summarized in Table I. By comparison of the analytic results with the numerical values for $\epsilon_{AB} = 0.0$, the same systematic deviation is observed.

In the following discussion we will focus our attention on the results presented in Table I. It should be realized that the average ratio of A to B segments for the random copolymer is 1.1, slightly different from the expected value of 1. Three values for the energy parameter are considered,

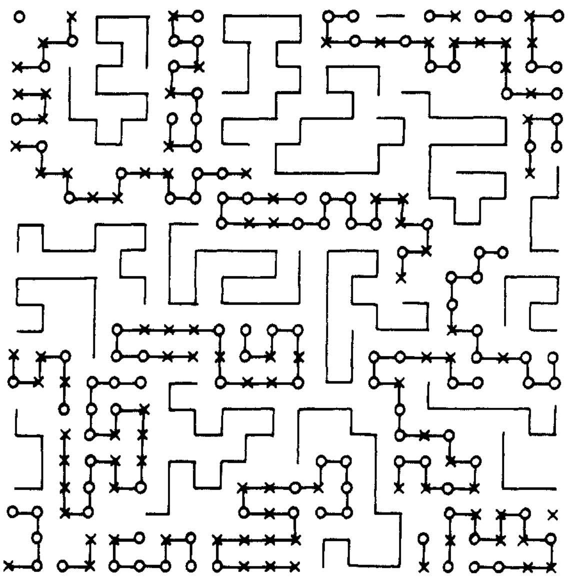

Figure 1. Snapshot pictures of random copolymer/homopolymer mixture, with $\epsilon_{AB}/k_BT = 0.0$, where A and B are the segments of the random copolymer. Situation obtained after 11×10^6 attempted reptation moves. (O) A; (×) B; solid line represents homopolymer.

$\epsilon_{AB}/k_BT = 0$, 0.5, and 1.0. From the data of Table I we notice on the average a slight swelling of the coils, for the energy parameter going from 0 to 1.0. Averaged over all chains in the system, random copolymers α as well as homopolymers β, the average degree of swelling λ^2 turns out to be approximately 1.1 for $\epsilon_{AB}/k_BT = 1.0$. This value is much lower than the value of 1.47 found by Cifra et al.[3] However, it has to be realized that in our case we are dealing with the intramolecular repulsion effect instead of intermolecular attraction. So the χ parameter has to be replaced by χ_{eff},[7-9] given by

$$\chi_{\text{eff}} \cong -\frac{z-2}{k_BT}x_Ax_B\epsilon_{AB} \qquad (16)$$

where $x_A \cong x_B \cong 0.5$. Hence, the actual value of the exchange interaction parameter for the same value of ϵ_{AB}/k_BT is four times as small. For our system, $\epsilon_{AB}/k_BT = 1.0$ corresponds to $\chi_{\text{eff}} \cong -0.5$, compared to a value of -1.0 used by Cifra et al.[3] According to Table I, the number of intramolecular A–B contacts decreases strongly as a function of ϵ_{AB}/k_BT. At the same time the number of intramolecular A–A and B–B contacts increases. This implies that intramolecular reorganization takes place. Hence, the coils of the random copolymer reorganize into a "micellelike" structure in order to relax the intramolecular repulsion effect. The number of intermolecular A–A and B–B contacts remains approximately constant. But, as expected, the number of intermolecular A–B contacts decreases considerably as a function of ϵ_{AB}/k_BT. These contacts are replaced by intermolecular A–C and B–C contacts. This is mainly the result of the system becoming more ordered on a whole chain scale, random copolymers preferring homopolymers as nearest neighbors. Snapshots taken for $\epsilon_{AB}/k_BT = 0$ and 1.0 are given in Figures 1 and 2. The segregation of the chains is clearly visible, although some chain interpenetration occurs in the last case. Figure 3 shows examples of the distribution of centers of mass for these energy values. The more ordered structure for $\epsilon_{AB}/k_BT = 1.0$ is obvious.

