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Polymer Miscibility in Capillaries

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SYNOPSIS

A thermodynamic analysis predicts an increase in miscibility, relative to that in the bulk state, for a polymer mixture confined in a capillary with a diameter of the order of the size of the polymer coils. This is derived by using both the concepts of growing domains and a consideration of the thickness of polymer-polymer interfaces. The analysis is combined with a Monte Carlo lattice simulation that provides results on such confined systems. Intermixing, described in terms of the number of heterocontacts and the dimensions of the polymer chains in the capillary parallel and perpendicular to the tubular axis, is investigated. The results confirm that demixing in homogeneous mixtures is hindered, whereas intermixing is enhanced, in the capillary relative to that in the unconfined mixture. © 1992 John Wiley & Sons, Inc.

Key words: miscibility of polymers in capillaries • capillary, effect on miscibility of polymers confined in • thermodynamics of miscibility of polymer mixtures in capillaries

INTRODUCTION

The importance of polymer interfaces, surfaces, and various confinements of polymer systems is generally accepted and plays an important role in practice. In the present contribution we study the effect of confinement of a polymer mixture in an infinite tube with a diameter of the order of magnitude of the polymer coils. The main objective is to determine the effect of such confinement on miscibility in the mixture. A possible application of this study is in systems with the following geometries: cylindrical microdomains in block copolymer mixtures, blends in porous media having many tubelike channels, filled blends, and processing problems. We have found only one reference¹ dealing specifically with this problem on the basis of thermodynamic considerations. In the present work we present simple thermodynamic arguments to assess changes in miscibility due to the confinement of a mixture in a tube; we also present the first results for such systems obtained by Monte Carlo simulation.

THERMODYNAMIC EFFECT OF CAPILLARY CONFINEMENT ON POLYMER MISCIBILITY

The work of Raphael¹ suggests that for a tube of diameter $D \ll aN^{1/4}$ (where N is the number of monomers per chain and a is a typical monomer size), the critical miscibility increases as

$$\chi_c \propto \left(\frac{a}{D}\right)^4 \quad (1)$$

where χ_c is the usual critical segmental interaction parameter. The respective tube walls are assumed here and throughout this contribution to be non-interactive and to present only a geometric constraint. This result suggests that miscibility is affected only for very small D/R ratios, i.e., for tube diameters smaller than the root mean square (RMS) of the coil dimension (R is the diameter of an unconfined polymer chain in the bulk melt, and for an ideal chain $R_0 = aN^{1/2}$). We anticipate here that miscibility is also affected for larger D/R ratios and for tube diameters equal to or greater than the coil dimension. We will first present simple phenomenological reasoning for this conclusion in morphological terms. Consider a binary polymer system undergoing demixing in a capillary tube. During demixing, when a growing domain reaches a char-

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acteristic dimension of the order D , larger domains cannot effectively be produced. Fusing domains of the same component along the length of the capillaries is restricted since a large potential energy barrier must be overcome. This barrier is formed by the presence of domains containing the other phase-separated component along the tube. Since a given domain of size D is constrained in two orthogonal directions and can grow only along the axis of the tube, it cannot mediate fusion of the other kinds of domains present on either side parallel to the tube axis. Deformation of the domain by narrowing to enable the neighboring domains of the opposite species to pass, leads to the growth of an unfavorable energy interface and thus has low probability. This situation is depicted in Figure 1.

The reasoning that a quasi-equilibrium domain size formed during demixing is of the order of the tube diameter is valid for ratios $D/R \geq 1$ because domains in very narrow tubes cannot decrease in size during demixing below the limits given by the chain dimensions. In fact, the domain length formed by "elongated cigars" comprising single chains in this case obviously increases.

