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Monte Carlo simulation of star/linear and star/star blends with chemically identical monomers

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Abstract

The effects of chain size and architectural asymmetry on the miscibility of blends with chemically identical monomers, differing only in their molecular weight and architecture, are studied via Monte Carlo simulation by using the bond fluctuation model. Namely, we consider blends composed of linear/linear, star/linear and star/star chains. We found that linear/linear blends are more miscible than the corresponding star/star mixtures. In star/linear blends, the increase in the volume fraction of the star chains increases the miscibility. For both star/linear and star/star blends, the miscibility decreases with the increase in star functionality. When we increase the molecular weight of linear chains of star/linear mixtures the miscibility decreases. Our findings are compared with recent analytical and experimental results.

1. Introduction

Polymer blends are very important in polymer science since they combine the properties of their components. In this way, polymer mixtures may have improved properties, so they can be considered as new materials. The miscibility of polymeric mixtures has been found to depend on various parameters [1], such as the temperature, the chemical mismatch, the chain molecular weight and the chain architecture [2]. In particular, the effect of the chain molecular weight and architecture are significant factors, which influence the miscibility of blends with chemically identical monomers, where the interactions between all units are the same [3–9]. In such blends, the magnitudes of the size and architectural asymmetry effects can be deduced by estimating the total effective thermodynamic interactions between two units of different species via the interaction parameter χ_{eff} [7–9].

Experimentally, there is a sufficient amount of work associated with blends of chemically identical monomers composed of linear and star chains [3, 4, 10, 11]. The χ_{eff} interaction parameter is obtained by means of the random phase approximation (RPA) equation

$$S = \frac{1}{S_{\text{col}}(q \rightarrow 0)} = \frac{1}{\Phi_A M_A} + \frac{1}{\Phi_B M_B} - 2\chi_{\text{eff}}, \quad (1)$$

where S is the second derivative of the free energy with respect to the volume fractions, $S_{\text{col}}(q)$ is the collective scattering function, and Φ_A, M_A and Φ_B, M_B are the volume fraction and the molecular weight of the two polymer species A and B, respectively. When S is positive, we are in the region of a homogeneous single phase, while the border $S = 0$ (spinodal line) and the beginning of negative S denotes the emergence of the instability region and the eventual appearance of different phases. χ_{eff} describes the effective interactions between the chains, and larger positive values of it mean larger repulsions between the different polymers, making S smaller and closer to the stability limit $S \rightarrow 0$ [6]. Therefore, higher values of S mean more miscible blends. For polystyrene (PS) star/linear blends it was found that the miscibility decreases as the number of the star arms increases [3, 4]. However, a different behavior was observed in polybutadiene (PB) star/linear [11] and star/star [5] blends. It was found that the miscibility varied non-monotonically with an increase in the number of arms from four to 12 [11]. The dependence of the miscibility on the volume fraction of star chains was an additional subject of experimental work. For PB blends, it was found that, in star/linear blends with chemically identical monomers, the miscibility increases with the increase in the volume fraction of the star chains in the mixture [11]. The results for PS star/linear mixtures contradict this behavior [4], showing that the miscibility decreases with the increase in the volume fraction of star chains.

Theory [7, 8] predicts the stability criteria for linear/star and star/star blends with chemically identical monomers. For star/star blends with the same number of arms and symmetric or asymmetric chains, it was shown that the miscibility decreases monotonically with star functionality. For star/linear blends, it was found that the miscibility increases as the volume fraction of the star chains increases.

The effect of chain architecture in blends with chemically identical monomers can be checked through appropriate simulation studies. In the present work, we have performed Monte Carlo (MC) simulations mainly for star/linear and star/star blends with chemically identical monomers using the bond fluctuation model [12–18] (BFM). We have actually considered a representative variety of molecular weights, volume fractions and star functionalities. We use the simple cubic lattice, and the total volume fraction of occupied lattice sites is $\Phi = 0.5$, which corresponds to dense polymer blends for this algorithm [13, 17]. Since the χ_{eff} interaction parameter takes very small values ($\sim 10^4$), as predicted by theory and shown by experiment, the determination of χ_{eff} by means of the extrapolation of $S_{\text{col}}(q)$ at $q \rightarrow 0$ in simulation is difficult. For this reason we calculate the mean number of heterocontacts per lattice site, which is more illustrative and expresses directly the miscibility of the blends. When this number is higher, the A and B units come closer in space, thus enhancing the miscibility. Conversely, when the number of heterocontacts per lattice site is small, the A and B units prefer to be far apart, resulting in less miscibility. The comparison of the miscibilities of various blends is thus easier and a check with other theories and experiments is possible.

