Second Virial Coefficient of A_xB_y Miktoarm Star Copolymers in Common Θ, Common Good, and Selective Solvents

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ABSTRACT: The mutual second virial coefficient A_2 between two identical ideal miktoarm star copolymer chains A_xB_y composed of A and B branches is determined up to the first order of the small parameter $\epsilon = 4 - d$ (d is the space dimensionality) by means of simple perturbation theory. Analytical expressions corresponding to various macroscopic states, as those are defined by the prevailing binary intermolecular interactions, are obtained as a function of the arm lengths N_A, N_B, their corresponding numbers x, y, and the interaction parameters, between units of similar or dissimilar kind u_{AA}, u_{BB}, and u_{AB}. The effect of the copolymer architecture is also studied in detail by calculating g_A, the ratio of the virial coefficient of a miktoarm star with respect to that of a linear diblock copolymer with the same number of A and B units; g_A is dimensionless and experimentally accessible.

1. Introduction

The osmotic second virial coefficient, A_2, is an interesting property useful for the understanding of the fundamental behavior of polymer solutions. A great deal of theoretical research has also been conducted on A_2 for flexible homopolymers since the early days of the development of polymer solution theory owing to its relatively easy access by experiment. It is obtained from the osmotic pressure Π in the limit of infinite dilution[1]

$$A_2 = \lim_{c \to 0} \frac{\mathrm{d}[\Pi/(RTc)]}{\mathrm{d}c} \tag{1.1}$$

and is determined by the average interactions between two polymeric chains. The second virial coefficient can take both positive and negative values depending on the temperature and the solvent quality. For the excluded volume regime (long chains in a good solvent) its dependence on molecular weight may be expressed as a power law, $A_2 \sim M^{-\gamma}$, where γ is a critical exponent independent of the nature of the polymer or the solvent. Renormalization group theory[1−4] and Monte Carlo simulation results[5−7] can reproduce the experimental findings on A_2 with reasonable accuracy; even though some problems still prevail,[8] our understanding of A_2 for homopolymer solutions is, in general, quite satisfactory.

On the other hand, information about copolymer A_2 is fragmentary since available theoretical[9] and experimental results[10] are extremely limited; this is especially true for the case of identical miktoarm[11] star copolymer chains (miktoarm is derived from the Greek word *μικτος*, meaning mixed), which are composed of x branches from the homopolymer A, each of molecular weight N_A, and y, from the homopolymer B, of molecular weight N_B. In the case of a copolymer, in addition to the "self" virial coefficients, A_{2AA} and A_{2BB}, between A−A and B−B arms belonging to different chains, there are four more virial coefficients: A_{2AB}, between arms A−B, A_{2AC} and A_{2BC} between arms A or B and the whole copolymer chain, and the mutual A_{2CC}, between two copolymer chains, respectively. A wide spectrum of mutual virial coefficient values can be achieved by changing either the solvent quality or the chain architecture by changing the number of A or B branches or their relative length. The effects of the architecture on A_{2CC} in various macroscopic states are clearer if one considers g_A, the ratio of mutual virial coefficients of the miktoarm to the linear diblock copolymer, having the same total molecular weight M:

$$g_A = A_{2\mathrm{CC,mikto}}/A_{2\mathrm{CC,diblock}} \tag{1.2}$$

g_A is dimensionless and may be readily measured.[3]

In the present work we perform a theoretical calculation of both quantities, the mutual second virial coefficient A_{2CC} of a miktoarm copolymer and the ratio g_A corresponding to the three possible macroscopic states of common Θ, common good, and selective solvent. The method follows the renormalization group approach of refs 1 and 2. Thus, the analytical expressions are obtained in a perturbation scheme, up to second order in the interaction parameters u_{AA}, u_{BB}, and u_{AB}. The calculations are made close to the critical dimensionality $d = 4$. The values of interaction parameters at the fixed points u_{AA}^*, u_{BB}^*, and u_{AB}^* have been evaluated up to first order in the small parameter $\epsilon = 4 - d$ and are universal since they do not depend on the chain architecture. This method has successfully been applied to the calculation of the conformational properties of miktoarm stars[11] and the second virial coefficient of homopolymers with various architectures.[1]

In the next chapter we present the sketch for the evaluation of A_2, while in subsequent sections the results for the mutual virial coefficients and the ratio g_A for different macroscopic states are discussed.

2. Evaluation of A_2

The mutual second virial coefficient A_{2CC} can be obtained from the following relation:[1]

$$A_{2\mathrm{CC}} = -\frac{VN_{\mathrm{avog}}}{2M^2}\left(\frac{C_2 - C_1^{\,2}}{C_1^{\,2}}\right) \tag{2.1}$$

C_2 is the conformational partition function of two chains and is defined in terms of the probability distribution function: $C_2 = \int \Pi \mathrm{d}^d\vec{R}_{1ci}\, \Pi \mathrm{d}^d\vec{R}_{2ci}\, P\{\vec{R}_{1ci},\vec{R}'_{2ci}\}$; C_1 is the same property for a single chain, V is the volume of the system, N_{avog} is the Avogadro number, and M is the total molecular weight of the miktoarm chain. To evaluate C_2, we substitute $P\{\vec{R}_{1ci},\vec{R}'_{2ci}\}$ from eq A.1 (see Appendix). In the resulting expression we are expanding the last three exponential terms, which represent the interexcluded interactions up to the second order of the interaction parameters u_{AA}, u_{BB}, u_{AB}. For convenience we use the notation w_{11}, w_{22}, w_{12} to describe all the intra- and interexcluded interactions of the u_{AA}, u_{BB}, and u_{AB} type, between the same or different miktoarm chains.

