On the Conformational Behavior of an ABC Triblock Copolymer Molecule

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Received December 7, 1989; Revised Manuscript Received August 28, 1990

ABSTRACT: The conformational properties of a triblock copolymer molecule with different kinds of interactions between units from the same or different blocks are studied as functions of the molecular weights of the three blocks. The analysis is based on calculations done about the critical dimension $d = 4$, where first-order perturbation theory is used. We calculate the end-to-end mean-square distances and the radii of gyration of the three blocks, the two subdiblocks, and the whole molecule, and from them we deduce the mean-square distances between the centers of mass of the blocks. Beyond the power law dependence of these properties on the molecular weight, which is the same as that of a homopolymer, their prefactors are determined at the various macroscopic states of the triblock copolymer. They depend both on the specific values of the interaction parameters at the fixed points and the ratios of the lengths of the blocks. The knowledge of the sizes of the parts of the macromolecule permits a comparison with the results from other methods as well as with experimental results of dilute solutions. A comparison between the behaviors of an AB diblock and that of an ABA triblock, special cases of the general ABC molecule, is included.

1. Introduction

Multiblock polymers, which can be obtained from the chemical junction of different homopolymers, have a richer spectrum of properties than those of the constituent homopolymers, and their study is interesting from both a theoretical and a technological point of view.[1-7] When the inter- and intrablock interactions of copolymers in solutions are varied by changing solvents or the temperature, different macroscopic behavior can be obtained. In the class of experiments on the special ABA type of triblocks,[8-17] the effects of the interactions between the end blocks are manifest and distinguish them from the AB diblock analogues.[12,15,18] A large influence on the size of the middle block is observed in the ABA case.[12,15] The variation of the molecular weights of the blocks affects the macroscopic properties of these species as well. It is characteristic, for example, that differences in the molecular weights of the blocks or the interactions between them cause differences in the morphology of films of these copolymers cast from their solutions.[2,3,5-7] Differences in the solubilities of the AB and ABA molecules in the same solvent systems have also been reported.[13,16] Theoretical studies have been made on the special ABA type triblocks by means of analytical theories,[14,19-21] and Monte Carlo techniques[16] and quantitative relations have been found to depend not only on the intensity of the unit-to-unit interactions but also on the relative lengths of the blocks.[16,19-21] With comparison of the properties of the ABA triblock with those of the AB diblock[22] of the same molecular weight, it has been found that the effects of the intramolecular interactions (repulsive or attractive) are more pronounced in the case of the ABA triblock. For repulsive intramolecular interactions larger expansion factors have been found for the ABA case, indicating that the triblock ABA has a larger mean size than the equimolar AB diblock under similar conditions. Association, on the other hand, between the side blocks of the ABA triblocks under certain conditions of attractions causes the collapse of these macromolecules; such behavior is not found in the case of the AB diblocks under similar conditions.[19,20]

Though a variety of experiments have been made on the triblock macromolecules of the general ABC type, a systematic theoretical description of the role of the molecular weights of the blocks and the various pair interactions on the conformational behavior of this large class of macromolecules has not yet been done. We present in this work such a systematic study in an effort to give the general characteristics of these macromolecules in solutions. First-order calculations are done at the critical dimension $d = 4$,[23-28] and the solution about $d = 4$ is used to describe the general effects of the chain behavior. The macroscopic states of the macromolecule can be found, and by means of first-order perturbation theory, the critical exponents and the prefactors of the various macroscopic properties can be determined to order $\epsilon = 4 - d$.[29] We extend our previous work concerning diblock copolymers of equal block lengths[27] to the study of triblock copolymers of different block lengths, in order to include effects coming from the variation of the sizes of the three blocks as well. The relations of the present study concerning the ABC macromolecule can both predict the behavior of this large class of block copolymers and prescribe interesting experiments. From these general relations, the corresponding relations of the special ABA and AB block copolymers are obtained as well and explain the main experimental behavior of these systems. They are an extension of previous renormalization group calculations[21,22c] and are in accord with other theoretical results.[14,16,19-21]

Generally, three different molecular weights N_A, N_B, and N_C of the three blocks and six different kinds of interactions between pairs of similar or dissimilar monomer units can exist. We use the previous notation[23,27] and write for the probability distribution of the positions $\{r_{iA}, r_{iB}, r_{iC}\}$ of all units the expression

$$P\{r_{iA},r_{iB},r_{iC}\} = P_0\{r_{iA},r_{iB},r_{iC}\} \exp\{-u_A\sum_{i=1}^{N_A}\sum_{j=1}^{N_A}{}_{i\neq j}\delta^d(r_{iA}-r_{jA}) - u_B\sum_{i=1}^{N_B}\sum_{j=1}^{N_B}{}_{i\neq j}\delta^d(r_{iB}-r_{jB}) - u_C\sum_{i=1}^{N_C}\sum_{j=1}^{N_C}{}_{i\neq j}\delta^d(r_{iC}-r_{jC}) - 2u_{AB}\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\delta^d(r_{iA}-r_{jB}) - 2u_{BC}\sum_{i=1}^{N_B}\sum_{j=1}^{N_C}\delta^d(r_{iB}-r_{jC}) - 2u_{CA}\sum_{i=1}^{N_C}\sum_{j=1}^{N_A}\delta^d(r_{iC}-r_{jA})\} \quad (1.1)$$

with

$$P_0\{r_{iA},r_{iB},r_{iC}\} = (d/2\pi l^2)^{3dN/2} \exp\{-(d/2l^2)[\sum_{i=1}^{N_A}(r_{iA} - r_{i+1,A})^2 + \sum_{i=1}^{N_B}(r_{iB} - r_{i+1,B})^2 + \sum_{i=1}^{N_C}(r_{iC} - r_{i+1,C})^2]\}$$

the probability distribution of the ideal chain of length N,

0024-9297/91/2224-1341$02.50/0

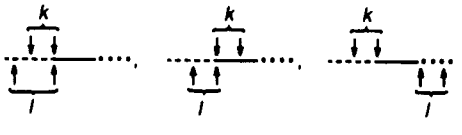
equal to the sum of the lengths of the three blocks $N = N_A + N_B + N_C$.[30] The first three exponential terms represent intrablock excluded-volume interactions while the last three represent excluded-volume interactions between different blocks. The macroscopic properties are determined as averages over the probability distribution $P\{r_{iA},r_{iB},r_{iC}\}$, by means of first-order perturbation theory with respect to the u's. In the next section we determine the mean-square distances between any pair of polymeric units and use them in the following sections to determine the end-to-end mean-square distances and the radii of gyration of the three blocks, the subdiblocks, and the whole macromolecule; from them, the mean-square distances of the centers of mass of the blocks are deduced. An analysis concerning the macroscopic states represented by the fixed points of the system is included.

2. Unit-to-Unit Mean-Square Distances

Starting quantities for the calculations that follow are the unit-to-unit mean-square distances, where the two units may belong to the same or different blocks, quantities that are also important in the evaluation of hydrodynamic properties. We use them here for the evaluation of conformational static properties. Though generally nine different combinations can be realized where the first and the second unit may belong to one of the three A, B, or C blocks, only four of them need to be calculated; the rest of the cases can be recovered from these four with symmetrical changes. If we denote the unit-to-unit mean-square distances as $\langle R_{X,Y}{}^2\rangle$ with the X and Y letters standing for two of the A, B, or C blocks where the two units belong, the four unit-to-unit distances needed are as follows: that with both units on an end block like $\langle R_{A,A}{}^2\rangle$ or $\langle R_{C,C}{}^2\rangle$, that with both units on the middle B block $\langle R_{B,B}{}^2\rangle$, the case with one unit on the central block and the other on an end block like $\langle R_{A,B}{}^2\rangle$, or $\langle R_{B,C}{}^2\rangle$, and finally $\langle R_{A,C}{}^2\rangle$ where the two units belong to the two end blocks. These mean-square distances are defined by means of the probability distribution $P\{r_{iA},r_{iB},r_{iC}\}$ (eq 1.1) as

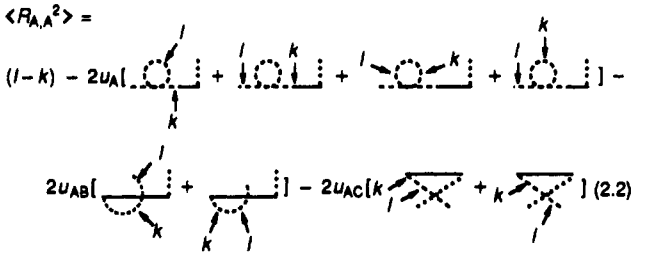
$$\langle R_{X,Y}{}^2\rangle = \int \pi d^d r_{iA}\pi d^d r_{iB}\pi d^d r_{iC} P\{r_{iA},r_{iB},r_{iC}\}\, R_{X,Y}{}^2 \Big/ \int \pi d^d r_{iA}\pi d^d r_{iB}\pi d^d r_{iC} P\{r_{iA},r_{iB},r_{iC}\}, \qquad X, Y = \mathrm{A, B, C} \quad (2.1)$$

and are functions of the positions of the two units on the blocks. These positions are determined by means of their contour lengths k and l, which are defined to be measured from the two junction points. If we denote the A block with a dashed line, the B block with a solid line, and the C block with a dotted line, the way of measuring the k and l distances is shown in the following examples:



For first-order calculations in the six u's, the probability distribution $P\{r_{iA},r_{iB},r_{iC}\}$ is needed up to first order in the u's. The ideal part of $P\{r_{iA},r_{iB},r_{iC}\}$ yields the ideal term of $\langle R_{X,Y}{}^2\rangle$, which is proportional to the length of the segment between the two points, that is, proportional to $l - k$ for the cases where both units belong to the same block, equal to $l + k$ when the units belong to adjacent blocks, and equal to $k + N_B + 1$ when the units belong the two end blocks. The rest of the terms with a δ function, bring in contact two chain units from the i and j positions on the chain, which can belong either to the same A, B, or C block for the intrablock excluded-volume interactions u_A, u_B, and u_C or to two different blocks for the interblock excluded-volume interactions u_{AB}, u_{BC}, and u_{AC}. Approximating the i and j summations with integrations, we end up with functions of l and k. In a diagrammatic language, we take for the case with both k and l in the A block the expression

