Conformational Properties of A_xB_{f-x} Star Copolymers

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Received April 13, 1992; Revised Manuscript Received July 13, 1992

ABSTRACT: The conformational properties of a star AB copolymer molecule composed of A and B branches with different kinds of interactions between units are studied as functions of the molecular weight, the number of branches, and the interaction parameters. By means of calculations at the critical dimensionality $d = 4$ up to first order in $\epsilon = 4 - d$, we obtain analytical expressions for the mean end-to-end square distances of one and two different branches, the sizes of homopolymers parts and the whole molecule, and the distance between the centers of mass of two different homopolymers. In our analysis we emphasize the region where only interactions between units of different homopolymers occur.

1. Introduction

During the recent years homopolymers with various architectures like stars, rings, or combs have been the subject of an intensive research[1-10] in order to understand the role that the chain topology plays in the determination of their macroscopic properties. Significant toward this direction is the contribution of synthetic chemistry,[5,6,9] which, by means of anionic polymerization, has achieved well-characterized polymers with large molecular weights. Theoretical studies, together with experimental findings, have given satisfactory answers to the above questions and now it is obvious that the differences in the behavior of these more compact polymers arise from their large density of monomers in space, which yields an increasing possibility of interactions between their units. Linear AB block copolymers on the other hand have been also studied[11-13] because their properties have large technological interest. These polymers consist of blocks of nonmixing homopolymers with different kinds of interactions between units from the same or different blocks, which are forced to have common junctions. A large spectrum of properties can be achieved with AB copolymers either by changing their molecular weights or by changing the solvent conditions that determine the intensities of interactions between their units.

The accumulated theoretical and experimental knowledge both for homopolymers with various architectures and for linear AB block copolymers lead to the synthesis[14,15] and the study[16] of polymers that combine the characteristics of two categories and have, therefore, great theoretical interest. From all the AB copolymers that can be synthesized, we study in this work the star AB copolymers with f branches, x from the homopolymer A, each of molecular weight N_A, and the rest from the homopolymer B, of molecular weight N_B, chains of which combine characteristics of stars with those of linear AB block copolymers (Figure 1). This study is based on statistical thermodynamic methods used extensively for polymer chains.[17] First-order calculations of the interaction parameters u_A, u_B, and u_{AB} between units of the same or different kinds are made at the critical dimensionality $d = 4$ in order to describe the basic conformational properties. The characteristic exponents of these properties and the various expansion factors that describe the general effects of the chain behavior are found by means of the fixed points that determine the macroscopic states of the macromolecule. The values of interaction parameters at the fixed points u_A^*, u_B^*, and u_{AB}^* have been found[11] up to the first order of small parameter $\epsilon = 4 - d$ and are universal, not depending on the chain architecture.[3] This method[18,19] has successfully been used to describe star,[3] ring,[8] and comb[10] homopolymers and also to investigate linear AB block copolymers.[11] It is also expected to give the analytical dependence of macroscopic properties of star AB copolymers on the molecular weight, the total number of branches, and the temperature.

If we consider the star copolymer composed from two different homopolymer stars joined at the origin (Figure 1) we can use the previously established notation of two indices[3] for the determination of the position vectors $\mathbf{R}_{\mathrm{nAiA}}$, $\mathbf{R}_{\mathrm{nBiB}}$ of chain units. The first index nA or nB determines the branch of homopolymer A or B where the unit lies and varies from 1 to x and from 1 to $f - x$, respectively, while the second index iA or iB indicates the exact position of the unit from the center of the molecule along the specific branch and varies from 1 to N_A and from 1 to N_B. Then the probability distribution function $P\{\mathbf{R}_{\mathrm{nAiA}},\mathbf{R}_{\mathrm{nBiB}}\}$ of these vectors is written as

$$P\{\mathbf{R}_{\mathrm{nAiA}},\mathbf{R}_{\mathrm{nBiB}}\} = P_0\{\mathbf{R}_{\mathrm{nAiA}},\mathbf{R}_{\mathrm{nBiB}}\} \times \exp\Big[-u_A \sum_{\mathrm{nA}=1}^{x} \sum_{\mathrm{nA'}=1}^{x} \sum_{\mathrm{iA}=1}^{N_A} \sum_{\mathrm{jA}=1}^{N_A} \delta^d(\mathbf{R}_{\mathrm{nAiA}} - \mathbf{R}_{\mathrm{nA'jA}}) - u_B \sum_{\mathrm{nB}=1}^{f-x} \sum_{\mathrm{nB'}=1}^{f-x} \sum_{\mathrm{iB}=1}^{N_B} \sum_{\mathrm{jB}=1}^{N_B} \delta^d(\mathbf{R}_{\mathrm{nBiB}} - \mathbf{R}_{\mathrm{nB'jB}}) - 2u_{AB} \sum_{\mathrm{nA}=1}^{x} \sum_{\mathrm{nB}=1}^{f-x} \sum_{\mathrm{iA}=1}^{N_A} \sum_{\mathrm{jB}=1}^{N_B} \delta^d(\mathbf{R}_{\mathrm{nAiA}} - \mathbf{R}_{\mathrm{nBjB}})\Big] \quad (1.1)$$

$P_0\{\mathbf{R}_{\mathrm{nAiA}},\mathbf{R}_{\mathrm{nBiB}}\}$ is the ideal distribution function expressing the connectivity of chain units, and in the Gaussian model it is given by[20]

$$P_0\{\mathbf{R}_{\mathrm{nAiA}},\mathbf{R}_{\mathrm{nBiB}}\} = (d/2\pi)^{dM/2} \exp\{-(d/2)[\sum_{\mathrm{nA}=1}^{x} \sum_{\mathrm{iA}=1}^{N_A} (R_{\mathrm{nAiA}} - R_{\mathrm{nAiA+1}})^2 + \sum_{\mathrm{nA}=1}^{f-x} \sum_{\mathrm{iA}=1}^{N_B} (R_{\mathrm{nBiB}} - R_{\mathrm{nBiB+1}})^2]\}, \quad M = xN_A + (f-x)N_B \quad (1.2)$$

with length units expressed in terms of the statistical unit

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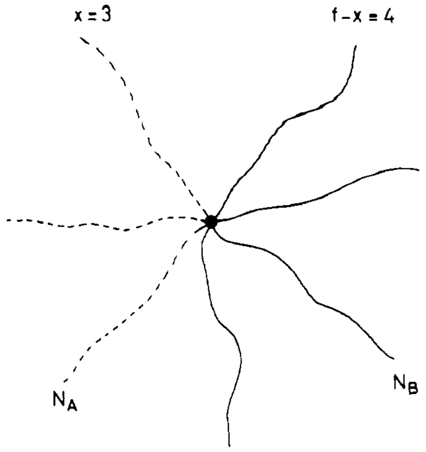


