Dilute Solutions of Block Copolymers. 1. Diblock Copolymers

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Received July 18, 1997; Revised Manuscript Received April 9, 1998

ABSTRACT: Pair configurations of symmetric diblock copolymers in a selective solvent (i.e. a good solvent for one block and a Θ-solvent for the other block) and of their constituent homopolymers were investigated. Cubic lattice chains of total length $N = 160$ were generated by use of Monte Carlo methods. Pair data were determined by exact enumeration of all possible pair configurations. When the separation between two copolymer chains reached zero ($r \to 0$) the pair distribution function $g(r)$ is about 0.18, which is slightly larger than the value found for athermal systems (≈0.14) but appreciably smaller than $g(0)$ of Θ-systems (0.6−0.8). The extent to which mean squared dimensions and shape parameters depend on intermolecular distance for block copolymers was similar to that of athermal chains, as well. Transformation of the data into a concentration dependence revealed that with increase in concentration chain dimensions decreased in the case of good and selective solvents while they increased for Θ-solvents. Concomitantly, the molecular shape became more globulelike in the former case, while it remained fairly unchanged in the latter. On the whole, diblock copolymers in a selective solvent were found to behave approximately like homopolymers in a relatively good solvent.

I. Introduction

Theoretical and numerical investigations of an “infinitely dilute” macromolecular solution usually are performed on *isolated* particles, as intermolecular interactions between dissolved molecules may be disregarded in this restricted case. The first step toward a slightly more concentrated (but nevertheless highly diluted) solution is to take into account pairwise interactions between dissolved particles. The information provided by the simulation of *isolated pairs* of macromolecules is 2-fold. On the one hand, quantities reflecting “integral” changes produced by the presence of another molecule may be calculated, regarding pairs of coils at any distance from one another. The most prominent property is the excluded volume u, i.e. the volume which is not accessible for a chain in the presence of another one due to (repulsive) interaction. Experimental evaluation of the excluded volume is substantiated by the second osmotic virial coefficient,[1] A_2. Both theoretical work[2−4] and computer simulations[3,5−13] have been carried out on this subject. Similarly, as u (or A_2) represents the *concentration dependence* of the (reduced) osmotic pressure (π/c), the volume integral of the relative deviation of any property associated with all compatible pairs with respect to the property of isolated chains may be interpreted as a concentration dependence of this property within the limits of infinite dilution.[14,15] These “integral” effects will be treated in section III.B. Another type of information, on the other hand, originates from simulation data at each specific intermolecular distance.[5,7,11,12,14,15] This provides one with a pseudo-dynamic picture reflecting the differential changes of the molecular properties which occur when another molecule approaches. The most important separation-dependent property is the pair distribution function $g(r) = e^{-U(r)/kT}$ ($U(r)$ being the pair potential[5,7,12,16−19] in the limit of zero concentration) which is a measure of the probability of finding two chains at a distance r between their centers of gravity. $g(r)$ is related to the (integral) excluded volume by

$$u = \int_0^{\infty} [1 - g(r)] 4\pi r^2 \, dr \qquad (1)$$

Separation-dependent changes will be treated in section III.A of this article.

This paper will focus on the investigation of symmetric diblock copolymers (and their constituent homopolymers) in a selective solvent while the following article[20] will deal with symmetric triblock copolymers.

II. The Model

The term “exact enumeration” usually refers to the numerical evaluation of all possible *chain* configurations of an isolated lattice chain. In the present context, it denotes the evaluation of the number of *pair* configurations which can be formed from *two* distinct lattice chains.[6] The data generation for isolated pairs therefore comprises two steps: chain generation by means of Monte Carlo methods and exact enumeration of pair configurations.