$\langle R_{A,A}{}^2\rangle =$

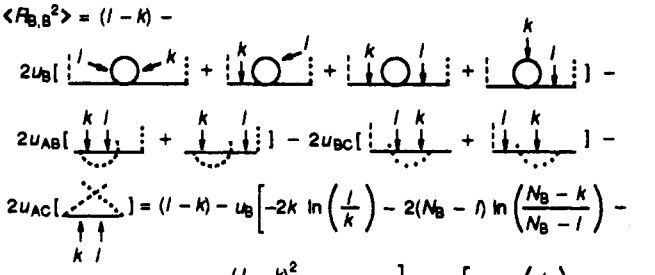


The diagrams represent intersected chains from the action of the δ functions while the l and k points are denoted on the A block. Diagrams where the (l,k) segment has not any part in common with the loop vanish and are not included. The forms of the surviving diagrams come from the simple rule of being equal to −(the length of the part of the (l,k) segment in the loop)^2/(length of the loop)$^{1+(d/2)}$ [31] and are further explained in section A of the supplementary material. Their values for $d = 4$ found after the integrations over i and j are quoted in Table A.1 in the supplementary material. By means of these values, the evaluation of $\langle R_{A,A}{}^2\rangle$ is possible. It is given by

$$\langle R_{A,A}{}^2\rangle = (l-k) - u_A\left[-2k\ln\left(\frac{l}{k}\right) - 2(N_A - l)\times \ln\left(\frac{N_A-k}{N_A-l}\right) - 2(l-k)\ln(l-k) - \frac{(l-k)^2}{N_A} + 3(l-k)\right] - u_{AB}\left[2k\ln\left(\frac{l}{k}\right) + 2(N_B+k)\ln\left(\frac{N_B+k}{N_B+l}\right) - \frac{(l-k)^2}{N_A+N_B} + \frac{(l-k)^2}{N_A}\right] - u_{AC}\left[2(N_B+N_C+k)\ln\left(\frac{N_B+N_C+k}{N_B+N_C+l}\right) + 2(N_B+k)\ln\left(\frac{N_B+l}{N_B+k}\right) - \frac{(l-k)^2}{N} + \frac{(l-k)^2}{N_A+N_B}\right] \quad (2.3)$$

and depends on both the molecular weights of the blocks and the excluded-volume interactions and also on the positions l and k of the two points in the A block. A symmetrical expression can be taken for $\langle R_{C,C}{}^2\rangle$ if we replace A of $\langle R_{A,A}{}^2\rangle$ with C. In a similar way, $\langle R_{B,B}{}^2\rangle$ where the two units are in the central block can be written as

$\langle R_{B,B}{}^2\rangle = (l-k) -$



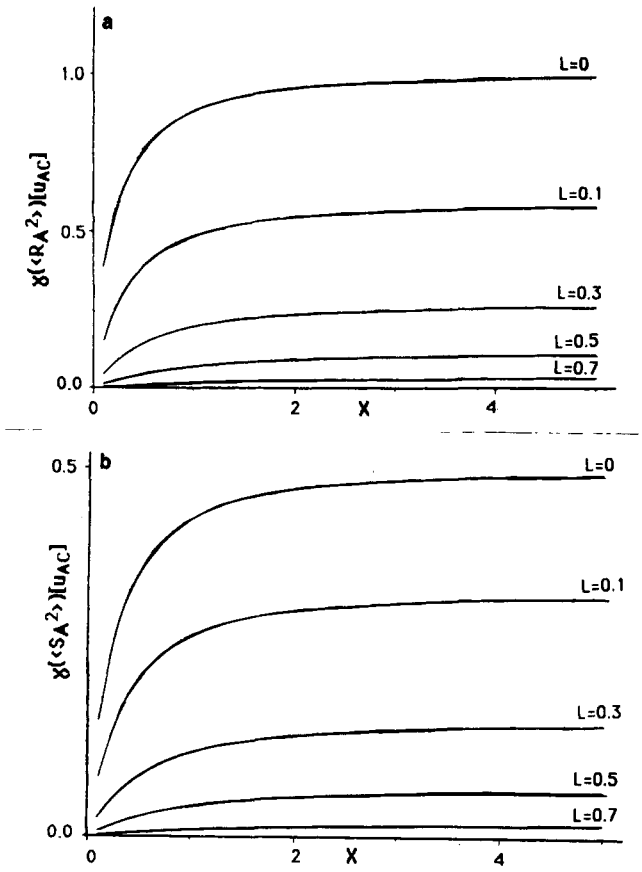
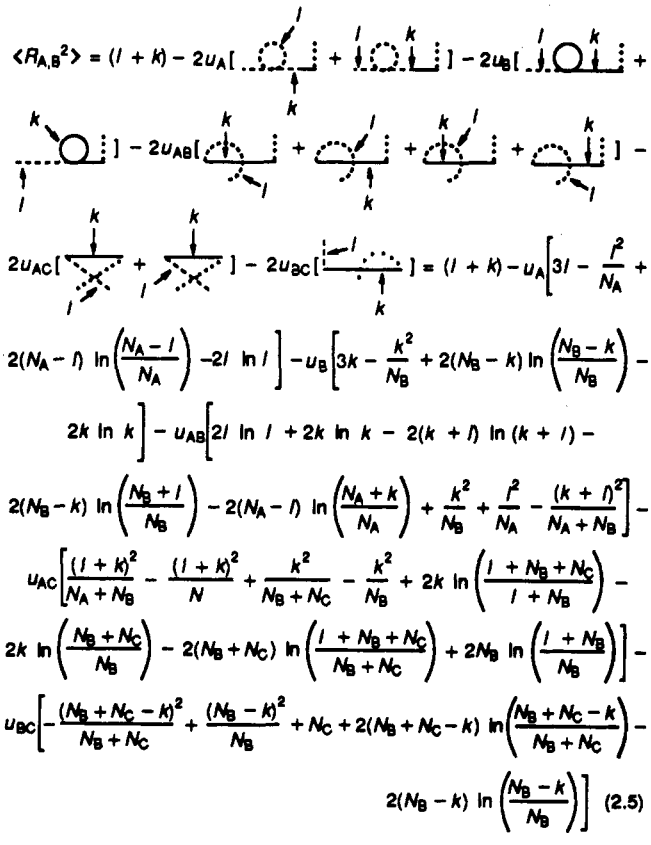
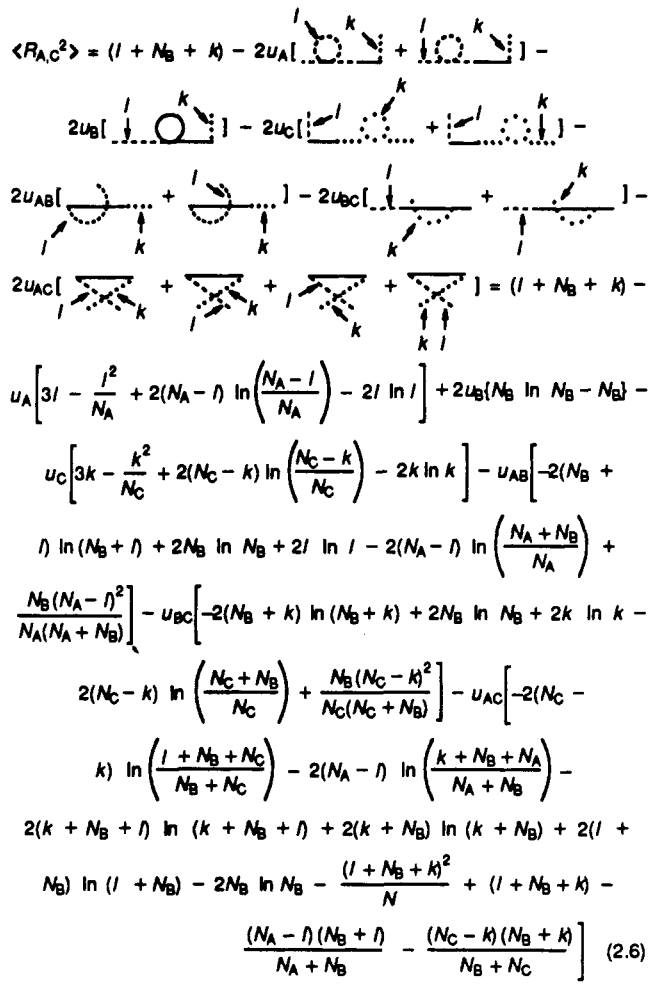


Figure 1. u_{AC} contributions to the (a) $\gamma(\langle R_A^2\rangle)$ ratio (eq 3.1) and the (b) $\gamma(\langle S_A^2\rangle)$ ratio (eq 4.3) as a function of the reduced variable $X = N_C/N_A$. $L = N_B/(N_A + N_B)$ increases with the length N_B of the middle block.

Going to the second category of unit-to-unit distances coming from positions at two adjacent blocks, we take for $\langle R_{A,B}^2\rangle$ the expression



with the values of the diagrams written in Table A.1 in the supplementary material. With a symmetrical change of A with C, $\langle R_{B,C}^2\rangle$ can be recovered from $\langle R_{A,B}^2\rangle$. The last combination $\langle R_{A,C}^2\rangle$ for positions on the two end blocks becomes



Equations 2.3–2.6 describe all possible unit-to-unit mean-square distances, and they can be employed for the evaluation of the macroscopic properties. We proceed and evaluate in the next sections the end-to-end mean-square distances and the radii of gyration of the three blocks, the two subdiblocks, and the whole molecule, and we deduce from them the mean-square distances between the centers of mass of the blocks.

3. End-to-End Mean-Square Distances

3.A. End-to-End Mean-Square Distances of the Blocks. By means of eq 2.3 of the unit-to-unit mean-square distances in the A block, we can find putting $l = N_A$ and $k = 0$ the end-to-end mean-square distance $\langle R_A^2\rangle$ of the A block.

$$\langle R_A^2\rangle = N_A\left\{1 + 2u_A[\ln N_A - 1] + 2u_{AB}\left[\frac{N_B}{N_A}\times \ln\left(\frac{N_A+N_B}{N_B}\right) - \frac{N_B}{2(N_A+N_B)}\right] + 2u_{AC}\left[\frac{N_B+N_C}{N_A}\times \ln\left(\frac{N}{N_B+N_C}\right) - \frac{N_B}{N_A}\ln\left(\frac{N_A+N_B}{N_B}\right) - \frac{N_AN_C}{2N(N_A+N_B)}\right]\right\} \quad (3.1)$$

In this way the study of the behavior of the extension of the A block is possible. The u_A term of eq 3.1 is the most dominant in the limit of large molecular weights, and it represents the intrablock excluded-volume interactions

Table I
γ Ratios at Two Characteristic Macroscopic States and the Expansion Factors α^2 at the State with $u_A^* = u_B^* = 0$ and $u_{AB}^* = \epsilon/8$, for the ABA Triblock and AB Diblock with Equal Length Fractions X of A and B[a]

