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# Effective interaction parameter of linear/star polymer blends and comparison with that of linear/linear and star/star blends

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The authors present a detailed study of the microscopic parameters, which control the miscibility in binary linear/star polymer blends. The effective interactions of linear/star polymer blends are studied by means of Monte Carlo simulations and comparison is made with linear/linear and star/star blends, which they also determined. Using the bond fluctuation model on a simple cubic lattice, the authors are able to simulate symmetric linear/linear, star/star, and, for the first time, linear/star blends with a moderate number of arms. The simulations were performed at a volume fraction of occupied lattice sites  $\varphi=0.5$ , which corresponds to dense polymer mixtures for this algorithm. In particular, we study star/star blends with 4, 8, and 12 arms and the respective linear/linear blends as well as linear/star blends, all having the same total number of units equal to 73 and 121. The authors find that linear/star blends are more miscible than the corresponding linear/linear blends, which is in agreement with recent experimental and theoretical results. They find that linear/star mixtures are less miscible than star/star blends, a result which is also verified by theoretical findings. © 2007 American Institute of Physics. [DOI: [10.1063/1.2731786](https://doi.org/10.1063/1.2731786)]

## I. INTRODUCTION

Throughout the last few decades, the subject of polymer blends has been studied extensively mainly as a result of the potential applications of polymer blends as new materials. The interactions between the chain units play a crucial role for the stability of polymer mixtures. Flory-Huggins theory<sup>1</sup> expressed these interactions through the interaction parameter  $\chi$ , which was believed to depend only on the temperature  $T$  of the mixture. However, experimental and recent theoretical results predict that the  $\chi$  parameter depends also on the volume fraction, the molecular weight, and the chain architecture.<sup>2–4</sup> The dependence of  $\chi$  on these parameters is included only in complex polymer theories<sup>5</sup> and in Monte Carlo (MC) simulations<sup>6</sup> via the effective interaction parameter  $\chi_{\text{eff}}$ . Under the same conditions, for different blends of the same molecular weight and composition, higher values of  $\chi_{\text{eff}}$  correspond to less miscibility. In our previous work,<sup>7</sup> we studied extensively the effect of the chain architecture on the miscibility of linear/linear and star/star polymer blends. By means of the collective scattering structure factor we found that star/star blends are more miscible than linear/linear mixtures, at least for short chains. With an increase in the number of arms, we found that the miscibility of star/star blends was enhanced significantly. This comes mainly from the shielding effect of the star cores, which reduces the number of heterocontacts. Experimentally, mixtures of linear

poly(vinyl methyl ether) (PVME) with 4 (Ref. 8) or 22 (Ref. 9) armed star polystyrene (PS) were studied to evaluate the effect of chain topology in the critical fluctuations in homogeneous polymer mixtures. It was found<sup>8</sup> that the cloud point curve of the PS/PVME mixtures was elevated by  $\sim 10^\circ\text{C}$  over that of the corresponding linear/linear mixtures. For longer chains<sup>9</sup> the elevation was about  $\sim 4^\circ\text{C}$ . This result indicates that the miscibility is higher for linear/star mixtures than it is for linear/linear mixtures. The behavior of the corresponding star/star blends has not been experimentally studied in such a way that direct comparison of linear/linear, linear/star, and star/star blends could be made. Conversely, analytical theory has already presented a detailed study of the behavior of linear/linear, linear/star, and star/star blends. Garas and Kosmas<sup>5</sup> incorporated chain correlations between the chains in the blend. The one loop diagrams that describe two point correlations between chains were determined at the critical dimensionality  $d=4$ . The contribution of the higher order diagrams is estimated through reexponentiation of the first order results. It was found that the linear/star blends were more miscible than the corresponding linear/linear blends in agreement with the experimental results.<sup>8,9</sup> Furthermore, they found that star/star blends are more miscible than the linear/star mixtures, when all the chains are of the same molecular weight and the stars of the same functionality. It was also pointed out that the difference in miscibility was decreased when the molecular

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weight of the polymer chains was increased. For constant molecular weight, the miscibility is increased when the functionality of star polymers is increased.