2. Simulation method

We use the BFM in a simple cubic lattice of length L with periodic boundary conditions to simulate linear A/linear B, star A/linear B, and star A/star B polymer blends with star chains

containing different numbers of arms f , equal to 4, 6, 8 and 12. Since we study blends with chemically identical monomers, we use types A and B just to distinguish our chains of different architecture or molecular weight. We place n_A and n_B molecules each composed of M_A and M_B units, respectively. 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 *et al* [13] when eight-site non-overlapping 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 should be high enough to ensure that the number of interactions between different replicas of the same molecules is negligible. Usually L is $L \geq 2R_{\text{span}}^2 / \sqrt{10} + 5\lambda$, where R_{span}^2 is the unperturbed mean square distance between pairs of end units in the star or linear chain. (This distance corresponds to the pairs of ends separated by the greatest number of bonds in the case of mixtures of different types of molecules.) λ is the root-mean-squared bond distance ($\lambda = 2.72$). The numbers of chains n_A and n_B derive from the desired number of sites blocked by each type of polymer beads A or B, and the total polymer volume fraction, $\Phi = 8(n_A M_A + n_B M_B) / L^3 = 0.5$ corresponding to dense polymer blends for this algorithm. Interactions between non-neighboring beads placed at distances smaller than $\sqrt{10}$ are considered according to the BFM proposed by Wittkop *et al* [15]. These interactions will be denoted as contacts and may involve different types of orientation between the BFM monomeric cubes. The model also considers different values of bond energies, depending also on the type of bond vector [16]. The interaction energies are expressed in terms of three energy parameters between A–A, B–B and A–B units: $\varepsilon'_{AA}/k_B T$, $\varepsilon'_{BB}/k_B T$ and $\varepsilon'_{AB}/k_B T$. In our case of blends with chemically identical monomers, these three parameters are equal and represented by a single value ε . In the majority of our simulation results we use self-avoiding chains ($\varepsilon = 0$) to study the blends with chemically identical monomers. For the dependence of the miscibility on temperature and a comparison with the theoretical results, we have also considered positive values of (repulsive interactions between units) ε , namely $\varepsilon = 0.001, 0.0015, 0.002, 0.0025$ and 0.003 .

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. The same number of steps for the calculation of properties follows these trajectories.

In the case of star/linear and star/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 [2]. In star/linear 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 star/linear and star/star mixtures through elementary bead jump for both linear and star chains, with displacement vectors $(\pm 1, 0, 0)$, $(0, \pm 1, 0)$, $(0, 0, \pm 1)$. Once the move has been made, the lengths of the new bonds are checked for compliance with the BFM lengths. The distance between the central units and its first neighbors is permitted to increase up to 4 instead of the value $\sqrt{10}$ established for the other units in order to facilitate the mobility of star chains. The new configuration is accepted if both the SAW and Metropolis criterion are fulfilled. Typical trajectories for star/linear and star/star blends consist of 10^7 attempted movements per bead for equilibration, followed by the same number of Monte Carlo steps for the calculation of properties. We have verified that the

number of equilibration steps that was used is sufficient to give constant values for the average acceptance rates in all the cases. We save the trajectory coordinates every 10^3 configurations for all the blends that we study and calculate properties of the blends, averaging the resulting samples.

In the current paper we also present, for comparison purposes, analytical results for the second derivative of the free energy S obtained from [8]. The analytical model considers Gaussian chains with excluded volume interactions between different chains $u > 0$. Using an Edwards-type Hamiltonian, the partition function and the resulting free energy of the blend are obtained through summation of the series of the one-loop diagrams at any dimensionality d . The second derivative of the free energy with respect to the volume fractions of the different species is obtained for star/star and star/linear blends for the fixed point value $u = u^* = 1/16$ corresponding to $d = 3$.

3. Results and discussion

3.1. Mean number of heterocontacts per lattice site and the second derivative S of the free energy

The first property that we have calculated for our mixtures is the mean number of heterocontacts per lattice site, defined as:

$$\langle N'_{AB} \rangle = \frac{\langle N_{AB} \rangle}{N\Phi_A\Phi_B}, \quad (2)$$

where N is the total number of occupied sites in the lattice and Φ_A and Φ_B are the volume fractions of the A and B polymers units. The use of the term ‘heterocontacts’ declares the number of beads N_{AB} of different type of units A and B placed at distances between 2 and $\sqrt{10}$. $\langle N'_{AB} \rangle$ is an important property and reflects the proximity miscibility of different chains. When $\langle N'_{AB} \rangle$ is higher, the components of the blends are more miscible, since they are allowed to be closer.