	ABA triblock: $x_A = 1/4$, $x_B = 1/2$, $x_A = 1/4$		AB diblock: $x_A = 1/2$, $x_B = 1/2$	
	$u_A^* = u_B^* = 0$, $u_{AB}^* = \epsilon/8$	$u_A^* = u_B^* = u_{AB}^* = \epsilon/16$	$u_A^* = u_B^* = 0$, $u_{AB}^* = \epsilon/8$	$u_A^* = u_B^* = u_{AB}^* = \epsilon/16$
property	value	value	value	value
$\gamma(\langle R_A^2\rangle)$	1.119 [~1.09 (16)]	1.061	*1.111 [1.09(22a)]	*1.055
$\gamma(\langle R_B^2\rangle)$	1.191 [1.17 (16)]	1.106	*1.111 [1.09(22a)]	*1.055
$\gamma(\langle S_A^2\rangle)$	1.059 [~1.02 (16)]	1.030	1.054 [1.02(22a)]	*1.027
$\gamma(\langle S_B^2\rangle)$	1.090 [1.07 (16)]	1.050	1.054 [1.02(22a)]	*1.027
$\gamma(\langle R_{AB}^2\rangle)$	1.064	1.042		
$\gamma(\langle S_{AB}^2\rangle)$	1.026	1.019		
$\gamma(\langle G_{AB}^2\rangle)$	1.014	1.016		
$\alpha^2(\langle R_A^2\rangle)$	1.119 [~1.09 (16)]		1.111 [1.09(22a)]	
$\alpha^2(\langle R_B^2\rangle)$	1.191 [1.17 (16)]		1.111 [1.09(22a)]	
$\alpha^2(\langle R_{AB}^2\rangle)$	1.223			
$\alpha^2(\langle R^2\rangle)$	1.239 [1.36 (16)]		1.173 [1.22(22a)]	
$\alpha^2(\langle S_A^2\rangle)$	1.059 [~1.02 (16)]		1.054 [1.02(22a)]	
$\alpha^2(\langle S_B^2\rangle)$	1.090 [1.07 (16)]		1.054 [1.02(22a)]	
$\alpha^2(\langle S_{AB}^2\rangle)$	1.186			
$\alpha^2(\langle S^2\rangle)$	1.227 [1.28 (16)]		*1.189 [1.22(22a)]	
$\alpha^2(\langle G_{AB}^2\rangle)$	1.314 [1.42 (16)]		1.324 [1.43(22a)]	
$\alpha^2(\langle S_{AA}^2\rangle)$	1.264			
$\alpha^2(\langle G_{AA}^2\rangle)$	1.315			

[a] The values in brackets are taken from the references in parentheses. The values with an asterisk concerning the AB diblock have first been given in ref 21.

familiar from the study of homopolymers.[23,27] What it does is to expand the block and yield a power law with respect to N_A. The $u_A \ln N_A$ term together with the fixed point value $u_A^* = \epsilon/16$ determines the critical exponent to order ϵ, which comes out identical with the critical exponent ν of the homopolymer case: $\langle R_A^2\rangle_{N_A\to\infty} \sim N_A(1 + 2u_A \ln N_A) \sim N_A^{1+2u_A^*} = N_A^{1+\epsilon/8}$, with $2\nu = 1 + \epsilon/8$. The rest of the u_{AB} and u_{AC} terms come from the AB and AC interactions, respectively, and determine the overall size of the A subchain. Their effects are more pronounced on the ratio $\gamma(\langle R_A^2\rangle) = \langle R_A^2\rangle/\langle R_A^2\rangle_{hom}$, expressing the relative expansion of the A block compared to that of the A homopolymer of molecular weight N_A. It is equal to

$$\gamma(\langle R_A^2\rangle) = 1 + 2u_{AB}\left[\frac{N_B}{N_A}\ln\left(\frac{N_A+N_B}{N_B}\right) - \frac{N_B}{2(N_A+N_B)}\right] + 2u_{AC}\left[\frac{N_B+N_C}{N_A}\ln\left(\frac{N}{N_B+N_C}\right) - \frac{N_B}{N_A}\ln\left(\frac{N_A+N_B}{N_B}\right) - \frac{N_AN_C}{2N(N_A+N_B)}\right] \quad (3.2)$$

and its value for various molecular weights and interaction parameters can be compared with the results from other methods (see section 6 and Table I). The u_{AB} contribution to $\gamma(\langle R_A^2\rangle)$ depends on ratios of molecular weights, including both N_A and N_B, but is independent of N_C. In the limit $N_B \to 0$ it vanishes because the B block that causes the expansion vanishes, while it increases on increasing N_B, tending to the limit 1. In the limit of a large B block the A block attains its greatest expansion for repulsive AB interactions ($u_{AB} > 0$). When we study the u_{AC} term of eq 3.1, which represents the AC interactions, similar conclusions are derived. In the limit $N_C \to 0$ the expansion of the A block due to the u_{AC} interactions also vanishes while it increases by increasing N_C, reaching a limiting state of a large C block where the A block obtains its maximum expansion. The difference now is that this maximum expansion of the A block depends on the length N_B of the middle B block, being smaller for larger N_B. The reason is that increasing N_B the A and C blocks get on average further apart, they mix less, and therefore the expanding u_{AC} effects reduce. This is shown in Figure 1a

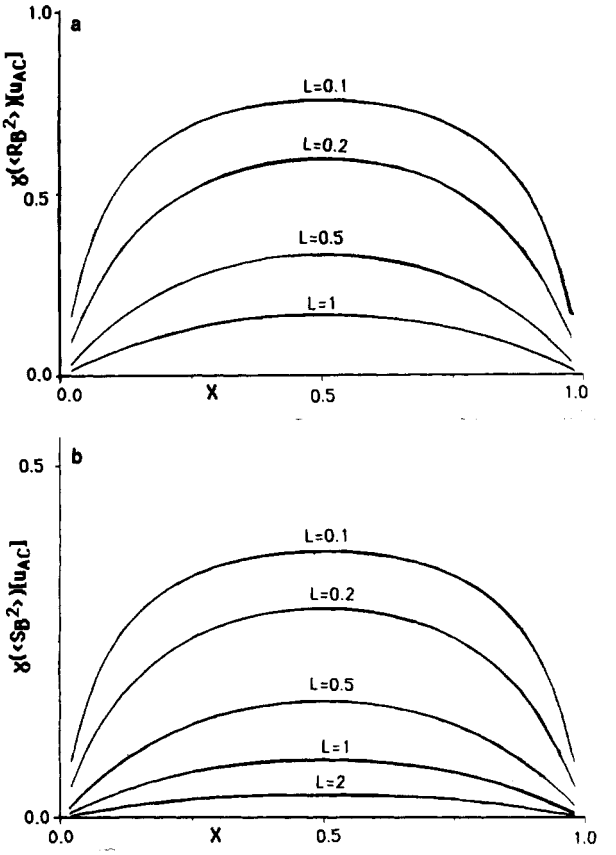


Figure 2. u_{AC} contributions to the (a) $\gamma(\langle R_B^2\rangle)$ ratio (eq 3.4) and the (b) $\gamma(\langle S_B^2\rangle)$ ratio (eq 4.4) as a function of the reduced variable $X = N_A/(N_A + N_C)$. $L = N_B/(N_A + N_C)$ increases with the length N_B of the middle block.

where the u_{AC} contributions to the $\gamma(\langle R_A^2\rangle)$ factor are plotted against the reduced variable $X = N_C/N_A$, for various values of $L = N_B/(N_A + N_B)$, which increases with the length N_B of the middle block. For larger values of L the curves and the limiting expansions obtain smaller values. The case with $N_B = 0$ ($L = 0$) corresponds to a diblock, and it is equivalent to the case of the u_{AB} interactions studied above. Similar is the behavior of the size of the other end block expressed by the symmetrical end-to-end mean-square distance $\langle R_C^2\rangle$.

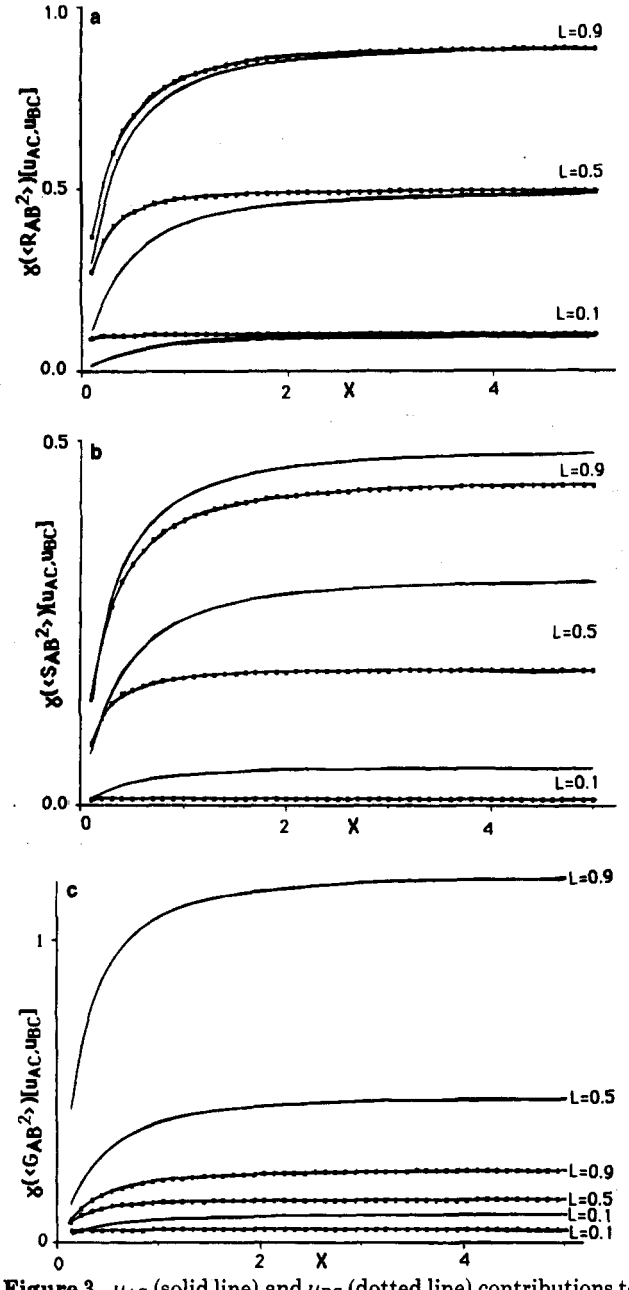


Figure 3. u_{AC} (solid line) and u_{BC} (dotted line) contributions to the ratios (a) $\gamma(\langle R_{AB}^2\rangle)$ (eq 3.5), (b) $\gamma(\langle S_{AB}^2\rangle)$ (eq 4.6), and (c) $\gamma(\langle G_{AB}^2\rangle)$ (eq B.1) as a function of the reduced variable $X = N_C/(N_A + N_B)$. $L = N_A/(N_A + N_B)$ for the u_{AC} and $L = N_B/(N_A + N_B)$ for the u_{BC} interactions, respectively.