Next we present an alternative approach based on a consideration of the interfaces present in a partially miscible blend. This approach not only will show that the effect is not limited to very narrow capillaries but also will provide a semiquantitative relation governing the effect of confinement on demixing. We start with a homogeneous, miscible blend in a tube. This mixture has in effect an infinite interfacial thickness L (1 in Fig. 2). As the mixture

Figure 1. Schematic representation of growing domains demixing in a capillary.

Figure 2. Schematic representations of decreasing interfacial thickness L during demixing, depicting composition profiles at the interface. When $L = D$, the first macrophase appears in the tube, effectively limiting further demixing.

begins to demix, the interfacial thickness decreases. While L exceeds D , demixing can proceed further since the diffusive miscible region is wider than D and the tube is fully open to the exchange of material. Panel 2a in Figure 2 depicts the situation in which the interfacial thickness is equal to the tube diameter, $L = D$, and shows a composition profile at the interface in the capillary for the case in which the interface is oriented parallel to the tube axis. For the orientation of the interface shown, a pure phase grows along the tube walls. Thus opposite walls develop pure polymer components A (or B). The orientation and position of the interface in the tube is, however, arbitrary. Panel 2b in Figure 2 shows the situation with different orientation of the interface in which the interfacial thickness is equal to the tube diameter, $L = D$. As pointed out above, a particular orientation of the interface within the tube cannot be preferred a priori. Situations 2a and 2b are then equivalent since we can expect both orientations of the interface to be present when the first macrophase appears in the system. In case 2b, instead of a thin layer of a new phase growing along the walls, a narrow layer of a single phase which spans the tube diameter appears. Since in both cases the first macrophase appears, at the same point in the demixing process, it must do so at the same $L = D$ interfacial thickness. (The redistribution of the interface orientation from a single long interface parallel to the tube to several perpendicular interfaces is expected and corresponds to a randomness in the formation of microdomains.) From this ar-

gument, we can see that the identity $L = D$ is critical for miscibility in a capillary. Further demixing narrows the interfacial thickness L , and this increases the domain size of each component across the tube diameter (3 and 4 in Fig. 2). This prevents further fusing of domains of the same type by separating the domains with an impenetrable area formed by the respective domains. From the above analysis we can obtain a simple relation for critical miscibility. We adopt the hypothesis that an interfacial thickness equal to the tube diameter is critical for miscibility and use the relation for L obtained by Helfand,² i.e.,

$$L = 2a \left(\frac{m}{\chi} \right)^{1/2} \quad (2)$$

where m is a lattice constant defined so that the number of nearest neighbors in the same layer parallel to the interface is $z(1 - 2m)$ and in the adjacent layers is zm , where z is the number of nearest neighbors of the lattice. For a simple cubic lattice, $m = 1/6$. From the critical condition $L_c = D$ we find

$$\chi_c \cong 4m \left(\frac{a}{D} \right)^2 \quad (3)$$

which is valid for $D \leq L$. For $D > L$, the system behaves as if it were unconfined, i.e., in a regime where the mixing/demixing transition is governed by $\chi N \sim 1$. For the limit $D = L$, we thus have $D = L \propto a\chi^{-1/2} \propto aN^{1/2}$. Inserting this D into (3), we recover the standard three-dimensional value $\chi_c \sim 1/N$.

In eq. (3) we recover the inverse proportionality of χ_c to D , similar to eq. (1) obtained by Raphael,¹ except that in eq. (3) the exponent is -2 rather than Raphael's value of -4 . It is worth mentioning that Roe³ obtained a proportionality, $L \propto \chi^{-1/4}$, for a polymer-polymer interfacial thickness; if we were to use this result, we would obtain the same scaling as Raphael. However, the proportional $L \propto \chi^{-1/2}$ used here appears to be generally accepted and is also related to a second generally accepted relation for the interfacial tension in which $\gamma \propto \chi^{1/2}$. Thus the main result from the above consideration is that we have obtained a relation for χ_c in a capillary with a different proportionality to D compared to that given in ref. 1, and an assertion that the validity of this relation is not restricted to very small D/R ratios, which is the main difference in the assumption made here and those in the paper of Raphael.