3.1.1. Star A/linear B blends. The dependence of the miscibility on the molecular weight of linear chains in star/linear blends is shown in figure 1. Star chains in the mixtures contain 73 units each, while the length of linear chains varies from 6 to 144 units. The composition of star chains in the blends is asymmetric and equal to $\Phi_A = 0.2$, a value which is widely used in experimental studies [3–5, 10, 11]. Blends with different star functionalities $f = 6, 8$ and 12 are considered. It can be observed that the increase in the molecular weight of linear chains results in a decrease in the miscibility of the blends. Such a dependence is stronger when the molecular weight of linear chains is equal to or less than the molecular weight of the corresponding star branch. This is because the short linear chain with a length less than or equal to the star polymer arm penetrates as a whole into the star molecule. By increasing the linear chain length, a part of the chain lies out of the star molecule and the number of heterocontacts per lattice site between linear and star chains, and consequently the miscibility, are reduced. A further increase in the length of linear chains from 30 to 144 units has a small effect on the miscibility of the blend, since the units of linear chains are far apart from the star units. In particular, it is shown that the increase in the functionality of star chains leads to an even slighter dependence of the blend’s miscibility on the molecular weight of linear chains due to the shorter branch length and the smaller size of the high functionality star chains. The latter conclusions are confirmed by the second derivative of the free energy S obtained by means of analytical theory [8] for two different linear chain molecular weights of 24 and 144, which

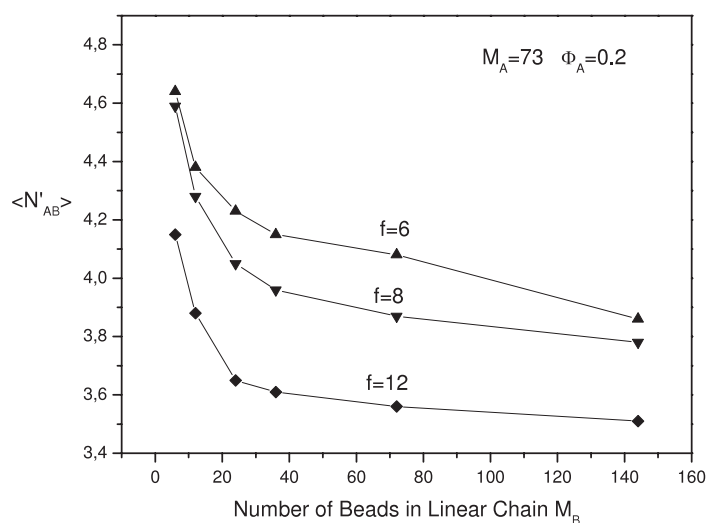


Figure 1. The mean number of heterocontacts per lattice site as a function of the molecular weight of the linear chains M_B for different star A/linear B blends; $\varepsilon = 0$.

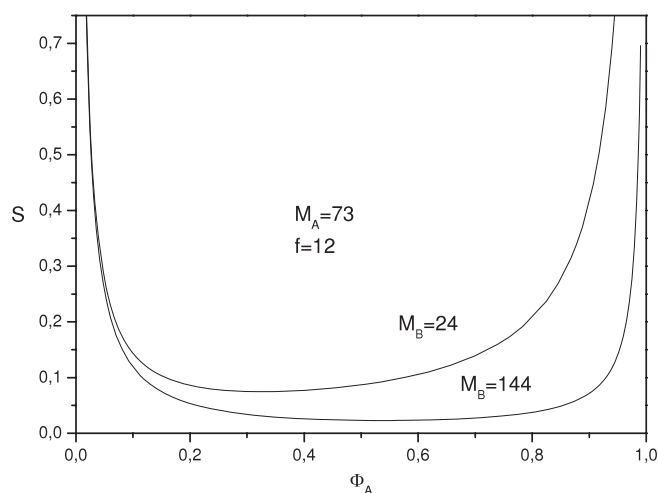


Figure 2. The second derivative of the free energy S for different star A/linear B blends; $u = 1/16$.

are shown in figure 2. We observe that the S for the blend with a lower molecular weight of linear chains lies higher than that a linear chain molecular weight equal to 144. Thus, the blend that contains the linear chains with a molecular weight of 24 is more miscible than the corresponding blend with linear chains of molecular weight 144.

The effect of the star functionality f on the miscibility of star/linear blends is also depicted in figure 1. We found that the increase in the star functionality leads to a linear decrease in the number of heterocontacts per lattice site and consequently to less miscible blends. This is because the increase in the star functionality leads to more compact molecules with shorter arm lengths, and thus the penetration of linear chains into a star chain and the number of heterocontacts are reduced. This monotonic increase in the miscibility when the functionality of star arms increases is consistent with the experimental results for PS blends [3, 4], and

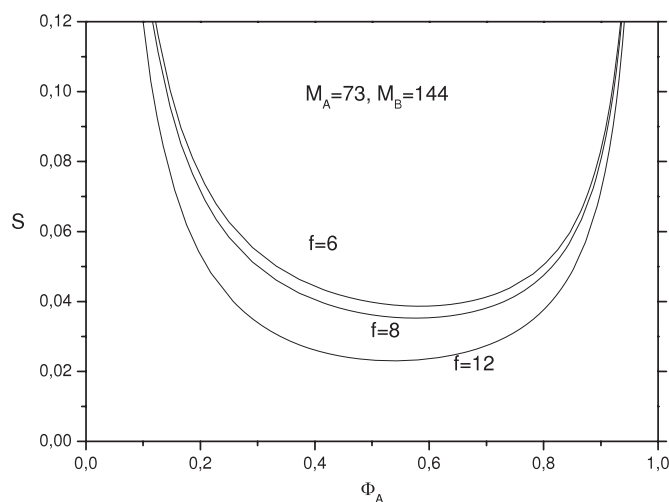


Figure 3. The second derivative of the free energy S for different star A/linear B blends; $u = 1/16$.

