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Effective Interaction Parameters of Star/Star, Ring/Ring, and Ring/Linear Chemically Identical Blends

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ABSTRACT: The effects of chain size and architectural asymmetry on the miscibility of chemically identical polymer blends composed of star/star, ring/ring, and ring/linear chains are studied by means of an analytical theory. The free energy of these blends is obtained through the summation of the series of the one-loop diagrams at any dimensionality d. From the spinodal equation, we find that for the same total molecular weights the effective repulsions between ring/ring species are higher than those of linear/linear blends and higher than those of the symmetrical star/star blends of four branches but smaller than the respective interactions of star/star blends where both species have five arms. At $d = 3$ no phase separation is found for blends composed of ring/ring and ring/linear chains at any size disparity or volume fraction. The same is true in the case of blends composed of star/star or star/linear chains with a few or a moderate number of arms in agreement with recent experimental and theoretical results.

Introduction

An important factor influencing polymer material properties is the architecture of the component polymer chains. Branched or ring architecture leads to more compact chains, the stiffnesses of which differ from those of the linear ones. This affects properties such as melt rheology, glass transition temperature, and crystallinity.[1] Blending and separating chemically identical polymers with different molecular weights or architecture allows a step further to be achieved, and thus materials with enhanced or even novel properties can be expected. This is because the excluded volume interactions between units belonging to different chains are not canceled as Flory's theory suggests[2] but remain, leading to a nonrandom mixing or even demixing in some circumstances.[3] Experimentally, small-angle neutron scattering (SANS) is used for the study of chemically identical blends, where the necessary contrast is achieved by deuterating one of the components. However, a distinction between chemically identical blends and blends of isotopic analogues[4−7] which can actually be studied experimentally should be made. The properties of the latter are due to a combination of architectural effects and labeling effects. The magnitudes of the architectural effects can be deduced[4−6] by estimating the total effective thermodynamic interactions ($\chi_{\mathrm{eff,total}}$) and then subtracting a measured value for χ in a linear/linear blend in which isotopic labeling is presumably the dominant effect. Using this technique, Greenberg and co-workers measured the thermodynamic interactions (χ_{eff}) in blends of star and linear polystyrene[4,5] (PS), and the respective star/linear chemically identical blends of polybutadiene[6] (PB) and poly(methyl methacrylate)[7] (PMMA). They found that in PS and PMMA star/linear blends (with stars having up to 12 arms), thermodynamic interactions always increase with the number of arms, while this change is not monotonic in PB blends. In both cases, the effective interaction parameter χ_{eff} decreases when the branch length and the star volume fraction in the blend increase whereas it increases when the length of the linear chains is increased.

The original Flory−Huggins theory needs nontrivial amendments in order to account properly for the interactions between similar units and thus to describe chemically identical blends. Fredrickson et al. employ the Gaussian field theory proposing entropic corrections in linear/linear, star/linear, and comb/linear chemically identical blends. Chain correlations are incorporated in their model through the scattering structure factor,[8] and the thermodynamic interactions are expressed in terms of the radii of gyration of the two parts, the number of branches, and the star volume fraction. χ_{eff} obtained from the Gaussian field theory for star/linear blends are in qualitative agreement with the experimental results, except in two cases related to the PB star/linear blends: the dependence of χ_{eff} on the linear molecular weight, where the theory anticipates the reverse behavior, and the nonlinear change of χ_{eff} with increasing f. Another conclusion of the theory is that bulk phase segregation due to architecture alone could be expected for star/linear blends, but only when stars have a large number of arms ($f > 20$). However, experimentally, phase separation is observed in two particular PB and PMMA blends of six- and seven-arm stars with sufficiently large linear chains.[6,7] Equivalent to the Gaussian field theory, we have recently incorporated correlations between all chains of the blends by means of the one-loop diagrams and found directly the spinodal line.[9] Our results for star/linear blends, presented in the next sections, are close to the theoretical findings of Fredrickson et al.

Despite the extensive literature that is available on the chemically identical star/linear blends[4−8] with moderate number of arms, the thermodynamic interactions in chemically identical ring/ring, ring/linear, and star/

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star blends remain largely unexplored. To the best of our knowledge, only two experimental studies on star/star and ring/ring blends have been reported,[10–12] but no theoretical work has yet appeared. Our aim is to investigate the thermodynamic interactions and the phase behavior of all the above-mentioned types of chemically identical blends using an analytical model. The partition function and the resulting free energy and stability conditions are obtained through the inclusion of the summation of the series of the one-loop diagrams[13–15] between chains at any dimensionality d. The model has been successfully applied in the case of chemically identical linear/linear blends[9,16] with chain size asymmetry. Thus, it is also expected to describe the ring/ring, ring/linear, and the star/star chemically identical blends having a moderate number of arms.