The end-to-end mean-square distance of the middle B block can be obtained from eq 2.4 if we put $l = N_B$ and $k = 0$. It goes as

$$\langle R_B^2\rangle = N_B\Bigg\{1 + 2u_B[\ln N_B - 1] + 2u_{AB}\Bigg[\frac{N_A}{N_B}\ln\left(\frac{N_A+N_B}{N_A}\right) - \frac{N_A}{2(N_A+N_B)}\Bigg] + 2u_{BC}\Bigg[\frac{N_C}{N_B}\ln\left(\frac{N_C+N_B}{N_C}\right) - \frac{N_C}{2(N_C+N_B)}\Bigg] + u_{AC}\Bigg[\frac{N_B}{N} - \frac{N_B}{N_A+N_B} - \frac{N_B}{N_B+N_C} + 1\Bigg]\Bigg\} \quad (3.3)$$

The $u_B \ln N_B$ term represents the intrablock excluded-volume interactions, and it is the same as that of a B homopolymer of length N_B, yielding the critical exponent ν of the B homopolymer. The effects of AB, BC, and AC interactions on the corresponding $\gamma(\langle R_B^2\rangle)$ factor

$$\gamma(\langle R_B^2\rangle) = \frac{\langle R_B^2\rangle}{\langle R_B^2\rangle_{hom}} = 1 + 2u_{AB}\Bigg[\frac{N_A}{N_B}\ln\left(\frac{N_A+N_B}{N_A}\right) - \frac{N_A}{2(N_A+N_B)}\Bigg] + 2u_{BC}\Bigg[\frac{N_C}{N_B}\ln\left(\frac{N_C+N_B}{N_C}\right) - \frac{N_C}{2(N_C+N_B)}\Bigg] + u_{AC}\Bigg[\frac{N_B}{N} - \frac{N_B}{N_A+N_B} - \frac{N_B}{N_B+N_C} + 1\Bigg] \quad (3.4)$$

are expressed by means of the u_{AB}, u_{BC}, and u_{AC} terms, respectively. The u_{AB} and u_{BC} terms are symmetrical and give the effects of the two side blocks on the middle B block. They increase on increasing the lengths N_A and N_C, respectively, reaching the limits of large A and C blocks where the extension of the B block becomes maximum. The u_{AC} term is positive, meaning that an extension of the B block also takes place due to the repulsions between the A and C blocks, which are joined with the two ends of the B block. The AC interactions get reduced by increasing the length N_B, since A and C blocks get further apart. These effects are shown in Figure 2a where for larger values of $L = N_B/(N_A + N_C)$ indicating larger values of N_B, we take smaller values of the u_{AC} coefficient. The u_{AC} interactions are symmetrical with respect to N_A and N_C, which is also illustrated in Figure 2a where we plot the u_{AC} contributions with respect to the reduced variable $X = N_A/(N_A + N_C)$, expressing the length fraction of the A units.

3.B. End-to-End Mean-Square Distance of the AB Subdiblock. From the unit-to-unit mean-square distances of the two adjacent blocks A and B, $\langle R_{A,B}^2\rangle$ (eq 2.5), we can find the end-to-end mean-square distance $\langle R_{AB}^2\rangle$ of the AB subdiblock, if we put $l = N_A$ and $k = N_B$

$$\langle R_{AB}^2\rangle = (N_A+N_B)\Bigg\{1 + 2u_A\Bigg[\frac{N_A}{N_A+N_B}(\ln N_A - 1)\Bigg] + 2u_B\Bigg[\frac{N_B}{N_A+N_B}(\ln N_B - 1)\Bigg] + 2u_{AB}\Bigg[\ln(N_A+N_B) - \frac{N_A}{N_A+N_B}\ln N_A - \frac{N_B}{N_A+N_B}\ln N_B\Bigg] + u_{BC}\Bigg[2\frac{N_C}{N_A+N_B}\times \ln\left(\frac{N_B+N_C}{N_C}\right) - \frac{N_BN_C}{(N_A+N_B)(N_B+N_C)}\Bigg] + u_{AC}\Bigg[-2\frac{N_C}{N_A+N_B}\ln\left(\frac{N_B+N_C}{N}\right) - \frac{N_AN_C^2}{(N_A+N_B)(N_B+N_C)N}\Bigg]\Bigg\} \quad (3.5)$$

The coefficients of u_{BC} and u_{AC} represent the effects of the third C block on the expansion of the AB subdiblock, and they are positive, indicating that the presence of the third C block causes an expansion of the subdiblock. Increasing the molecular weight N_C of the third block causes this expansion to increase and reach the state of large C where the AB subdiblock attains its maximum expansion, like in the cases of the single blocks. We can compare the contributions of the BC and AC interactions by studying the u_{BC} and u_{AC} terms of eq 3.5. For small finite N_C the u_{BC} term due to its $\ln(N_B/N_C)$ is larger than the u_{AC} term, indicating stronger BC effects. This happens because the distance between the B and the C block is smaller than the distance between the A and the C block. In the limit $N_C \to \infty$ this difference smooths out. The C

block because of its enormous length forgets its beginning at the end of the B block and sees both A and B blocks in the same way. This is shown in Figure 3a where though the coefficient of u_{AC} obtains smaller values than that of u_{BC}, in the limit $X = N_C/(N_A + N_B) \to \infty$, both of them tend to the same limit for equivalent L's, equal to $N_A/(N_A + N_B)$ for the u_{AC} and $N_B/(N_A + N_B)$ for the u_{BC} interactions.

3.C. End-to-End Mean-Square Distance of the Triblock. The end-to-end mean-square distance $\langle R^2 \rangle$ of the whole molecule can be found by putting $l = N_A$ and $k = N_C$ in eq 2.6.

$$\langle R^2 \rangle = N\Big\{1 + 2u_A\frac{N_A}{N}(\ln N_A - 1) + 2u_B\frac{N_B}{N}(\ln N_B - 1) + 2u_C\frac{N_C}{N}(\ln N_C - 1) + 2u_{AB}\Big[\frac{N_A + N_B}{N}\ln (N_A + N_B) - \frac{N_A}{N}\ln N_A - \frac{N_B}{N}\ln N_B\Big] + 2u_{BC}\Big[\frac{N_B + N_C}{N}\ln (N_B + N_C) - \frac{N_C}{N}\ln N_C - \frac{N_B}{N}\ln N_B\Big] + 2u_{AC}\Big[\ln N - \frac{N_A + N_B}{N}\times \ln (N_A + N_B) - \frac{N_B + N_C}{N}\ln (N_B + N_C) + \frac{N_B}{N}\ln N_B\Big]\Big\} \quad (3.6)$$

The u_A, u_B, and u_C terms are the contributions from the intrablock interactions and together with the respective parts of the ideal term are equivalent to the end-to-end mean-square distances of the three independent homopolymers. The effects of the interblock interactions are represented by the other three u_{AB}, u_{BC}, and u_{AC} terms, the first two of them being symmetrical. They are positive, indicating extra expansions. These expansions are larger when the two interacting blocks are of equal length. Increasing N_B, the u_{AC} contributions decrease because the A and C blocks get further apart and interact less. This decrease appears in Figure 4a, where the plot of the u_{AC} contributions against $X = N_A/(N_A + N_C)$ for various values of $L = N_B/(N_A + N_C)$ is shown. Larger values of L, which means larger values of N_B, yield smaller contributions. The same plot shows that the effects get less for the asymmetrical cases with $X \neq {}^1/_2$.

4. Mean Radii of Gyration

The unit-to-unit mean-square distances analyzed in section 2 are used now for the evaluation of the various radii of gyration of the parts and the whole triblock molecule. These evaluations are based on the general formula[30]

$$\langle S^2 \rangle = \frac{1}{2M^2}\sum_l\sum_k \langle (r_l - r_k)^2 \rangle \quad (4.1)$$

where M is the molecular weight of the molecule or the part and the summations of l and k run over all units of the molecule or the part under study.

4.A. Radii of Gyration of the Blocks. In analogy to the end-to-end mean-square distances, section 3A, we find in this section the radii of gyration of the three blocks. The radius of gyration $\langle S_A^2 \rangle$ of the A block can be defined in terms of the unit-to-unit mean-square distances $\langle R_{A,A}^2 \rangle$ in the A block, eq 2.3, if we sum over all l and k in the A block

$$\langle S_A^2 \rangle = \frac{1}{2N_A^2}\sum_l^{N_A}\sum_{k\neq l}^{N_A} \langle R_{A,A}^2 \rangle \quad (4.2)$$

The replacement of the summations with integrations yields for $\langle S_A^2 \rangle$ the expression

$$\langle S_A^2 \rangle = \frac{N_A}{6}\Big\{1 + 2u_A\Big[\ln N_A - \frac{13}{12}\Big] + u_{AB}\Big[\frac{6N_B^2(N_A + N_B)}{N_A^3}\ln\Big(\frac{N_B}{N_A + N_B}\Big) + \frac{N_B(5N_A^2 + 18N_AN_B + 12N_B^2)}{2N_A^2(N_A + N_B)}\Big] + u_{AC}\Big[\frac{6N_B^2(N_A + N_B)}{N_A^3}\ln\Big(\frac{N_A + N_B}{N_B}\Big) + \frac{6(N_B + N_C)^2N}{N_A^3}\times \ln\Big(\frac{N_B + N_C}{N}\Big) + \frac{3N_C(N_A + 4N_B + 2N_C)}{N_A^2} - \frac{N_AN_C}{2N(N_A + N_B)}\Big]\Big\} \quad (4.3)$$

The behavior of $\langle S_A^2 \rangle$ goes as that of $\langle R_A^2 \rangle$ (Figure 1). The larger expansion of $\langle R_A^2 \rangle$ compared to that of $\langle S_A^2 \rangle$, which includes the expansions of all segments in the block, indicates that the interior of the block expands less than its exterior. Similar behavior can be obtained for the symmetrical radius of gyration $\langle S_C^2 \rangle$ of the C block.

The radius of gyration $\langle S_B^2 \rangle$ of the middle block can be found by means of the unit-to-unit distances $\langle R_{B,B}^2 \rangle$ (eq 2.4) as

$$\langle S_B^2 \rangle = \frac{N_B}{6}\Big\{1 + 2u_B\Big[\ln N_B - \frac{13}{12}\Big] + u_{AB}\Big[\frac{6N_A^2(N_A + N_B)}{N_B^3}\ln\Big(\frac{N_A}{N_A + N_B}\Big) + \frac{N_A(5N_B^2 + 18N_AN_B + 12N_A^2)}{2N_B^2(N_A + N_B)}\Big] + u_{BC}\Big[\frac{6N_C^2(N_C + N_B)}{N_B^3}\ln\Big(\frac{N_C}{N_C + N_B}\Big) + \frac{N_C(5N_B^2 + 18N_CN_B + 12N_C^2)}{2N_B^2(N_C + N_B)}\Big] + u_{AC}\Big[\frac{N_AN_C(N + N_B)}{2(N_A + N_B)(N_C + N_B)N}\Big]\Big\} \quad (4.4)$$

$\langle S_B^2 \rangle$ (Figure 2b) behaves like $\langle R_B^2 \rangle$ (Figure 2a). The fact that the expansion of $\langle R_B^2 \rangle$ is larger than the expansion of $\langle S_B^2 \rangle$ means also that the interior of the middle block is less sensitive to the u_{AC} interactions than its exterior.