Possible verification of the theory can be achieved through adequate MC simulations or experiments. In the present work, we have performed extensive MC simulations for linear/linear, star/star, and linear/star blends using the bond fluctuation model<sup>10–14</sup> (BFM). For linear/star mixtures with all chains having the same molecular weight in each blend equal to 73 or 121 units, we calculate the interaction parameter  $\chi_{\text{eff}}$  in the homogenous phase. The same parameter is also estimated for the star/star and the linear/linear blends at the same temperature and the same molecular weight in order to determine the dependence of  $\chi_{\text{eff}}$  on the functionality of star chains, the molecular weight, as well as the volume fraction of both components of the mixtures. By increasing the temperature of the mixtures, the systems approach the spinodal line, which is determined by means of the collective scattering structure factor. In linear/star mixtures, we finally compute the radius of gyration of the polymer chains at a certain range of temperatures and we compare the behavior of linear and star chains with the respective linear/linear and star/star blends. Thus, we are able to determine accurately the effect of the chain architecture on the miscibility of different blends.

## II. SIMULATION METHOD

We use the BFM in a simple cubic lattice of length  $L$  with periodic boundary conditions to simulate linear/linear, star/star, and linear/star polymer blends with different numbers of arms (4, 8, and 12). For all the blends we place  $n$  molecules, each composed of 73 or 121 units. These particular values of molecular weights are chosen in order to enable the simulation of star chains of functionality 4, 8, and 12 with the same molecular weight. 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 by self-avoiding walk (SAW) polymers. This SAW condition is completely equivalent to the description given in the original model of Carmesin and Kremer,<sup>10</sup> when eight-site nonoverlapping monomers are replaced by single-site beads. Bonds linking the beads can have lengths ranging from 2 to  $\sqrt{10}$ , but bond 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,  $L \geq 2N^{1/2} + 5\lambda$ , where  $\lambda$  is the root-mean-squared bond distance ( $\lambda=2.72$ ). The number of chains derives from the desired number of sites blocked by the polymer beads,<sup>12</sup> which is equivalent to the polymer volume fraction,  $\Phi=8nN/L^3=0.5$ . Depending on the volume fraction ( $\Phi_A=0.2, 0.35, 0.5, 0.65$ , and  $0.80$ ), some chains are assigned randomly as  $A$ -type polymer chains, and the rest are assigned as  $B$ -type chains. In this way, the initial configuration for blends is obtained. Interactions between non-neighboring beads placed at distances smaller than  $\sqrt{10}$  are considered according to the BFM proposed by Wittkop *et al.*<sup>13</sup> The model also considers

different values of bond energies, depending also on the type of bond vector.<sup>14</sup> The interaction energies are expressed in terms of three energy parameters between similar  $A$ - $A$ ,  $B$ - $B$ , or dissimilar  $A$ - $B$  units,  $\varepsilon'_{AA}/k_B T=0$ ,  $\varepsilon'_{BB}/k_B T=0$ , and  $\varepsilon'_{AB}/k_B T=\varepsilon_{AB}>0$ . These thermodynamic interactions are chosen for the blends to exhibit a phase separation when the temperature is lowered and the lattice voids to be neutral.

In linear/linear blends, 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 either 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. These trajectories are followed by the same number of steps for the calculation of properties.

In the case of star/star and linear/star blends, it is difficult to reach the high density of the mixture ( $\Phi=0.5$ ). In order to overcome this problem, the initial configurations for the star chains were generated as described in Ref. 7. In linear/star blends, the linear chains are positioned using the same procedure that we followed for the star chains. Equilibration can be performed from these initial configurations of linear/star and star/star mixtures through elementary bead jump for both linear and star chains, 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, 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. Typical trajectories for linear/star and star/star blends consist of  $10^6$  attempted movements per bead for equilibration and followed by the same number of Monte Carlo steps for the calculation of properties. We save the trajectory coordinates every  $10^3$  configurations for all the blends we study and calculate properties of the blends averaging the resulting samples.