Figure 1. Star copolymer molecule with seven branches. Three of these consist of homopolymer A (dashed lines), each of molecular weight N_A, and the rest of homopolymer B, with molecular weight N_B.

length, l. The first two exponential terms in eq 1.1 represent the long-range interactions between two units of the same homopolymer and the third the cross interactions between two units of dissimilar homopolymers. The excluded volume parameters u_A, u_B, and u_{AB} in front of the summations express the strength of these interactions and are temperature dependent. In good solvents, where repulsions occur between the units, they take positive values, while they vanish in Θ solvents. The probability distribution function $P\{\mathbf{R}_{nAiA},\mathbf{R}_{nBiB}\}$ is a central quantity in the statistical thermodynamics of polymers and, therefore, most conformational properties can be determined from it. In the following sections we give expressions for the mean end-to-end square distances corresponding to one and two different branches, the radii of gyration of various parts and the whole molecule, in star AB copolymers, and the distance between the centers of mass of two homopolymer parts.

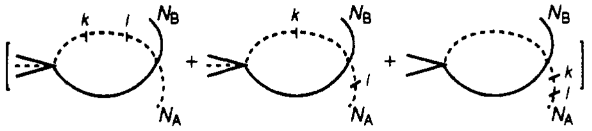
2. End-to-End Mean Square Distances

The different conformational properties determined in this work can be obtained from unit-to-unit mean square distances $\langle (R_l - R_k)^2 \rangle$. Thus we can calculate the mean end-to-end square distances, where the units k,l are placed at the ends of one or two branches, or the radii of gyration, obtained after the summation over all the chain unit positions belonging to the selected part of the molecule. Generally only the following three averages need to be calculated from the five different combinations of unit-to-unit distances that are possible when one considers the units belonging to the same or a different branch of similar or dissimilar homopolymers: $\langle (R_{1lA} - R_{1kA})^2 \rangle$, $\langle (R_{1lA} - R_{2kA})^2 \rangle$, $\langle (R_{1lA} - R_{2kB})^2 \rangle$. The remaining averages, $\langle (R_{1lB} - R_{1kB})^2 \rangle$, $\langle (R_{1lB} - R_{2kB})^2 \rangle$, can be obtained from the ones previously enumerated with symmetric changes between the excluded volume parameters, the number of branches, and the molecular weights: $u_A \rightarrow u_B$, $x \rightarrow f - x$, and $N_A \rightarrow N_B$. The evaluation of unit-to-unit mean square distances is based on the definition of these quantities and according to the probability distribution function $P\{\mathbf{R}_{nAiA},\mathbf{R}_{mBiB}\}$, i.e.

$$\langle (R_{1lA} - R_{tky})^2 \rangle = \frac{\int \Pi d^d\mathbf{R}_{nAiA} \Pi d^d\mathbf{R}_{nBiB} (R_{1lA} - R_{tky})^2 P\{\mathbf{R}_{nAiA},\mathbf{R}_{nBiB}\}}{\int \Pi d^d\mathbf{R}_{nAiA} \Pi d^d\mathbf{R}_{nBiB} P\{\mathbf{R}_{nAiA},\mathbf{R}_{nBiB}\}} \quad y = \mathrm{A, B} \quad t = 1, 2 \qquad (2.1)$$

Under Θ solvent conditions $P\{\mathbf{R}_{nAiA},\mathbf{R}_{nBiB}\}$ is described by the Gaussian function (eq 1.2) and the problem can be solved exactly. In this case $\langle (R_{1lA} - R_{tky})^2 \rangle$ is proportional to the length of the chain segment between the two units, that is, proportional to $l - k$ when the units belong to the same branch and equal to $l + k$ when the units belong to different branches. Under good solvent conditions, the excluded volume interactions between units increase the complexity of the problem, but the solution can be approximately obtained in a perturbation scheme. Accordingly, we expand the exponential of $P\{\mathbf{R}_{nAiA},\mathbf{R}_{nBiB}\}$ in eq 2.1 and, after the integrations over all the position vectors $\mathbf{R}_{nAiA}$, $\mathbf{R}_{nBiB}$ are accomplished, we finally arrive to the follow diagrammatic expression, for the case where both k and l belong to the same branch of homopolymer A (dashed line)

$$<(R_{1lA} - R_{1kA})^2> = (l - k) - u_A \left[B(k,l,x) \right] - 2u_{AB}(f - x) \times$$



(2.2)