$$
\begin{aligned}
C_2 = \int \Pi \mathrm{d}^d\vec{R}_{1i}\, \Pi \mathrm{d}^d\vec{R}_{2i}\, P_0\{\vec{R}_{1i},\vec{R}_{2i}\} \times \\
\exp[-w_{11}\sum_{i=1}^{M}\sum_{j=1}^{M}\delta^d(\vec{R}_{1i}-\vec{R}_{1j}) - \\
w_{22}\sum_{i=1}^{M}\sum_{j=1}^{M}\delta^d(\vec{R}_{2i}-\vec{R}_{2j})]\{1 - 2w_{12}\sum_{i=1}^{M}\sum_{j=1}^{M}\mathrm{d}^d(\vec{R}_{1i}-\vec{R}_{2j}) + \\
2{w_{12}}^2\sum_{i=1}^{M}\sum_{j=1}^{M}\sum_{k=1}^{M}\sum_{l=1}^{M}\mathrm{d}^d(\vec{R}_{1i}-\vec{R}_{2j})\,\mathrm{d}^d(\vec{R}_{1k}-\vec{R}_{2l})\}
\end{aligned}
\quad (2.2)
$$

The first term in the above expansion represents the product from two independent chains and is equal to C_1^2. The second term, which involves w_{12}, represents two miktoarm chains intersected at their ith and jth points due to the action of the delta function pseudopotential $\delta^d(\vec{R}_{1i} - \vec{R}_{2j})$. Finally, the third term, ${w_{12}}^2$, represents two chains intersected at two different pairs of points i, j and k, l due to the action of two delta functions. In the diagrammatic representation, eq 2.2 takes the form

$$C_2 = C_1^2 - 2w_{12}\ \overline{\underline{\quad\vdots\quad}}\ - 2w_{12}^2\ \overline{\underline{\ \ \vdots\ \ \vdots\ \ }} \qquad (2.3)$$

Here the solid lines represent the miktoarm chains, while the broken ones, the delta function type interaction that brings them in contact. Substituting C_2 in eq 2.1, the mutual second virial coefficient becomes

$$A_2 = -\frac{VN_{\mathrm{avog}}}{2C_1^2M^2}[-2w_{12}\ \overline{\underline{\quad\vdots\quad}}\ - 2w_{12}^2\ \overline{\underline{\ \ \vdots\ \ \vdots\ \ }}\ ] \qquad (2.4)$$

In the first-order diagram (first term in eq 2.4), the single point of intersection does not change the intrachain character of the miktoarm star so that each chain “produces” a C_1 factor. This, however, differs from the case of two independent chains in that the two intersecting chains “move” together in all available space of volume V, so that a factor V should appear in the denominator of the expression of the diagram. Each point of the single contact runs through all possible positions of the two miktoarm chains so that a double summation over all u_{AA}, u_{BB}, and u_{AB} terms is produced.

$$\overline{\underline{\quad\vdots\quad}} = \frac{C_1^2}{V}[u_{\mathrm{AA}}x^2\sum_{i=1}^{N_{\mathrm{A}}}\sum_{j=1}^{N_{\mathrm{A}}} + 2u_{\mathrm{AB}}xy\sum_{i=1}^{N_{\mathrm{A}}}\sum_{j=1}^{N_{\mathrm{B}}} + u_{\mathrm{BB}}y^2\sum_{i=1}^{N_{\mathrm{B}}}\sum_{j=1}^{N_{\mathrm{B}}}] \qquad (2.5)$$

In the limit of large N we may approximate summations with integrations and the diagram becomes equal to

$$\overline{\underline{\quad\vdots\quad}} = ({C_1}^2{N_{\mathrm{A}}}^2/V)[u_{\mathrm{AA}}x^2 + 2u_{\mathrm{AB}}xyp + u_{\mathrm{BB}}y^2p^2], \qquad \text{where } p = N_{\mathrm{B}}/N_{\mathrm{A}} \quad (2.6)$$

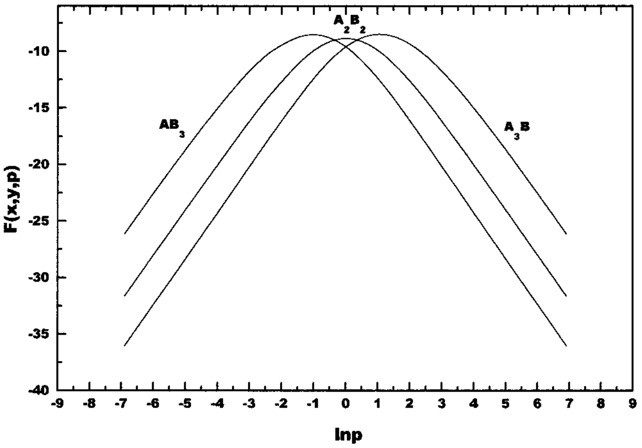

Figure 1. Function $F(x,y,p)$ vs ln p ($p = N_{\mathrm{B}}/N_{\mathrm{A}}$) for the macroscopic state in a common Θ solvent ($u_{\mathrm{AA}}^* = u_{\mathrm{BB}}^* = 0$, $u_{\mathrm{AB}}^* = \epsilon/8$).

In the second-order diagram (second term in eq 2.4), the two simple contacts i, j and k, l caused by the action of the two delta function type pseudopotentials $\delta^d(\vec{R}_{1i} - \vec{R}_{2j})$, $\delta^d(\vec{R}_{1k} - \vec{R}_{2l})$ form a single loop. The value of this diagram and the final expressions for the A_2 of a miktoarm star and the respective linear diblock copolymer with the same total molecular weight M are presented in the Appendix.