Model

We consider a system composed of two macromolecular species A and B with population n_A and n_B chains each, having different molecular weights N_A and N_B respectively. The chains fully occupy a volume V and are represented by continuous curves in d dimensions. In the canonical ensemble the configurational partition function can be written as $Z = Z_0 \int D\vec{R} \exp[-H(\vec{R})/k_BT]$ where Z_0 is the unperturbed partition function

$$Z_0^{ss} = \frac{V^{n_A+n_B}}{n_A!n_B!},\quad Z_0^{rr} = \left(\frac{d}{2\pi\ell^2 N_A}\right)^{n_A d/2}\left(\frac{d}{2\pi\ell^2 N_B}\right)^{n_B d/2}\frac{V^{n_A+n_B}}{n_A!n_B!},$$
$$Z_0^{rl} = \left(\frac{d}{2\pi\ell^2 N_r}\right)^{n_r d/2}\frac{V^{n_r+n_B}}{n_r!n_B!}$$

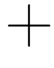
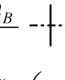
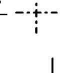
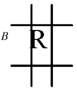
for the star/star, ring/ring, and ring/linear blends, respectively. $\int D\vec{R}$ denotes integration over the positions of all statistical segments of each species and $H(\vec{R})$is an Edwards type Hamiltonian for a collection of n_A and n_B interacting chains.

$$H/k_BT = \sum_{i=A;B}\sum_{j=1}^{n_i}\int_0^{N_i} ds\left(\frac{d\vec{R}_j(s)}{ds}\right)^2 + \sum_{i,j=A;B}\sum_{i'=1}^{n_i}\sum_{j'=1}^{n_i}\int_0^{N_i} ds\int_0^{N_j} ds'\,\delta^d((\vec{R}_{i'}(s) - \vec{R}_{j'}(s'))w_{ij} \quad (1)$$

The first term counts for the connectivity of the chains, with the $\vec{R}_j(s)$ representing the spatial position of the sth statistical segment of the jth chain, while the second stands for the interactions between nonadjacent parts of the chains. Notice that**,** strictly speaking, N in eq 1 is defined as a contour chain length and it is equal to the number of units N/ℓ times the length ℓ of each unit, ℓ considered, however for simplicity to be equal to 1. All excluded volume interaction parameters w_{AA}, w_{BB}, and w_{AB} are taken in the present work equal to u due to the chemical identity of the species A and B. Following previous works[13,14] and expanding the configurational-partition function with respect to inter-excluded-volume interactions, we take

$$Z = Z_0\left\langle 1 - u\sum_{i,j=A;B}\sum_{i'=1}^{n_i}\sum_{j'=1}^{n_j}\int_0^{N_i} ds\int_0^{N_j} ds'\,\delta^d\left((\vec{R}_{i'}(s) - \vec{R}_{j'}(s')\right) + \sum_{m>2}\frac{(-1)^m u^m}{m!}\left[\sum_{i,j=A;B}\sum_{i'=1}^{n_i}\sum_{j'=1}^{n_{ji}}\int_0^{N_i} ds\int_0^{N_j} ds'\,\delta^d\left((\vec{R}_{i'}(s) - \vec{R}_{j'}(s')\right)\right]^m\right\rangle \quad (2)$$

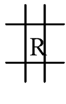
Each δ function of eq 2 brings into contact segments of different chains and diagrams to all orders of u are produced. These diagrams can be classified in three major categories according to the number of contacts i, and the number of chains m involved in them. The case $i = m - 1$ corresponds to the well-known RPA open connected diagrams with no loops while the cases $i < m - 1$ and $i = m$ correspond to the open-disconnected and ring diagrams, respectively. Every line of these diagrams stand for a chain either of the species A or B. The RPA diagrams in eq 2 sum into an exponential while among all connected diagrams, which survive in the expression of ln$Z$ the ring diagrams play a dominant role. Including these two classes of diagrams ln$Z$ can be written as

$$\ell nZ = \ell nZ_0 - u[\frac{n_A^2}{V}$$

$$+2\frac{n_A n_B}{V}$$

$$+\frac{n_B^2}{V}$$

$$] + \sum_{m>1}\frac{(-u)^m}{m!}2^{m-1}(m-1)!\frac{1}{V^{m-1}}\sum_{m_A=0}^{m}\binom{m}{m_A}n_A^{m_A}n_B^{m_B}$$

$$(3)$$

where the ring diagrams are represented by the last summation of eq 3. The number of these ring diagrams involving $m = m_A + m_B$ chains from species A and B, comes (a) from the $\binom{m}{m_A} n_A^{m_A} n_B^{m_B}$ different ways the m chains can be chosen among all the $n_A + n_B$ of chains, (b) from the different $(m-1)!$ arrangements of the m chains to form the ring, and (c) from the two ways that each chain can be placed in a position inside a ring, in total 2^{m-1} ways. The ring diagrams can be written in terms of the Debye or Debye-like integrals

$$J_A^l = \int_0^1 dx\,(1-x)e^{-px} = (e^{-p} - 1 + p)/p^2,$$
$$J_B^l = \int_0^1 dx\,(1-x)e^{-prx} = (e^{-pr} - 1 + pr)/p^2r^2,\quad J_A^r = (^1/_2)\int_0^1 dx\,e^{-px(1-x)}$$
$$J_B^r = (^1/_2)\int_0^1 dx\,e^{-prx(1-x)}$$

for the linear and ring chains respectively as


$$= (N_A^{2m-d/2}r^m/\Gamma(d/2))\int_0^\infty dp\,p^{d/2-1}J_A^{m_A}J_B^{m_B} \quad (4)$$

where p is a dummy integration variable, Γ is the gamma function and $r = N_B/N_A$ is the size asymmetry ratio of the two polymer species. Using the values of all diagrams in eq 3 and performing the trivial summation of ring diagrams, we obtain the following expressions of the partition function of the ring/ring and ring/linear chemically identical blends

$$\ln Z^{\mathrm{rr}} = \ln Z_0^{\mathrm{rr}} - uV + \frac{V}{2\Gamma(d/2)N_{\mathrm{A}}^{d/2}}\int_0^\infty \mathrm{d}p\, p^{d/2-1} [-\ln[1 + (4uN_{\mathrm{A}}\varphi_{\mathrm{A}}J_{\mathrm{A}}^{\mathrm{r}}) + (4uN_{\mathrm{A}}r\varphi_{\mathrm{B}}J_{\mathrm{B}}^{\mathrm{r}})]] \quad (5)$$