The function $B(k,l,x)$ describes all the interactions between the units of the different x branches corresponding to the same homopolymer A and has been calculated previously[3] for star homopolymer chains, up to the first order in u_A. The diagrams of the remaining term, u_{AB}, are new and represent the cross interactions between units belonging to asymmetric branches of different homopolymers. The forms of these diagrams arise also from the simple rule of being equal to −(the length of the part of (l,k) segment in the loop)^2/(length of the loop)$^{d/2+1}$, and their values for d = 4 are obtained in a way similar to that described in a previous paper.[3] Using these values in eq 2.2, we obtain the following expression for the $\langle (R_{1lA} - R_{1kA})^2 \rangle$

$$\begin{aligned} \langle (R_{1lA} - R_{1kA})^2 \rangle = {} & (l - k) + u_A \Bigg\{ 2k \ln \frac{l}{k} + 2(N_A - l) \ln \left(\frac{N_A - k}{N_A - l} \right) + 2(l - k) \ln (l - k) + \frac{(l - k)^2}{N_A} - \\ & 3(l - k) + (x - 1) \left[-\frac{(l - k)^2}{2N_A} + 2k \ln \frac{k}{l} + 2(k + N_A) \times \ln \left(\frac{N_A + l}{N_A + k} \right) \right] \Bigg\} + u_{AB}(f - x) \left[\frac{(l - k)^2}{(N_A + N_B)} - \frac{(l - k)^2}{N_A} + \right. \\ & \left. 2k \ln \frac{k}{l} + 2(k + N_B) \ln \left(\frac{N_B + l}{N_B + k} \right) \right] \end{aligned} \qquad (2.3)$$

The effects of the $(f - x)$ branches of the homopolymer B on the l to k distance can be determined from the u_{AB} term. This depends both on the molecular weights N_A, N_B and the positions of the l and k units in the A branch. For repulsions between A and B units, the u_{AB} term is always positive and causes an expansion in the l to k distances. The expansion is larger for segments that are closer to the core than to the rest, because the density of interactions is higher there and increases for higher molecular weight and number of B branches. Similar results are obtained for the distances, $\langle (R_{1lB} - R_{1kB})^2 \rangle$, between units lying in the same branch of homopolymer B.

The end-to-end mean square distance $\langle R^2{}_A \rangle$, which expresses the mean square length of whole branch of

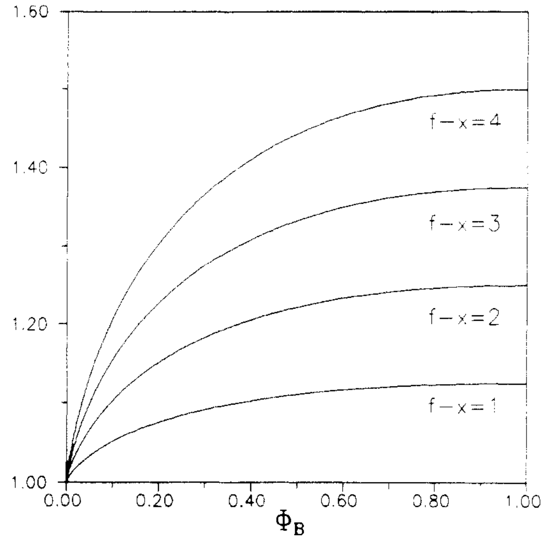


Figure 2. Ratio g_A as a function of the length fraction of the B branch, $\Phi_B = N_B/(N_A + N_B)$, and various values of $f - x$. $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$.

homopolymer A, can be calculated from eq 2.3, setting $l = N_A$ and $k = 0$.

$$\langle R^2{}_A\rangle = N_A\left\{1 + 2u_A\left[(\ln N_A - 1) - (x-1)\left(\frac{1}{4} - \ln 2\right)\right] - 2u_{AB}(f-x)\left[\frac{\rho}{2(1+\rho)} + \rho\ln\left(\frac{\rho}{1+\rho}\right)\right]\right\},\quad \rho = (N_B/N_A) \tag{2.4}$$

This way we can study the behavior of A branch in various macroscopic states. The u_A term, which describes the excluded volume interactions between units of the same homopolymer A, causes an expansion of the A branch that is higher when the molecular weight N_A increases. In the limit of long branches, the $u_A \ln N_A$ term is predominant and $\langle R^2{}_A\rangle$ becomes a power law of the molecular weight $\langle R^2{}_A\rangle = N^{2\nu}$. The critical exponent ν can be obtained by means of the fixed point value $u^*_A = \epsilon/16$, $\langle R^2{}_A\rangle = N_A\{1 + 2u_A \ln N_A\} = N_A{}^{1+2u^*_A} = N_A{}^{2\nu} \rightarrow \nu = 1/2 + \epsilon/16$, and coincides with the respective exponent of linear chains.[19] For Θ solvents and $u_{AB} > 0$, the extension of $\langle R^2{}_A\rangle$ is determined from the u_{AB} term, which does not affect the critical exponent but only determines the prefactor. The influence of the other branches of the same or different homopolymer on $\langle R^2{}_A\rangle$ is obviously noticed in the ratio $g_A = \langle R^2{}_A\rangle_{\text{star}}/\langle R^2\rangle_{\text{linear}}$, which is independent of the molecular weight. g_A expresses the relative expansion of the A branch compared to that of the linear homopolymer[19] with the same molecular weight and is equal to

$$g_A = \left\{1 + 2u_A\left[(x-1)\left(\ln 2 - \frac{1}{4}\right)\right] - 2u_{AB}(f-x)\left[\frac{\rho}{2(1+\rho)} + \rho\ln\left(\frac{\rho}{1+\rho}\right)\right]\right\} \tag{2.5}$$

The interactions within the branches of the same homopolymer A increase linearly with x and cause the extension of the branch. The effects of B branches are given for[11] $u^*_A = 0$, $u^*_{AB} = \epsilon/8$ in Figure 2 as a function of their length fraction $\Phi_B = \rho/(1 + \rho)$. We can observe from the figure that a higher value of Φ_B, due to the increase of the branch length N_B, causes a further expansion of branch A until a limiting value is reached. This limit depends on $f - x$. The interpretation of this behavior can be made by taking into account the u_{AB} interactions. Initially, the presence of B branches leads to the expansion of the A branch, which is longer for larger masses of B branches in its vicinity. With further increase of Φ_B the B branches are extended away from the A branch and they can no longer interact with it. In this region the limiting behavior of g_A is reached. The limiting values of g_A can be found by applying eq 2.5 with $\Phi_B \rightarrow 1$ ($\rho \rightarrow \infty$). Then we get $g_A = 1 + (\epsilon/8))(f - x)$, to first order in ϵ, which shows that the expansion limit of the A branch increases linearly with the number of B branches.

