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# Effects of the Chain Architecture on the Miscibility of Symmetric Linear/Linear and Star/Star Polymer Blends

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ABSTRACT: The effects of chain architecture on the miscibility of polymer blends were studied by means of Monte Carlo simulations. Using the bond fluctuation model on a simple cubic lattice, we were able to simulate symmetric linear/linear and—for the first time—star/star blends with a moderate number of arms. The simulations were made at a volume fraction of occupied lattice sites $\varphi = 0.5$, which corresponds to dense polymer mixtures for this algorithm. In particular, we studied star/star blends with 4, 8, and 12 arms and the respective linear blends, all having the same total number of units equal to 121. The critical points for the different blends indicated that the miscibility increased greatly when the number of arms $f$ was increased. Our results are in agreement with recent analytical findings.

## Introduction

Many polymeric materials are multicomponent systems. In an effort to design a material that can combine favorable characteristics of individual components, one can alloy chemically different polymers. The question of miscibility and immiscibility arises for each particular blend. In general, miscibility is unusual for blends of high molecular weight polymers. In recent years it has been increasingly noted that the phase behavior of multicomponent polymers can be changed not only by varying their molecular weight and their intercomponent interactions $\chi$ but also by modifying the molecular design of the molecules.[1−3] Factors such as the stiffness and the chain architecture can affect the phase behavior of a material. The substitution of star polymers for linear ones of the same type and molecular weights causes changes in the phase diagram due to shielding in the core region.[1,2] Neighboring molecules, both linear and star, are not able to penetrate the star center since the concentration of monomers in the core is high. The extent of the changes in the phase diagram would be expected to vary with the number and length of star polymers. Experimentally, the phase behavior of the poly(vinyl methyl ether) (PVME)/polystyrene (PS) blends, which exhibit a lower critical solution temperature (LCST), was studied.[1,2] The cloud-point curve, allowing determination of the demixing temperature, was detected by wide-angle light scattering or by optical microscopy. Faust et al.[1] compared samples containing a 22-arm PS star blended with linear PVME to the linear/linear blend comprising components of the same molecular weight ($M_{\mathrm{w,star}} = 1\,280\,000$, $M_{\mathrm{w,linear}} = 99\,000$). They found that the cloud-point curve for the star/linear blend was elevated by ∼4 °C. Russell et al.[2] studied the same chemical blends, but using star polymers with four arms having a much shorter arm length ($M_{\mathrm{w,star}} = 221\,000$, $M_{\mathrm{w,linear}} = 149\,000$). In their case, the elevation of the cloud-point curve was ∼10 °C. To describe polymer blends having nonlinear architecture, the original Flory−Huggins theory[4] required nontrivial improvements due to the single contact interactions between chains considered in this model. Garas et al.[3] incorporated chain correlations between the chains in the blend. The one-loop diagrams that describe the two-point correlations between Gaussian chains are determined at the critical dimensionality $d = 4$. The contribution of the higher order diagrams is estimated through reexponentiation of the first-order results. The model was able to explain the experimental findings.[1,2] The main conclusion of the theory is that star/linear blends are more miscible than are the respective linear/linear blends, and the difference in miscibility is decreased when the molecular weight of the polymer chains is increased. Moreover, it was found that star/star blends are more miscible than the linear/linear blends, and for constant molecular weights this miscibility increases when the functionality of star polymers is increased.

Because of the lack of any experimental results concerning star/star blends, the results of the theory can be checked only through appropriate simulation studies. In the present work we have performed Monte Carlo simulations for linear/linear and star/star blends using the bond fluctuation model[5−11] (BFM). All blends are symmetric having the same number of A or B type chains of the same length and functionality. We have considered stars with 4, 8, and 12 arms in a simple cubic lattice at a volume fraction of occupied lattice sites $\varphi = 0.5$, which corresponds to dense polymer blends for this algorithm.[6,10] We have computed the radius of gyration of polymer chains, the ratio between the distances of the center of masses between A−B and A−A type chains and the collective scattering of the blends. The critical points obtained from the latter properties were used for the comparison with the theory.[3]