$$\ln Z^{\mathrm{rl}} = \ln Z_0^{\mathrm{rl}} - uV + \frac{V}{2\Gamma(d/2)N_{\mathrm{A}}^{d/2}}\int_0^\infty \mathrm{d}p\, p^{d/2-1} [-\ln[1 + (4uN_{\mathrm{A}}\varphi_{\mathrm{A}}J_{\mathrm{A}}^{\mathrm{r}}) + (4uN_{\mathrm{A}}r\varphi_{\mathrm{B}}J_{\mathrm{B}}^{\mathrm{l}})]] \quad (6)$$

where φ_{A} and φ_{B} are the volume fractions of the A and B species equal to $n_{\mathrm{A}}N_{\mathrm{A}}v_{\mathrm{A}}/V$ and $n_{\mathrm{B}}N_{\mathrm{B}}v_{\mathrm{B}}/V$ respectively. v_{A} and v_{B} are the effective volumes of the A and B units considered for simplicity to be both equal to unity, $v_{\mathrm{A}} = v_{\mathrm{B}} = 1$, without changing the analysis and the conclusions which follow. This of course makes V equal to $V = n_{\mathrm{A}}N_{\mathrm{A}}v_{\mathrm{A}} + n_{\mathrm{B}}N_{\mathrm{B}}v_{\mathrm{B}} = n_{\mathrm{A}}N_{\mathrm{A}} + n_{\mathrm{B}}N_{\mathrm{B}}$, and it appears to be dimensionless though it has the units of volume.

More complicated is the case of the star/star chemically identical blends due to the two different ways that each star chain can participate in the ring diagrams: the two indices of the excluded volume interactions i, j in eq 2 can lie on the same or on the different branches. This leads to the following expression of the partition function

$$\ln Z^{\mathrm{ss}} = \ln Z_0^{\mathrm{ss}} - uV + \frac{V}{2\Gamma(d/2)N_{\mathrm{A}}^{d/2}}\left(\frac{d}{2\pi}\right)^{d/2}\int_0^\infty \mathrm{d}p\, p^{d/2-1} [-\ln[1 + (4uN_{\mathrm{A}}\varphi_{\mathrm{A}}J_{\mathrm{A}}^{\mathrm{l}} + 2u(f_{\mathrm{A}} - 1)N_{\mathrm{A}}\varphi_{\mathrm{A}}{h_{\mathrm{A}}}^2) + (4uN_{\mathrm{A}}r\varphi_{\mathrm{B}}J_{\mathrm{B}}^{\mathrm{l}} + 2u(f_{\mathrm{B}} - 1)N_{\mathrm{A}}r\varphi_{\mathrm{B}}{h_{\mathrm{B}}}^2)]], \quad r = N_{\mathrm{B}}/N_{\mathrm{A}} \quad (7)$$

where f_{A} and f_{B} are the number of branches of the A and B star polymers, N_{A} and N_{B} the branch lengths, and h_{A}, h_{B} the Debye-like functions $h_{\mathrm{A}} = (1/p)(1 - e^{-p})$, $h_{\mathrm{B}} = (1/pr)(1 - e^{-pr})$.

Results and Discussion

(a) Star/Star Chemically Identical Blends. The Helmoltz free energy density of mixing for the chemically identical blends of A and B star polymer species $\Delta F/K_{\mathrm{B}}TV = -\ln Z^{\mathrm{ss}} + \ln Z_{\mathrm{A}}^{\mathrm{s}} + \ln Z_{\mathrm{B}}^{\mathrm{s}}$, can be obtained by means of the partition functions of the blend (eq 7) and the respective of the homopolymer melts $Z_{\mathrm{A}}^{\mathrm{s}} = V_{\mathrm{A}}^{n_{\mathrm{A}}}/n_{\mathrm{A}}!$ and $Z_{\mathrm{B}}^{\mathrm{s}} = V_{\mathrm{B}}^{n_{\mathrm{B}}}/n_{\mathrm{B}}!$

$$\frac{\Delta F}{K_{\mathrm{B}}TV} = \frac{\varphi_{\mathrm{A}}}{N_{\mathrm{A}}}\ln\varphi_{\mathrm{A}} + \frac{\varphi_{\mathrm{B}}}{N_{\mathrm{A}}r}\ln\varphi_{\mathrm{B}} + u + \frac{V}{2\Gamma(d/2)N_{\mathrm{A}}^{d/2}}\left(\frac{d}{2\pi}\right)^{d/2}\int_0^\infty \mathrm{d}p\, p^{d/2-1}[-\ln[1 + \zeta_{\mathrm{A}}\varphi_{\mathrm{A}}(2J_{\mathrm{A}}^{\mathrm{l}} + (f_{\mathrm{A}} - 1){h_{\mathrm{A}}}^2) + \zeta_{\mathrm{B}}\varphi_{\mathrm{B}}(2J_{\mathrm{B}}^{\mathrm{l}} + (f_{\mathrm{B}} - 1){h_{\mathrm{B}}}^2)]], \quad \zeta_{\mathrm{A}} = 2uN_{\mathrm{A}}, \quad \zeta_{\mathrm{B}} = 2uN_{\mathrm{A}}r \quad (8)$$