The next category of unit-to-unit distances corresponding to units of different homopolymer at different branches can be evaluated in a similar way as $\langle(R_{1lA} - R_{1kA})^2\rangle$, i.e., from eq 2.1. Then, after expanding the exponential term of $P\{\mathbf{R}_{nAiA},\mathbf{R}_{nBiB}\}$ and performing all the necessary integrations, $\langle(R_{1lA} - R_{2kB})^2\rangle$ takes the form

$$\begin{aligned}\langle(R_{1lA} - R_{2kB})^2\rangle = {}& (l+k) + \\ & u_A\left\{\left[\frac{l^2}{N_A} + 2(N_A - l)\ln\left(\frac{N_A}{N_A - l}\right) + 2l\ln l - 3l\right] + (x-1)\left[-\frac{l^2}{2N_A} + 2N_A\ln\left(\frac{N_A + l}{N_A}\right)\right]\right\} + \\ & u_B\left\{\left[\frac{k^2}{N_B} + 2(N_B - k)\ln\left(\frac{N_B}{N_B - k}\right) + 2k\ln k - 3k\right] + (f-x-1)\left[-\frac{k^2}{2N_B} + 2N_B\ln\left(\frac{N_B + k}{N_B}\right)\right]\right\} + \\ & u_{AB}\left\{(f-x-1)\left[\frac{l^2}{(N_A + N_B)} + 2N_B\ln\left(\frac{N_B + l}{N_B}\right) - \frac{l^2}{N_A}\right] + (x-1)\left[\frac{k^2}{(N_A + N_B)} + 2N_A\ln\left(\frac{N_A + k}{N_A}\right) - \frac{k^2}{N_B}\right] + \right. \\ & \left[-\frac{k^2}{N_B} - \frac{l^2}{N_A} + \frac{(k+l)^2}{(N_A + N_B)} + 2k\ln\left(\frac{l+k}{k}\right) + 2l\ln\left(\frac{l+k}{l}\right) + \right. \\ & \left.\left. 2(N_B - k)\ln\left(\frac{N_B + l}{N_B}\right) + 2(N_A - l)\ln\left(\frac{N_A + k}{N_A}\right)\right]\right\}\end{aligned} \tag{2.6}$$

This form reveals that the presence of the remaining $f - 2$ branches causes a further expansion of the l to k distance in any nonideal macroscopic state characterized by repulsions between units. The mean end-to-end square distance $\langle R^2{}_{AB}\rangle$, which expresses the dimensions of two branches of different homopolymers, can be extracted from eq 2.6 if we set $l = N_A$ and $k = N_B$

$$\begin{aligned}\langle R^2{}_{AB}\rangle = {}& (N_A + N_B)\{1 + 2u_A[\Phi_A(\ln N_A - 1) + (x-1)\Phi_A(\ln 2 - {}^1/_4)] + 2u_B[\Phi_B(\ln N_B - 1) + \\ & (f-x-1)\Phi_B(\ln 2 - {}^1/_4)] - 2u_{AB}[(f-x-1)(\Phi_A\Phi_B/2 + \Phi_B\ln\Phi_B) + (x-1)(\Phi_A\Phi_B/2 + \Phi_A\ln\Phi_A) + \\ & \Phi_B\ln\Phi_B + \Phi_A\ln\Phi_A]\}\end{aligned} \tag{2.7}$$

Φ_A, Φ_B are the length fractions of A and B branches, $\Phi_A = N_A/(N_A + N_B)$, $\Phi_B = N_B/(N_A + N_B)$, and also can be written in terms of parameter $\rho = N_B/N_A$ since $\Phi_A = 1/(1 + \rho)$, $\Phi_B = \rho/(1 + \rho)$.

The $u_A\Phi_A \ln N_A$ and $u_B\Phi_B \ln N_B$ terms, which represent the excluded volume interactions between branches of the same homopolymer, determine the critical exponent of $\langle R^2{}_{AB}\rangle$. This exponent is independent of the values of length fractions Φ_A, Φ_B and also identical with the exponent of the end-to-end distance of linear homopolymers,[19] $\langle R^2{}_{AB}\rangle = (N_A + N_B)\{1 + 2u_A\Phi_A \ln N_A + 2u_B\Phi_B \ln N_B\} = (1 + \rho)N_A{}^{2\nu}$, $2\nu = 1 + 2u^*_A[1/(1 + \rho)] + 2u^*_B[\rho/(1 + \rho)] = 1 + \epsilon/8$. In analogy with the study of the previous terms, we define the ratio $g_{AB} = \langle R^2{}_{AB}\rangle_{\text{star}}/(\langle R^2{}_A\rangle_{\text{linear}} + \langle R^2{}_B\rangle_{\text{linear}})$. g_{AB} expresses the relative expansion of the AB block

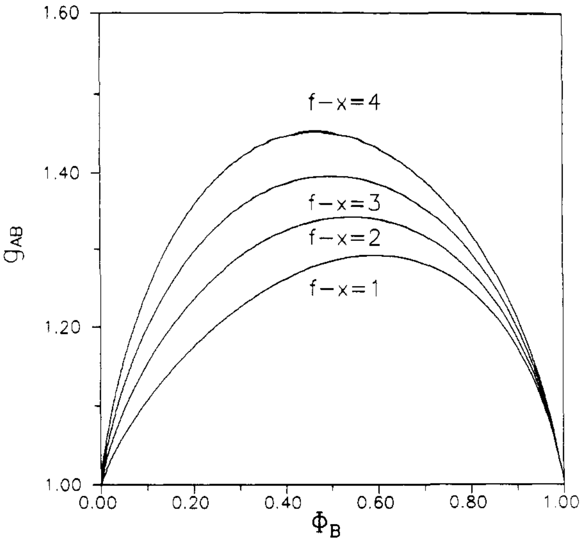


Figure 3. Ratio g_{AB} as a function of the length fraction of the B branch, Φ_B, for star copolymers with $x = 3$ and various values of $f - x$. $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$.