## III. RESULTS AND DISCUSSION

We consider linear  $A$ /linear  $B$ , linear  $A$ /star  $B$ , and star  $A$ /star  $B$  polymer blends consisting of two different types of units  $A$  and  $B$  with asymmetric composition  $\Phi_A$  equal to 0.2, 0.35, 0.5, 0.65, and 0.8. All chains in the mixtures are symmetric and contain 73 units each. A weak repulsive potential  $\varepsilon'_{AB}/k_B T=0.003$  is considered to describe interactions between different units. For this potential, all the blends are in the one-phase region. The first property we have calculated for the above mixtures is the effective interaction parameter  $\chi_{\text{eff}}$  as a configurational average. In BFM this interaction parameter is given by the following relation:<sup>6</sup>

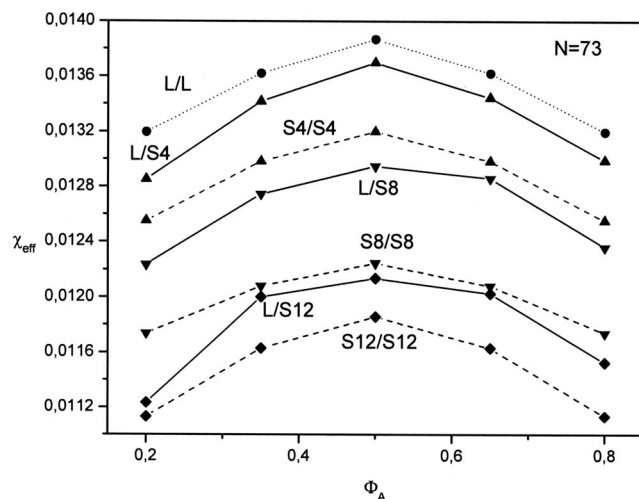


FIG. 1.  $\chi_{\text{eff}}$  interaction parameter vs the volume fraction of the A units  $\Phi_A$ . (L/L) Linear A/linear B blend. (L/S4) Blend of linear chains and 4-arm stars. (S12/S12) Blend of 12-arm stars. All chains contain 73 monomer units. (Lines in all figures are guide for the eyes.)

$$\chi_{\text{eff}} = \frac{\sum_{r_{AB}} N_{AB}(r_{AB}) E_{AB}(r_{AB}, \varepsilon'_{AB})}{\Phi_A \Phi_B N k_B T}, \quad (1)$$

where  $N_{AB}$  is the number of heterocontacts for a specific distance  $r_{AB}$  between dissimilar beads, and  $N$  is the total number of occupied lattice sites. For a given temperature,  $E_{AB}$  is the energy of heterointeractions corresponding to the distance  $r_{AB}$ . The summation in the numerator is over all possible distances  $r_{AB}$  between beads of different type. In Fig. 1 we present our results for all mixtures as a function of the A-type chain volume fraction  $\Phi_A$ . It can be observed that for a constant value of volume fraction  $\Phi_A$ ,  $\chi_{\text{eff}}$  has the highest value in the case of linear/linear polymer blend and the lowest for star/star blend with stars having 12 arms. The respective value for the linear/star blend with stars of the same functionality (12 arms) lies between the previous two values but closer to the one corresponding to star/star blend. By decreasing the number of arms,  $\chi_{\text{eff}}$  increases for all blends, but the corresponding value for linear/star blends always remains between the ones of linear/linear and star/star blends of stars with the same functionality. However, when the functionality of star chains decreases,  $\chi_{\text{eff}}$  increases faster for linear/star blends than for the corresponding star/star blends. In fact, the case of stars with 4 arms shows a value close to that of the linear/linear blend. The dependence of  $\chi_{\text{eff}}$  on the volume fraction of the A-type chains  $\Phi_A$  is given by a flattened parabolic curve. For the case of linear/linear and star/star mixtures this curve is symmetric, having the maximum value at  $\Phi_A = 0.5$ , due to the equal molecular weight of all chains in the mixtures. In Fig. 2 we present our results of the effective interaction parameter  $\chi_{\text{eff}}$  for the case of linear A/linear B, linear A/star B and star A/star B polymer blends, in which both type A and type B polymer chains contain 121 units each. It can be observed again that  $\chi_{\text{eff}}$  values for linear/star blends lies between the respective values of  $\chi_{\text{eff}}$  of linear/linear and star/star polymer blends as in the previous case of blends with chains containing 73 units