It depends on V only through the volume fractions φ_{A} and φ_{B} and exactly reproduces the first two ideal terms in the well-known Flory–Huggins expression. The third u term, due to the absence of a prefactor that depends on the second order of the volume fractions, is eliminated in the spinodal equation, which takes the form

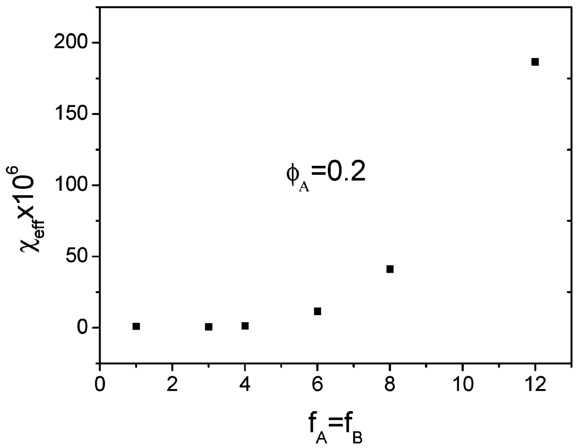


Figure 1. χ_{eff} as a function of star functionality for star A/star B chemically identical blends with the same number of arms $f_{\mathrm{A}} = f_{\mathrm{B}}$ and constant total molecular weights $M_{\mathrm{A}} = 3000$ and $M_{\mathrm{B}} = 18000$ ($u = 1/16$).

$$\frac{\partial^2 \Delta F}{\partial {\varphi_{\mathrm{A}}}^2} = \frac{1}{\varphi_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{(1 - \varphi_{\mathrm{A}})N_{\mathrm{A}}r} - 2\chi_{\mathrm{eff}} = 0 \quad (9)$$

where χ_{eff} is defined according to the Flory expression, and it is equal to

$$\chi_{\mathrm{eff}} = \frac{1}{\Gamma(d/2)N_{\mathrm{A}}^{d/2}}\left(\frac{d}{2\pi}\right)^{d/2}\int_0^\infty \mathrm{d}p\, p^{d/2-1} \frac{[[2\zeta_{\mathrm{A}}j_{\mathrm{A}}^{\mathrm{l}} + \zeta_{\mathrm{A}}(f_{\mathrm{A}} - 1){h_{\mathrm{A}}}^2] - [2\zeta_{\mathrm{B}}j_{\mathrm{B}}^{\mathrm{l}} + \zeta_{\mathrm{B}}(f_{\mathrm{B}} - 1){h_{\mathrm{B}}}^2]]^2}{[1 + 2\zeta_{\mathrm{A}}\varphi_{\mathrm{A}}j_{\mathrm{A}}^{\mathrm{l}} + \zeta_{\mathrm{A}}\varphi_{\mathrm{A}}(f_{\mathrm{A}} - 1){h_{\mathrm{A}}}^2 + 2\zeta_{\mathrm{B}}\varphi_{\mathrm{A}}j_{\mathrm{B}}^{\mathrm{l}} + \zeta_{\mathrm{B}}\varphi_{\mathrm{A}}(f_{\mathrm{B}} - 1){h_{\mathrm{B}}}^2]^2} \quad (10)$$

The spinodal equation can obtain an analytic form if we replace the Debye functions with the approximants $j_{\mathrm{A}}^{\mathrm{l}} = (p + 2)^{-1}$, $j_{\mathrm{B}}^{\mathrm{l}} = (pr + 2)^{-1}$, $h_{\mathrm{A}} = (p + 1)^{-1}$, and $h_{\mathrm{B}} = (pr + 1)^{-1}$. However, this approximation, while it correctly reproduces the $p \to 0$, and the $p \to \infty$ limits of the exact expressions, introduces an error in the case of ${h_{\mathrm{A}}}^2$, which can reach 60% of the true values. Thus, to maintain accuracy, we decided to calculate numerically eqs 9 and 10, via the MATHEMATICA package. The functionals of these eqs are continuous functions for the entire range of the integration variable p in contrast to the Fredrickson analytical formulas for star/linear blends where cutoffs are needed to avoid singularities. This is because the summation of one-loop diagrams we follow here explicitly reproduces the unity in the denominator which prevents singularities in the limit $p \to 0$ where the Debye functions have their maximum values.

In our analysis, we initially consider star A/star B chemically identical blends with the same number of arms $f_{\mathrm{A}} = f_{\mathrm{B}}$, but with different molecular weights (size asymmetry). Our aim is to find how the effective repulsions between different chains, due to size asymmetry, depend on the number of arms f, the branch length N_{A} and N_{B} of the two species, and the volume fractions φ_{A}, φ_{B}. In Figure 1, we present the effective interactions χ_{eff} for chemically identical star/star blends with $f_{\mathrm{A}} = f_{\mathrm{B}} = 1$ (linear), 3, 4, 6, 8 and 12 and constant