copolymer, formed inside the star from the two different branches, compared to the summation of two homopolymers with the same characteristics as the two branches, and is equal to

$$g_{AB} = \{1 + 2u_A(x-1)\Phi_A(\ln 2 - {}^1/_4) + 2u_B(f-x-1)\Phi_B(\ln 2 - {}^1/_4) - 2u_{AB}[(f-x-1)(\Phi_A\Phi_B/2 + \Phi_B \ln \Phi_B) + (x-1)(\Phi_A\Phi_B/2 + \Phi_A \ln \Phi_A) + \Phi_A \ln \Phi_A + \Phi_B \ln \Phi_B]\} \quad (2.8)$$

The contribution of the excluded volume interactions between the A branch and the other $(x - 1)$ branches of the same homopolymer A, which arise when Φ_B increases by increasing the molecular weight N_B, is of opposite nature to that of branch B with respect to the other $(f - x - 1)$ branches of the same homopolymer B. For $L = (f - x)/x > 1$, increasing Φ_B means that more segments of the homopolymer B interact with branch B. Then the u_B interactions are predominant and g_{AB} increases linearly for increasing values of Φ_B and the slope increases for increasing L. The reverse behavior is observed by increasing Φ_B for $L < 1$. Opposite behavior is also shown by the cross interactions between the $f - x - 1$ and $x - 1$ branches with the A and B branch. These two competetive effects are nonmonotonic as we see for the general case considered through this work, $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$ in Figure 3. An increase of g_{AB} is observed in the beginning, when the length of the B branch increases, a maximum is reached where the two opposite effects cancel, and, then, a decrease onsets when the B branches are extended far away of the A branch and cannot further interact with it. In the case where the number of A and B branches are equal ($L = 1$), the curve is symmetrical and the maximum is reached for equal molecular weights ($\Phi_B = 0.5$). The contribution of B branches increases by increasing L and therefore the maximum is obtained for smaller values of the length fraction Φ_B. In Figure 4, we keep the total number of branches f constant and we change simultaneously x and $f - x$. For the extreme values of L, the maximum has the highest value because the interactions are high, while they are reduced when L goes to unity. For $L = 1$, the maximum has the lowest value at $\Phi_A = 0.5$. In this point, all the interactions are equivalent and all the curves intersected at the same point.

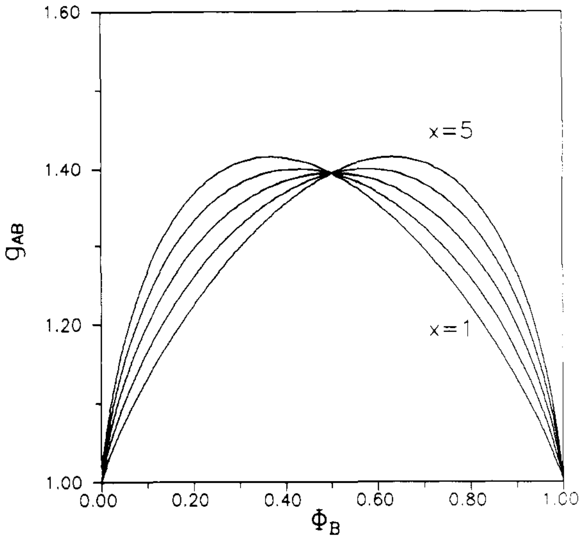


Figure 4. Ratio g_{AB} as a function of the length fraction of the B branch, Φ_B, for star copolymers with six branches ($f = 6$) and various x, $x = 1, 2, 3, 4$, and 5. $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$.

The last combination for units on different branches of the same homopolymer A leads to

$$\langle (R_{1lA} - R_{2kA})^2 \rangle = (l + k) + u_A\left\{2(N_A - k)\ln\left(\frac{N_A + l}{N_A - k}\right) + 2(N_A - l)\ln\left(\frac{N_A + k}{N_A - l}\right) + 2(l + k)\ln(l + k) + \frac{(l + k)^2}{2N_A} - 3(l + k) + 2(x - 2)\left[-\frac{k^2 + l^2}{4N_A} + N_A \ln\left(\frac{N_A + k}{N_A}\right) + N_A \ln\left(\frac{N_A + l}{N_A}\right)\right]\right\} + 2u_{AB}(f - x)\left[-\frac{k^2 + l^2}{2N_A} + \frac{(k^2 + l^2)}{2(N_A + N_B)} + N_B \ln\left(\frac{N_B + k}{N_B}\right) + N_B \ln\left(\frac{N_B + l}{N_B}\right)\right] \quad (2.9)$$

The mean end-to-end square distance of these two branches $\langle R^2{}_{AA} \rangle$ can be obtained from eq 2.9 setting $k = N_A$, $l = N_A$:

$$\langle R^2{}_{AA} \rangle = 2N_A\left\{1 + 2u_A\left[\ln(2N_A) - 1 - (x - 2)\left(\frac{1}{4} - \ln 2\right)\right] - 2u_{AB}(f - x)\left[\frac{\rho}{2(1 + \rho)} + \rho \ln\left(\frac{\rho}{1 + \rho}\right)\right]\right\} \quad (2.10)$$

The dependence of the remaining $f - 2$ branches of the same or different homopolymer is the same as in eq 2.4, discussed in a previous paragraph. Equations 2.3, 2.6, and 2.9 and the symmetric expressions obtained by the substitutions $u_A \rightarrow u_B$, $N_A \rightarrow N_B$, $x \rightarrow (f - x)$ can be employed for the evaluation of the other macroscopic properties. In the following section we evaluate the radii of gyration for the homopolymer parts and the whole molecule and the average distance between the two centers of mass.