4.B. Radii of Gyration of the Subdiblocks and the Mean-Square Distances of the Centers of Mass of Adjacent Blocks. For the evaluation of the mean radius of gyration $\langle S_{AB}^2 \rangle$ of the AB subdiblock, we sum l and k over all units of the subdiblock, which is equivalent to three summations over the A and B blocks:

$$\langle S_{AB}^2 \rangle = \frac{1}{2(N_A + N_B)^2}\Big\{\sum_{k=1}^{N_A}\sum_{l=1\neq k}^{N_A} \langle R_{A,A}^2 \rangle + 2\sum_{k=1}^{N_A}\sum_{l=1}^{N_B}\langle R_{A,B}^2 \rangle + \sum_{k=1}^{N_B}\sum_{l=1\neq k}^{N_B} \langle R_{B,B}^2 \rangle\Big\} \quad (4.5)$$

By means of eqs 2.3–2.5 for $\langle R_{A,A}^2 \rangle$, $\langle R_{B,B}^2 \rangle$, and $\langle R_{A,B}^2 \rangle$, respectively, and upon replacement of the summations

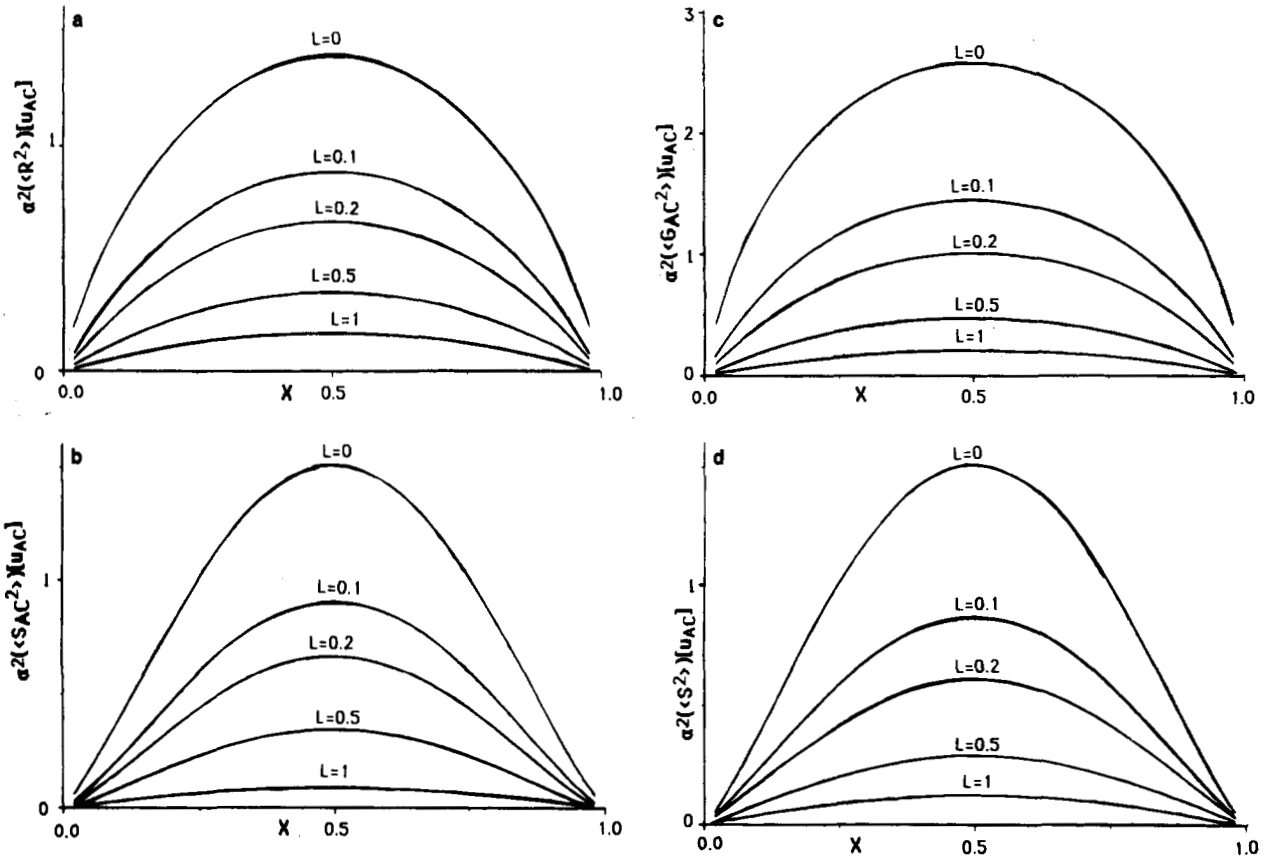


Figure 4. u_{AC} contributions to the expansion factor (a) $\alpha^2(\langle R^2\rangle)$ (eq 3.6), (b) $\alpha^2(\langle S_{AC}^2\rangle)$ (eq 4.9), (c) $\alpha^2(\langle G_{AC}^2\rangle)$ (eq B.2), and (d) $\alpha^2(\langle S^2\rangle)$ (eq B.3) as a function of the reduced variable $X = N_A/(N_A + N_C)$, for various values of $L = N_B/(N_A + N_C)$.

with the straightforward, to be performed, integrations we get:

$$\langle S_{AB}^2\rangle = \frac{N_A+N_B}{6}\Bigg\{1 + 2u_A\frac{N_A^2}{(N_A+N_B)^3}\Bigg[(N_A + 3N_B)\ln N_A - \frac{13N_A+42N_B}{12}\Bigg] + 2u_B\frac{N_B^2}{(N_A+N_B)^3}\Bigg[(N_B + 3N_A)\ln N_B - \frac{13N_B+42N_A}{12}\Bigg] + u_{AB}\Bigg[\frac{2N_A^2(N_A+3N_B)}{(N_A+N_B)^3}\times \ln\left(\frac{N_A+N_B}{N_A}\right) + \frac{2N_B^2(N_B+3N_A)}{(N_A+N_B)^3}\ln\left(\frac{N_A+N_B}{N_B}\right) + \frac{N_AN_B}{2(N_A+N_B)^2}\Bigg] + u_{BC}\Bigg[\frac{6N_C^2N}{(N_A+N_B)^3}\ln\left(\frac{N_C}{N_B+N_C}\right) + \frac{N_BN_C(5N_B^2+8N_AN_B+12N_AN_C+18N_BN_C+12N_C^2)}{2(N_B+N_C)(N_A+N_B)^3}\Bigg] + u_{AC}\Bigg[\frac{6N_C^2N}{(N_A+N_B)^3}\ln\left(\frac{N_B+N_C}{N}\right) + \frac{N_AN_C(6N_A+N_B+12N_C)}{2(N_A+N_B)^3} + \frac{N_AN_C(-N_A^2+3N_BN_C)}{2(N_A+N_B)^3N} + \frac{N_AN_BN_C(N_B^2-4N_CN)}{2(N_B+N_C)(N_A+N_B)^3N}\Bigg]\Bigg\} \quad (4.6)$$

The contributions to the expansion of $\langle S_{AB}^2\rangle$ from the various u terms behave as those of the expansion of the end-to-end mean-square distance of the diblock $\langle R_{AB}^2\rangle$ as discussed in section 3B. The influence of the C block on the radius of gyration of the AB subdiblock through the u_{BC} and u_{AC} interactions is shown in Figure 3b. The mean radius of gyration $\langle S_{AB}^2\rangle$ has two components. The first one consists of the radii of gyration $\langle S_A^2\rangle$ and $\langle S_B^2\rangle$ of the two blocks and the second of the mean-square distance $\langle G_{AB}^2\rangle$ between the centers of mass of the two blocks. It can be written as

$$\langle S_{AB}^2\rangle = x_A\langle S_A^2\rangle + x_B\langle S_B^2\rangle + x_Ax_B\langle G_{AB}^2\rangle \quad (4.7)$$

where $x_A = N_A/(N_A + N_B)$ and $x_B = N_B/(N_A + N_B)$ are the mole fractions of the blocks in the subdiblock. Increasing either the mean radii of gyration of the two blocks or the mean-square distance between them increases $\langle S_{AB}^2\rangle$. By means of eq 4.6 and the expressions of $\langle S_A^2\rangle$ (eq 4.3) and $\langle S_B^2\rangle$ (eq 4.4), we can find from eq 4.7 and analyze the second component $\langle G_{AB}^2\rangle$, the expression of which is given in section B of supplementary material. The u_A and u_B terms of $\langle G_{AB}^2\rangle$ have large positive values, indicating that the expansion of the two blocks get their centers of mass further apart. The positive u_{AB} term is a segregation term expressing the repulsions of the centers of mass of the two blocks, and it is symmetrical with respect to N_A and N_B. Finally, the positive u_{AC} and u_{BC} terms express the expansion of the subdiblock AB caused by the presence of the C block. Of some interest is the detailing study and the comparison of these last two terms in both properties $\langle S_{AB}^2\rangle$ and $\langle G_{AB}^2\rangle$. We plot the u_{AC} and u_{BC} terms in parts b and c of Figure 3 as functions of $X = N_C/(N_A + N_B)$ for various values of $L = N_A/(N_A + N_B)$ and $L = N_B/(N_A + N_B)$, respectively. The general behavior is that for $N_C \to \infty$ we take limiting values of these terms showing the approach to the limit of large C. The u_{AC} terms are generally larger than the u_{BC} ones, and this looks like a paradox since the AC chain distance is larger than the BC one. It is easy to understand the effect if we realize that the AC interactions both expand the A block and also push it away from the C block, causing an indirect expansion of the overall AB subdiblock. On the contrary,

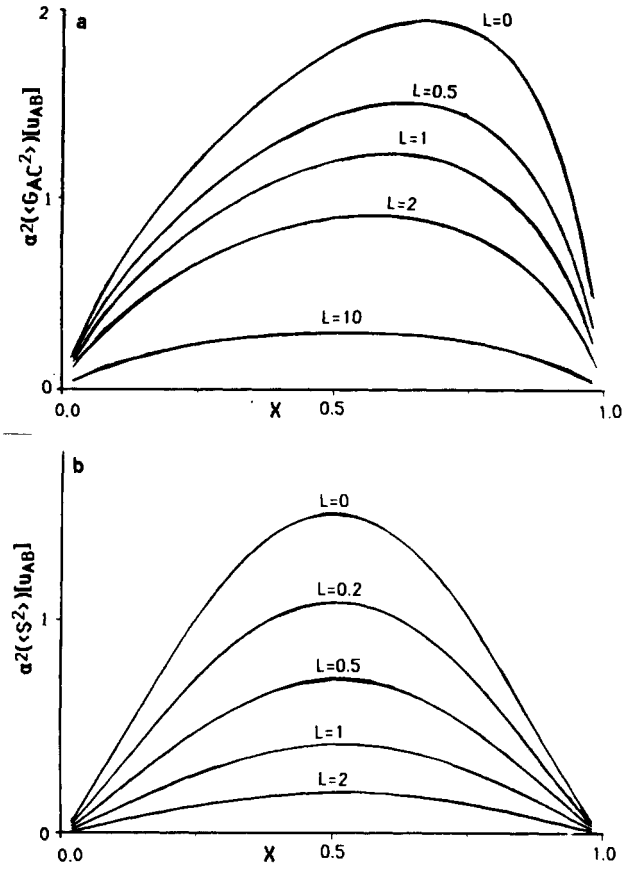


Figure 5. u_{AB} contributions to the expansion factor (a) $\alpha^2(\langle G_{AC}^2\rangle)$ (eq B.2) and (b) $\alpha^2(\langle S^2\rangle)$ (eq B.3) as a function of the reduced variable $X = N_A/(N_A + N_B)$, for various values of $L = N_C/(N_A + N_B)$.