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## Simulation Method

**(a) Linear/Linear Blends.** In our simulations, we place $n$ linear molecules, each composed of 121 units in a cubic lattice of length $L$ with periodic boundary conditions. The distance between adjusted sites, $b$, is taken as the unit of length. Each unit blocks the other 26 lattice sites contained in the elementary cube centered at the bead location. In this way, the model complies with the restriction imposed for self-avoiding walk (SAW) polymers. This SAW condition is completely equivalent to the description given for the original model of Carmesin et al.[6] when eight-site nonoverlapping monomers are replaced by single-site beads. Bonds linking the beads can have lengths ranging between 2 and $\sqrt{10}$, but bonds vectors of the type ($\pm 2, \pm 2, 0$) are excluded in order to avoid bond crossing during the simulation. The value of $L$ ($L = 124$) should be high enough to ensure that the number of interactions between different replicas of the same molecules is very small, $L \geq 2N^{1/2} + 5l$, where $l$ is the root-mean-squared bond distance ($l = 2.72$). The number of chains is determined from the desired number of sites blocked by the polymer beads,[7] equivalent to the polymer volume fraction, $\Phi = 8nN/L^3 = 0.5$, corresponding to the polymer blend for this model. Half of the chains are assigned randomly as A type polymer chains, and the rest are assigned as B type chains. This way the initial configuration for symmetric linear/linear blends is obtained. Interactions between nonneighboring beads placed at distances smaller than $\sqrt{10}$ are considered according to the BFM proposed by Wittkop et al.[8] This model takes into consideration interactions between the sites blocked by each pair of chain units in the original description. Actually, the global interaction energy for a specific pair of units can be extracted from a set of values depending only on the distance between the central sites of these units. The model also considers different values of bond energies, depending also on the type of bond vector.[9] The interaction energies are expressed in terms of three energy parameters between similar A−A, B−B or dissimilar A−B units, $\epsilon'_{AA}/k_BT = 0$, $\epsilon'_{BB}/k_BT = 0$, $\epsilon'_{AB}/k_BT = \epsilon_{AB} > 0$. These thermodynamic interactions are chosen so that as the blends exhibit a phase separation when the temperature is lowered, and so that the lattice voids are neutral.

The total energy of a configuration that complies with the SAW condition is the sum of all bond energies, together with all energies corresponding to intramolecular and intermolecular interactions between pairs of nonneighboring units. Configuration changes are obtained by using the "slithering snake" or "reptation" moves in which a bead is removed from a randomly chosen end of the chain and a new bead is inserted in a random position at the other end. If the SAW condition is fulfilled, the configuration is accepted or not through comparison of this new energy with the energy of the previous configuration, according to the standard Metropolis criterion. Typical trajectories for linear/linear blends consist of $10^7$ attempted movements per chain for equilibration followed by the same number of trajectories for the calculation of properties. We save the trajectory coordinates every $10^3$ configurations and calculate properties averaging the resulting samples.