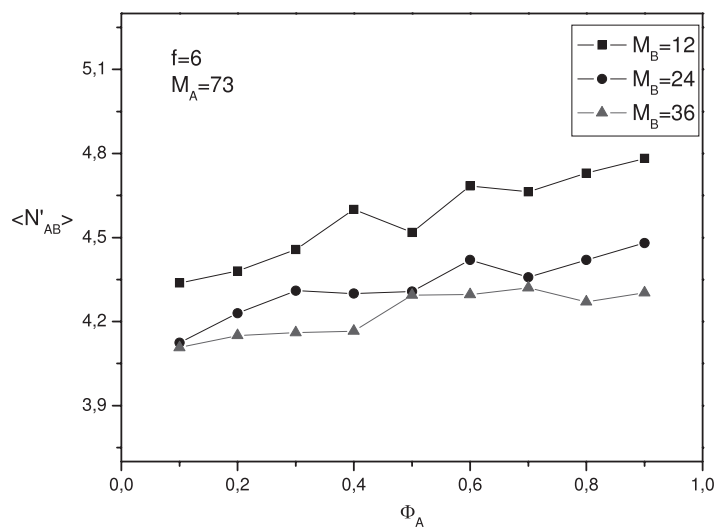


Figure 4. The mean number of heterocontacts per lattice site as a function of the volume fraction of star chains Φ_A for different star A/linear B blends; $\varepsilon = 0$.

is inconsistent with the experimental findings for PB blends [11]. The second derivative of the free energy S of figure 3 obtained by means of analytical theory [8] confirms the latter conclusions. We see that an increase in the functionality of star chains results in a decrease in the miscibility.

In figure 4 we present the results of the mean number of heterocontacts per lattice site for star/linear blends as a function of the star volume fraction Φ_A for three different molecular weights of linear chains 12, 24 and 36. In all blends, star chains have six arms and contain 73 beads. We found that an increase in the volume fraction of star chains leads to an increase in the miscibility of the blends for all molecular weights of linear chains that we have used in the

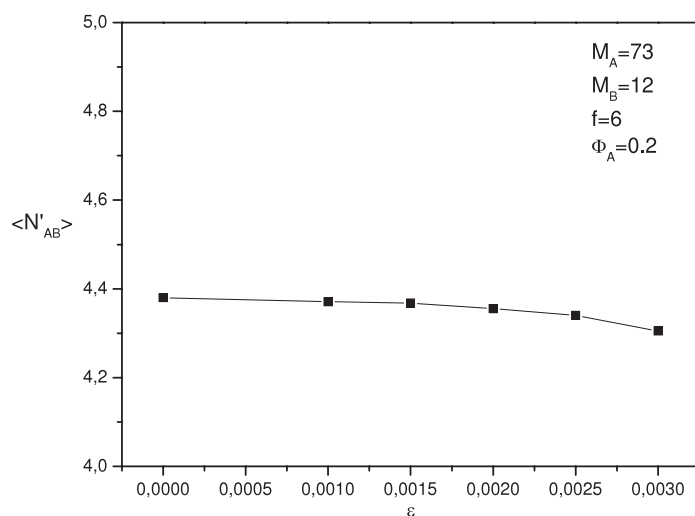


Figure 5. The mean number of heterocontacts per lattice as a function of the interaction parameter ε ($\sim 1/T$) of a star A/linear B blend.

current simulation. This increase is significant and has also been verified by theory [8] (figure 2) and experiment [4, 11]. Furthermore, the miscibility is always higher when the molecular weight of linear chains is smaller; this is a conclusion fully and more clearly supported by the results of figures 1 and 2. The increase in heterocontacts per lattice site by increasing the star chain's volume fraction Φ_A can be explained as follows. The linear chains with two ends can penetrate more than one star chain as the number of star molecules increases due to the higher dimensions of linear chains. In this way, the blend miscibility increases when the volume fraction of star chains increases. As the length of linear chains increases, many of the linear chain units are placed far from the star units. Therefore, the number of heterocontacts and the miscibility of the blends are reduced. The limiting behavior of the mean number of heterocontacts when $\Phi_A \rightarrow 0$ or $\Phi_A \rightarrow 1$ is expected to be similar to that predicted by theory (figure 2), since the factor $\Phi_A \Phi_B$ approaches the zero faster than the mean number of heterocontacts per lattice site.