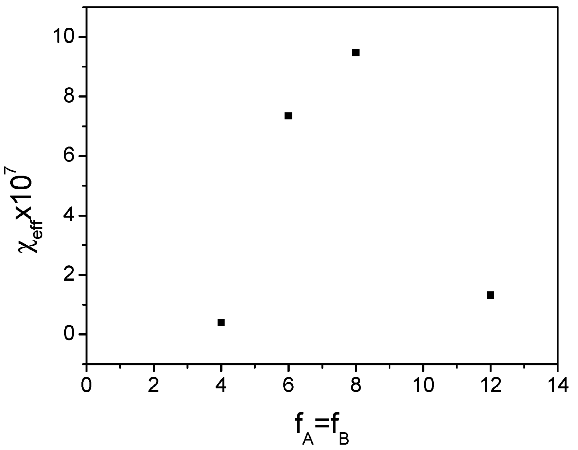


Figure 2. $\chi_{\rm eff}$ as a function of star functionality for star A/star B chemically identical blends with the same number of arms $f_{\rm A} = f_{\rm B}$ and different arm lengths. ($f = 4$, $N_{\rm A} = 405$, $N_{\rm B} = 445$, $\varphi_{\rm A} = 0.17$), ($f = 6$, $N_{\rm A} = 310$, $N_{\rm B} = 378$, $\varphi_{\rm A} = 0.18$), ($f = 8$, $N_{\rm A} = 236$, $N_{\rm B} = 268$, $\varphi_{\rm A} = 0.16$), ($f = 12$, $N_{\rm A} = 163$, $N_{\rm B} = 167$, $\varphi_{\rm A} = 0.16$). $u = {}^1\!/_{16}$.

total molecular weights $M_{\rm A} = f_{\rm A}N_{\rm A} = 3000$ and $M_{\rm B} = f_{\rm B}N_{\rm B} = 18000$. In all cases, the excluded volume parameter u has been set equal to the fixed point value of $u^* = \epsilon/16 = {}^1\!/_{16}$ ($\epsilon = 4 - d$, $d = 3$), as in our previous works.[9,16] It can be observed that $\chi_{\rm eff}$ is increased when the functionality of star polymers increases, except in the case of the three-arm stars, where $\chi_{\rm eff}$ takes the lowest value. This special behavior of three-arm star is also observed[17] in dilute solutions, where the nonideal contribution to the partition function is canceled at $f = 3$. Experimentally, star polymers with different functionalities, but exactly the same total molecular weight, are very difficult to synthesize. Martter and co-workers[10] using deuterated (PB) star blends with narrow, but different molecular weights, found that $\chi_{\rm eff}$ shows a nonmonotonic behavior when the star functionality increases. Their $\chi_{\rm eff}$ decreases when f increases from 4 to 8, and then increases in the 12 arm star blends reaching a value similar to that of $f = 4$ blends. Using the molecular characteristics of the deuterated PB star/star blends from ref 10 ($f = 4$, $N_{\rm A} = 405$, $N_{\rm B} = 445$, $\varphi_{\rm A} = 0.17$), ($f = 6$, $N_{\rm A} = 310$, $N_{\rm B} = 378$, $\varphi_{\rm A} = 0.18$), ($f = 8$, $N_{\rm A} = 236$, $N_{\rm B} = 268$, $\varphi_{\rm A} = 0.16$), ($f = 12$, $N_{\rm A} = 163$, $N_{\rm B} = 167$, $\varphi_{\rm A} = 0.16$), we calculate the theoretical values of $\chi_{\rm eff}$ for these blends. Our results presented in Figure 2 are in agreement with the experimental findings for star/star blends with $f = 4$ and 12 arms, while the other values of $\chi_{\rm eff}$ for $f = 6$, 8 are higher. In any case, it is clear that the nonmonotonic behavior of $\chi_{\rm eff}$ observed experimentally arises from the subtle differences of the arm lengths. As regards the dependence of the effective interactions on the branch length of the A star species, $N_{\rm A}$, for constant asymmetry ratio $r = N_{\rm B}/N_{\rm A}$ and volume fractions, this is illustrated in Figure 3. Here we consider star/star blends with $f_{\rm A} = f_{\rm B} = 6$ and ($r = 3$, $\varphi_{\rm A} = 0.8$, $u = {}^1\!/_{16}$). An increase in branch length $N_{\rm A}$ entails a decrease in $\chi_{\rm eff}$. Now the variation of $\chi_{\rm eff}$ with r and $\varphi_{\rm A}$is presented in Figure 4, and it is similar to what we have found for linear/linear chemically identical blends. For $r = 1$, all chains in the star/star blend are equivalent and $\chi_{\rm eff} = 0$. With an increase of the asymmetry ratio, the effective interactions also increase, taking maximum values when we have a few large star chains in a sea of small chains ($\varphi_{\rm A} \rightarrow 1$), in agreement with the notion of depletion potential.[18]

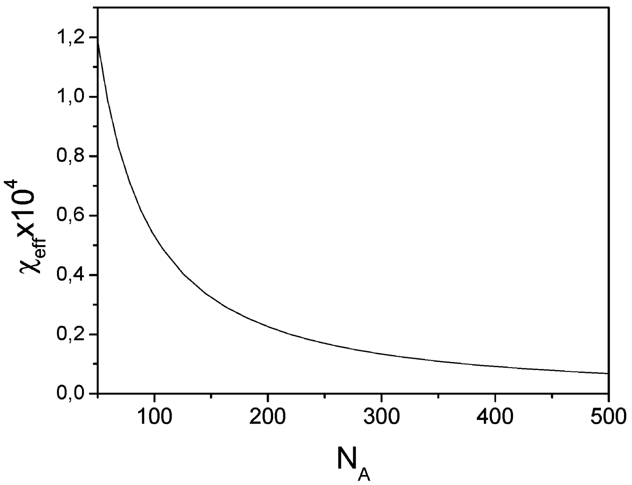


Figure 3. $\chi_{\rm eff}$ as a function of the star A arm length for star A/star B chemically identical blends with the same number of arms $f_{\rm A} = f_{\rm B} = 6$ ($r = 3$, $\varphi_{\rm A} = 0.8$, $u = {}^1\!/_{16}$).