**(b) Star/Star Blends.** We use the BFM to simulate melts of symmetric star/star polymer blends with different numbers of arms (4, 8, and 12). All the arms are of the same length in a given star molecule. As in the case of linear/linear blends, the total number of units in each molecule is 121 and the volume fraction is $\Phi = 0.5$. Because of the compact size of star polymers, we use much shorter boxes, namely $L = 84$, 72, and 56 for star blends with 4, 8, and 12 arms, respectively. To reach the melt density is especially difficult in the case of star blends with many arms. To overcome this problem, we consider an initial configuration in which the stars occupy regularly arranged initial positions (Figure 1). The arms run parallel from their second bead (neighboring to central unit) to their end, with straight bonds of $l = 1$ violating the BFM condition for the minimum bond length in a given direction. (In a previous paper,[5] we were unable to simulate star chains with $\Phi > 0.3$ using $l = 2$.) In the case of 12-arm stars these second beads are placed to comply with the model specifications using eight vectors ($\pm 2, \pm 2, \pm 1$), two vectors ($0, \pm 3, 0$), and two vectors ($0, 0, \pm 3$) with origins at the central unit. For the cases of 8- and 4-arm stars, eight vector ($\pm 2, \pm 2, \pm 1$) and four vectors ($\pm 2, -2, \pm 1$) are used respectively to connect the second beads to the central unit. The central units of different molecules are placed regularly in the system so that the maximum number of stars (usually not more than two in the $y$ direction) can be included in the simulation box. Equilibration can be performed from these preinitial configurations through elementary bead jump, with displacement vectors ($\pm 1, 0, 0$), ($0, \pm 1, 0$), and ($0, 0, \pm 1$). Once the move has been made, the lengths of the new bonds are checked for compliance with the BFM lengths. To facilitate further the mobility of star chains, a larger area of blocked units is established around the central unit. The distance between the central units and its first neighbors is permitted to increase up to 5 instead of the value $\sqrt{10}$ established for the other units. The new configuration is accepted if both the SAW and Metropolis criterion are fulfilled. Typically, $10^6$ Monte Carlo steps are required for equilibration from the initial configuration and to meet the conditions imposed on the BFM bond lengths. The assignment of A and B type chains and the calculation of properties are performed following the specifications described above for the linear/linear blends.

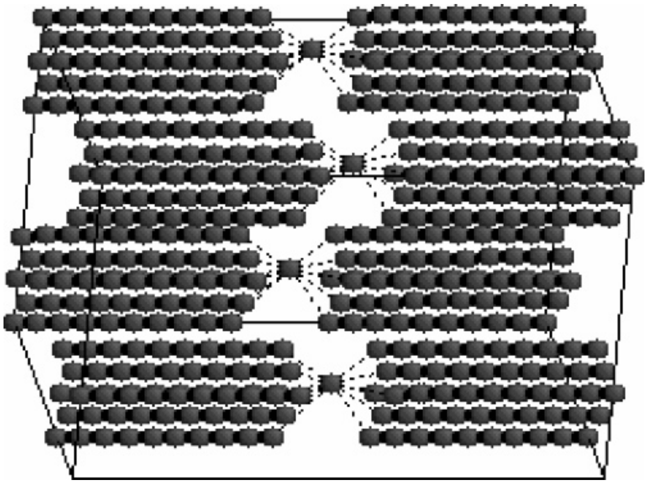

**Figure 1.** Preinitial configuration for star polymers with 12 arms and $N_A = N_B = 121$ in a cubic lattice. Only a part of the box is shown.

## Results and Discussion

The first property we have calculated here is the dimensionless ratio

$$\gamma = \frac{\langle R^2_{\mathrm{AB,centers}} \rangle^{1/2}}{\langle R^2_{\mathrm{AA,centers}} \rangle^{1/2}} \quad (1)$$

of the mean distances between the centers of mass of dissimilar chain species (A, B) to similar ones (A, A) or (B, B). This ratio plays the role of the "ordering parameter". In the case of chemically identical blends symmetrical in size and architecture,

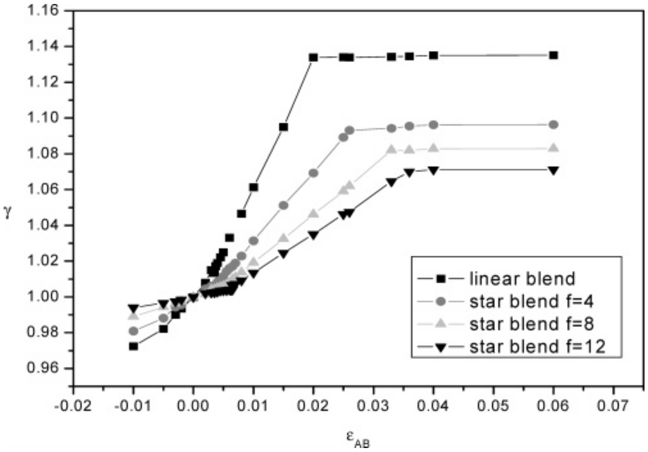

**Figure 2.** Ordering parameter $\gamma$ illustrated as a function of the interaction parameter between dissimilar units $\epsilon_{AB}$ for linear/linear and star/star blends.