Chain Generation. One could generate two completely new chains from scratch and compare these two chains by counting all possible pair configurations. For nonathermal conditions, however, this is very time-consuming as each configuration would have to be equilibrated in accordance with the thermodynamic conditions chosen. Therefore, a pool of 400 chains was chosen to start with. The chains were generated either by a self-avoiding walk procedure[21] (for $N = 40$, 80; N indicating the chain length) or by dimerization[22] (for the longest chains examined, $N = 160$). These athermal chains were equilibrated to the chosen solvent conditions by the pivot algorithm.[23] Acceptance of the new configuration was subjected to the Metropolis−Rosenbluth criterion[24] through comparison of the Boltzmann factor of the new chain to that of the preceding one. In practice, two chains were chosen at random from the pool, compared with each other, afterwards modified by use of the pivot algorithm ($N/2$ pivot relaxations per chain) and finally restored to the pool. The probability of choosing a specific pair of chains is $2/(400 \times 399)$; between two successive comparisons of two specific

S0024-9297(97)01087-5 CCC: $15.00

chains, each of them is relaxed on average 399 × $N/2$ times. As the correlation times are of order N for the slowest relaxation modes,[25,26] any correlation between the old and the new (pair) configuration is completely disrupted after 399 × $N/2$ pivot relaxations.

Exact Enumeration of Pair Configurations. For the determination of pair configurations, two chains were chosen at random from the pool of 400 equilibrated chains, and their characteristic properties (mean square radius of gyration $\langle s^2\rangle$, center of gravity, etc.) were determined. In order to calculate the number of overlapping configurations of the two chains, all N^2 distance vectors between all N segments of one chain and all N segments of the other chain were determined (the two centers of gravity, rounded to integer positions, being forced to coincide). Quite generally, the number of different vectors should equal the number of *forbidden* pair configurations, N_{forb}, the multiplicity of a given vector representing the number of overlaps between the two chains for a displacement characterized by this vector. In addition, as the (rounded) centers of gravity of both chains were located at the origin of the coordinate system, the length of the vector had to equal the distance between the two centers of gravity after shifting one of the chains. In this way, distance-dependent quantities became available. Together with the *total* number of possible configurations in the lattice, N_{total}, one can determine the number of all "allowed" configurations, N_{allowed}, being free of overlaps.

$$N_{\text{allowed}} = N_{\text{total}} - N_{\text{forb}} \tag{2}$$

For nonathermal conditions, one must also take into account the number of nearest-neighbor contacts between the two chains in order to arrive at the statistical weight of the pair configuration, expressed by the intermolecular Boltzmann factor (intramolecular Boltzmann factors need not be considered because all chains have the same probability due to the chosen algorithm of chain generation). It may be determined by calculating the $6N^2$ distance vectors between the N segments of one chain and the six neighbor positions of the N segments of the other chain.

After elimination of all vectors which have already appeared in counting overlaps, the number of different vectors is equal to the number of configurations, $N_{\text{cont,allowed}}$, which are free of overlaps but exhibit at least one contact. The actual number of contacts (when displacing the first chain by this vector) is determined by the multiplicity of the vector. Finally the number of allowed configurations without any contact between the chains

$$N_{\text{no cont,allowed}} = N_{\text{allowed}} - N_{\text{cont,allowed}} \tag{3}$$

has to be calculated. In this way the number of allowed configurations having a certain number of intermolecular contacts becomes accessible. As previously mentioned, all of these numbers may be separated into the contributions which come from the individual distances between the centers of gravity, r, of the two chains by storing the distance vectors. Thus the pair distribution function as well as other separation-dependent quantities may be evaluated. Since the centers of gravity were rounded to (integer) lattice units before calculating the distance vectors, r had to be corrected by adding the mean error[5] caused by rounding, which amounts to 0.5. Moreover, the distance between the centers of gravity of the two chains was normalized by their mean square radius of gyration, $\langle s^2\rangle$, in order to get the reduced distance

$$r_{\text{red}} = \sqrt{\frac{r^2 + 0.5}{\langle s^2\rangle}} \tag{4}$$

The data presented is based on 10^6 investigated pairs.