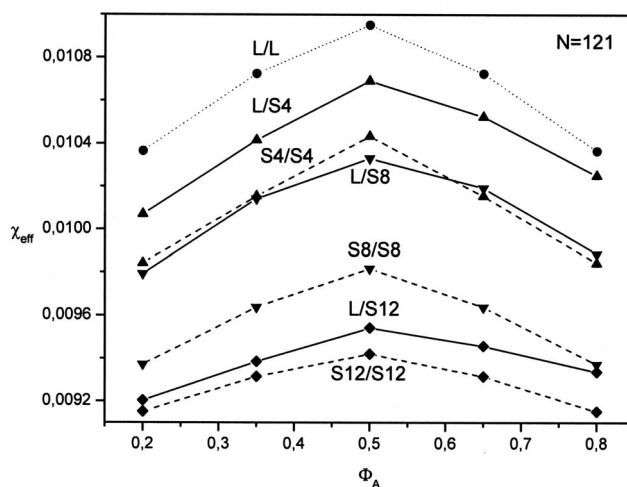


FIG. 2.  $\chi_{\text{eff}}$  interaction parameter vs the volume fraction of the A units  $\Phi_A$ . Same notation as in Fig. 1. All chains contain 121 units.

each. However, comparing the values of  $\chi_{\text{eff}}$  of blends (of the same type) with chains containing 73 and 121 units (Fig. 3), we find that the increase of the chain molecular weight leads to a decrease of  $\chi_{\text{eff}}$ .

A detailed explanation of our findings on the effects of both the architecture and the chain molecular weight can be done by calculating the average number of heterocontacts per lattice site as a function of the distance  $r$  between dissimilar interacting units A and B. In Fig. 4, we present our results for compositionally symmetric ( $\Phi_A = 0.5$ ) linear/linear and 12-arm star/star polymer blends for the two different chain lengths corresponding to 73 and 121 units in order to examine the effect of the chain molecular weight on  $\chi_{\text{eff}}$ . In linear/linear blends, we notice that the mixture with the chains of the lower molecular weight ( $N=73$ ) has more heterocontacts at small distances  $r$  than the blends with 121 unit chains. This mainly arises from the higher interpenetration of the chains with the lower molecular weight ( $N=73$ ). For higher values of distance  $r$ , it can be seen that the differences

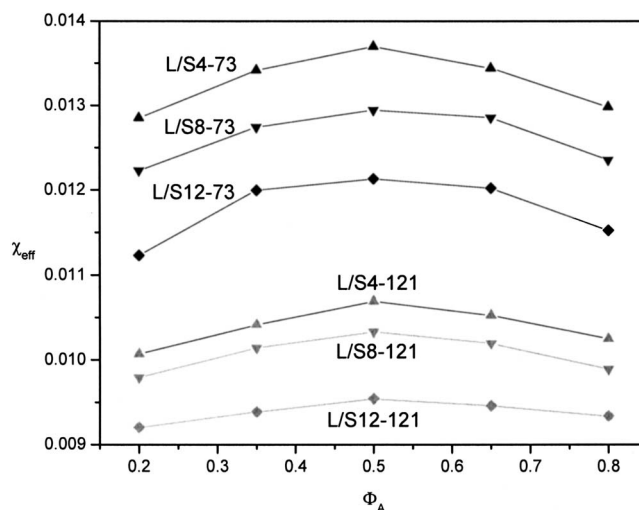


FIG. 3.  $\chi_{\text{eff}}$  interaction parameter for linear A/star B blends vs the volume fraction of the A units  $\Phi_A$ . (L/S4-73) Blend of linear chains and 4-arm stars, both containing 73 monomer units.



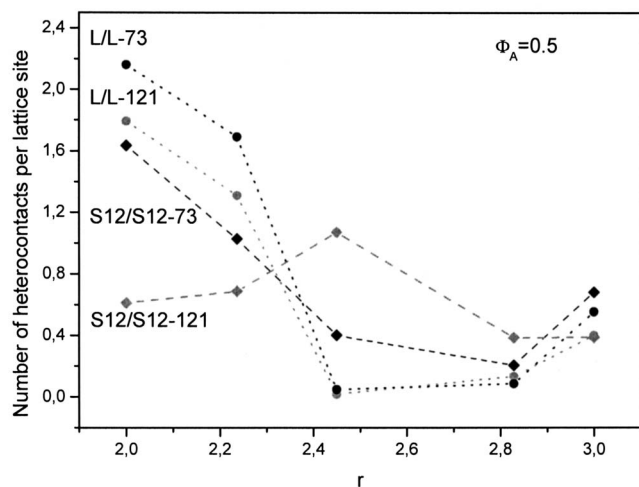


FIG. 4. The number of heterocontacts per lattice site as a function of the distance  $r$ . (S12/S12-73) Blend of 12-arm star chains, both containing 73 monomer units.