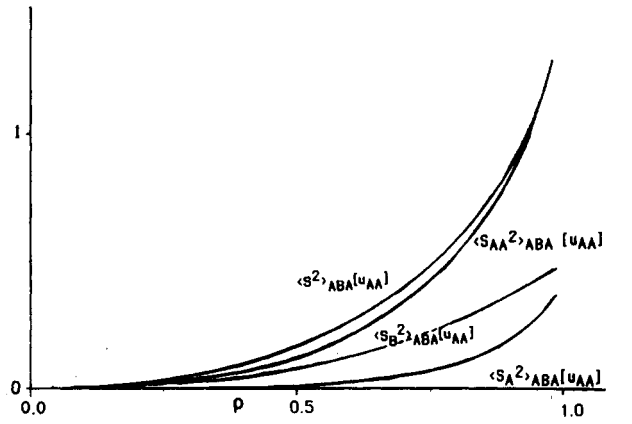


Figure 6. u_{AA} interblock effects on the radii of gyration for the case of the ABA triblock copolymer, as functions of the length fraction $\rho = N_A/N$ of the total number N_A of the A units.

the BC interactions cause only an expansion to the B block but not a pushing since the two interacting blocks are joined. Although the contribution to the enlargement of the subdiblock from the expansion of the B block is larger than that of the A block, the double effect of AC interactions dominates. A residual difference of these effects remains for $N_C \to \infty$ (Figure 3b,c), contrary to what happens to the positions of the two ends A and B expressed by $\langle R_{AB}^2\rangle$ (Figure 3a). This result indicates a distortion of the AB subdiblock caused by the presence of the C block.

4.C. System of the Two Side Blocks A and C and the Radius of Gyration of the Triblock. The radius of gyration $\langle S_{AC}^2\rangle$ of the system of the two end blocks is given by

$$\langle S_{AC}^2\rangle = \frac{1}{2(N_A+N_C)^2}\left\{\sum_{k=1}^{N_A}\sum_{l=1,l\neq k}^{N_A}\langle R_{A,A}^2\rangle + 2\sum_{k=1}^{N_A}\sum_{l=1}^{N_C}\langle R_{A,C}^2\rangle + \sum_{k=1}^{N_C}\sum_{l=1,l\neq k}^{N_C}\langle R_{C,C}^2\rangle\right\} \quad (4.8)$$

where the summations are taken over all units of the two end blocks A and C. By means of the expressions of $\langle R_{A,A}^2\rangle$ and $\langle R_{C,C}^2\rangle$ (eq 2.3) and $\langle R_{A,C}^2\rangle$ (eq 2.6), we find for the radius of gyration of the system of the two end blocks the relation

$$\begin{aligned}\langle S_{AC}^2\rangle = {} & \left\{\frac{N_A+N_C}{6}+\frac{N_AN_BN_C}{(N_A+N_C)^2}\right\}\times \\ & \left\{1+u_A\left[\frac{2N_A^2}{(N_A+N_C)^3+6N_AN_BN_C}\right]\left[(N_A+3N_C)\ln N_A-\frac{13N_A+42N_C}{12}\right]+u_B\left[\frac{12N_AN_BN_C}{(N_A+N_C)^3+6N_AN_BN_C}\right]\times\right. \\ & [\ln N_B-1]+u_C\left[\frac{2N_C^2}{(N_A+N_C)^3+6N_AN_BN_C}\right]\left[(N_C+3N_A)\ln N_C-\frac{13N_C+42N_A}{12}\right]+ \\ & u_{AB}\left[\frac{6}{(N_A+N_C)^3+6N_AN_BN_C}\right]\times \\ & \left[[-N_B^2N+2N_C(N_A^2+N_AN_B+N_B^2)]\ln\left(\frac{N_A+N_B}{N}\right)-2N_A^2N_C\ln\left(\frac{N_A}{N}\right)-N_B[-N_BN+2N_C(N_A+N_B)]\ln\left(\frac{N_B}{N}\right)+\right. \\ & \left.\left.\frac{N_AN_B(5N_A^2+18N_AN_B-12N_AN_C-12N_BN_C+12N_B^2)}{12(N_A+N_B)}\right]+ \\ & u_{BC}\left[\frac{6}{(N_A+N_C)^3+6N_AN_BN_C}\right]\left[[-N_B^2N+2N_A(N_C^2+N_BN_C+N_B^2)]\ln\left(\frac{N_B+N_C}{N}\right)-2N_C^2N_A\ln\left(\frac{N_C}{N}\right)-\right. \\ & N_B[-N_BN+2N_A(N_B+N_C)]\ln\left(\frac{N_B}{N}\right)+ \\ & \left.\left.\frac{N_BN_C(5N_C^2+18N_BN_C-12N_AN_B-12N_AN_C+12N_B^2)}{12(N_B+N_C)}\right]+ \\ & u_{AC}\left[\frac{1}{(N_A+N_C)^3+6N_AN_BN_C}\right]\left[2[(N_A+N_B)[3N_B^2+2(N_A+N_B)^2]-3N_A^2N]\ln\left(\frac{N_A+N_B}{N}\right)+2[(N_B+N_C)[3N_B^2+2(N_B+N_C)^2]-3N_C^2N]\ln\left(\frac{N_B+N_C}{N}\right)-\right. \\ & 2N_B(5N_B^2-6N_AN_C)\ln\left(\frac{N_B}{N}\right)-\frac{(N_A+N_B)^4+(N_B+N_C)^4}{2N}- \\ & \frac{1}{3}(N_A+N_B)^2(N_A+N_B-9N_C)-\frac{1}{3}(N_B+N_C)^2(N_B+N_C-9N_A)-3N_AN_C(N_A-2N_B+N_C)-\frac{N_A^3N_C(N_A+4N)}{2(N_A+N_B)N}- \\ & \left.\left.\frac{N_AN_C^3(4N+N_C)}{2(N_B+N_C)N}+\frac{N_B^4}{2N}+\frac{10}{3}N_B^3-3N_B^2N+\frac{5}{6}N^3\right]\right\} \quad (4.9)\end{aligned}$$

Increasing N_B, the ideal part $\langle S_{AC}^2\rangle_0 = (N_A + N_C)/6 +$

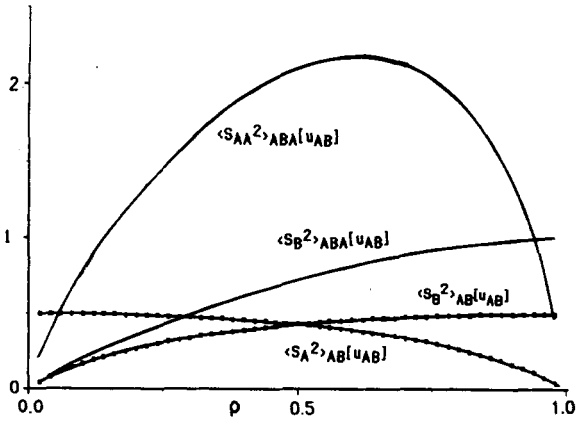


Figure 7. u_{AB} effects on the radii of gyration for the cases of the AB (dotted line) and the ABA (solid line) block copolymers as functions of $\rho = N_A/N$.

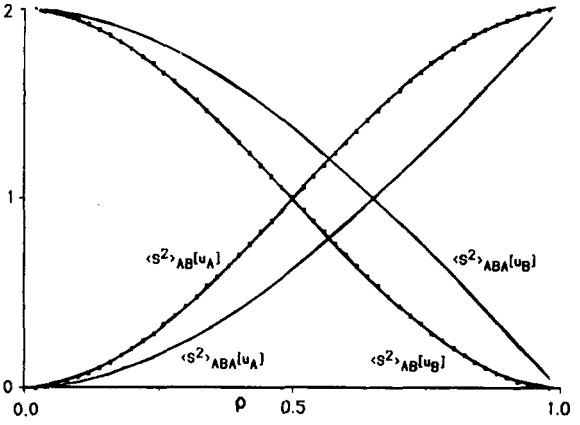


Figure 8. u_A and u_B intrablock effects of order ln N on the radius of gyration of the whole molecule for the cases of the AB (dotted line) and the ABA (solid line) block copolymers as functions of $\rho = N_A/N$.