Energy Calculation. In a lattice, the energy is proportional to the number of contacts, z_{ij}, between the different components i and j of the system, wherein each contact contributes to the total energy with its specific contact energy. Thus, a system of two kinds of monomers (polymer segments), X and Y, and a solvent, S, gave rise to six types of contact energies, ϵ_{ij} (i, j = X, Y, S) which were combined to give exchange energies[27−30]

$$\Delta\epsilon_{\text{XY}} = (\epsilon_{\text{XY}} + \epsilon_{\text{SS}}) - (\epsilon_{\text{XS}} + \epsilon_{\text{YS}}) \tag{5}$$

summarizing the energy differences between polymer−polymer, polymer−solvent, and solvent−solvent contacts. In the simulation, the most important parameter was the interaction parameter

$$\varphi_{\text{XY}} = \frac{\Delta\epsilon_{\text{XY}}}{kT} \tag{6}$$

Whenever two types of monomers, X and Y, exist in a solvent, there are three relevant interaction parameters, φ_{XX}, φ_{YY}, and φ_{XY}. Following eq 5, they describe the energy gain or loss if a polymer−polymer contact is formed from two polymer−solvent contacts. The total energy of a configuration (in multiples of kT) equals $z_{\text{XX}}\varphi_{\text{XX}} + z_{\text{YY}}\varphi_{\text{YY}} + z_{\text{XY}}\varphi_{\text{XY}}$, where z_{XY} is the total number of contacts between segments of type X and Y as stated above. Alternatively, a (different) interaction parameter φ'_{XY} may be defined which is based on the gain or loss of energy when establishing two XY contacts simultaneously breaking one XX contact and one YY contact. Of course, φ_{XY} and φ'_{XY} are not independent of each other. The relationship between the two quantities is given by eq 7.

$$\varphi'_{\text{XY}} = 2\varphi_{\text{XY}} - (\varphi_{\text{XX}} + \varphi_{\text{YY}}) \tag{7}$$

Nomenclature. In order to deal with systems of different solvent quality, symbols A and B (for X and Y) have been introduced. Contrary to common understanding, they not only designate monomer units of different type in the chain but also refer to the type of interaction with the solvent. Thus A describes a segment (or a block) which forms an athermal solution in the solvent given while B characterizes a monomer unit (or a block) which is part of a chain for which the solvent is a Θ-solvent. In this sense, true homopolymers are those for which $\varphi_{\text{XX}} = \varphi_{\text{YY}} = \varphi_{\text{XY}} \equiv \varphi$; they are either named AA (two identical "blocks" in an athermal solution; $\varphi = 0$) or BB (two identical "blocks" in a Θ-solvent; $\varphi = \varphi_\Theta$). The determination of the parameter φ_Θ is, to some extent, problematic: φ_Θ parameters obtained numerically either by use of an intramolecular criterion ($\langle s^2\rangle \sim N - 1$) or by an intermolecular criterion (zero excluded volume) should coincide within the limit of infinitely long chains. On the basis of the intramolecular criterion, an energy parameter $\varphi_\Theta \approx -0.275$ is expected[31] within the limits of $N \to \infty$. For short chains, however, it is well-known that the φ_Θ parameter defined

Table 1. Interaction Parameters for the Systems Investigated

system XY	φ_{XX}	φ_{YY}	φ_{XY}	φ'_{XY}
AA	0	0	0	0
BB	−0.270	−0.270	−0.270	0
AB	0	−0.270	0	+0.270
CC	−0.0675	−0.0675	−0.0675	0

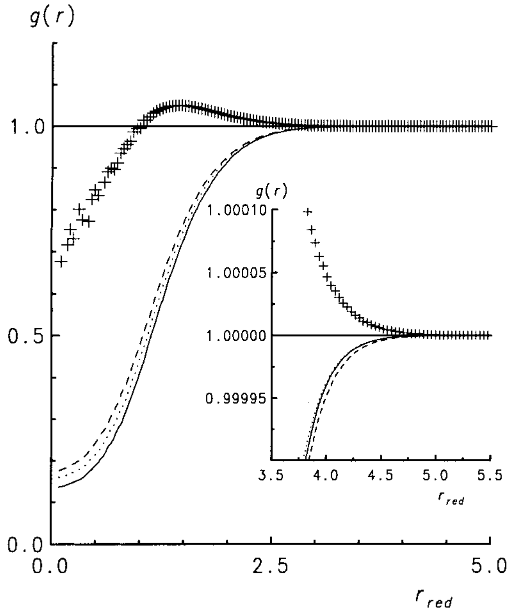

Figure 1. Pair distribution function $g(r)$ vs r_{red} (r_{red} being the distance between the centers of gravity of the two chains normalized by their root mean square radius of gyration) for the homopolymers AA (—), BB (+), CC (···) and the diblock copolymer AB (− −). The inset shows $g(r)$ for large values of r. Apart from BB (where scattering is quite large) lines are used instead of symbols (indicating discrete values) for the purpose of better resolution.