In figure 5, we present the dependence of the mean number of heterocontacts with the repulsive potential between units of the mixture. It is shown that the increase in the potential results in a small decrease in the miscibility by reducing the number of heterocontacts per lattice site. By increasing the strength of the excluded volume interactions, the penetration of linear chains becomes slightly more difficult, because the increased repulsions tend to decrease the miscibility of the blend. By means of analytical theory [8] we have verified the same effect by calculating the second derivative of the free energy S for different u , namely $u = 1/32, 1/16, 1/8$. The results are presented in figure 6, confirming the obtained Monte Carlo simulation results of figure 5. However, this does not mean that the increase in the interaction parameter can lead to a phase separation in blends with chemically identical monomers. In the case of blends with chemically identical monomers, the increase in the interaction (decrease in the temperature) affects all interactions A–A and B–B and A–B almost in the same way. Therefore, the Flory parameter χ , which is approximately $(\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB})$, is not affected significantly (shown in figure 5 and also in figure 2 of [3]). Thus, the effect of the temperature is not significant in blends with chemically identical monomers, but the size and architectural disparity play the main role on the miscibility of these blends.

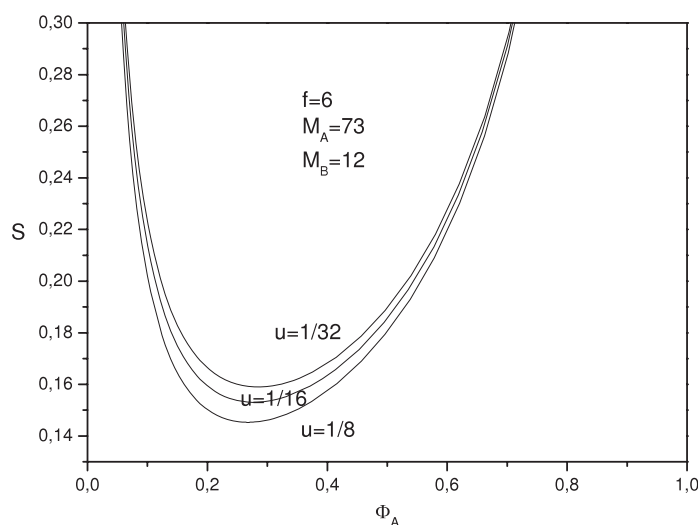


Figure 6. The second derivative of the free energy S of star A/linear B blend for various values of interaction parameter u .

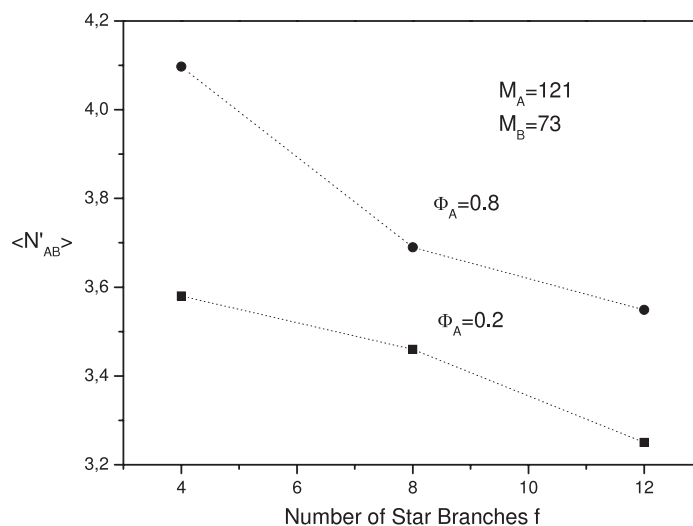


Figure 7. The mean number of heterocontacts per lattice site as a function of the star functionality f for different star A/star B blends with chemically identical monomers; $\varepsilon = 0$.

3.1.2. Star A/star B blends. In order to estimate the dependence of the miscibility on the star functionality f and composition Φ_A , we simulate star A/star B mixtures with star chains having functionalities of $f = 4, 8$ and 12 , and molecular weights equal to $M_A = 121$ and $M_B = 73$. In figure 7, we present our results for two different volume fractions of A species, $\Phi_A = 0.2$ and 0.8 . For both cases, we find that an increase in the number of branches results in a decrease in the miscibility. By increasing the star functionality for constant total molecular weight the star chains become more compact and the penetration of the two different star chains becomes difficult, thus reducing the number of heterocontacts and the miscibility of the blend. The same behavior also appeared in star/linear chains when we altered the star functionality.