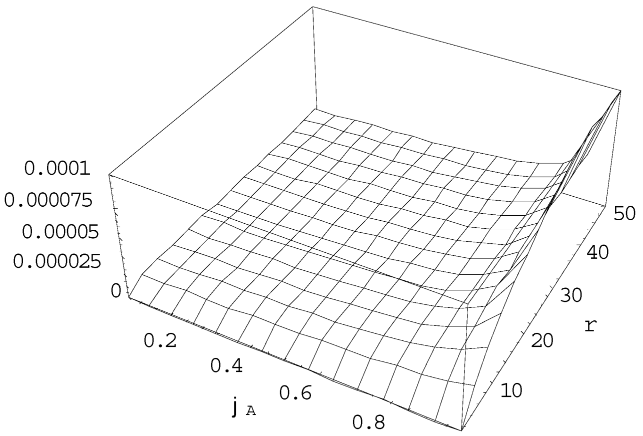


Figure 4. $\chi_{\rm eff}$ as a function of the star A volume fraction $\varphi_{\rm A}$ and the asymmetry ratio $r = N_{\rm B}/N_{\rm A}$ star A/star B chemically identical blends with the same number of arms $f_{\rm A} = f_{\rm B} = 4$ ($N_{\rm A} = 200$, $u = {}^1\!/_{16}$).

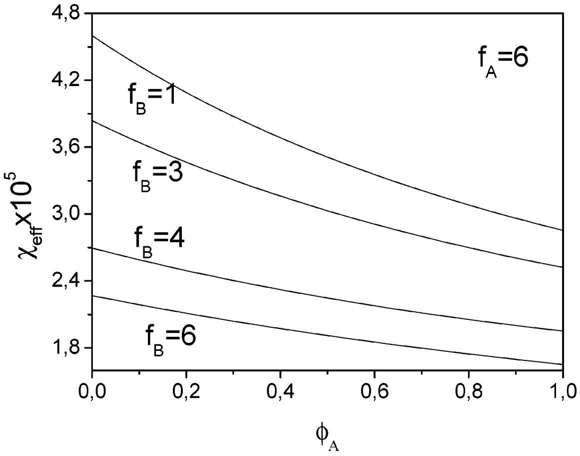


Figure 5. $\chi_{\rm eff}$ as a function of the star A volume fraction for various star A/star B chemically identical blends. $M_{\rm A} = 1800$, $M_{\rm B} = 3600$, $u = {}^1\!/_{16}$.

Next we consider chemically identical star/star blends of components having different numbers of arms. Our aim is to determine the effects of architectural asymmetry on the effective interactions for various branch lengths and volume fractions. In Figure 5, we present $\chi_{\rm eff}$ for star/star blends as a function of the A stars'

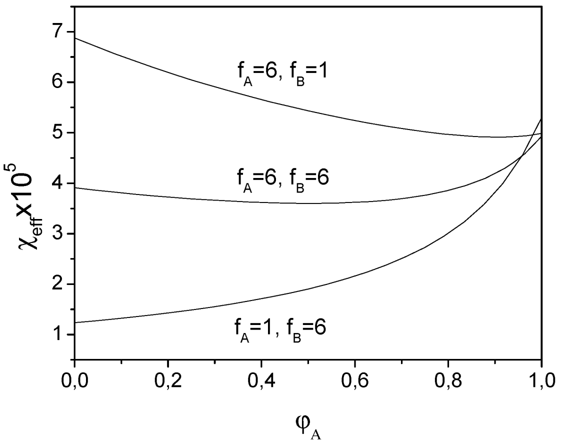


Figure 6. χ_{eff} as a function of volume fraction of A species for various star/star and star/linear chemically identical blends. $M_A = 1200$, $M_B = 7200$, $u = 1/16$.

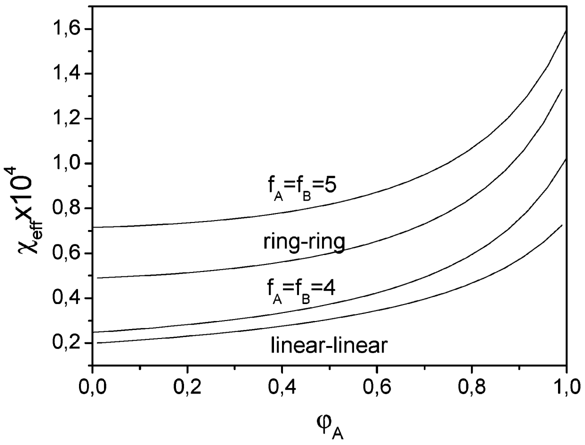


Figure 7. Comparison between χ_{eff} of various chemically identical blends. $M_A = 300$, $M_B = 1500$, $u = 1/16$.

volume fraction. Both species, A and B, have fixed total molecular weights equal to $M_A = 1800$, $M_B = 3600$. It can be observed that the effective interactions increase when the difference between the numbers of arms increases, obtaining the highest value when the star chain of the one component becomes a linear polymer ($f = 1$). Experimentally, changes on the χ_{eff} value resulting from small dissimilarities in the number of arms of the two components in star/star blends were too small to determine except in the case of star/linear blends. Our results for the star/linear blends show that thermodynamic interactions always increase with the number of arms, while they decrease when the branch length and the star volume fraction in the blend increase. χ_{eff} also decreases when the length of the linear chains increases, in agreement with the Fredrickson's theoretical results. Overall, the experimental values of χ_{eff} for star A/star B blends lie more or less between the values of the corresponding star A/linear B and linear A/star B blends, moving up as the number of arms increases. Our theoretical values of χ_{eff} for the six-arm star blends and total molecular weights $M_A = 1200$, $M_B = 7200$ with respect to the A species volume fraction presented in Figure 6 confirm the experimental findings. However, we verify that for higher size asymmetries e.g ($M_A = 1200$, $M_B = 16000$), χ_{eff} in star/star blends becomes slightly higher than both χ_{eff} values of star/linear blends for a range of volume fractions values φ_A greater than 0.7. For smaller asymmetries ($M_A = 1200$, $M_B = 2400$), χ_{eff} in star/star blends is found to be lower than the respective χ_{eff} values of both star/linear blends.