by *zero excluded volume* depends rather heavily on chain length.[9] For short chains (as compared to longer ones) an energy parameter $\varphi > -0.275$ would be sufficient to compensate for the intermolecular excluded volume, e.g. −0.255 for $N = 50$ and −0.27 for $N = 160$, the chain length examined in this paper.

Finally, the diblock copolymer, designated AB, was characterized by $\varphi_{XX} = 0$, $\varphi_{YY} = -0.27$, and $\varphi_{XY} = 0$. Thus the solvent was an athermal one for segments (or blocks) of type A. For type B, solvent molecules (actually empty sites) as well as segments of type A acted as a bad solvent. Between the two types of monomers (or blocks), repulsive interactions were dominant ($\varphi'_{XY} = +0.27$). For comparison, another homopolymer, CC, with the value $\varphi_{XX} = -0.0675$ was investigated as well. The interaction parameters of all these systems are summarized in Table 1. Contacts between two different chains were treated in the same way as intramolecular contacts of the same type.

III. Results and Discussion

A. Differential Changes. Pair Distribution Function.

As previously stated, the pair distribution function $g(r)$—depicted in Figure 1 for the systems investigated—is a measure for the compatibility of two macromolecules at a given distance r. Starting from infinite separation, $g(r)$ slowly begins to deviate from 1 at $r_{red} \approx 4.5$ (see closeup of Figure 1) and diminishes to an astonishingly high value of 0.13 at zero intermolecular distance (see Table 2 and ref 5). The reasons for the relatively good compatibility at $r \to 0$ are characteristic changes in size, shape and orientation of the chains.[14,15] As chain length increases, $g(0)$ increases, however the effect levels off for very large chain lengths as shown in Figure 2.

Table 2. Pair Distribution Function at Vanishing Intermolecular Distance, $g(r = 0)$

system XY	$N = 160$	$N = 80$	$N = 40$
AA	0.1358/0.1358[a]	0.1217	0.1025
BB	0.6767/0.7967[a]	0.6206	0.5320
AB	0.1756		
CC	0.1593		

[a] The two values correspond to two independent ensembles.

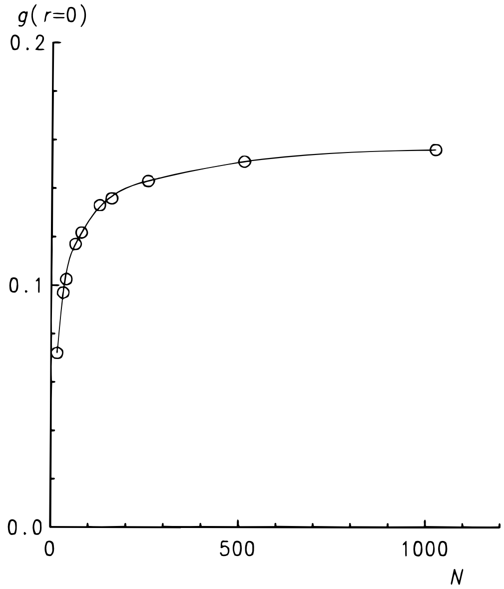

Figure 2. Pair distribution function at vanishing intermolecular separation, $g(r = 0)$, of athermal homopolymers[41] vs the chain length N. The interpolation line is a guide for the eye.