3. Radii of Gyration and the Average Distance between the Centers of Mass

The radii of gyration $\langle S^2 \rangle$ of the molecule or the homopolymer parts are important macroscopic properties because they are experimentally accessible through hydrodynamic or scattering methods and also because they measure the size and the shape of parts of the chain that consists of more than two branches. $\langle S^2 \rangle$ is defined as the mean square distance of units of the considered part from their center of masses and also can be expressed in terms of unit-to-unit distances as[20]

$$\langle S^2\rangle = \frac{1}{2M^2}\sum_k\sum_l\langle(R_l - R_k)^2\rangle \tag{3.1}$$

In the case of the radius of gyration $\langle S_A^2\rangle$ of the homopolymer part A, the distances $\langle(R_l-R_k)^2\rangle$ can either correspond to units lying on the same branch $\langle(R_{1lA} - R_{1kA})^2\rangle$ or to different branches $\langle(R_{1lA} - R_{2kA})^2\rangle$ and consequently $\langle S_A^2\rangle$ can be written as

$$\langle S_A^2\rangle = \frac{1}{2(xN_A)^2}\Big[x\sum_{k=1}^{N_A}\sum_{l=1}^{N_A}\langle(R_{1lA} - R_{1kA})^2\rangle + x(x-1)\sum_{k=1}^{N_A}\sum_{l=1}^{N_A}\langle(R_{1lA} - R_{2kA})^2\rangle\Big] \tag{3.2}$$

Substituting the expressions for these distances, eqs 2.3 and 2.9, in eq 3.2 and replacing the summations with straightforward integrations which are subsequently performed, we get

$$\langle S_A^2\rangle = \frac{N_A(3x-2)}{6x}\left\{1 + 2u_A\left[\ln N_A + 4\frac{(x-1)(3x-5)}{(3x-2)}\ln 2 - \frac{13}{12}\left[\frac{1 + 3(x-1)(2x-3)}{(3x-2)}\right]\right] + 2u_{AB}\frac{(f-x)}{(3x-2)}\left[3\rho^2(1+\rho)\ln\left(\frac{\rho}{1+\rho}\right) + \frac{\rho(12\rho^2 + 18\rho + 5)}{4(1+\rho)}\right] - 2u_{AB}\frac{(f-x)(x-1)}{(3x-2)}\times\left[6\rho(1+\rho)\ln\left(\frac{\rho}{1+\rho}\right) + \frac{\rho(6\rho+7)}{(1+\rho)}\right]\right\} \tag{3.3}$$

An analysis of eq 3.3 shows that both ideal and u_A terms are similar to the corresponding ones for a homopolymer star[3] of the same characteristics, and they increase with increasing molecular weight and number of branches. For the study of the other term in u_{AB}, which expresses the enlargement of the expansion of $\langle S_A^2\rangle$ compared to that of homopolymer star $\langle S^2\rangle_{\text{star hom}}$, we define the quantity $g_{SA} = \langle S_A^2\rangle/\langle S^2\rangle_{\text{star hom}}$. This quantity depends on the ratio of molecular weights $\rho = N_B/N_A$ and both the numbers x and $f - x$

$$g_{SA} = 1 + 2u_{AB}\frac{(f-x)}{(3x-2)}\left[3\rho^2(1+\rho)\ln\left(\frac{\rho}{1+\rho}\right) + \frac{\rho(12\rho^2 + 18\rho + 5)}{4(1+\rho)}\right] - 2u_{AB}\frac{(f-x)(x-1)}{(3x-2)}\times\left[6\rho(1+\rho)\ln\left(\frac{\rho}{1+\rho}\right) + \frac{\rho(6\rho+7)}{(1+\rho)}\right] \tag{3.4}$$

In the limit $\rho \to 0$ ($N_B \to 0$), the contribution of the u_{AB} term vanishes because the branches causing the expansion shrink and $g_{SA} \to 1$. Increasing ρ for constant number of branches, we observe a behavior for $\langle S_A^2\rangle$ similar to that of $\langle R_A^2\rangle$ of the single branch. Initially, $\langle S_A^2\rangle$ increases and then it adopts a limiting value, reached when the A and B branches go further apart and cannot interact (Figure 5). The values of g_{SA} can be obtained in this case from eq 3.4 for $\rho \to \infty$ and are expressed as

$$g_{SA}(N_B \to \infty) = 1 + (1/16)[(f-x)(8x-7)/(3x-2)] \tag{3.5}$$

Increasing the number of B branches for constant x,ρ, we place more segments of the homopolymer B near the A branches and consequently $\langle S_A^2\rangle$ expands. For $x = 1$, the ratio g_{SA} expresses the relative expansion of the single branch and can be directly compared to g_A, calculated from the end-to-end square distance for the macroscopic states with $u^*_A = 0$. We observe from eqs 2.5 and 3.4 that, for any value of ρ, g_A is always greater that g_{SA}, which means that $\langle S_A^2\rangle$ is less sensitive to the excluded volume interactions than $\langle R_A^2\rangle$. For greater values of x, g_{SA} increases because the cross interactions increase and reaches for $x \to \infty$ and $f - x$ constant the limit $g_{SA}(\rho \to \infty) = 1 + (f - x)/6$. The behavior of the size of the other homopolymer part B, expressed by the symmetrical radius of gyration $\langle S_B^2\rangle$, is, of course, similar.

In the case of the radius of gyration $\langle S^2\rangle_{\text{star copo}}$ of the whole molecule, the different averages $\langle(R_l - R_k)^2\rangle$ correspond to distances between two units, which can belong to the same or different branches of the same or different homopolymers. Then

$$\langle S^2\rangle_{\text{star copo}} = \frac{1}{2[xN_A + (f-x)N_B]^2}\Big[x\sum_{k=1}^{N_A}\sum_{l=1}^{N_A}\langle(R_{1lA} - R_{1kA})^2\rangle + x(x-1)\sum_{l=1}^{N_A}\sum_{l=1}^{N_A}\langle(R_{1lA} - R_{2kA})^2\rangle + (f-x)\sum_{k=1}^{N_B}\sum_{l=1}^{N_B}\langle(R_{1lB} - R_{1kB})^2\rangle + (f-x)(f-x-1)\sum_{k=1}^{N_B}\sum_{l=1}^{N_B}\langle(R_{1lB} - R_{2kB})^2\rangle + 2x(f-x)\sum_{k=1}^{N_B}\sum_{l=1}^{N_A}\langle(R_{1lA} - R_{2kB})^2\rangle\Big] \tag{3.6}$$