in the number of heterocontacts are small, thus the main difference in  $\chi_{\text{eff}}$  comes from the effective heterocontacts corresponding to small distances. The same behavior is observed in the case of 12-arm star/star mixtures. Therefore,  $\chi_{\text{eff}}$  is higher in mixtures with shorter chains.

The influence of the chain architecture on the number of heterocontacts per lattice site is illustrated in Fig. 5. All blends are compositionally symmetric ( $\Phi_A=0.5$ ) and they have chains composed of 73 units. For short distances ( $r=2, \sqrt{5}$ ), the number of heterocontacts per lattice site is higher in linear/linear blends and decreases when the functionality of star chains increases in linear/star and star/star blends. For higher distances  $r$ , the order of heterocontacts becomes inverted, with the linear/linear blends having the smallest value of heterocontacts compared to the linear/star and star/star mixtures. In the linear/star blend with 12 arms, the number of heterocontacts per lattice site for  $r=2, \sqrt{5}$  lies between those of linear/linear and star/star blends with stars of the same functionality, while at the distance  $r=3$  we ob-

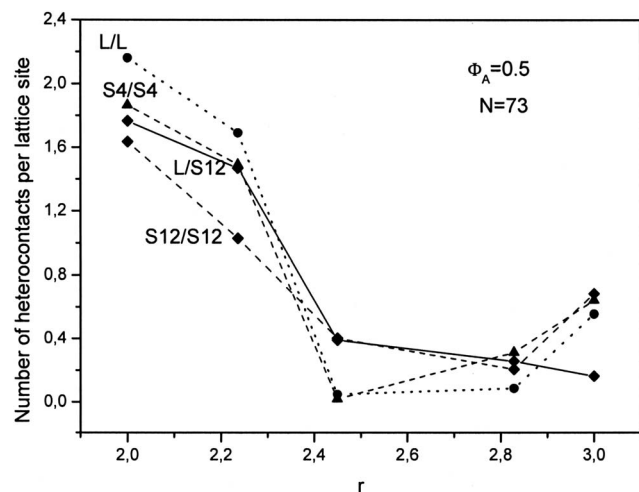


FIG. 5. The number of heterocontacts per lattice site as a function of the distance  $r$ . Same notation as in Fig. 1. All blends contain chains with 73 units.

tain a smaller value even when it is compared with that of the linear/linear blends. Thus,  $\chi_{\text{eff}}$  values of linear/star mixtures are closer to star/star blends with 12 arms. As a conclusion, when the number of arms increases, the shielding effect of the star architecture, reduces the number of  $A$ - $B$  heterocontacts by protecting the interior units of the chain from the presence of the units of different type, resulting in the decrease of  $\chi_{\text{eff}}$  for heteropolymer mixtures.

By decreasing the temperature, the effective interactions increase and the blends approach the spinodal curve. For blends composed of chains with the same molecular weight, higher values of  $\chi_{\text{eff}}$  means more immiscible mixtures. However, even in the case of compositionally symmetric blends ( $\Phi_A=0.5$ ), the relation  $\chi_{\text{eff}} N=2$  is not accurate for the detection of the spinodal curve.<sup>15</sup>

An accurate estimation of the spinodal curves can be obtained through the collective scattering function of the blends. The collective scattering function is computed as<sup>7</sup>

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

where  $f_i$  is the occupation state of the different sites located at  $\mathbf{R}_i$ , within the simulation box lattice.  $f_i$  is given by  $f_i = 2(I - \Phi_A)$  if site  $i$  is occupied by unit  $A$ ,  $f_i = -2\Phi_A$  if site  $i$  is occupied by unit  $B$ , or  $f_i = 0$  if site  $i$  is vacant or blocked. For compositionally symmetric mixtures ( $\Phi_A = \Phi_B$ ) this leads to the coefficient values  $f_i = 1, -1, 0$  used in our previous work.<sup>7</sup> In order to compute  $S_{\text{col}}(q)$ , we must comply with the following restrictions imposed on  $q$  by the periodic boundary conditions, according to the chosen box length,