MONTE CARLO SIMULATION

The simulation of a polymer mixture consisting of A and B chains in a tube was performed on a cubic lattice where the tube was approximated by a rectangular section formed by $d \times d \times l$ lattice sites, where l is the length of the capillary. The side walls of the section (the outer layers of the $d \times l$ sites on each of the four sides) were occupied by noninteractive beads representing hard wall excluded volume constraints for the chains. Excluding this outer layer of sites forming the walls of the tube, the tube diameter representing the confinement is then $D = d - 2$. In contrast, at both the top and bottom of the parallelepiped, periodic boundary conditions were applied to these end caps in the direction of the tube axis. Two cases were investigated. System 1 was a system with chains comprising $N = 20$ segments and with $l = 22$, $D = 2, 4$, and ∞ . (The results for infinite D were identical to previous results⁴ for bulk unconfined blends with periodic boundary conditions applied in all directions.) The volume fraction occupied by the polymer segment was $\phi = 0.909$; polymer segment occupied one site. The residual fractional volume of 0.0909 was occupied by empty sites. System 2 was less dense and contained longer chains: $\phi = 0.789$, $N = 30$, $l = 38$, and $D = 2, 4, 6, 8$, and 18.

For both cases, the calculations for a given D started with a randomized configuration obtained from an assembly of parallel alternating A and B chains located on the lattice. All chains had equal numbers of segments and the mixture composition was always 50/50 in A/B chains. Order then was erased by allowing the chains to reptate until a random configuration was attained. Such a configuration represents a situation with a zero segmental interaction energy (i.e., $\epsilon = 0$). The equilibration of all states then began from this random configuration. The simulation of different states was initiated by imposing a nonzero reduced interaction energy $\epsilon' \equiv \epsilon/kT$ between adjacent lattice sites occupied by different segments. All other nearest-neighbor interactions between segments of the same type and between void sites and polymer segments were considered to be of zero energy. The system was subjected to random reptation of the chains until equilibrium representing the balance between the imposed energy and the entropy arising from sampling of possible multichain configurations was reached.

Thermodynamic averages were calculated according to the usual Metropolis rules. The number of needed reptation trial moves was dependent on statistics; for narrow tubes, longer equilibration

times were necessary. In fact, we experienced a considerable "slowing down" in comparison to the previously investigated analogous unconfined systems.⁴ Equilibration was terminated after the derived thermodynamic quantities began to fluctuate around the average values. The longest equilibration times involved 3.5×10^8 trial moves. The acceptance ratio of trial moves was in the range 0.1 to 0.22.

The thermodynamic variables calculated included the average number of heterocontacts N_{AB} per chain characterizing the level of intermixing, and the dimensions of the chains in the tube. We calculated the overall mean square end-to-end distance of the chains $\langle R^2 \rangle$ and one of the components parallel or perpendicular to the tube axis, since

$$\langle R^2 \rangle = \langle R^2 \rangle_{\perp} + \langle R^2 \rangle_{\parallel} \quad (4)$$

where $\langle R^2 \rangle_{\parallel} \equiv \langle R_z^2 \rangle$ is the contribution along the tube axis z and $\langle R^2 \rangle_{\perp} \equiv \langle R_x^2 \rangle + \langle R_y^2 \rangle$ is that perpendicular to the tube. Chains traversing the top or bottom of the tube had to be "unwrapped" to calculate their geometric averages. The chain dimensions could be accumulated into a single calculated variable because of the symmetric composition of the blend and the identical lengths of both chain types.

RESULTS AND DISCUSSION

Figures 3 and 5 show raw data on the intermixing level in the tube in terms of the number of heterocontacts N_{AB} per chain as a function of the reduced

Figure 3. Number of heterocontacts per chain in system 1 as a function of reduced interaction energy ϵ' for various confinements: (●) $D = 2$; (◇) $D = 4$; (○) $D = \infty$.