the absence of repulsions between chains A and B leads to the random mixing of the chains and the ratio $\gamma$ takes the value 1. With the introduction of repulsion between A and B units, $\gamma$ increases since the distance between chains A and B also increases. In the thermodynamic limit, $\gamma$ is infinite for the phase-separated blends. In Figure 2, we present our results for the ordering parameter $\gamma$ for the linear/linear and star/star blends for various temperatures ($\epsilon_{AB} \sim 1/T$). The simulations start from the chemically identical blends, and then the temperature is lowered in increasingly larger steps. The last configuration of each blend was used as an initial configuration for the next run at the new (lower) temperature. It can be observed that the dependence of the ordering parameter on the interaction potential $\epsilon_{AB}$ between dissimilar units is sigmoidal. To show this behavior more clearly, we have also performed some simulations for blends with attractions between units A and B where the results for ratio $\gamma$ are smaller than 1. With an increase in $\epsilon_{AB}$ in star/star blends with 12 arms, the ordering parameter $\gamma$ increases linearly up to $\epsilon_{AB} = 0.0065$, a value that correspond to the critical temperature of the blend since we are dealing with a symmetric mixture. A further increase of the interaction parameter $\epsilon_{AB}$ leads to an abrupt breaking of symmetry, since the blend enters the two-phase region and ratio $\gamma$ shows the steepest increase with $\epsilon_{AB}$. The ordering parameter $\gamma$ reaches a plateau after $\epsilon_{AB} = 0.035$, a value in which chains A and B cannot be further separated because of geometrical constraints arising from the finite size box $L$ we use in the simulations. With an increase in the total volume the plateau value of $\gamma$ increases since the mean-square distances of the centers of dissimilar chains $\langle R^2_{AB,centers}\rangle$ increase, tending to infinity for $L \to \infty$. The variation of the ordering parameter $\gamma$ with the interaction parameter $\epsilon_{AB}$ for the rest of star/star and linear/linear blends is also sigmoidal. In the case of star/star blends with 8 arms, $\gamma$ also increases with $\epsilon_{AB}$, always showing higher values than those with 12 arms. This is a clear indication that a 12-arm star/star blend is more miscible than a star/star blend with 8 arms. A further decrease in the number of arms results in increased immiscibility, as can been observed in Figure 2, in accordance with recent theoretical results.[3] The critical temperatures obtained from this figure are $\epsilon_{AB} = 0.0036$, 0.0045, 0.0054, and 0.0064 for the linear/linear and the star/star blends with 4, 8, and 12 arms, respectively. The miscibility difference between a linear/linear and a 12-arm star/star blend, at least for short chains (121 segments $\sim M_w = 39\,000$ for PS), is very significant, remarking the interest of a possible experimental verification. An intuitive explanation of the miscibility difference between the linear and star blends is the following: In the linear/linear blends, the chains interpenetrate each other. Therefore, when the intensity of the heterointeractions is increased, the blend separates into two phases in order to reduce the heterointeractions. In the case of star/star blends with 4 arms, the interpenetration of units between different chains is difficult because of the small dimensions of the macromolecule which leads to a smaller number of heterointeractions, thus enhancing miscibility. The miscibility is increased when a higher number of arms is considered because the star chain becomes very dense, protecting even more units in the interior of the macromolecule from the presence of dissimilar units.