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

According to the random phase approximation,<sup>1</sup> the inverse of the collective scattering function  $[S_{\text{col}}(\mathbf{q})]^{-1}$  in the homogeneous phase region should vary linearly with  $q^2$ . The extrapolated values  $[S_{\text{col}}(q \rightarrow 0)]^{-1}$  at  $q \rightarrow 0$  are small positive numbers. The points of the spinodal line ( $1/S_{\text{col}}(q \rightarrow 0) = 0$ ) can be estimated from plots of  $[S_{\text{col}}(q \rightarrow 0)]^{-1}$  vs  $\epsilon_{AB}$ , assuming a linear relation between the extrapolated inverse collective scattering function and the inverse temperature  $\epsilon_{AB} \sim 1/T$ ,

$$[S_{\text{col}}(\mathbf{q} \rightarrow 0)]^{-1} \sim \epsilon_{AB}. \quad (4)$$

In Fig. 6, we present our results for the spinodal lines of linear/linear, linear/star, and star/star blends with chains containing 121 units and functionalities of star chains equal to  $f=4, 8$ , and 12 for the linear/star mixtures, while  $f=12$  for the corresponding star/star blends. It is obvious that the linear/linear blend demixes first as the temperature decreases. The linear/star blend composed of star chains with functionality  $f=4$  and the same chain molecular weight remains miscible at this temperature, which is in full agreement with the experimental<sup>8</sup> and theoretical<sup>5</sup> results. As we decrease further the temperature, we find that linear/star blends are more miscible as the number of arms of star chains increases due to

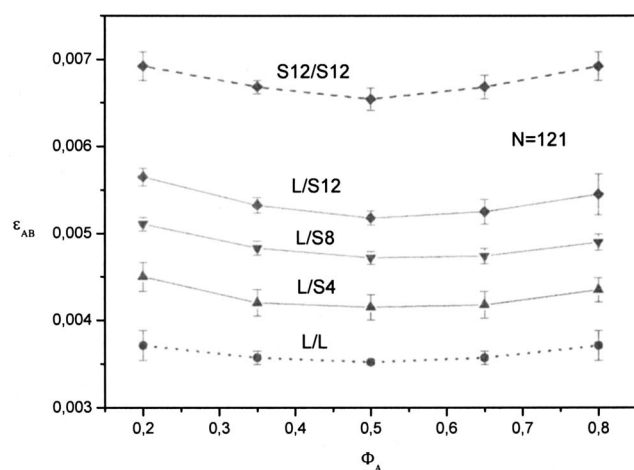


FIG. 6. The phase diagram. Same notation as in Fig. 1. Blends contain chains with 121 units.

the shielding effect of the star architecture, which reduces the number of heterointeractions. The star/star blend with 12 arms is more miscible than the respective linear/star blend, in agreement with the predictions of the analytical theory.<sup>5</sup> In Fig. 7, we present the spinodal lines for the corresponding linear/linear, linear/star, and star/star blends for the short chains containing 73 units per chain. It can be seen that both blends containing 73 or 121 units perform the same behavior when we change the chain architecture. However, the variations of spinodal curves with blend composition are more pronounced in the case of short chains. Moreover, comparing Figs. 6 and 7, we also conclude that the increase of the molecular weight results in smaller differences in the miscibility between linear/linear, linear/star, and star/star blends since the differences in  $\epsilon_{AB} \sim 1/T$  are smaller. This result is in agreement with the theoretical results<sup>5</sup> and the experimental findings.<sup>9</sup> By substantially increasing the molecular weight of the polymer chains, the beads “forget” their origin (i.e., they do not distinguish if they belong to a linear or a star chain) and the effects of architecture are diminished. Further simulations are needed in order to determine the molecular