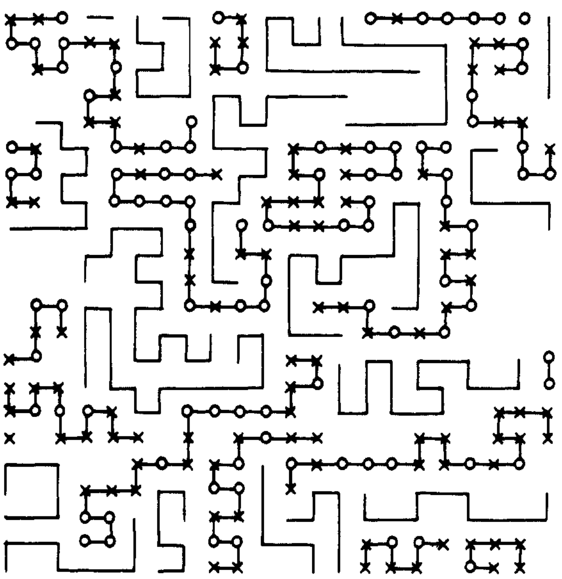

Figure 2. Snapshot pictures of random copolymer/homopolymer mixture, with $\epsilon_{AB}/k_BT = 1.0$, where A and B are the segments of the random copolymer. Situation obtained after 11×10^6 attempted reptation moves. (O) A; (×) B; solid line represents homopolymer.

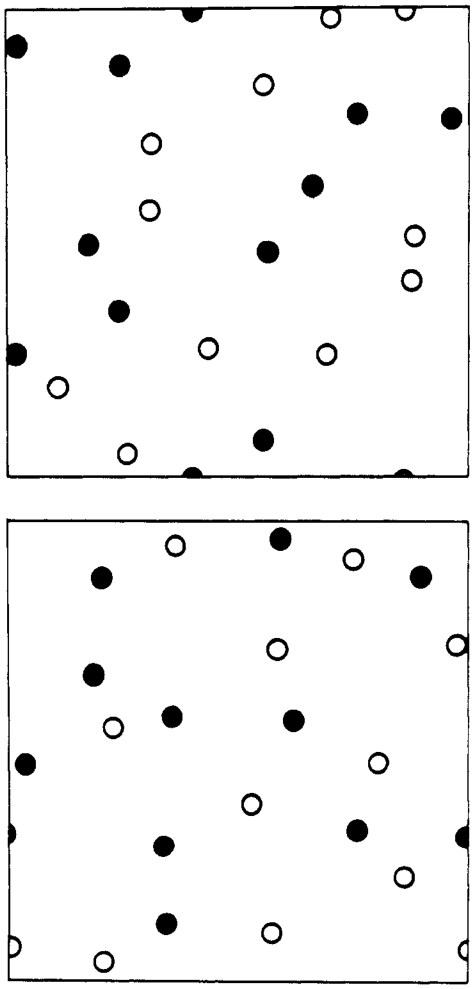

Figure 3. Snapshot pictures of the distribution of the centers of mass of the chains for a random copolymer/homopolymer mixture. Situation obtained after 11×10^6 attempted reptation moves. (O) homopolymer chain; (●) random copolymer chain; (top) $\epsilon_{AB}/k_BT = 0.0$; (bottom) $\epsilon_{AB}/k_BT = 1.0$.

In summary we see that the presence of the repulsion effect does not lead to substantial interpenetration of chains for moderate values of ϵ_{AB}/k_BT. Entropically, it is less unfavorable to have both an internal reorganization of the random copolymer and a more ordered external structure. Since in many blends of homopolymers the relatively strong endothermic interactions between the

Macromolecules 1989, *22*, 4631–4635

structural groups of the pure components are the real driving force for miscibility, this conclusion may well be valid for a large class of systems.

Concluding Remarks

The main objective of this study was to investigate in some detail the effect of the intramolecular repulsion on the chain conformations for mixtures of polymers. A new aspect turned out to be the reorganization of the random copolymer into "micellelike" structures, a feature already observed experimentally. There are strong indications that the shape of the polymers is influenced as well. At present this is investigated in detail.[30]

Another interesting observation concerns the possibility that polymers that are immiscible in three dimensions become miscible in two dimensions. This is due to the fact that the number of segmental interactions that one chain has with all other chains is proportional to the number of segments, N, per chain in the first case, whereas in two dimensions this number is proportional to the square root of N, because in two dimensions segregation dominates at least as long as the interactions are slightly unfavorable, which is the relevant situation to consider. Monte Carlo simulations to study the influence of crossover from three dimensions to two dimensions on the miscibility and the conformations of polymers have been started.

Acknowledgment. J.H.V. thanks H. van der Werff for computational assistance. The critical remarks by one of the reviewers are gratefully acknowledged.