Figure 4. Reduced number of heterocontacts $N_{AB}(\epsilon')/N_{AB}(\epsilon' = 0)$ in system 1 as a function of ϵ' for different D : (○) $D = \infty$; (◇) $D = 4$; (●) $D = 2$. The points are connected for illustrative purposes only.

interaction energy ϵ' for different tube diameters. In Figure 3 it is seen that the confined mixture generally shows lower values of N_{AB} relative to the unconfined mixture. This reflects the presence of walls in the confined system. The walls effectively reduce the number of contacts between the chain segments since a fraction of the possible chain contacts is necessarily ascribed to wall-segment geometries. This effect is of course more pronounced for smaller tube diameters. We can express the wall effect on the number of heterocontacts for each tube diameter in terms of the fraction $f = N_{AB}(D, \epsilon' = 0)/N_{AB}(D = \infty, \epsilon' = 0)$, using data for the athermal mixture. Thus for the system with $N = 20$, we obtain $f = 0.68$ for $D = 4$ and $f = 0.3$ for $D = 2$, which illustrates the extent of the wall effect. To determine the true effect of confinement on the intermixing of A and B chains in a system, the raw N_{AB} data were normalized by subtracting the effect of the walls. This could be done in several ways. A mean-field estimate for the effect using lattice considerations and occupation probabilities could be made, but we prefer to avoid mixing mean-field and Monte Carlo results. Another possibility is to directly calculate the number of contacts with the walls in the MC calculation, but this approach would lead to a large increase in computation time. For self-consistency, a different concept was adopted. When comparing data for different D , we have divided the number of calculated heterocontacts by a factor $N_{AB}(\epsilon' = 0)$ calculated for the athermal homogeneous system with the same D . The normalized values $N_{AB}(\epsilon')/N_{AB}(\epsilon' = 0)$ for a range of D 's could then be compared. Results for tubes of different diameters have the same value for

the athermal case, $\epsilon' = 0$. The results of this treatment are shown in Figure 4, in which it is seen that the decrease in intermixing when considering more positive interactions is more pronounced for large D (i.e., miscibility is enhanced in narrower tubes). This can also be seen directly in Figure 3. The decrease in N_{AB} on going from the athermal system (in the miscibility region) to demixing is larger for an unconfined (or large D) system than for one with a small tube diameter. From our previous study,⁴ the demixing transition of an unconfined system containing these chain lengths is at $\epsilon'_c = 0.05$. The same trend as seen in the $N = 20$ system can also be seen for the second case where $N = 30$, $\phi = 0.789$; these results are shown in Figure 5.

The above discussion has concentrated on the demixing process. Intermixing in the miscibility region is also of interest. Data from the $N = 20$, $\phi = 0.909$ case yields values of $N_{AB}(\epsilon' = -0.2)/N_{AB}(\epsilon' = 0) = 1.28, 1.38$, and 2.06 for $D = \infty, 4$, and 2 , respectively, showing an increased intermixing for narrow tubes in the homogeneous region. Data from the $N = 30$, $\phi = 0.789$ system exhibit the same effect: i.e., $N_{AB}(\epsilon' = -0.1)/N_{AB}(\epsilon' = 0) = 1.27, 1.4$, and 2.38 for $D = 8, 4$, and 2 , respectively.

As shown above, miscibility is affected for strong confinements where the tube diameters decrease to the order of the polymer chain dimensions. The question of how individual chains behave under these conditions in terms of their shape also arises. With this in mind, the mean-square end-to-end dis-

Figure 5. Number of heterocontacts per chain in system 2 as a function of reduced interaction energy ϵ' for various confinements: ($\diamond$) $D = 2$; ($\circ$) $D = 3$; ($\blacktriangle$) $D = 6$; ($\triangle$) $D = 8$; ($\bullet$) $D = 18$.