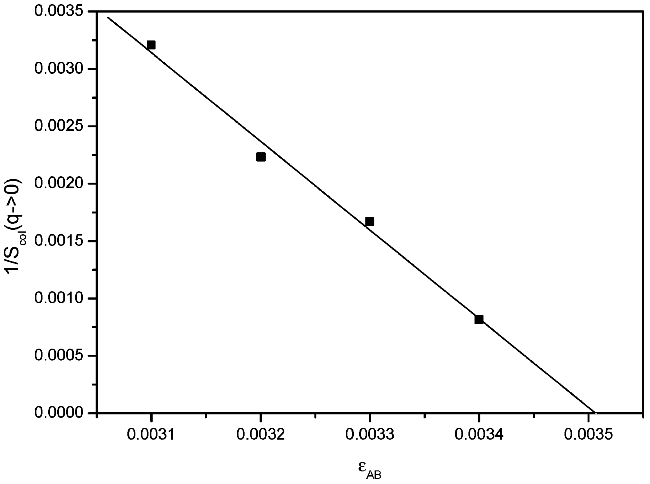

**Figure 3.** Plot of $1/S_{col}(q \to 0)$ vs the interaction parameter between dissimilar units $\epsilon_{AB}$ for linear/linear blends. The $x$ axis intersect estimates the critical temperature of the blend ($\epsilon_{AB} \sim 1/T$).

A more accurate estimate of the critical points can be obtained through the collective scattering function of the blends. The collective scattering function is computed as[7]

$$S_{col}(q) = 8L^{-3}\langle[\sum_i^{L^3} f_i \cos(\vec{q}\cdot\vec{R}_i)]^2 + [\sum_i^{L^3} f_i \sin(\vec{q}\cdot\vec{R}_i)]^2\rangle \quad (2)$$

where $f_i$ is the occupation state of the different sites located at $\vec{R}_i$, within the simulation box lattice. $f_i$ is given by $f_i = 1$ if site $i$ is occupied by unit A, $f_i = -1$ if site $i$ is occupied by unit B, or, finally, $f_i = 0$ if site $i$ is vacant or blocked. To compute $S_{col}(q)$, we must comply with the following restrictions imposed on $q$ by the periodic boundary conditions, according to the chosen box length

$$q_k = (2\pi/L)n_k, \quad k = x, y, z, \quad n_k = 1, 2, ... \quad (3)$$

According to the random phase approximation,[4] the inverse of the collective scattering function $[S_{col}(\vec{q})]^{-1}$ in the homogeneous phase region should vary linearly with $q^2$. The extrapolated values $[S_{col}(q \to 0)]^{-1}$ at $q \to 0$ are small positive numbers. With an increase in the repulsions between unlike units, a symmetric ($N_A = N_B$, $\Phi_A = \Phi_B$) polymer blend approaches the spinodal at the critical point, and $S_{col}(q \to 0)$ diverges. The critical point can be estimated from plots $[S_{col}(q \to 0)]^{-1}$ vs $\epsilon_{AB}$, assuming a linear relation[10] between the extrapolated inverse collective scattering function and the inverse temperature $\epsilon_{AB} \sim 1/T$

$$[S_{col}(\vec{q} \to 0)]^{-1} \sim \epsilon_{AB} \quad (4)$$

In Figures 3−6 we present our simulation results. To avoid possible microscale ordering phenomena in star/star blends, however, we have used greater $q$ vectors to obtain the

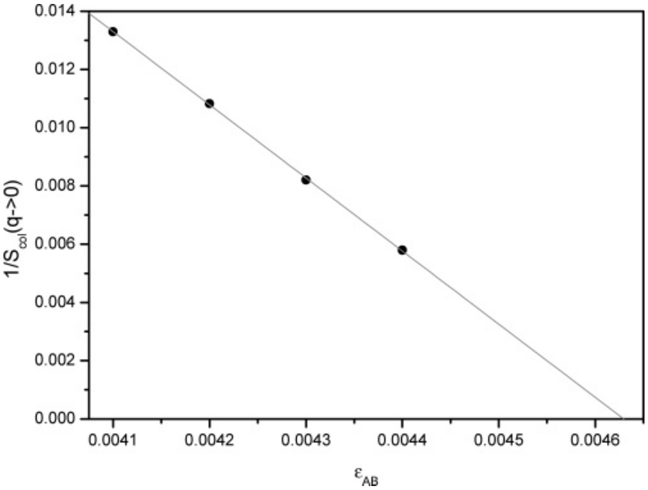

**Figure 4.** Plot of $1/S_{\mathrm{col}}(q\rightarrow 0)$ vs the interaction parameter between dissimilar units $\epsilon_{AB}$ for star/star blends with $f = 4$ arms. The *x* axis intersect estimates the critical temperature of the blend ($\epsilon_{AB} \sim 1/T$).