For repulsive heterointeractions ($u_{\mathrm{AB}} > 0$) both mutual second virial coefficients become zero only when u_{AA} and u_{BB} take negative values; this suggests lower Θ temperatures when compared with the respective Θ temperatures of homopolymers having the same number of arms $f = x + y$. This has also been concluded from MC calculations.[12]

3. Results for Different Macroscopic States

a. Common Θ Solvent. We first consider the case of two miktoarm stars with both homopolymer parts, A and B, under Θ conditions and subject to excluded volume heterointeractions. This case can be quantified by assigning the following special values to the interaction parameters: $u_{\mathrm{AA}}^* = 0$, $u_{\mathrm{BB}}^* = 0$, $u_{\mathrm{AB}}^* = \epsilon/8$ (these are the fixed points). By introducing the first two in eq A.3, we obtain a simplified expression for the second virial coefficient, which is now equal to $A_{2\mathrm{CC,mikto}} = N_{\mathrm{avog}}u_{\mathrm{AB}}'(2pxy/(x + py)^2)\{1 - u_{\mathrm{AB}}[4 \ln M + F(x,y,p)]\}$; i.e., only the third term, u_{AB}, survives. By increasing the strength of heterointeractions, $A_{2\mathrm{CC,mikto}}$ is also increasing; this increase is initially sharp but more gradual for larger u_{AB} values. An increase of the molecular weight causes a corresponding decrease of the mutual second virial coefficient, and in the limit of large molecular weights this dependence assumes a power law form: $A_{2\mathrm{CC,mikto}} \sim M^{-\gamma}$. The critical exponent γ may be evaluated from the last expression up to first order in ϵ. For large M, the ln M term is much larger than the function $F(x,y,p)$ and the mutual second virial coefficient becomes $A_{2\mathrm{CC,mikto}} = N_{\mathrm{avog}}u_{\mathrm{AB}}'(2pxy/(x + py)^2)\{1 - 4u_{\mathrm{AB}} \ln M\} \Rightarrow A_{2\mathrm{CC,mikto}} \sim \exp(-4u_{\mathrm{AB}}^* \ln M) \sim \mathrm{M}^{-4u_{\mathrm{AB}}^*}$. Using the fixed point value of $u_{\mathrm{AB}}^* = \epsilon/8$ we find $\gamma = \epsilon/2$. This value is double the one established for homopolymers in a common good solvent.[1] For smaller molecular weights, the $F(x,y,p)$ contribution is not negligible and the effects of architecture start to become important. In Figure 1, $F(x,y,p)$ is presented as a function of the ratio $p = N_{\mathrm{B}}/N_{\mathrm{A}}$, for three different miktoarm stars, AB_3, $\mathrm{A}_2\mathrm{B}_2$, and $\mathrm{A}_3\mathrm{B}$, having the same total molecular weight. Higher values of $F(x,y,p)$ means that the mutual second virial coefficient and the heterointeractions are decreasing. At the same time, however, the factor $(2pxy/(x + py)^2)$, which in essence is equal to the product of mass fractions $2\Phi_A\Phi_B$, is also changing, and the final behavior of $A_{2\mathrm{CC,mikto}}$ is derived from the competitive action of these two terms. The latter term may be eliminated by calculating the ratio g_A of the mutual second virial coefficients of a miktoarm star to that of a diblock having the same number of A and B units. For the current macroscopic state, g_A is given by the following analytical expression

$$g_A = A_{2\mathrm{CC,mikto}}/A_{2\mathrm{CC,diblock}} = \{1 - u_{\mathrm{AB}}[(4 + 3py - 2pxy)\ln p - [2(p + 1)^2/p](4xy - 3x - 3y + 5)\ln(p + 1) + [(p + 2)^2/p](2xy - 2x - y + 2)\ln(p + 2) + [(1 + 2p)^2/p](2xy - 2y - x + 2)\ln(1 + 2p) - 4[p(2xy - 2y - x + 2) + (2xy - 2x - 2y + 3) + (2xy - 2x - y + 2)/p]\ln 2 + 4[(x^2 + pxy + p^2y^2)/xyp]\ln 2 + 6[(x + yp)^2/xyp]\ln(x + yp) - [(2x + yp)^2/xyp]\ln(2x + yp) - [(x + 2yp)^2/xyp]\ln(x + 2yp) - [(4x + yp)/x]\ln(yp) - [(x + 4py)/yp]\ln x]\} \quad (3.1)$$

g_A encapsulates the effects of macromolecular architecture and therefore depends on the number of branches x, y and the asymmetry ratio p while is independent of the molecular weight of the arms. Experimental[3] and theoretical[5] studies in the case of homopolymers indicate that the contribution of higher order terms in the interaction parameters is very important. Moreover, the naive first-order results like the ones of eq 3.1 predict unphysically negative values of g_A for f (=$x + y$) higher than 7. To address these issues, we exponentiate the ratio g_A in the following manner