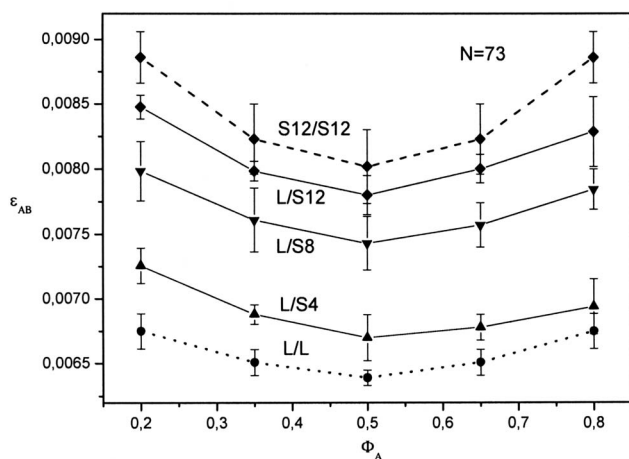


FIG. 7. The phase diagram. Same notation as in Fig. 1. Blends contain chains with 73 units.

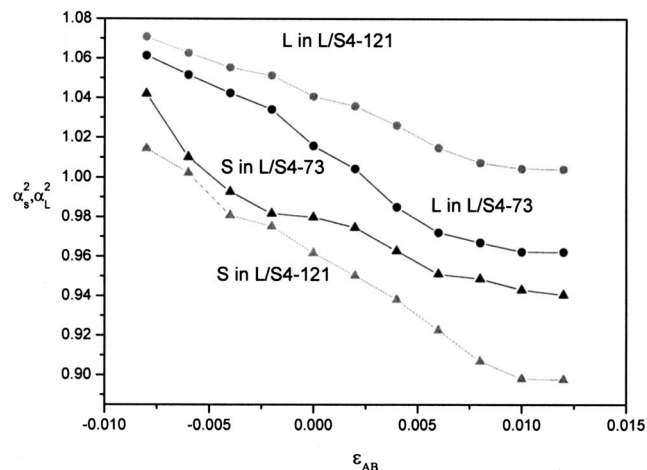


FIG. 8. The expansion factors  $\alpha_s^2$  and  $\alpha_L^2$  of star and linear coils in linear/star blends. (L in L/S4-121) Linear chains in blends of linear chains and 4-arm stars, both having 121 monomer units. (S in L/S4-73) Star chains in blends of linear chains and 4-arm stars, both containing 73 monomer units.

weight for which the spinodal lines of linear/linear, linear/star, and star/star blends collapse into a single curve.

The last properties we calculate in this work are the expansion factors  $\alpha_L^2$  and  $\alpha_s^2$  of radii of gyration of linear and star coils in binary linear/star polymer blends. For linear chains the expansion factor  $\alpha_L^2$  is defined as

$$\alpha_L^2 = \frac{\langle S_{\text{linear}}^2 \rangle}{\langle S_{\text{linear},0}^2 \rangle}, \quad (5)$$

where  $\langle S_{\text{linear}}^2 \rangle$  is the mean square radius of gyration of linear chains in a linear/star mixture and  $\langle S_{\text{linear},0}^2 \rangle$  are the unperturbed dimensions of the linear coils in their melt. For star chains the expansion factor  $\alpha_s^2$  is defined similarly. In a previous work,<sup>7</sup> studying symmetric linear/linear and star/star blends, we found that the polymer coils contract when the repulsive interactions increase. This contraction becomes more substantial 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). For linear chains, the maximum contraction

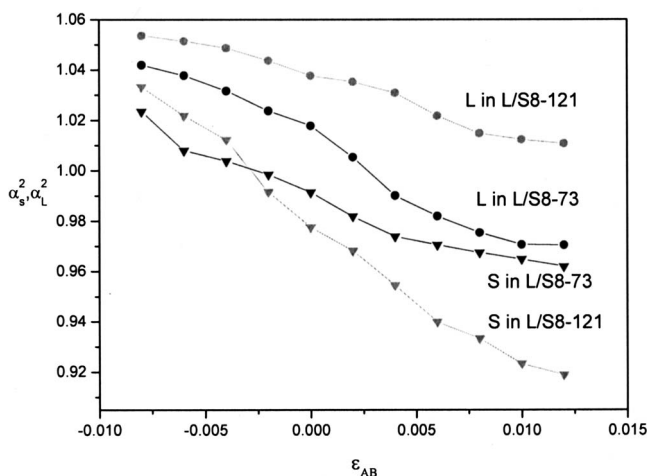


FIG. 9. The expansion factors  $\alpha_s^2$  and  $\alpha_L^2$  of star and linear coils in linear/star blends. Same notation as in Fig. 8.