Are the effective interactions strong enough to cause phase separation in star/linear chemically identical blends? For large asymmetries: short arm length $N_A = 10$ and long linear chains $N_B = 13000$ corresponding to $M_{wA} = 3000$, $M_{wB} \cong 4000000$ for PS, our results obtained from the spinodal equation (eq 9) show that there is no phase separation in star/linear blends for stars having up to 12 arms. For smaller asymmetries, star/linear blends remain miscible for stars of up to 18 arms or a few more. It is known, however, from the study of dilute solutions that the one-loop models for star chains overestimate the excluded volume interactions. This is a weakness for star chains with a high number of arms, and occurs when higher loop orders are not included.[19] Another crucial point to mention here is the value of the excluded volume interaction parameter u. We have set u equal to the fixed point value $u^* = \epsilon/16$. Despite the fact that this value is excellent for obtaining the critical exponents of various macroscopic properties of polymers or for comparing the χ_{eff} values of different chemically identical blends, it is not clear whether it is appropriate for use in the spinodal equation. An unusually large value of the interaction parameter u, which may include a contribution from the labeling effects too, can lead to phase separation in star/linear blends with six arm stars and long linear chains in agreement with the experimental findings.[6]

(b) Ring/Ring Chemically Identical Blends. The spinodal equation and the effective interactions for chemically identical ring/ring blends can be obtained by means of eq 5 with a procedure similar to that described in the previous section for star/star blends.

$$\frac{1}{\varphi_A N_A} + \frac{1}{(1-\varphi_A)N_A r} - 2\chi_{eff}^{rr} = 0, \quad r = N_B/N_A \quad (11)$$

$$\chi_{eff}^{rr} = \frac{{\lambda_r}^2}{\Gamma(d/2)N_A^{d/2}} \left(\frac{d}{2\pi}\right)^{d/2} \int_0^\infty \mathrm{d}p\, p^{d/2-1} \frac{(j_A^r - r j_B^r)^2}{[1 + \lambda_r[\varphi_A j_A^r + (1-\varphi_A) r j_B^r]]^2}, \quad \lambda_r = 4uN_A \quad (12)$$

The first regularity for chemically identical ring/ring blends with $N_A > N_B$ is that the effective interactions χ_{eff}^{rr} decrease when the volume fraction φ_A of the long chains increases. With an increase in the size disparity between the two species χ_{eff}^{rr} is also increases. Furthermore, the effective interactions χ_{eff}^{rr} for the same asymmetry ratio $r = N_B/N_A$ are stronger when the molecular weights of the two species are smaller. In Figure 7, we compare the values of the effective interactions between linear/linear, star/star and ring/ring blends. In all cases the molecular weights for the two species A and B are constant, equal to $M_A = 300$ and $M_B = 1500$. The values of the effective interactions of linear/linear blends are obtained from eq 10 with $f_A = f_B = 1$. It can be observed that χ_{eff}^{rr} interactions between ring/ring species are higher than those of linear/linear blends, higher than those of the symmetrical star/star blends of four branches but smaller than the respective interactions of star/star blends where both species have five arms. Changing the molecular weights of the two species, we always obtain the same trends. Small-angle neutron scattering has

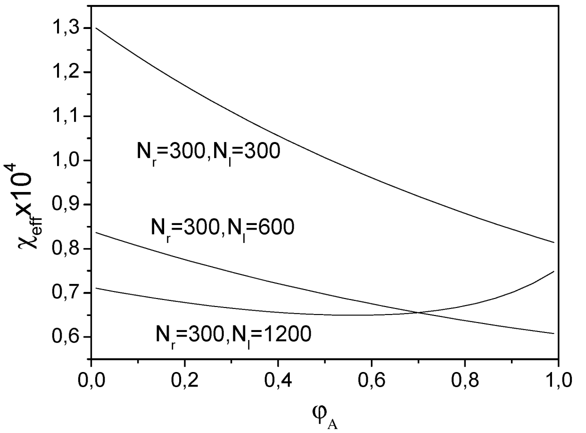


Figure 8. χ_{eff} as a function of volume fraction of the ring polymer for various ring/linear chemically identical blends. $u = {}^1/_{16}$.

been used experimentally to investigate the conformations of linear/linear and ring/ring poly(dimethylsiloxanes) PDMS in chemically identical blends over a range of molar mass and compositions. Both hydrogenated and deuterated linear chains were shown to have radii of gyration, which agree with the theoretical prediction of random walk model. In contrast, ring chains in labeled ring/ring blends adopt more expanded average conformations.[12] The experimental findings are in accordance with our theoretical results, which predict that the effective interactions in linear/linear blends are too weak to cause size expansion, while the respective interactions for ring/ring blends are much stronger and expand the ring chains. From the discussion of the previous section it is obvious that ring/ring effective interactions which are lower than the respective ones of star/star blends with five arms are not strong enough to cause phase separation in chemically identical ring /ring blends.