$$g_A = \exp\{-u_{\mathrm{AB}}D\} \quad (3.2)$$

where D is the prefactor of the u_{AB} term in eq 3.1. Using the fixed point value of $u_{\mathrm{AB}}^* = \epsilon/8$, we plot in Figure 2 g_A (eq 3.2) vs the length fractions $\Phi_B = yp/(x + yp)$ for several types of miktoarm stars. In general, it can be observed that g_A is always smaller than unity and is decreasing by increasing the total number of branches, f. In the case of an A_2B miktoarm star with an extremely short B arm ($\Phi_B \rightarrow 0$), the mutual second virial coefficient that accounts for the cross interexcluded volume interactions u_{AB} is equal to the respective one for the diblock copolymer ($g_A = 1$) since the B units feel a cloud of A units of the other chain around the space without being able to distinguish their architecture. By increasing Φ_B, g_A is decreasing. In the case an A block of the diblock copolymer, which is double in length compared to the A arm of miktoarm star, the A block is interacting more with the B block than the shorter A arms. The same value of $g_A = 1$ is obtained for the other limit of very long B arms ($\Phi_B \rightarrow 1$). For the A_2B_2 miktoarm stars, g_A is smaller compared to that of A_2B with the same Φ_B, since both arms of the miktoarm star are half the length of that of the diblocks, while the limiting values of g_A for $\Phi_B \rightarrow 0$ and $\Phi_B \rightarrow 1$ are again equal to 1. These values can be obtained from eq 3.2 by setting $p \rightarrow 0$ and $p \rightarrow \infty$, respectively, and are equal to $g_A = \exp\{-0.125[4(y - 1)\ln 2 - 4\ln y]\}$ and $g_A = \exp\{-0.125[4(x - 1)\ln 2 - 4\ln x]\}$. It may be observed in both cases that only the number of the very short arms determines the intensity of heterointeractions. The corresponding plots for the other miktoarm stars A_3B, A_4B, A_3B_3, and A_4B_2 illustrated in Figure 2 can also be explained in a similar manner. The comparison between miktoarm stars having the same total number of arms, f, but different x and y is also of some importance. From the A_2B_2, A_3B and A_3B_3, A_4B_2 curves in Figure 2 it is obvious that an increase of the total number of arms decreases the differences in g values in the major part of the Φ_B range. In the latter case (A_4B_2, A_3B_3) there are Φ_B values where the ratio g_A for A_4B_2 is smaller than the respective ratio of A_3B_3 and vice versa.

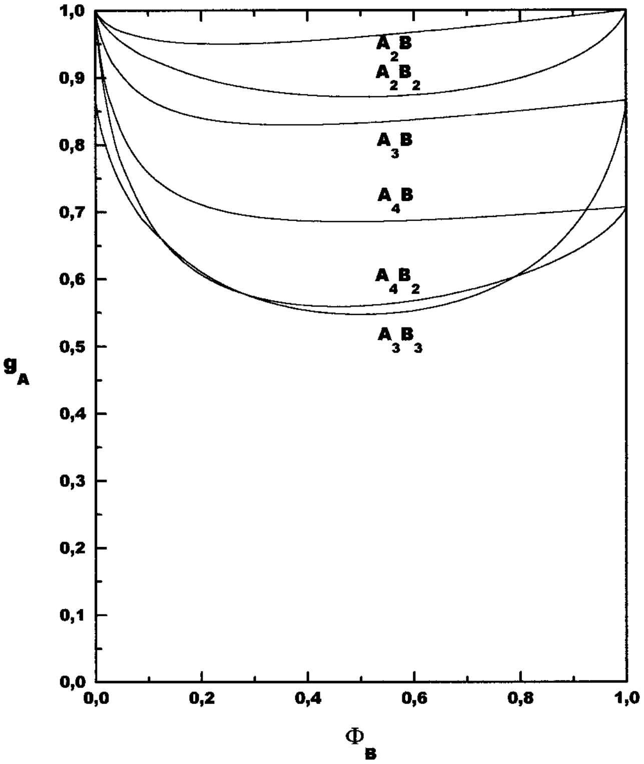

Figure 2. Exponentiated ratio g_A as a function of $\Phi_B = yp/(x + yp)$ for the macroscopic state in a common Θ solvent ($u_{\mathrm{AA}}^* = u_{\mathrm{BB}}^* = 0$, $u_{\mathrm{AB}}^* = \epsilon/8$).

b. Selective Solvent. Next we study the macroscopic state in a selective solvent. In particular, we consider the case of two identical miktoarm copolymers without A−A interchain interactions while the interactions of the A−B and B−B type obey the excluded volume regime. In our model the current macroscopic state corresponds to the special values of the interaction parameters at fixed points equal to $u_{\mathrm{AA}}^* = 0$, $u_{\mathrm{BB}}^* = \epsilon/16$, and $u_{\mathrm{AB}}^* = 3\epsilon/32$ (it is remembered that $\epsilon = 4 - d$). By introducing these values in eqs A.3 and A.4, we calculate the dimensionless ratio g_A and then its exponentiated form as previously described. Plots of g_A for various miktoarm chains are illustrated in Figure 3 where it can be seen that g_A is again smaller than unity and decreases by increasing the total number of branches. Compared, however, with the respective values of g_A for the common Θ solvent, the g_A values are significantly smaller. In the case of miktoarm stars having the same total number branches, there is an accentuated differentiation in the g_A behavior for $\Phi_B > 0.5$, where g_A is decreasing in the following order $A_3B > A_2B_2 > AB_3$, while the opposite is true for $\Phi_B < 0.5$. This may be explained by the inevitable rotation of two approaching copolymers that place the A homopolymer parts closer