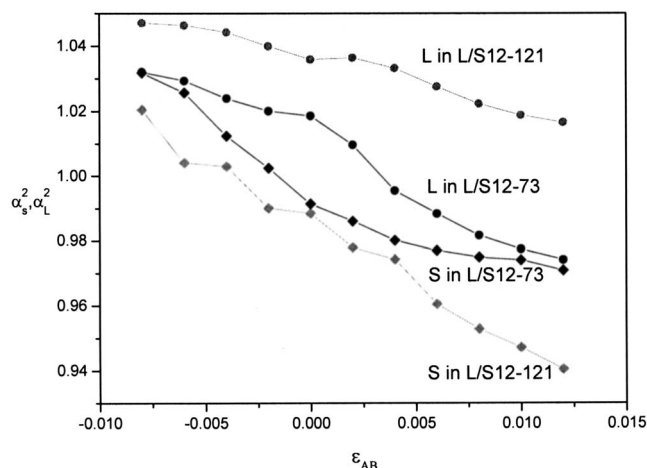


FIG. 10. The expansion factors  $\alpha_s^2$  and  $\alpha_L^2$  of star and linear coils in linear/star blends. Same notation as in Fig. 8.

is about 8%, while that for the star blends is smaller depending on the functionality of star chains.<sup>7</sup> Our results for compositionally symmetric linear/star blends ( $\Phi_A = \Phi_B = 0.5$ ) with star chains having  $f=4, 8$ , and 12 arms are presented in Figs. 8–10, respectively, where we observe the same effect of the polymer coils as described above for the case of linear/linear and star/star blends.

In the current case, as linear/star blends contain two types of chains with architectural asymmetry, the effect is different on linear chains from that on star chains. In linear/star blends, linear chains are more expanded and this is due to the lower proportion of heterocontacts they undergo compared to the linear chains of the corresponding linear/linear blends with the same molecular weight. Conversely, in linear/star blends, star chains contract more in comparison with star chains in the corresponding star/star binary blends. When the number of arms increases, the shielding effects of the star architecture reduces the number of heterocontacts, resulting in less significant contraction of star chains. Moreover, it can be observed that the effect of contraction or expansion of coils is more pronounced in the case of blends with 121 units than those of 73 units. However, for bond fluctuation models, the observed changes of radii of gyration are 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.<sup>13</sup> In our study this complexity is further enhanced by the architectural asymmetry.

#### IV. CONCLUDING REMARKS

In this paper, we presented the study of the microscopic parameters which control the miscibility of linear *A*/linear *B*, linear *A*/star *B*, and star *A*/star *B* blends composed of two different types of units *A* and *B*. Using the bond fluctuation

model we were able to study linear/star and star/star blends with 4, 8, and 12 arms and the respective linear/linear blends, all having the same total number of units of 73 and 121. We found that  $\chi_{\text{eff}}$  interaction parameter between dissimilar units *A* and *B* is higher in the case of linear/linear blends.  $\chi_{\text{eff}}$  has a lower value for the corresponding linear *A*/star *B* blends with the same molecular weight and also has the lowest value for the corresponding star *A*/star *B* blends with the same number of arms. By increasing the molecular weight of polymer chains,  $\chi_{\text{eff}}$  decreases for all blends. By increasing the temperature of the system, blends come into the spinodal regime and separate in two different phases. We found that linear *A*/star *B* blends are more miscible than the corresponding linear/linear blends, which is in agreement with recent experimental and analytical results. Respectively, we found that linear *A*/star *B* mixtures are less miscible than star *A*/star *B* blends, a result which is also verified by theoretical findings. In linear/star blends, linear chains are more expanded due to the lower proportion of heterocontacts they undergo, compared to the linear chains of the corresponding linear/linear blends with the same molecular weight. On the other hand, in linear *A*/star *B* blends, star chains contract more compared to star chains in the corresponding star *A*/star *B* binary blends.

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