Figure 6. Configurational properties of chains expressed as $\langle R^2 \rangle$, $\langle R^2 \rangle_{\perp}$, $\langle R^2 \rangle_{\parallel}$ for the athermal ($\epsilon' = 0$) system 2 as a function of tube diameter D shown in lattice spacing units. The points are connected for convenience.

tance of the chains $\langle R^2 \rangle$ and the decomposed components parallel and perpendicular to the tube, $\langle R^2 \rangle_{\parallel}$ and $\langle R^2 \rangle_{\perp}$, have been investigated. The results are shown in Figure 6 for the $N = 30$ athermal mixture, $\epsilon' = 0$. The result for large D asymptotically approaches a value close to that obtained by Olaj and Lantschbauer⁵ for an unconfined pure polymer melt (i.e., $\langle R^2 \rangle = 45.9$ for $N = 30$, $\phi = 1$ also obtained by Monte Carlo simulation on a cubic lattice). As the tube thickness is decreased from large D , the overall chain dimension slightly decreases, and we see that it is the perpendicular component $\langle R^2 \rangle_{\perp}$ that accounts for this while the $\langle R^2 \rangle_{\parallel}$ component remains constant. In this regime, the walls merely bend those chains lying at the boundary and reflect parts of these chains back into the bulk mixture, an effect that decreases $\langle R^2 \rangle$. After a critical confinement is reached, the chains have less freedom in configuration space and can only extend along the tube axis. For strong confinements with small D , there is therefore a sharp increase in $\langle R^2 \rangle_{\parallel}$ and $\langle R^2 \rangle$. A minimum appears in $\langle R^2 \rangle$ versus D as a result of opposing tendencies in $\langle R^2 \rangle_{\perp}$ and $\langle R^2 \rangle_{\parallel}$ because of the functional dependence of these parameters on D .

Further analysis of both components $\langle R^2 \rangle_{\perp}$ and $\langle R^2 \rangle_{\parallel}$ is useful. According to Daoud and de Gennes,⁶ the predicted dimension of polymer chains in a concentrated system of chains in a capillary measured along the capillary axis varies as $R_{\parallel} \propto N/D$ for confinements in which D is less than the size of a free polymer coil. Later this proportionality was

corrected^{7,8} by the relation $R_{\parallel} \propto N/D^2$ for confinements with $D \ll aN^{1/4}$ and this latter was used also by Raphael.¹ The data for $\langle R^2 \rangle_{\parallel}^{1/2}$ are plotted in Figure 7 against both $1/D$ and $1/D^2$ and we find more support for the second proportionality over the whole range of confinements, including a weaker than expected confinement for the entire valid range of the second proportionality. The perpendicular component $\langle R^2 \rangle_{\perp}^{1/2}$ varies linearly (see Fig. 8) with D below the critical tube thickness, approximately $D = 7$; for large D , $\langle R^2 \rangle_{\perp}^{1/2}$ asymptotically approaches its value in the bulk unconfined state $\langle R^2 \rangle_{\perp} = 2\langle R^2 \rangle/3$. Using these results, we found it instructive to express the degree of confinement λ relative to the free chain dimensions and to estimate its value where the individual chains become affected by the geometric boundaries. We define the coefficient, $\lambda \equiv D/2R_g$, where the radius of gyration of a linear unconfined chain is given as usual by $R_g = (\langle R^2 \rangle/6)^{1/2}$. If we use the value of Olaj and Lantschbauer⁵ for $\langle R^2 \rangle$ of unconfined chains and $D = 7$ for the start of the change in behavior in both $\langle R^2 \rangle_{\perp}$ and $\langle R^2 \rangle_{\parallel}$, then we obtain a value for the critical confinement of $\lambda = 1.27$. Even though the present data are limited, it is possible to estimate the parameter λ at the onset of the effect of confinement on the mixing process. From Figure 4, a rough estimation of λ is 1.1 for the $N = 20$ case, using $D = 5$ and the value of $\langle R^2 \rangle$ for unconfined chains from our previous investigation.⁴ From Figure 5, an analogous estimate for the $N = 30$ case, using $D = 7$ leads to the same value $\lambda = 1.27$ for λ as that obtained from the configurational properties above. These estimates suggest again that miscibility in the