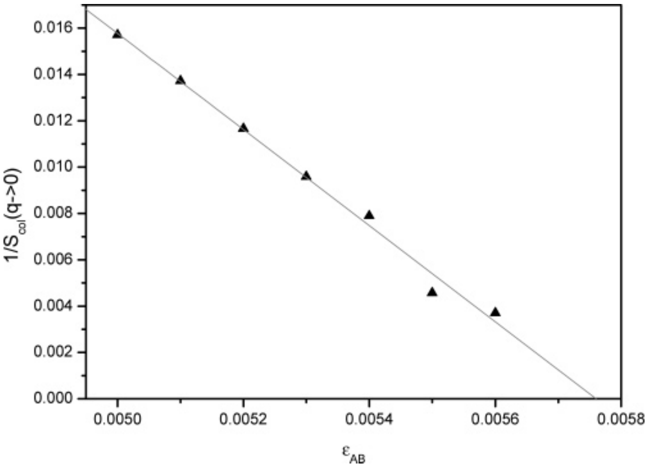

**Figure 5.** Plot of $1/S_{\mathrm{col}}(q\rightarrow 0)$ vs the interaction parameter between dissimilar units $\epsilon_{AB}$ for star/star blends with $f = 8$ arms. The *x* axis intersect estimates the critical temperature of the blend ($\epsilon_{AB} \sim 1/T$).

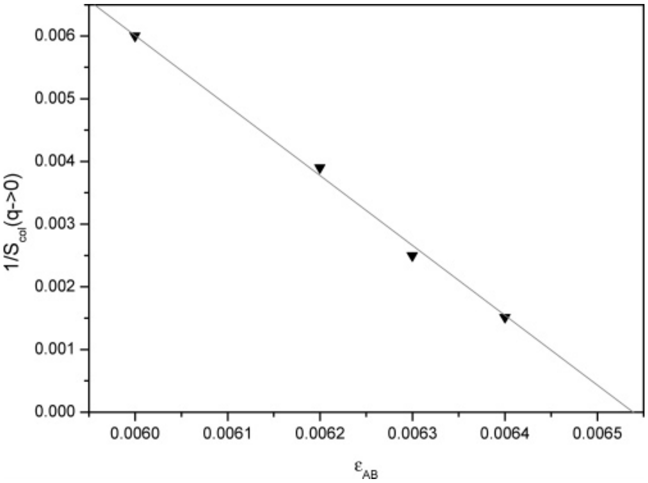

**Figure 6.** Plot of $1/S_{\mathrm{col}}(q\rightarrow 0)$ vs the interaction parameter between dissimilar units $\epsilon_{AB}$ for star/star blends with $f = 12$ arms. The *x* axis intersect estimates the critical temperature of the blend ($\epsilon_{AB} \sim 1/T$).

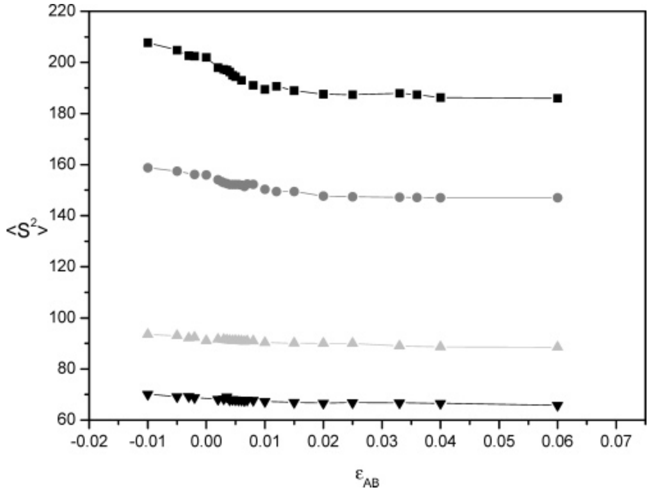

**Figure 7.** Mean-square radius of gyration vs the interaction parameter between dissimilar units $\epsilon_{AB}$ for linear/linear (squares) and star/star blends with 4 (circles), 8 (triangles), and 12 (upside-down triangles) arms.