By means of the expressions for $\langle(R_{1lA} - R_{1kA})^2\rangle$, $\langle(R_{1lA} - R_{2kA})^2\rangle$, and $\langle(R_{1lA} - R_{2kB})^2\rangle$, eqs 2.3, 2.6, and 2.9 and the symmetric for $\langle(R_{1lB} - R_{1kB})^2\rangle$, $\langle(R_{1lB} - R_{2kB})^2\rangle$, we find the following relation for the $\langle S^2\rangle_{\text{star copo}}$

$$\langle S^2\rangle_{\text{star copo}} = \frac{N_A}{6[x + (f-x)\rho]^2}\Big\{x[(3x-2) + 3\rho(f-x)] + (f-x)\rho^2[3\rho(f-x) - 2\rho + 3x] + 2u_A[x[(3x-2) + 3\rho(f-x)]\ln N_A + x(x-1)[4 + 12(x-2) + 12\rho(f-x)]\ln 2 - (x/12)[13 + 39(x-1)(2x-3) + 6\rho(f-x)(13x-6)]] + 2u_B[(f-x)\rho^2[3\rho(f-x) - 2\rho + 3x]\ln(\rho N_A) + (f-x)(f-x-1)\rho^2[4\rho + 12x + 12\rho(f-x-2)]\ln 2 - [(f-x)\rho^2/12][13\rho + 39\rho(f-x-1)[2(f-x) - 3] + 6x[13(f-x) - 6)]] - 2u_{AB}\Big[x(f-x)[\rho(\rho+1)[\rho + 6(x-1) + 6\rho(f-x-1)] + 2\rho^2]\ln\left(\frac{\rho}{1+\rho}\right) + x(f-x)[(\rho + 1)[1 + 6\rho(f-x-1) + 6(x-1)] + 2\rho]\ln\left(\frac{1}{1+\rho}\right) + [x(f-x)\rho/4][52\rho(f-x-1) + 52(x-1) - (1+\rho)]\Big]\Big\} \tag{3.7}$$

The ideal term, $\langle S_o^2\rangle_{\text{star copo}}$ increases with increasing both the number of branches and their length since the size of the macromolecule is then increased. For $\rho = 1$ all branches become equivalent and this term is described from the well-known Zimm–Stockmayer expression[21] for a homopolymer star with f branches. The u_A and u_B terms represent the interactions between units of the same homopolymer, which increase by increasing the corresponding number of branches and decrease when the

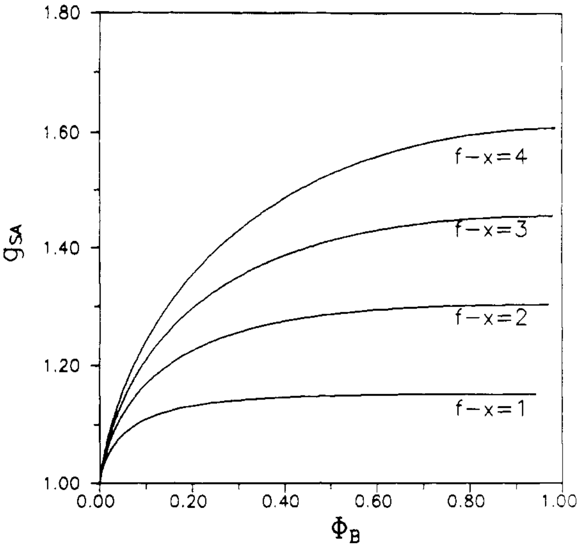


Figure 5. Ratio g_{SA} as a function of Φ_B for star copolymers with $x = 3$ and various $f - x$. $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$.

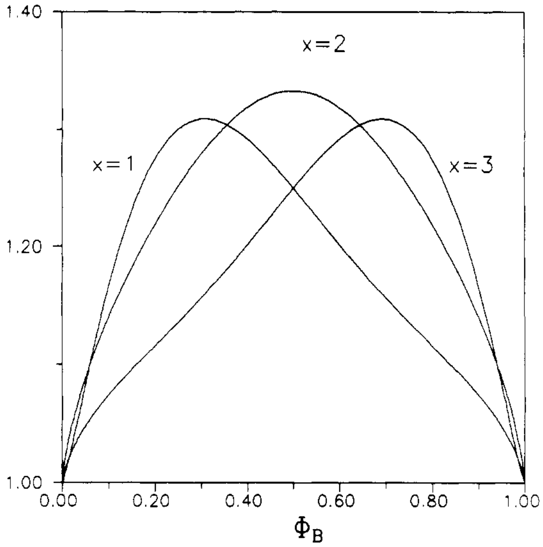


Figure 6. Expansion factor α^2 of the radius of gyration as a function of Φ_B for star copolymers with $f = 4$ and various x. $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$.

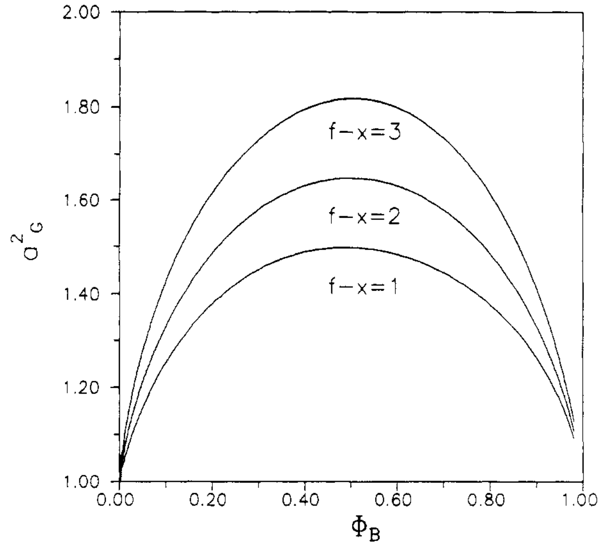


Figure 7. Expansion factor α_G^2 of the mean square distance between the two centers of mass as a function of Φ_B for star copolymers with $x = 2$ and various $f - x$. $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$.