References and Notes

(1) Baumgärtner, A. *Polymer* **1982**, *23*, 334.
(2) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell Univ. Press: Ithaca, NY, 1979.
(3) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Polym. Commun.* **1987**, *28*, 180.
(4) Baumgärtner, A. *Polymer* **1986**, *27*, 1777.
(5) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1988**, *21*, 446.
(6) Kremer, K.; Binder, K. *Comp. Phys. Rep.* **1988**, *7*, 259.
(7) Kambour, R. P.; Bendler, T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(8) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(9) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(10) Lai, C. H.; Paul, D. R.; Barlow, J. W. *Macromolecules* **1988**, *21*, 2432.
(11) Ellis, T. S. *Macromolecules* **1989**, *22*, 742.
(12) Liquori, A. M.; Anzuino, G.; Coiro, V. M.; d'Alagni, M.; de Santis, P.; Savino, M. *Nature* **1965**, *206*, 358.
(13) Michaels, A. S. *Ind. Eng. Chem.* **1965**, *57*, 32.
(14) Sutton, R. C.; Thai, L.; Hewitt, J. M.; Voycheck, C. L.; Tan, J. S. *Macromolecules* **1988**, *21*, 2432.
(15) Kron, A. K. *Polym. Sci.* **1965**, *7*, 1361. Kron, A. K.; Ptitsyn, O. B. *Polym. Sci. USSR* **1967**, *9*, 847. Kron, A. K.; Ptitsyn, O. B.; Skvortsov, A. K. *Mol. Biol.* **1967**, *1*, 487.
(16) Wall, F. T.; Mandel, F. *J. Chem. Phys.* **1975**, *63*, 4592. Mandel, F. *J. Chem. Phys.* **1979**, *70*, 334.
(17) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(18) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *84*, 1922.
(19) Bishop, M.; Frinks, S. *J. Chem. Phys.* **1987**, *87*, 3675.
(20) Straatsma, T. P.; Berendsen, H. J. C.; Stam, A. *J. Mol. Phys.* **1986**, *57*, 89.
(21) Allan, G. A. T. *Phys. Rev. B.* **1970**, *1*, 352.
(22) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(23) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* **1951**, *73*, 1904.
(24) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper: London, 1971.
(25) Wall, F. T., Seitz, W. A. *J. Chem. Phys.* **1977**, *67*, 3722.
(26) Curro, J. G. *Macromolecules* **1979**, *12*, 463.
(27) Domb, C.; Fisher, M. E. *Proc. Cambridge Philos. Soc.* **1958**, *54*, 48.
(28) Sariban, A.; Binder, K. *Macromolecules* **1988**, *21*, 711.
(29) ten Brinke, G.; Ausserre, D.; Hadziioannou, G. *J. Chem. Phys.* **1988**, *89*, 4374.
(30) van Vliet, J. H.; ten Brinke, G., unpublished results.
(31) Experimentally a thickness effect on the phase separation temperature of polystyrene–poly(vinyl methyl ether) blends was found for film thicknesses smaller than 1 μm. Reich, S.; Cohen, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1255.
(32) Note added in proof: In a recent publication (*J. Phys.* (*Les Ulis, Fr.*) **1989**, *50*, 803) E. Raphaël argued that the critical value of χ for a monolayer is given by the usual three-dimensional expression $\chi_c \sim 1/N$. This conclusion is based on the assumption that two adjacent chains overlap in a region with an interface thickness inversely proportional to the square root of χ. This assumption implies that the interface thickness diverges for $\chi \to 0$, which is not at all obvious for a polymer system confined to a plane, since there chains are segregated even for $\chi = 0$.

Thermal Characterization of Block Copolymer Interfaces

X. Quan,* H. E. Bair, and G. E. Johnson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974.

Received February 21, 1989; Revised Manuscript Received May 2, 1989

ABSTRACT: A thermal technique to determine the volume fraction of interfacial material in microphase-separated block copolymers is described. By measurement of the enthalpy relaxation that results from annealing at a temperature between the glass transition temperatures of the blocks, the total content of interfacial material can be determined. The technique assumes that the interface can be modeled as a series of discrete fractions with glass transition temperatures (T_g's) between the T_g's of the blocks which contribute independently to the excess enthalpy observed in a differential scanning calorimetry experiment. Several examples involving block copolymers and block copolymers blended with homopolymers are given to illustrate the utility of the method, which also may be extended to study other microphase-separated systems, such as filled composites and semicrystalline polymers.

Introduction

Interfacial or "interphase" material plays an important role in the mechanical properties of microphase-separated block copolymer systems. This is true especially for weakly segregated systems where the interfacial volume fraction is high. Due to conformational constraints on the polymer chains, the thickness of interfacial regions in polymer systems is large compared to those in low molecular weight mixtures and is generally on the order of a few nanometers.[1] However, the regions become much thicker, on the order of tens of nanometers and approaching the size of the microdomains, as the interaction energy and micro-