(c) Ring/Linear Chemically Identical Blends. In this last section we discuss the ring/linear chemically identical blends. Component A is a ring homopolymer consisting of N_{A} statistical segments. Component B is a linear homopolymer having the same chemical constitution of N_{B} segments. The spinodal equation and the resulting effective interactions of these blends are obtained by means of eq 6 as

$$\frac{1}{\varphi_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{(1-\varphi_{\mathrm{A}})N_{\mathrm{A}}r} - 2\chi_{\mathrm{eff}}^{\mathrm{rl}} = 0,\ r = N_{\mathrm{B}}/N_{\mathrm{A}} \quad (13)$$

$$\chi_{\mathrm{eff}}^{\mathrm{rl}} = \frac{{\lambda_{\mathrm{r}}}^2}{2\Gamma(d/2)N_{\mathrm{A}}^{d/2}} \left(\frac{d}{2\pi}\right)^{d/2}\int_0^\infty \mathrm{d}p\, p^{d/2-1}\frac{(j_{\mathrm{A}}^{\mathrm{r}} - rj_{\mathrm{B}}^{\mathrm{l}})^2}{[1+\lambda_r\varphi_{\mathrm{A}}j_{\mathrm{A}}^{\mathrm{r}} + \lambda_r(1-\varphi_{\mathrm{A}})rj_{\mathrm{B}}^{\mathrm{l}}]]^2},\quad \lambda_{\mathrm{r}} = 4uN_{\mathrm{A}} \quad (14)$$

In Figure 8 , we present our numerical results for $\chi_{\mathrm{eff}}^{\mathrm{rl}}$ obtained using the MATHEMATICA package. We consider ring chains with $N_{\mathrm{A}} = 300$ segments and linear chains with $N_{\mathrm{B}} = 300$, 600, and 1200 respectively. For the size symmetric case ($N_{\mathrm{A}} = N_{\mathrm{B}} = 300$), where only architectural asymmetry is present, it is observed that with an increase in the volume fraction of the ring chains the effective interactions decrease. In other words, the addition of a small concentration of ring molecules to a linear melt is less favorable thermodynamically than is the addition of a small concentration of linear chains to a ring melt. This is also true in ring/linear blends where the linear chains are twice as long as the ring ones ($N_{\mathrm{A}} = 300$; $N_{\mathrm{B}} = 600$). The evidence from this of the easier penetration of linear chains into rings is clear. With a further increase of the linear chain size, this penetration ceases to be easy and leads to the opposite result. Indeed, with an increase in the asymmetry ratio $r = N_{\mathrm{B}}/N_{\mathrm{A}}$ there is a decrease in $\chi_{\mathrm{eff}}^{\mathrm{rl}}$ up to the ring chains' volume fraction $\varphi_{\mathrm{A}} = 0.7$. For higher values of φ_{A}, $\chi_{\mathrm{eff}}^{\mathrm{rl}}$ increases when the linear chains molecular weight N_{B} increases. At that point a compensation occurs between the many ring chains, with the large number of units of the linear chains. Similar trends of $\chi_{\mathrm{eff}}^{\mathrm{rl}}$ are obtained with an increase in the ring chains' molecular weight. Considering blends with constant linear molecular weight $N_{\mathrm{B}} = 300$ and ring chain lengths varying from $N_{\mathrm{A}} = 600$ to 1200, we find that $\chi_{\mathrm{eff}}^{\mathrm{rl}}$ increases with an increase of N_{A} up to the ring chains' volume fraction $\varphi_{\mathrm{A}} = 0.3$. For higher values of φ_{A}, $\chi_{\mathrm{eff}}^{\mathrm{rl}}$ decreases with an increase in N_{A}. For small and moderate size disparities, the effective interactions between ring/linear chemically identical blends are larger than the respective interactions for ring/ring blends. For higher disparities $r = 20$, there are φ_{A} volume fraction regions where ring/ring interactions are higher than ring/linear ones and vice versa. Further experimental studies are needed to confirm the predicted trends of our theoretical results.

Up to now the corrections to the free energy density of mixing in chemically identical blends have been obtained when the excluded volume interactions between segments are not identically zero ($u \neq 0$). However, for the case $u = 0$ an extra potential can be included for the description of the effects of voids as we have done previously for the study of the θ point of chains of various architectures.[20]

Conclusion

Using a molecular model which takes into account chain correlation between the same or different species in a polymer blend, we are able to predict the macroscopic properties of star/star, ring/ring, and ring/linear chemically identical blends. In particular, our analytical results explain the experimentally observed size expansion of the hydrogenated and deuterated ring chains in ring/ring blends and the Gaussian dimensions in linear/linear chemically identical blends. Moreover, we find that the nonmonotonic change of the effective interactions with an increase in *f* in star/star PB blends arises from the subtle differences in the molecular weights of the two species. Experimental indication that star/linear chemically identical blends with six arms are phase separated may be due to labeling effects. More experimental and theoretical attention should be paid to this important class of asymmetric materials.

Supporting Information Available: A .zip file containing the code for the numerical evaluation of the effective interaction and spinodal functions for star/star, ring/ring and ring/linear chemically identical blends (eqs 9, 10, 11, 12, 13, and 14) obtained using MATHEMATICA's notebook. This material is available free of charge via the Internet at http://pubs.acs.org.

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