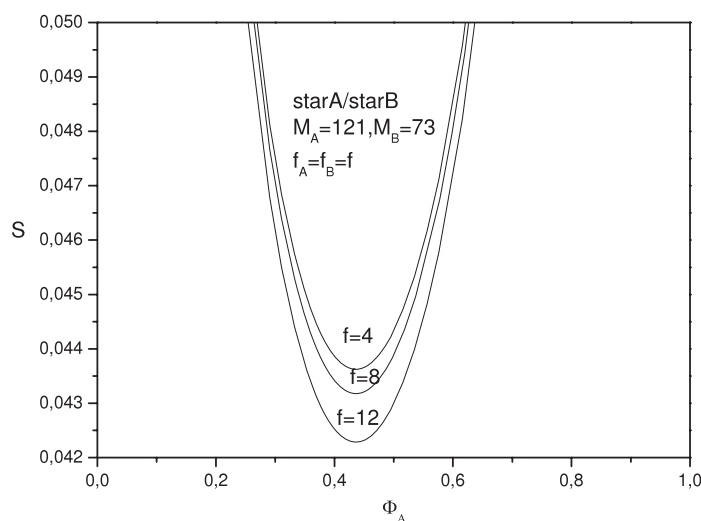


Figure 8. The second derivative of the free energy S for star A/star B blends with chemically identical monomers of different functionality; $u = 1/16$.

Our results are in full agreement with the theoretical results [8], but again are in disagreement with experimental findings of PB star/star mixtures [5]. However, in the case of star/star blends, this dependence is not completely linear. Furthermore, we can also notice in figure 7 that the miscibility is higher when the volume fraction Φ_A of the chains with the higher molecular weight is higher. This is because the stars with longer arms can penetrate more easily than star chains with short arms increasing in this way the number of heterocontacts and finally the miscibility of the blends. Our results are in full agreement with the theoretically calculated second derivative of the free energy S shown in figure 8. The values of S for $\Phi_A = 0.2$ and different functionalities $f = 4, 8$ and 12 are $0.0589, 0.0584$ and 0.0576 m, respectively. The corresponding values for $\Phi_A = 0.8$ are $0.0798, 0.0793$ and 0.0784 . This behavior is in accordance to the notion of the depletion potential of Asakura–Oosawa [19]. The depletion potential increases when we have few large chains in a ‘sea’ of short ones. We have also simulated star A/star B blends with chains of variable molecular weight keeping constant the size asymmetry ratio ρ (ratio of the molecular weight of star A to molecular weight of star B). This way the dependence of the miscibility on the chain size can be estimated. In particular, we studied two different blends with star chains having functionality $f = 6$. In the first case, star chains A and B contain 37 and 73 beads each, while in the other 73 and 145 beads respectively. The blends are compositionally symmetric $\Phi_A = \Phi_B = 0.5$. We find that the increase of the molecular weight of star chains results in the decrease of the miscibility obtaining for the number of heterocontacts the values 4.240 and 3.929 respectively. The increase of the arm molecular weight (for constant functionality of star chains f) reduces the penetration of the arms thus decreasing the number of heterocontacts and the miscibility of the blends.

The comparison of the miscibility of a star/star, linear/linear and star/linear blend is also interesting. We simulate compositionally symmetric star A/star B blends with $M_A = 121$ and $M_B = 73$ units per chain. The functionality of both type A and B chains varies, taking the values 4, 8 and 12. The obtained values for the number of heterocontacts per lattice site are 4.020, 3.720 and 3.472. The number of heterocontacts per lattice site of the corresponding linear A/linear B blend is 4.050. Thus, the linear/linear blend is more miscible than the

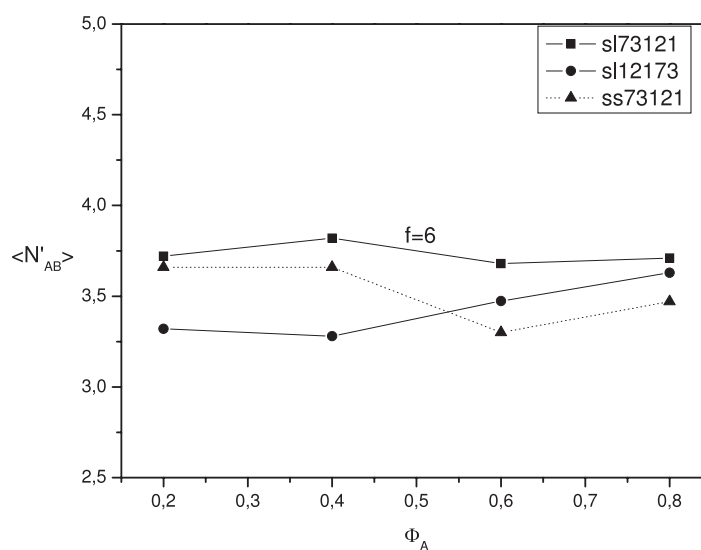


Figure 9. The mean number of heterocontacts as a function of the A species volume fraction Φ_A of star chains for star/star and star/linear blends with chemically identical monomers; $\varepsilon = 0$. sl73121 is star A/linear B blend with $M_A = 73$ and $M_B = 121$, sl12173 is a star A/linear B blend with $M_A = 121$ and $M_B = 73$ and ss73121 is the star A/star B mixture with $M_A = 73$ and $M_B = 121$. The functionality of star chains is $f = 6$ in all blends.