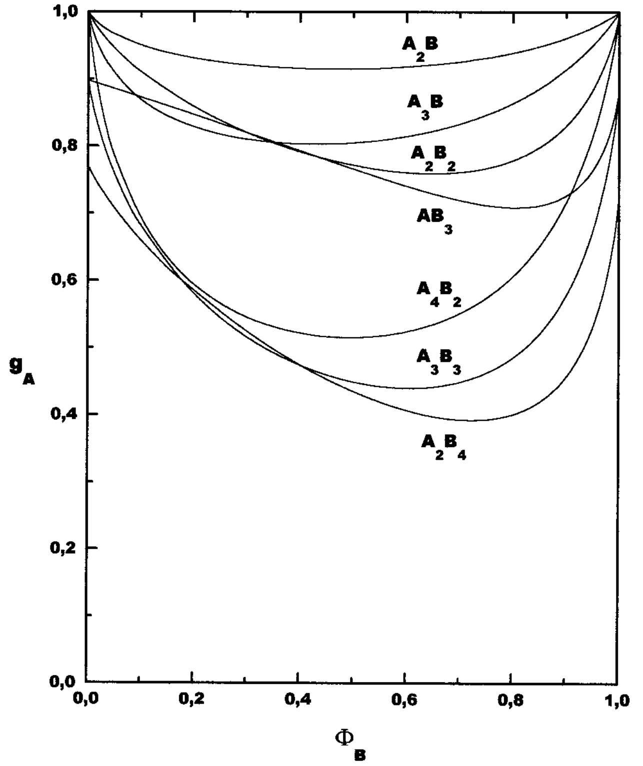

Figure 3. Exponentiated ratio g_A vs Φ_B for the macroscopic state in a selective solvent ($u_{AA}^* = 0$, $u_{BB}^* = \epsilon/16$, $u_{AB}^* = 3\epsilon/32$).

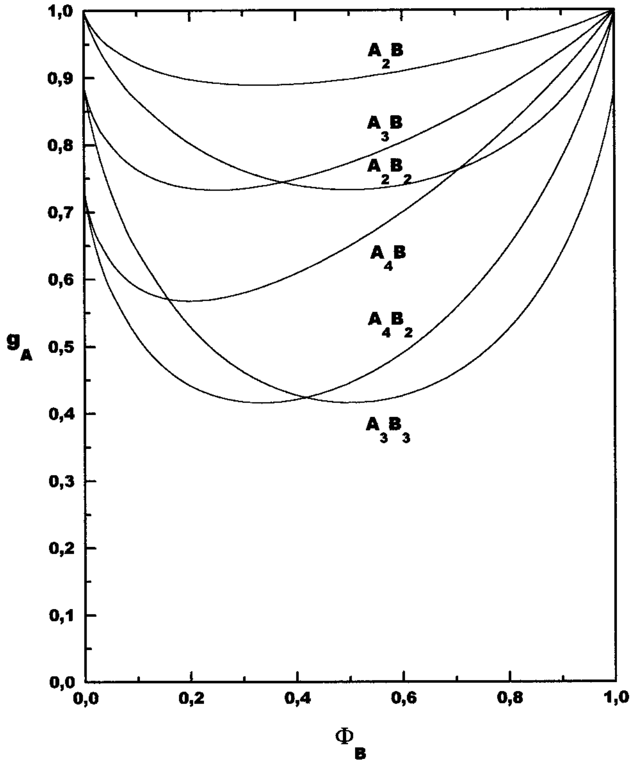

Figure 4. Exponentiated ratio g_A vs Φ_B for the macroscopic state in a common good solvent ($u_{AA}^* = u_{BB}^* = u_{AB}^* = u = \epsilon/16$).

Table 1. Experimental and Theoretical Values of the Ratio g_A for Symmetric Homopolymer Stars with Different Numbers of Arms f in a Good Solvent

f	exp[13]	Douglas and Freed[3,4]	current work
3	1.13		
4	0.94 ± 0.03	0.923	
6	0.86 ± 0.02	0.816	0.603
8		0.668	
12	0.51–0.70	0.336	0.341
18			0.236
32	0.20–0.25		0.138
64	0.13–0.15		0.071
128	0.06–0.09		0.036

and thus minimize the total number of interactions. In miktoarms with many short A arms, the two chains come closer while the longer B arms interact more with the A and B arms of the other chain. Almost similar is the behavior of a miktoarm with six branches. The limiting g_A values in both cases $\Phi_B \rightarrow 0$, $\Phi_B \rightarrow 1$ are only dependent on the number of y arms. In the first case, the short B arms determine the cross interactions, as previously explained (Θ-solvent state), and also the B–B interactions. In the second case of large B arms, the B–B interactions are predominant and again the limiting values depend on the number of the y arms.