extrapolated values of $[S_{\mathrm{col}}(q\rightarrow 0)]^{-1}$ at $q \rightarrow 0$ than the ones used for linear/linear blends. The extrapolated critical temperatures are $\epsilon_{AB} = 0.003\,52$ for linear/linear blends (close to the 0.0038 proposed by the equation $1/\epsilon_{AB} \approx 2.15N + 1.35$ of ref 10) and $\epsilon_{AB} = 0.004\,63$, $0.005\,76$, and $0.006\,54$ for star/star blends with 4, 8, and 12 arms, respectively. It is obvious that with an increase in the functionality of star polymers the miscibility increases almost linearly with the number of arms up to $f = 8$ while the critical temperature difference becomes smaller with a change from 8 to 12 arms. These extrapolated critical temperatures are very close to the ones obtained in Figure 2 from the ordering parameter $\gamma$ ($\epsilon_{AB} = 0.0036$, 0.0045, 0.0054, and 0.0064).

The last property we have calculated in this paper is the radius of gyration of polymer coils in binary polymer blends. Analytical calculations[12] confirmed by Monte Carlo simulations[13] and experiments[14,15] show that chain correlations play an important role in the behavior of linear/linear polymer blends with positive interactions, especially when these interactions are strong enough to bring the systems close to the spinodal curve. The effect of chain correlations on the individual macromolecules in this area of repelling interactions is to reduce their dimensions relative to their unperturbed state. This contraction becomes stronger as the system comes close to the phase separation where the radius of gyration takes on reasonably small values. (The opposite behavior is obtained for attraction between units.) Our results presented in Figure 7 are in agreement with the previous analytical results. For the linear/linear blends, we found that the polymer coil contracts when the repulsive interactions increases by about 8%, while for the star blends the effects of the chain correlations are less effective. The ratio of the radii of gyration of star chains in the blend to the unperturbed ones

$$\alpha^2 = \frac{\langle S^2_{\mathrm{star,blend}}\rangle}{\langle S^2_{\mathrm{star,0}}\rangle} \qquad (5)$$

take the values 0.94, 0.975, and 0.97 for stars with 4, 8, and 12 arms, respectively. When the number of arms is increased, the shielding effects of the star architecture reduce the number of heterocontacts, resulting in a less significant contraction of the star chains. However, for bond fluctuation models observed changes of radii of gyration is a complex combination of short- and long-range interactions. At low temperatures, for example, long bonds have been found to be more favored, leading to more expanded chains.[8] Our algorithm can be easily extended to describe asymmetric star/star blends having different number of A and B chains of different length and functionality.

Chemically identical star/star blends[16] also can be studied. This will be the subject of further coming work.

## Concluding Remarks

In this paper we use the bond fluctuation model to study the effects of the architecture on the miscibility of symmetric polymer blends. In particular, linear/linear blends with $N_A = N_B = 121$, $\Phi_A = \Phi_B$ and, for the first time, star/star blends with 4, 8, and 12 arms of the same length and density are simulated. The critical points obtained by means of the ordering parameter $\gamma$ and the collective scattering structure factors indicate that star/star blends are more miscible than linear/linear ones, at least for short chains. With an increase in the number of arms, miscibility is enhanced significantly. This comes mainly from the shielding effect of the star cores, which reduces the number of heterocontacts. This also reflects on the size of star chains in the blend. There is a smaller reduction in star coil dimensions relative to their unperturbed state than there is in the respective dimensions in linear/linear blends.

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