Figure 7. Chain dimensions parallel to the tube axis $\langle R^2 \rangle_{\parallel}^{1/2}$ as a function of $1/D$ ($\diamond$) and $1/D^2$ ($\circ$) in the athermal ($\epsilon' = 0$) system 2.

Figure 8. Chain dimensions perpendicular to the tube axis, $\langle R^2 \rangle_{\perp}^{1/2}$, as a function of D in the athermal system 2.

capillary begins to be affected when the tube diameter decreases to the size of the polymer chains.

Figures 9 and 10 show the chain dimensions in the mixture after interaction between chains is introduced for the system with $N = 30$. In Figure 9 we see that a negative ϵ' leading to intermixing also leads to the expansion of the chains. However, expansion is experienced only along the tube axis while $\langle R^2 \rangle_{\perp}$ is constant with ϵ' because in this case the confinement $D = 4$ is below the critical level ($D = 7$) and the very narrow capillary in this case does not allow coil expansion in the perpendicular direction.

Figure 9. Number of heterocontacts per chain, N_{AB} ($\square$), and chain dimensions: ($\blacktriangle$) $\langle R^2 \rangle$, ($\circ$) $\langle R^2 \rangle_{\perp}$, as a function of ϵ' for a single confinement, $D = 4$, in system 2.

Figure 10. Mean chain dimensions $\langle R^2 \rangle$, $\langle R^2 \rangle_{\perp}$, $\langle R^2 \rangle_{\parallel}$ in system 2 as a function of D for interaction energy $\epsilon' = 0.1$: ($\diamond$) $\langle R^2 \rangle$; ($\bullet$) $\langle R^2 \rangle_{\perp}$; ($\circ$) $\langle R^2 \rangle_{\parallel}$; and for interaction energy $\epsilon' = -0.1$: ($\triangle$) $\langle R^2 \rangle$.

Figure 10 depicts $\langle R^2 \rangle$ and its components as a function of D for a positive, $\epsilon' = 0.1$, and a negative, $\epsilon' = -0.1$, value. In the former case of repulsion, demixing leads to a decrease in chain dimensions. However, this decrease is relatively small since most of the chains experience the homopolymer melt environment in their own domains after demixing in the blend that is symmetric in composition. This was also observed previously for a symmetric unconfined blend.⁴ In the case of a compositional asymmetry, the minority chains collapse in the partially miscible blend, leading to a pronounced decrease in chain dimensions; this has been observed in recent experiments.⁹ Apart from a vertical shift depicting the decrease in dimension, the shape of the curves for $\epsilon' = 0.1$ is unchanged. For negative interactive energies, $\epsilon' = -0.1$, we also observe expansion of the chains in unconfined systems.⁴ The effect of expansion is more pronounced for strong confinements with smaller D . A strong tube confinement may possibly be coupled with an attractive interaction leading to intertwined extended chains or to a parallel chain register.

These results are quantitatively influenced by the lattice approximation used; however, qualitative differences in the results obtained by off-lattice simulations or by using a different lattice is not anticipated. The effect of corners present in the rectangular lattice section used may also perturb the quantitative results relative to the cylindrical case.

CONCLUSIONS

We present the first data on polymer blend miscibility in a capillary and show that miscibility in the tube begins to be affected in the same range of confinement λ in which the polymer chain configuration itself begins to be influenced (i.e., where the tube diameter D approaches the dimensions of the chains in the mixture). This indicates that miscibility is increased in a broader region of confinements relative to the polymer chain dimension than had been predicted previously.

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