c. Common Good Solvent. The last macroscopic state considered here is the one in a common good solvent. In that case, all types of interchain interactions between units A–A, B–B, and A–B, obey the excluded volume regime: $u_{AA}^* = u_{BB}^* = u_{AB}^* = u^* = \epsilon/16$, and the miktoarm chains behave like an asymmetric homopolymer star with the same total molecular weight, M. The critical exponent is obtained in the limit of large M using the fixed point value of $u^* = \epsilon/16$ and is equal to $A_{2CC} = (N_{avog}/(x + py)^2)u\{(x + py)^2 - 4u(x + py)^2 \ln M\} \sim M^{-4u} \sim M^{-\epsilon/4} \sim M^{-0.25}$ (where $\epsilon = 4 - d$); i.e., it coincides with the respective of homopolymer chains. The analytical expression for the second virial coefficient of symmetric homopolymer stars[1] is recovered by setting in eq A.4 $p = 1$ and is equal to $A_{2S} = uN_{avog}[1 - 4u(\ln M + F(f))]$, $F(f) = -2 \ln 2 - {}^1/_2 - \ln f + (-7f^2 + 22f - 15) \ln 2 + [({}^9/_2)f^2 - ({}^{27}/_2)f + 9] \ln 3$. This result is an indication of the correctness of our calculations. The dimensionless ratio g_A and its exponentiated form can be obtained as described for the previous two macroscopic states (Θ and selective solvent case). The results are illustrated in Figure 4 as a function of the mass fraction Φ_B; it can be observed that for the limiting values $\Phi_B \rightarrow 0$, $\Phi_B \rightarrow 1$ the ratio g_A becomes equal to that of a symmetric homopolymer star with x and y branches, respectively, while for Φ_B values different than these two extremes g_A is decreasing by increasing f, the total number of arms. Compared to the respective g_A values in a common Θ solvent, g_A values are smaller for any value of Φ_B. In the case of the selective solvent, which provides Θ conditions for the A units, the g_A values are smaller for small values of Φ_B and higher for higher Φ_B values. The experimental values of g_A[13] for symmetric homopolymer stars (see Table 1) are higher than the ones predicted by this work. By calculating the third-order term (in the interaction parameter u^3), Kosmas[1] has shown that the A_2 of homopolymers stars may be written in a closed form of the type $A_{2S} = uN_{avog}[1 + 8u(\ln M + F(f))]^{-1/2}$. The parameters 8 and $-{}^1/_2$ have been determined from the first two terms of the series, and their values were consisted to the third-order term. (For a more explicit description of how the higher order terms are included, see ref 14.) Writing our results (eqs A.3 and A.4) for the common good solvent in a closed form following the Kosmas approach,[1,14] we are able to derive an improved estimation for the g_A ratio. These values illustrated in Figure 5 for miktoarm chains up to $A_{64}B_{64}$ and in Table 1 for selected symmetric stars. It can be seen that the

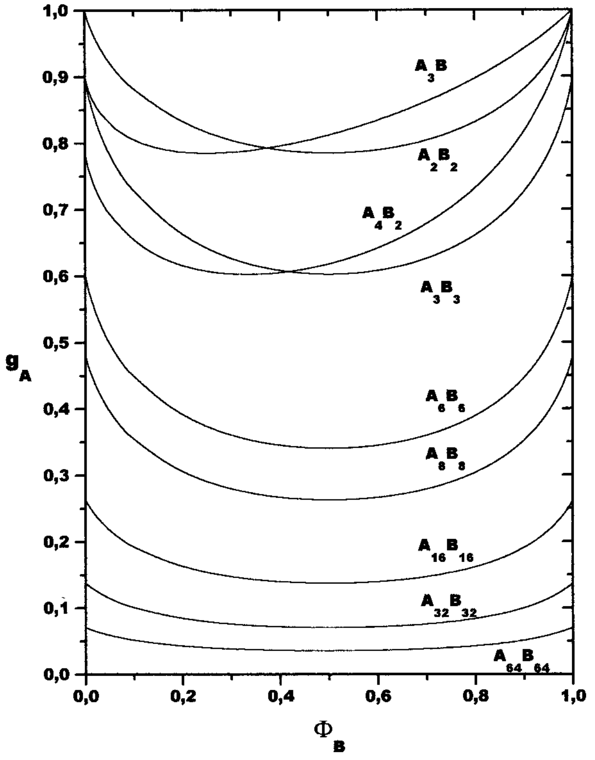

Figure 5. Ratio g_A obtained in a closed form vs Φ_B for the macroscopic state in a common good solvent ($u_{AA}^* = u_{BB}^* = u_{AB}^* = u = \epsilon/16$).

agreement with the experimental values is better now than in the previous case (Figure 4). The exponentiated results of Douglas and Freed[3,4] fit better the experimental values up to $f = 8$ but become unphysically negative for $f \geq 18$. From the comparison of our estimates with the experimental data for the g_A ratio, it is obvious that the proper inclusion of higher order terms is very significant. Douglas and Freed[15] in their RG analysis of diblock copolymers in the Gell–Mann–Low scheme consider limits where exact results are known and use this nonperturbative information to guide the resummation whenever possible. This will be the aim of future work.

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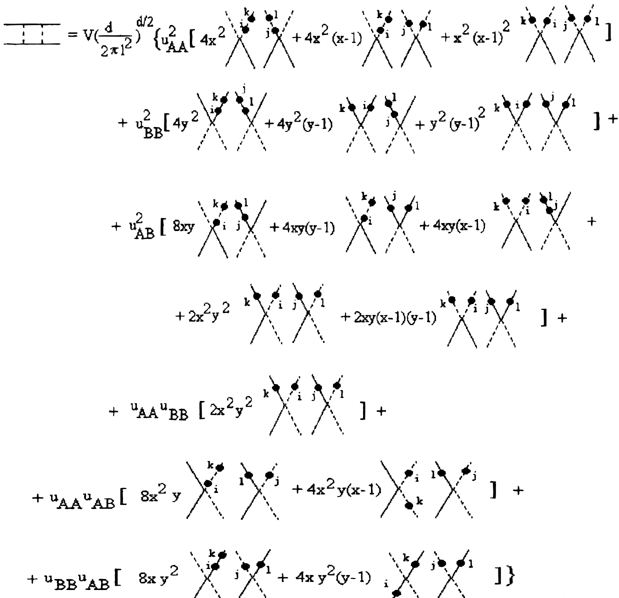
Appendix