corresponding star/star blends in agreement to the theoretical and experimental findings based on both PS and PB polymers. This is due to the higher penetration of linear chains compared to that of the corresponding star chains. In the case of star chains, the presence of the core decreases the penetration of the arms. Therefore, the miscibility is higher in the case of linear/linear blends. Overall, the miscibility for star A/star B blends lies more or less between the values of the corresponding star A/linear B and linear A/star B blends is moving down as the number of arms increases [5]. Our Monte Carlo results presented in figure 9 for the six arm blends confirm the latter experimental conclusion showing that the number of heterocontacts per lattice site of the star A/star B blend is between those of the star A/linear B blend with $M_A = 73$, $M_B = 121$ and the star A/linear B blend with $M_A = 121$, $M_B = 73$ for values of star volume fraction lower than 0.5. Moreover, figure 9 shows that the star A/star B blend with $M_A = 73$ and $M_B = 121$ has the same dependence on the volume fraction of star chains Φ_A , as in the case of the star A/linear B blend with $M_A = 73$ and $M_B = 121$. However, the corresponding values for the star A/star B blends for the number of heterocontacts per lattice site are always smaller than those for star A/linear B blend. The star A/linear B blend with $M_A = 121$ and $M_B = 73$ shows the opposite behavior with star volume fraction compared to the above star A/linear B and star A/star B mixtures. For small volume fraction of star chains the star A/linear B blend with $M_A = 121$ and $M_B = 73$ is the less miscible blend, but for a high concentration of star chains it becomes more miscible than the corresponding star A/star B blend. Overall, the star A/linear B blend with $M_A = 73$ and $M_B = 121$ for any volume fraction of star chains is the more miscible blend. We have calculated the second derivative of the free energy S of the above mixtures for comparison purposes. The analytical results are presented in figure 10. It can be seen that the star A/star B mixture with $M_A = 73$ and $M_B = 121$ and the star A/linear B blend with $M_A = 73$ and $M_B = 121$ show almost the same behavior with the star volume fraction and star A/linear B blend is always more miscible than

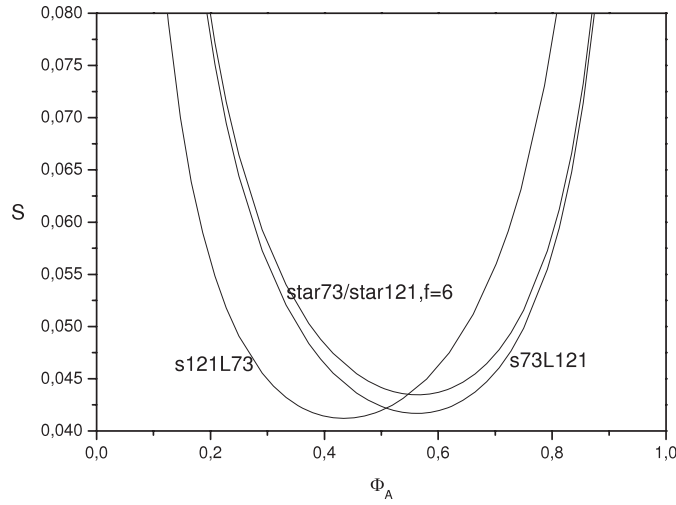


Figure 10. The second derivative of the free energy S for the corresponding star/linear and star/star mixtures of figure 9; $u = 1/16$.

the corresponding star A/star B mixture, in agreement with the simulation results. However, the analytical results indicate that the miscibility of star/star blends lies between the values of the corresponding star A/linear B and linear A/star B blends for the values of Φ_A species higher than $\Phi_A > 0.5$, while the simulation results shows the opposite behavior. There is not a simple explanation of this disagreement between the theory and the Monte Carlo simulations, since it is a complex combination of the effects of the architecture, the volume fraction and the chain molecular weight.

3.2. Collective scattering function

We study the case of star/linear blends with high size asymmetry in order to verify possible phase separation for specific mixtures. The collective scattering function is computed as [14]

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

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 $f_i = 2(1 - \Phi_A)$ if site i is occupied by unit A, $f_i = -2\Phi_A$ if site i is occupied by unit B, and also $f_i = 0$ if site i is vacant or blocked [20]. For compositionally symmetric mixtures ($\Phi_A = \Phi_B = 0.5$) this leads to the coefficient values $f_i = 1, -1, 0$ respectively, used in our previous work [2]. 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 L ,

$$q_k = (2\pi/L)n_k, \quad k = x, y, z, \quad n_k = 1, 2, \dots \quad (4)$$

According to the random phase approximation [1], the inverse of the collective scattering function $[S_{\text{col}}(\vec{q})]^{-1}$ in the homogeneous phase region should vary linearly with q^2 . If the extrapolated values of $[S_{\text{col}}(q)]^{-1}$ at $q \rightarrow 0$ are small positive numbers, then the blend remains homogeneous. However, if zero or negative values are obtained, then phase separations occur. An experimental study [11] of a unique PB star A/linear B blend with star chains containing six