length of the branch of the other homopolymer increases. For $\rho = 1$ the respective terms of an homopolymer star are also obtained.[3] The behavior of the segregated u_{AB} term is similar to that of $\langle R^2_{AB}\rangle$. In Figure 6, the expansion factor $\alpha^2 = \langle S^2\rangle_{\text{star copo}}/\langle S_0^2\rangle_{\text{star copo}}$ that includes only this term for the macroscopic state $u^*_A = u^*_B = 0$, $u^*_{AB} = \epsilon/8$ is illustrated as a function of the length fraction $\Phi_B = \rho/(1 + \rho)$, for constant f. On increasing Φ_B (starting from $\Phi_B = 0$) the expansion factor increases and a maximum value is obtained when the competetive contribution of the two homopolymer parts is balanced. The absolute value of the maximum increase by increasing the product $x(f - x)$, adopting its highest value when $x = (f - x)$. The u_{AB} interactions increase when f increases, and then the expansion factor takes higher values.

From eqs 3.3 and 3.7, expressions for the radius of gyration of special cases can be easily obtained. For instance by setting $f = 3$ and $x = 1$ in eq 3.7, the case of simple graft polymer can be recovered. Some of the expressions for special cases like the AB block copolymers are already well-known,[11,12] so that we only used them here to check the correctness of our calculations. The expressions of the radii of gyration of the two homopolymer parts and the whole molecule can also be used to evaluate the mean square distance between the centers of mass of the two homopolymers by means of the relation[12]

$$\langle S^2\rangle_{\text{star copo}} = x_A\langle S_A^{\,2}\rangle + x_B\langle S_B^{\,2}\rangle + x_A x_B\langle G^2\rangle \quad (3.8)$$

where $x_A = xN_A/[xN_A + (f - x)N_B]$ and $x_B = 1 - x_A$ are the mass fractions of the two homopolymer parts A and B. After the straightforward calculations, we obtain the following expression for $\langle G^2\rangle$

$$\begin{aligned}\langle G^2\rangle = \frac{N_A}{3x}\{1 + 2u_A[\ln N_A + 10(x - 1)\ln 2 - \\ (159x - 130)/24]\} + \frac{\rho N_A}{3(f - x)}\{1 + 2u_B[\ln(\rho N_A) + \\ 10(f - x - 1)\ln 2 - [159(f - x) - 130]/24]\} - \\ 2u_{AB}\Bigl\{[[3(f - x)(1 + \rho)(\rho + 2)\rho - 2x\rho^2]/6x]\ln\left(\frac{\rho}{1 + \rho}\right) + \\ [[3x(1 + \rho)(1 + 2\rho) - 2(f - x)\rho]/6(f - x)\rho^2]\ln\left(\frac{1}{1 + \rho}\right) + \\ [12\rho^4(f - x)^2 + \rho^3(f - x)(42f - 50x) + \rho^2(88x^2 + 33f^2 - \\ 88xf) + \rho(50x^2 - 8xf) + 12x^2]/[24x(f - x)\rho(\rho + 1)]\Bigr\} \quad (3.9)\end{aligned}$$

This expression has three components. The first one, $\langle G_A^2\rangle$, represents the mean square distance between the center of mass of homopolymer A from the star origin.[22] The second one, $\langle G_B^2\rangle$, corresponds to the respective quantity for the homopolymer part B, and the third component is the segregation term, expressing the repulsion of two centers of mass from the star origin. The ideal forms[22] for $\langle G_A^2\rangle$ and $\langle G_B^2\rangle$ are $N_A/3x$ and $\rho N_A/3(f - x)$ and increase with increasing the respective branch molecular weight, since the arms reach regions far away from the star origin. However, each homopolymer part becomes more symmetrical when the respective number of branches is increased and, therefore, the distance between the centers of mass decreases. The u_A and u_B terms have high positive values when the number of branches and the molecular weight are high, indicating that the expansion of the two homopolymers causes a further separation of the mass centers. The segregation term is symmetrical with respect to the length fraction, Φ_B, of branch B as we can see in Figure 7, where we show the expansion factor $\alpha_G^2 = \langle G^2\rangle/\langle G_0^2\rangle$, with respect to $\langle G_0^2\rangle = N_A/3x + \rho N_A/3(f - x)$. This factor includes only the u_{AB} term for the macroscopic state $u^*_A = u^*_B = 0, u^*_{AB} = \epsilon/8$ and is plotted for various values of Φ_B. For constant x and N_A, the enlargement of the B branches increases the distance between centers of masses until a maximum value is reached for branches A and B of equal length. The interactions increase by increasing the number of branches of B homopolymer and, consequently, the molecule becomes more asymmetric, with the A and B branches still more separated.

4. Conclusions

The conformational properties of the A_xB_{f-x} star copolymer molecule, which incorporate the characteristics of a star homopolymer together with those of a linear AB block copolymer, are studied for various macroscopic states in terms of the number of branches and their molecular weight. By means of a perturbation theory scheme, we obtain expressions for the unit-to-unit distances, the end-to-end distances, the radii of gyration, and the distances between the centers of mass of two homopolymers. A limit in the extension of the homopolymer parts is observed when the size of the other homopolymer part increases, while typical nonmonotonic behavior characterizes the size of the whole molecule or parts consisting of two or more branches of different homopolymers. The largest effects in the latter depend both on the branch length fraction and on the product of the number of different branches, which determines the intensity of the cross interactions, together with the conditions for which these interactions are balanced.

Acknowledgment. C.V. expresses his sincere thanks for the hospitality of Professors Freire and Horta and their groups in the Complutense and UNED Universities. He also acknowledges the Spanish Ministry of Education for financial support in the form of the programm "Estancias Temporales de Cientificos y Tecnólogos Extranjeros en España". This work has been in part supported by Grant PB89-093 of the DGICYT (Spain).

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