a. Probability Distribution Function. We use a three-index notation to determine the position vectors $\mathbf{R}_{cbi}$ of any two units belonging to the same or different miktoarm chains. The first two indices c and b, which determine the miktoarm chain and the specific branch on which the unit lies, respectively take the values $c = 1$ or 2 and $b = 1$ to f (where $f = x + y$). The first x branches are assigned to be of the A type (consisting of A homopolymer units), and the remaining y branches are therefore of type B. The third index determines the exact position of the unit along a specific arm (starting from the junction point) and varies from $i = 1, ..., N_A$ or $i = 1, ..., N_B$. For a configuration where the ends of the segments of the two chains are at the position vectors $\mathbf{R}_{cbi}$ and $\mathbf{R}_{cbi}'$, the probability distribution function is given by

$$
\begin{aligned}
P\{\vec{R}_{1bi},\vec{R}_{2b'j}'\} = P_0\{\vec{R}_{1bi},\vec{R}_{2b'j}'\} \times \\
\exp\{-u_{AA}\sum_{b=1}^{x}\sum_{b'=1}^{x}\sum_{i=1}^{N_A}\sum_{j=1}^{N_A}\delta^d(\vec{R}_{1bi} - \vec{R}_{1b'j}) - \\
u_{BB}\sum_{b=x+1}^{f}\sum_{b'=x+1}^{f}\sum_{i=1}^{N_B}\sum_{j=1}^{N_B}\delta^d(\vec{R}_{1bi} - \vec{R}_{1b'j}) - \\
2u_{AB}\sum_{b=1}^{x}\sum_{b'=x+1}^{f}\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\delta^d(\vec{R}_{1bi} - \vec{R}_{1b'j}) - \\
u_{AA}\sum_{b=1}^{x}\sum_{b'=1}^{x}\sum_{i=1}^{N_A}\sum_{j=1}^{N_A}\delta^d(\vec{R}_{2bi}' - \vec{R}_{2b'j}') - \\
u_{BB}\sum_{b=x+1}^{f}\sum_{b'=x+1}^{f}\sum_{i=1}^{N_B}\sum_{j=1}^{N_B}\delta^d(\vec{R}_{2bi}' - \vec{R}_{2b'j}') - \\
2u_{AB}\sum_{b=1}^{x}\sum_{b'=x+1}^{f}\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\delta^d(\vec{R}_{2bi}' - \vec{R}_{2b'j}') - \\
2u_{AA}\sum_{b=1}^{x}\sum_{b'=1}^{x}\sum_{i=1}^{N_A}\sum_{j=1}^{N_A}\delta^d(\vec{R}_{1bi} - \vec{R}_{2b'j}') - \\
2u_{BB}\sum_{b=x+1}^{f}\sum_{b'=x+1}^{f}\sum_{i=1}^{N_B}\sum_{j=1}^{N_B}\delta^d(\vec{R}_{1bi} - \vec{R}_{2b'j}') - \\
4u_{AB}\sum_{b=1}^{x}\sum_{b'=x+1}^{f}\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\delta^d(\vec{R}_{1bi} - \vec{R}_{2b'j}')\}
\end{aligned}
\quad (A.1)
$$

$P_0\{\vec{R}_{1bi},\vec{R}_{2b'i}\}$ stands for the probability distribution of the two ideal (Gaussian) noninteracting miktoarm chains. The first six exponential terms in eq 1.4 represent the long-range intramolecular interactions between units belonging in the same chain, labeled $c = 1$ or 2. The remaining three terms are the intermolecular interactions between units of the different chains. The form of these interactions for two chain points at position vectors $\mathbf{R}_{cbi}$ and $\mathbf{R}_{cbj}$ is approximated with a d-dimensional delta function pseudopotential, $u\delta^d(\mathbf{R}_{cbi} - \mathbf{R}_{cbj})$, which takes nonzero values only when $\mathbf{R}_{cbi}$ is close to $\mathbf{R}_{cbj}$. The intensity of the interactions is proportional to the excluded volume parameters u_{AA}, u_{BB}, u_{AB}, which can be written in terms of the mean average potential between the two chain points at positions separated by vector $\vec{r}$ as $u = (^1/_2)\int d\vec{r}\,\{1 - \exp[-V(\vec{r})/kT]\}$. The probability distribution function is a central quantity in the statistical thermodynamics of polymers and simple liquids alike, and all the macroscopic properties are expressed in terms of it.

b. Second-Order Diagram and the Analytical Expression for A_2. In the second-order diagram (second term in eq 2.4), the two simple contacts i, j and k, l caused by the action of the two delta function type pseudopotentials $\delta^d(\vec{R}_{1i} - \vec{R}_{2j})$, $\delta^d(\vec{R}_{1k} - \vec{R}_{2l})$ form a single loop. A loop may be created from two, three, or four intersecting branches of the same or different homopolymers A or B. Therefore, the following cases of the u_{AA}^2, u_{BB}^2, u_{AB}^2, and $u_{AA}u_{AB}$, $u_{BB}u_{AB}$, $u_{AA}u_{BB}$ interactions exists; their respective multiplicities appear as prefactors:



(A.2)

Due to the fact that this calculation is up to second order in the interaction parameters, the diagrams in eq A.2 are calculated up to zero order in intraexcluded volume interactions ($C_1 = V$). Their forms arise from the simple rule that each diagram represents an integral of the following type: $\int_M \mathrm{d}i_1 \int_M \mathrm{d}k_1 \int_M \mathrm{d}j_2 \int_M \mathrm{d}l_2\, (d/2\pi l^2)^{d/2}/(\text{length of the loop})^{d/2}$. The integral values corresponding to the critical dimensionality $d = 4$ are obtained by way similar to that described previously.[1,2] Introducing the obtained diagram values in eq A.2 and substituting the resulting expressions for the general first- and second-order diagrams (eqs 2.6 and A.2) into eq 2.4, we finally arrive at the following analytical expression for the mutual second virial coefficient of identical miktoarm star polymers, corresponding to any component length ratio $p = N_B/N_A$ and solvent conditions.