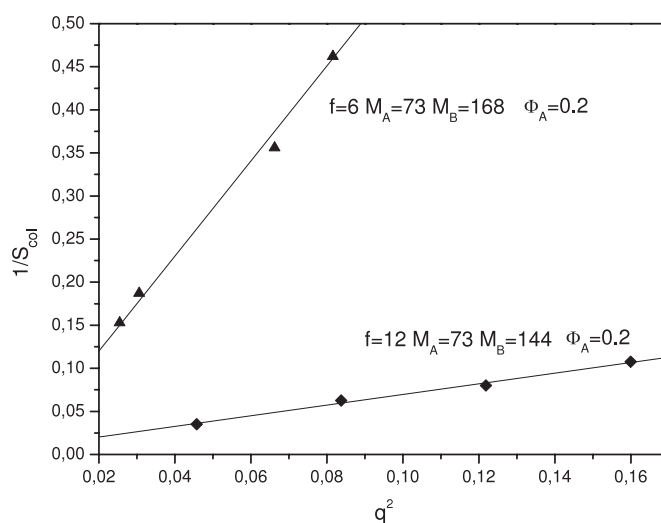


Figure 11. Plot of $1/S_{col}$ versus q^2 for different star A/linear B blends with chemically identical monomers; $\varepsilon = 0.001$.

arms and adequate long linear chains (14 times longer than the star arm length) has found that this blend is de-mixed. In this case, the volume fraction of the star chains was $\Phi_A = 0.2$. In the current work, we simulate a similar star A/linear B blend. The star chains with functionality $f = 6$ contain 73 units, while the linear ones have 168 units. Moreover, another blend with star chains containing 12 arms and 73 beads per chain is also considered. The linear chains in this blend contain 144 units, being, therefore, 24 times longer than the star arms in these mixtures.

In figure 11 we present our results. It is shown that the extrapolation of $1/S_{col}$ for ($q \rightarrow 0$) has a positive value for both cases. Therefore, for these blends with chemically identical monomers we conclude that there is no phase separation even in this case that the ratio ρ is sufficiently high. This result opposes experimental findings. Theoretical studies [7, 8], which state that no phase separation is possible for star/linear blends if the number of branches of star chains is less than 18 are confirmed at least for stars up to 12 arms.

4. Concluding remarks

In this paper we studied the effect of the architecture and the size asymmetry on the miscibility of star/linear and star/star mixtures with chemically identical monomers via MC simulations by using the BFM. Our results (presented in the appendix) are in agreement with the findings of the analytical theories and with those obtained experimentally in the case of PS blends with chemically identical monomers. However, in some cases our findings are not consistent with the obtained experimental results for PB mixtures. Since the only difference between PS and PB blends is the strength of the excluded volume interactions, the different behavior of PB blends may not be attributed to the architectural or the size asymmetry. The excluded volume interactions u between units in PB chains may be smaller due to the absence of the phenyl groups presented in PS polymers. Thus, the labeling effect and small differences in the molecular weights in PB blends may introduce a significant contribution to these smaller excluded volume interactions, and could lead to the different behavior of PB blends. Further experimental work is needed to clarify the observed differences between PS and PB blends.

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Appendix

The following tables contain concisely the main conclusions of this study.

Star A/linear B blends

Volume fraction	Property	Miscibility
$\Phi_A = 0.2$	Increase in the molecular weight of linear chains ($M_B \leq M_{\text{branch}}$)	Decrease
$\Phi_A = 0.2$	Increase in the molecular weight of linear chains ($M_B > M_{\text{branch}}$)	Slight decrease
$\Phi_A = 0.2$	Increase in the star functionality f	Decrease
	Increase of the Φ_A ($M_A > M_B$)	Increase
$\Phi_A = 0.2$	Decrease in the temperature	Slight decrease

Star A/star B ($f_A = f_B$)

Volume fraction	Property	Miscibility
Any Φ_A	Increase in star functionality f ($M_A > M_B$)	Decrease
	Increase Φ_A ($M_A > M_B$)	Increase
$\Phi_A = 0.5$	Increase of the molecular weight for constant $\rho = M_A/M_B$ ($f = \text{constant}$)	Decrease

Comparison between linear A/linear B, star A/star B, star A/linear B and star B/linear A

Linear/linear are more miscible than star/star and linear/star blends for the same volume fraction and total molecular weights.

For $\Phi_A < 0.5$ the miscibility of star A/star B lies between star A/linear B and linear A/star B blends. For $\Phi_A > 0.5$ star A/star B ($M_A < M_B$) is less miscible than star A/linear B and linear A/star B mixtures.

Phase separation

No phase separation found for star A/linear B blends with functionality $f = 12$ and molecular weight of linear chains 24 times longer than the star arm.

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