$N_AN_BN_C/(N_A+N_C)^2$ increases because the two end blocks get further apart. The three u_A, u_B, and u_C terms, representing intrablock excluded-volume effects, increase with the enlargement of the corresponding blocks, and they decrease when the lengths of the other blocks increase. The three u_{AB}, u_{BC}, and u_{AC} terms obtain their maximum values for comparable sizes of the interacting blocks, and the u_{AC} term representing interactions between the two end blocks reduces with the increase of the size of the middle B block (Figure 4b). $\langle S_{AC}^2\rangle$ has also two components. The first comes from the radii of gyration of the two A and C blocks while the second comes from the end-to-end mean-square distance $\langle G_{AC}^2\rangle$ of the centers of mass of the two end blocks. It can be written as

$$\langle S_{AC}^2\rangle = x_A\langle S_A^2\rangle + x_C\langle S_C^2\rangle + x_Ax_C\langle G_{AC}^2\rangle \quad (4.10)$$

where $x_A = N_A/(N_A + N_C)$ and $x_C = N_C/(N_A + N_C)$ are the mole fractions of the A and C units, respectively, in the subdiblock. By means of the expressions of $\langle S_{AC}^2\rangle$ (eq 4.9) and of $\langle S_A^2\rangle$ and $\langle S_C^2\rangle$ (eq 4.3), $\langle G_{AC}^2\rangle$ can be found. Its form is given in the section B of supplementary material (eq B.2), and graphs of it are shown in Figures 4c and 5a. The ideal center-to-center mean-square distance $\langle G_{AC}^2\rangle_0 = (N_A+2N_B+N_C)/3$ increases on increasing both N_A and N_C since larger blocks mean also larger distances between their centers of mass. It also increases on increasing N_B since the enlargement of the length of the middle block takes the two end blocks further apart. The intrablock excluded-volume effects represented by its u_A, u_B, and u_C terms (eq B.2 of supplementary material) increase on increasing the lengths of the corresponding blocks and decrease on increasing the lengths of the other blocks. The u_{AB} contributions symmetrical with the u_{BC} ones are shown in Figure 5a. Increasing N_A, a maximum is reached for comparable sizes of N_A and N_B of the two interacting blocks. Similar behavior is observed for the u_{AC} interactions, which obtain their maximum for $N_A = N_C$ (Figure 4c). The latter reduce on increasing N_B since the two interacting blocks get further apart.

The radius of gyration $\langle S^2\rangle$ of the whole molecule is related to the radii of gyration $\langle S_A^2\rangle$, $\langle S_B^2\rangle$, and $\langle S_C^2\rangle$ of the three blocks and the three mean-square distances $\langle G_{AB}^2\rangle$, $\langle G_{BC}^2\rangle$ and $\langle G_{AC}^2\rangle$ of the centers of mass of the three blocks in the triblock

$$\langle S^2\rangle = x_A\langle S_A^2\rangle + x_B\langle S_B^2\rangle + x_C\langle S_C^2\rangle + x_Ax_B\langle G_{AB}^2\rangle + x_Bx_C\langle G_{BC}^2\rangle + x_Ax_C\langle G_{AC}^2\rangle \quad (4.11)$$

where $x_A = N_A/N$, $x_B = N_B/N$, and $x_C = N_C/N$ are the length fractions of the three blocks. All quantities have been found so $\langle S^2\rangle$ can be calculated, and it is given in the section B of supplementary material (eq B.3). The behavior of $\langle S^2\rangle$ is similar to those of $\langle R^2\rangle$, $\langle S_{AC}^2\rangle$, and $\langle G_{AC}^2\rangle$ as it is shown in Figures 4d and 5b where the dependence of its expansion due to the interblock effects and the molecular weights of the blocks are shown.

5. ABA and AB Block Copolymers

Many efforts have been devoted to the study of the special block copolymers of the ABA and AB type and a comparison between the properties of equimolar molecules of the two kinds shows the effects that different architectures can cause on species made of the same monomers.[8,10,12,13,15-21] Once the expressions of the general ABC triblock copolymer have been found, expressions for all special cases of block copolymers up to three blocks can easily be produced. The relations of the ABA and the AB molecules for example come straight from those of the ABC molecule, putting $u_A = u_{AC} = u_C$ and $u_{AB} = u_{BC}$ for the former and $u_C = u_{AC} = u_{BC} = 0$ for the latter. Some of the relations taken in this way have already been given in refs 21 and 22c (see also ref 27), and a check on the correctness of the present general results can be done by recovering these known results. From eq 3.5 we can take for example the end-to-end mean-square distance $\langle R^2\rangle_{AB}$ of the AB diblock, putting $u_{BC} = u_{AC} = 0$. The ratio then $\langle R^2\rangle_{AB}/[\langle R_A^2\rangle_{hom} + \langle R_B^2\rangle_{hom}] = 1 - 2u_{AB}[x_A \ln x_A + x_B \ln x_B]$, with x_A and x_B the mole fractions of the two blocks ($x_A + x_B = 1$), can be found, and it is identical with that of ref 21 (eq 4.8), with our u's defined half to those of ref 21. As far as the radii of gyration are concerned, the ratio $\gamma(\langle S_A^2\rangle_{AB}) = \langle S_A^2\rangle_{AB}/\langle S_A^2\rangle_{hom} = 1 + (2u_{AB}/x_A)[(x_B/4x_A) - (12 - 6x_A - x_A^2) + 3(x_B^2/x_A^2) \ln x_B]$ taken from eq 4.3 is the same as that of eq 28 of ref 22c. Similarly, the same expression as that of eq 22 of ref 22c for $\delta_1 = [\langle S^2\rangle_{AB} - x_A\langle S_A^2\rangle_{hom} - x_B\langle S_B^2\rangle_{hom}]/[2x_Ax_B(\langle S_A^2\rangle_{hom} + \langle S_B^2\rangle_{hom})]$ concerning the radius of gyration $\langle S^2\rangle_{AB}$ of a diblock is taken by means of $\langle S^2\rangle_{AB}$ from eq 4.6 with $u_{BC} = u_{AC} = 0$ and the radii of gyration of the isolated blocks $\langle S_i^2\rangle_{hom} = (N_i/6)[1 + 2u_i(\ln N_i - (13/12))]$ (i = A, B).

In the relations of the ABA and AB macromolecules taken from those of the ABC triblock, the length fraction ρ of all the A units equals to $\rho = N_A/(N_A + N_B)$. For symmetrical AB and ABA species of the same chain length, N_A in the case of the ABA stands for the sum of the lengths of the two A side blocks each of length $N_A/2$. Previous theoretical studies comparing the radii of gyration of the one A block $\langle S_A^2\rangle_{ABA}$ and $\langle S_A^2\rangle_{AB}$ for the two cases[16,19] find that for large N_B (small ρ) they are of comparable size, $\langle S_A^2\rangle_{ABA} \sim \langle S_A^2\rangle_{AB}$. This is seen to be true from the

graph of Figure 6, where the extra interblock u_{AA} excluded-volume component of the expansion factor $\alpha^2(\langle S_A^2\rangle_{ABA}) = \langle S_A^2\rangle_{ABA}/(N_A/12)$ is drawn as a function of ρ. For small ρ it is negligible so that $\langle S_A^2\rangle_{ABA}$ is close to $\langle S_A^2\rangle_{AB}$. For larger values of ρ the u_{AA} interblock interactions become important and expand more the size of the A blocks in the ABA case; thus the equivalence breaks and $\langle S_A^2\rangle_{ABA}$ becomes larger than $\langle S_A^2\rangle_{AB}$. The more pronounced excluded-volume effects on the B block in the case of ABA[16,19] can also be explained. Indeed, as is shown in Figure 6, the u_{AA} interblock contributions to the expansion factor of $\langle S_B^2\rangle_{ABA}$ are positive, proving that the middle B block is larger in the ABA triblock than in the AB diblock. Increasing ρ (decreasing N_B), the interblock u_{AA} interactions become stronger and the expansion of the middle B block increases. The u_{AB} effects are also stronger on $\langle S_B^2\rangle_{ABA}$ than on $\langle S_B^2\rangle_{AB}$ (Figure 7) because, though the amount of the A units is the same for the two cases, their symmetrical distribution from the two ends of the B block in the ABA case brings them on average closer to the B block. In the same Figure 7 the size of the A system of the two end blocks as is expressed by means of $\langle S_{AA}^2\rangle_{ABA}$ is seen to be larger than the corresponding $\langle S_A^2\rangle_{AB}$, expressing the size of the A block in the AB molecule, because of the insertion of the B block in the former case. Of some interest is the study of the effects of the intrablock u_A and u_B interactions of order ln N, on the overall radius of gyration $\langle S^2\rangle$ as a function of ρ (Figure 8). We see that in the case of the ABA the u_A interactions become less effective while the u_B ones appear stronger in agreement with previous findings.[16,19] The reason for this is that every A monomer interacts mainly with only half of the total amount of A units coming from the same block of length $N_A/2$, while in the case of AB it interacts with all N_A units of the A block. Furthermore, the u_B interactions appear stronger in the ABA case because they do affect not only the size of the B subchain but also the system of the two A blocks by pushing them away in space; such a distinction does not happen in the case of the AB diblock.

On the basis of the above analysis, the explanation of the experimental peculiarities found for the AB and ABA copolymers is straightforward. The dependence of $\langle S_B^2\rangle_{ABA}$ on the u_{AA} (Figure 6) representing the AA interactions between the two end blocks, which are positive for repulsions ($u_{AA} > 0$) and negative for attractions ($u_{AA} < 0$), reveals that the solubility of the A component affects the dimensions of the B block. This explains the results of the experimental measurements on the size of the B block found in the ABA case, significantly smaller than those of the parent B homopolymer in A unfavorable solutions (u_{AA} small negative). Such a thing is not observed at the respective measurements of the AB diblock molecule.[12,15] It has been observed experimentally[9,10] that the ABA molecule of almost equimolar components ($\rho \approx 0.5$) gives larger intrinsic viscosities and second virial coefficients in B selective solvents than in A selective ones. These two properties increase with the average size of the macromolecules in the solution, and their behavior can be explained from the fact that the u_B intrablock effects on $\langle S^2\rangle_{ABA}$ are significantly greater than those of the u_A ones for ρ up to 0.6 (Figure 8). Furthermore, since the u_B effects are larger than the u_A ones, triblocks of the same total molecular weight are expected to give larger values of viscosity in good solvents when they are richer in the B component, and this is in accord with previous theoretical and experimental results.[9,10,16,19]

6. Fixed Points and the Values of the Various Universal Ratios

One of the achievements of renormalization group (RG) theories is to produce correctly the characteristics of the macroscopic states at which the macromolecules can exist. Such features can be the values of the critical exponents that determine the dependence of the macroscopic properties on the molecular weights, as well as the values of the universal ratios like the γ ratios or the expansion factors α^2. The various macroscopic states are described by the fixed points of RG theories where the interaction parameters obtain specific values. For a homopolymer like A, B, or C isolated chains, for example, the two fixed point values $u_x^* = 0$ and $u_x^* = \epsilon/16$ (x = A, B, C) describe the ideal and the expanded states, respectively. For a diblock like the AB or BC isolated diblocks further macroscopic states are possible. The values of the three interaction parameters u_x^*, u_y^*, and u_{xy}^* (x, y = A, B or B, C) at the fixed points are related by means of $u_{xy}^* = \epsilon/8 - 1/2\,(u_x^* + u_y^*)$, which permits u_{xy}^* to obtain larger values than $\epsilon/16$ as well.[22b,27] While for two expanded blocks ($u_x^* = u_y^* = \epsilon/16$) u_{xy}^* can be either 0 or take the value $\epsilon/16$, it can obtain the larger values of $3\epsilon/32$ or $\epsilon/8$ when the one block or both blocks are in their ideal states, respectively, indicating that the segregation state with positive u_{xy}^* is reached more when the blocks are hardly in their ideal states.[22b,27] For the general ABC triblock the fixed point equation for the u_{AC} interaction parameter obeys the equation $u_{AC}^* = \epsilon/8 - 1/2(u_A^* + u_C^*)$ and it is identical with those of the two subdiblocks. The reason for this is the universal character of the fixed points. The values of the interaction parameters at the fixed points do not depend on the specific details of each macromolecule. They do not change for example if we change the molecular weights of the three blocks. Since the middle B block can vary from the limit of very small values (limit of AC diblock) to the limit of large values (ABC triblock), u_{AC}^* has to obey the same equation for both limits. So generally the following equations determine the fixed points of the ABC triblock

$$8u_x^{*2} - \frac{1}{2}u_x^*\epsilon = 0$$

$$u_{xy}^* = \frac{\epsilon}{8} - \frac{1}{2}(u_x^* + u_y^*), \quad x, y = \text{A, B, C} \qquad (6.1)$$

and describe all macroscopic states at which a triblock can exist. Although eq 6.1 has been given before for the homopolymer and the diblock copolymer molecules, as far as the general ABC triblock is concerned, they include the new result $u_{AC}^* = \epsilon/8 - 1/2(u_A^* + u_C^*)$ for the fixed point value u_{AC}^* of the interaction parameter between the two end blocks.