$$A_{2CC,\mathrm{mikto}} = \frac{N_{\mathrm{avog}}}{(x + py)^2}\{u_{AA}' x^2\{1 - u_{AA}[4 \ln M - 4 \ln(x + py) + 18(x - 1)(x - 2) \ln 3 + 4(-7x^2 + 22x - 17) \ln 2 - 2] - u_{BB}y^2[-4(1 + p + p^2) \ln 2 - p^2 \ln p - 4(p + 1)^2 \ln(p + 1) + (p + 2)^2 \ln(p + 2) + (1 + 2p)^2 \ln(1 + 2p)] - 2u_{AB}y[-(x - 1)(p + 3)^2 \ln(p + 3) + (3x - 5)(p + 2)^2 \ln(p + 2) + (p + 1)[-3(x - 1)(p + 1) + 4(p + 2)] \ln(p + 1) + p[-2(p + 2) + p(x - 1)] \ln p + 9(x - 1) \ln 3 - 4(3x - 5) \ln 2]\} + p^2y^2u_{BB}'\{1 - u_{BB}[4 \ln M - 4 \ln(x + yp) + 4 \ln p + 18(y - 1)(y - 2) \ln 3 + 4(-7y^2 + 22y - 17) \ln 2 - 2] - u_{AA}(x^2/p^2)[-4(1 + p + p^2) \ln 2 - p^2 \ln p - 4(p + 1)^2 \ln(1 + p) + (p + 2)^2 \ln (p + 2) + (1 + 2p)^2 \ln(1 + 2p)] - 2u_{AB}(x/p^2)[- (y - 1)(1 + 3p)^2 \ln(1 + 3p) + (1 + 2p)^2(3y - 5) \ln(1 + 2p) + (p + 1)[4(2p + 1) - 3(y - 1)(1 + p)] \ln(p + 1) + 9p^2(y - 1) \ln 3 - 4p^2(3y - 5) \ln 2]\} + 2pxyu_{AB}'\{1 - u_{AB}[4 \ln M - 4 \ln(x + yp) + (4 + 3py - 2pxy) \ln p - 2[(p + 1)^2/p](4xy - 3x - 3y + 5) \ln(p + 1) + [(p + 2)^2/p](2xy - 2x - y + 2) \ln(p + 2) + [(1 + 2p)^2/p](2xy - 2y - x + 2) \ln(1 + 2p) - 4[p(2xy - 2y - x + 2) + (2xy - 2x - 2y + 3) + (2xy - 2x - y + 2)/p] \ln 2 - 2]\}\} \quad (A.3)$$

The excluded volume parameters u_{AA}, u_{BB}, and u_{AB} are dimensionless, while u_{AA}', u_{BB}', and u_{AB}' have volume dimensions and are equal to $u_{AA}' = u_{AA}/(d/2\pi l^2)^{d/2}$, $u_{BB}' = u_{BB}/(d/2\pi l^2)^{d/2}$, and $u_{AB}' = u_{AB}/(d/2\pi l^2)^{d/2}$. From that last expression the mutual virial coefficient of a span diblock copolymer chain $A_{2CC,\mathrm{diblock}}$, may be obtained by setting $x = 1$ and $y = 1$. The respective virial coefficient for a diblock chain with the same total molecular weight M is obtained in an earlier stage using $N_{\mathrm{blockA}} = xN_A$ and $N_{\mathrm{blockB}} = yN_B$ and is equal to

$$A_{2CC,\mathrm{diblock}} = \frac{N_{\mathrm{avog}}}{(x + py)^2}\{u_{AA}' x^2\{1 - u_{AA}[4 \ln M - 4 \ln(x + py) + 4 \ln x - 8 \ln 2 - 2] - u_{BB}(1/x^2)[-4(x^2 + pxy + p^2y^2) \ln 2 - p^2y^2 \ln(py) - x^2 \ln x - 4(x + py)^2 \ln(x + py) + (2x + py)^2 \ln(2x + py) + (x + 2py)^2 \ln(x + 2py)] - 4u_{AB}(1/x^2)[-(2x + py)^2 \ln(2x + py) + 4x^2 \ln 2 - py(2x + py) \ln(py) + 2(x + py)(2x + py) \ln(x + py)]\} + p^2y^2u_{BB}'\{1 - u_{BB}[4 \ln M - 4 \ln(x + yp) + 4 \ln(py) - 8 \ln 2 - 2] - u_{AA}(1/p^2y^2)[-4(x^2 + pxy + p^2y^2) \ln 2 - p^2y^2 \ln(py) - x^2 \ln x - 4(x + py)^2 \ln(x + py) + (2x + py)^2 \ln(2x + py) + (x + 2py)^2 \ln(x + 2py)] - 4u_{AB}(1/p^2y^2)[4p^2y^2 \ln 2 - x(x + 2py) \ln x + 2(x + py)(x + 2py) \ln(x + py) - (x + 2py)^2 \ln(x + 2py)]\} + 2pxyu_{AB}'\{1 - u_{AB}(1/pxy)[4pxy \ln M - 4pxy \ln(x + yp) + py(4x + py) \ln(py) + x(x + 4py) \ln x - 6(x + py)^2 \ln(x + py) + (x + 2py)^2 \ln(x + 2py) + (2x + py)^2 \ln(2x + py) - 4(x^2 + pxy + p^2y^2) \ln 2 - 2pxy]\}\} \quad (A.4)$$

References and Notes

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