From the expressions of the macroscopic properties that have been studied, many characteristic ratios independent of the molecular weights and depending only on ratios of them can be found. These universal quantities obtain different values at the various macroscopic states and depend on the values that the u's obtain at these states. In what follows, we will concern ourselves, following the literature, with only two such ratios. The one kind is the γ ratios denoting the ratio of a quantity to the similar quantity of the homopolymer under the same conditions. In the case of γ ratios of subdiblocks of the triblock, the property is divided by the same property of the corresponding isolated diblock under similar conditions. The second category of ratios are the expansion factors α^2, which denote the ratios of properties to their ideal values

with all interaction parameters equal to zero. In all these states the γ ratios or the expansion factors α^2 can be determined to order ϵ, simply by putting in their expressions taken from the relations of the previous sections the values of the interaction parameters of eq 6.1. As an example of the way this can be applied, we find the ratio $\gamma(\langle S_B^2\rangle)$, taken from eq 4.4, for an ABC triblock with $N_B = 2N_A$ and $N_C = N_A/3$, and for the macroscopic state with $u_A^* = \epsilon/16$ (expanded A block), $u_B^* = 0$ (ideal B block), $u_C^* = \epsilon/16$ (expanded C block), $u_{AB}^* = 3\epsilon/32$ (A and B blocks in segregation), $u_{BC}^* = 0$ (B and C blocks not in segregation), and $u_{AC}^* = \epsilon/16$ (A and C blocks in segregation). Once the ratios of the lengths of the blocks are specified, the coefficients of the u terms can be found, and after using the values of the interaction parameters as they are given for the specific state, the ratio can be calculated, and to order $\epsilon(\epsilon=1)$, it is equal to $\gamma(\langle S_B^2\rangle) = 1.036$.

The expansion factors of the various properties for the AB and ABA macromolecules have been estimated by means of Monte Carlo methods,[16,22a] for the case of zero intrablock excluded-volume interactions and self-avoidance between dissimilar units, for $x_A = x_B = {}^1/_2$ for the AB case and $x_A = {}^1/_4$, $x_B = {}^1/_2$, and $x_A = {}^1/_4$ for the ABA case. Their values are quoted in Table I. We can also find these expansion factors from our general relations. The self-avoidance condition between different ideal blocks ($u_A^* = u_B^* = 0$) corresponds to the fixed point value $u_{AB}^* = \epsilon/8$.[27,29] The values of the γ ratios and the expansion factors α^2 are written in Table I for two macroscopic states and for $\epsilon = 1$. We see that the general trends of the first-order ϵ calculations go as those of the results from computer calculations. Both sets of results agree for example in that the expansion factors of the end-to-end mean-square distances are larger than the expansion factors of the corresponding radii of gyration. This applies to the whole molecule or to parts of it. Also, the middle block in the ABA triblock, according to both methods, is more expanded than the end ones. A thing to mention at this stage is that, though better numerical agreement is expected from second-order ϵ calculations, closer results to those of Monte Carlo calculations can be achieved by reexponentiating the first-order ϵ results. This has been done in refs 21 and 22c and found for example that the expansion factor $\alpha^2(\langle S^2\rangle_{AB}) = 1.23$ for the state $u_A^* = u_B^* = 0$, $u_{AB} = \epsilon/8$, closer to the Monte Carlo result 1.22 than the value 1.19 of first-order ϵ calculations. For the ratio $\langle G_{AB}^2\rangle/2[\langle R_A^2\rangle_{hom} + \langle R_B^2\rangle_{hom}]$ from eq B.1 with $u_{AC} = u_{BC} = 0$, the first-order ϵ results yield the value 1.32 for the state $u_A^* = u_B^* = 0$, $u_{AB}^* = \epsilon/8$, while the result given in ref 22c is 1.36 and closer to the Monte Carlo value 1.43.

7. Conclusions

The dilute-solution behavior of the triblock copolymers of the general ABC type is described in terms of the intensity of the intra- and interblock interactions and the molecular weights of the three blocks. Starting with the unit-to-unit mean-square distances, the end-to-end mean-square distances, and the mean-square radii of gyration of the three blocks, the two subdiblocks and the whole molecule are evaluated, and from them the mean-square distances between the centers of mass of the blocks are deduced. Limiting states of maximum expansions, created by parts of the molecule for the rest of the molecule when the sizes of the former grow enormously are detected. Maximum effects between interacting blocks are found for comparable molecular weights of these blocks. The critical exponent $\nu = (1/2) + (\epsilon/16)$ characterizing the size of the various parts of the triblock is the same as that of homopolymers, but the prefactors depend on both the intensity of the interactions and the ratios of the molecular weights of the three blocks. The macroscopic states at which the triblock can exist have been found by finding the fixed points of the system and determining the values of the interaction parameters at the fixed points to order ϵ. All prefactors and characteristic ratios of the ABC triblock can be found at these states. The γ ratios and the expansion factors α^2 of the various properties of equimolar ABA and AB molecules, special cases of the general ABC molecule, are given to order ϵ. These results are compared and found to be consistent with the results of Monte Carlo enumerations.

Acknowledgment. We thank the Greek General Secretariat of Research and Technology for partial support.

Supplementary Material Available: Section A including examples of evaluation of diagrams and Table A.1 with the values of all diagrams and Section B including the expressions of $\langle G_{AB}^2\rangle$, $\langle G_{AC}^2\rangle$, and $\langle S^2\rangle$ (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Noshay, A.; McGrath, J. *Block Copolymer Overview and Critical Survay*; Academic Press: New York, 1977.
(2) Matsushita, Y.; Choshi, H.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1980**, *13*, 1053.
(3) (a) Arai, K.; Kotaka, T.; Kitano, Y.; Yoshimura, K. *Macromolecules* **1980**, *13*, 455. (b) Arai, K.; Kotaka, T.; Kitano, Y.; Yoshimura, K. *Macromolecules* **1980**, *13*, 1670.
(4) Kotaka, T.; Miki, T.; Arai, K. *J. Macromol. Sci. Phys.* **1980**, *B17*, 303.
(5) Watanabe, H.; Kotaka, T. *Polym. J.* **1981**, *13*, 149.
(6) Kudose, I.; Kotaka, T. *Macromolecules* **1984**, *17*, 2325.
(7) (a) Kudose, I.; Arai, K.; Kotaka, T. *Polym. J.* **1984**, *16*, 241. (b) Arai, K.; Ueda-Mashima, C.; Kotaka, T.; Yoshimura, K.; Murayama, K. *Polymer* **1984**, *25*, 230.
(8) Inagaki, H. D. *Makromol. Chem.* **1965**, *86*, 289.
(9) Inagaki, H.; Miyamoto, T. D. *Makromol. Chem.* **1965**, *87*, 166.
(10) Utracki, L. A.; Simha, R.; Fetters, L. J. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 2051.
(11) Kotaka, T.; Ohnuma, H.; Inagaki, H. *Polymer* **1969**, *10*, 517.
(12) Ohnuma, H.; Kotaka, T.; Inagaki, H. *Polym. J.* **1970**, *1*, 716.
(13) Kotaka, T.; Ohnuma, H.; Inagaki, H. *Colloidal and Morphological Behaviour of Block and Graft Copolymers*; Molau, G. E., Ed.; Plenum Press: New York, 1971; p 259.
(14) Dondos, A. D. *Makromol. Chem.* **1971**, *147*, 123.
(15) Tanaka, T.; Kotaka, T.; Inagaki, H. *Polym. J.* **1972**, *3*, 338.
(16) Tanaka, T.; Kotaka, T.; Ban, K.; Hattori, M.; Inagaki, H. *Macromolecules* **1977**, *10*, 960.
(17) Henderson, C. P.; Williams, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1001.
(18) Kotaka, T.; Tanaka, T.; Hattori, M.; Inagaki, H. *Macromolecules* **1978**, *11*, 138.
(19) Tanaka, T.; Kotaka, T. *Bull. Inst. Chem. Res.* **1972**, *50*, 107.
(20) Kurata, M.; Kimura, T. *J. Polym., Sci., Polym. Phys. Ed.* **1979**, *17*, 2133.
(21) Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *86*, 4280.
(22) (a) Tanaka, T.; Kotaka, T.; Inagaki, H. *Macromolecules* **1976**, *9*, 561. (b) Joanny, J.; Leibler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640. (c) McMullen, W.; Freed, K.; Cherayil, B. *Macromolecules* **1989**, *22*, 1853.
(23) Kosmas, M. K. *J. Phys. A: Math. Gen.* **1981**, *14*, 931.
(24) Kosmas, M. K. *J. Phys. A: Math. Gen.* **1981**, *14*, 2779.
(25) Kosmas, M. K. *J. Phys. A: Math. Gen.* **1982**, *15*, 1667.
(26) Vlahos, C. H.; Kosmas, M. K. *Polymer* **1984**, *25*, 1607.
(27) Sdranis, Y. S.; Kosmas, M. K. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 819.
(28) Vlahos, C. H.; Kosmas, M. K. *J. Phys. A: Math. Gen.* **1987**, *20*, 1471.
(29) Whittington, S. G.; Kosmas, M. K.; Gaunt, D. S. *J. Phys. A: Math. Gen.* **1988**, *21*, 4211.
(30) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(31) Fixman, M. *J. Phys. A: Math. Gen.* **1955**, *23*, 1656.