As previously mentioned, Θ-chains—by an intermolecular criterion—are characterized by zero excluded volume. This may either be realized by $g(r) \equiv 1$ for all distances r (as assumed in many theoretical approaches) or by a compensation for the positive (repulsive) intermolecular excluded volume by equal negative contributions to $u = \int[1 - g(r)]4\pi r^2\,dr$ arising from attractive interaction. Actually, the latter is the case as outlined in refs 5 and 14 and depicted in Figure 1. Admittedly, $g(r)$ for $r \approx 0$ increases (and the maximum $g(r)$ value decreases) with increasing chain length. Thus $g(r) \approx 1$ for all distances, as proposed by Flory and Krigbaum,[16,17] can be valid within the limits of $N \to \infty$ only. Indeed, $g(0)$ increases very slowly—approximately with $N^{1/4}$ (see Figure 3)—so that even fairly long chains still exhibit the characteristic shape of $g(r)$ depicted in Figure 1.

The pair distribution function of AB diblock copolymers does *not* show any positive deviation from unity. Starting from infinite separation, the (first) contacts may be either of type A−A or of type B−B or of type A−B, depending on the relative orientation of the two chains. As only B−B contacts contribute to the pair distribution function with a Boltzmann factor greater than unity, the attraction between the chains is obviously too small to produce positive deviations from unity, $g(r) > 1$. For $r_{red} < 4.5$, $g(r)$ decreases to ≈0.17 at $r = 0$.

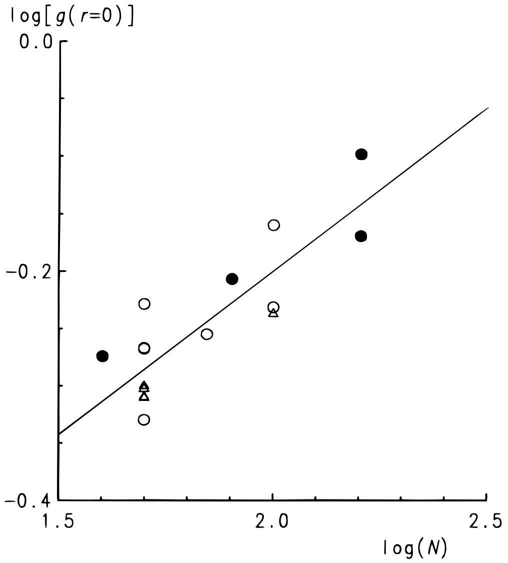

Figure 3. Pair distribution function at vanishing intermolecular separation, $g(r = 0)$, of Θ-homopolymers vs the chain-length N in a double-logarithmic plot. The symbols indicate different values for the interaction parameter φ: $\varphi = -0.255$ (○), $\varphi = -0.26$ (△), and $\varphi = -0.27$ (●). The interpolation line results from all given data points.

In case of a purely statistical distribution of contacts (to be expected in case of random copolymers but admittedly not pertinent to block copolymers), the contact numbers should obey a ratio z_{AA}:z_{BB}:z_{AB} = 1:1:2. As the energy of a (pair) configuration is simply $\sum z_{ij}\varphi_{ij} = z_{BB}\varphi_{BB}$ (as $\varphi_{AA} = \varphi_{AB} = 0$), a homopolymer subject to $\varphi_{XX} = \varphi_{BB}/4$ (type C) could serve as comparison. The pair distribution function of CC (dotted line in Figure 1) is located between that of AB and $g(r)$ of AA. Thus, $g(r)$ of AB is slightly larger than the pair distribution function of the homopolymer CC for all values of r. This indicates that intermolecular B−B contacts are still preferred to A−A and A−B contacts (which do not contribute to the Boltzmann factor), necessarily leading to deviations from the relationship z_{AA}:z_{BB}:z_{AB} = 1:1:2.

It should be noted that the properties of an ensemble might basically be determined by a few configurations which are characterized by extremely large Boltzmann factors. The more negative the energy parameter and the larger the number of contacts is, the higher this risk. Therefore relatively large fluctuations are encountered in the case of Θ-chains while smooth statistics are recorded for the other systems.

Mean Square Chain Dimensions. The behavior of the mean square chain dimensions of chains in good and in selective solvents, respectively, differs significantly from that of Θ-chains as seen in Figure 4. This figure shows

$$s_{\mathrm{rel}}^{2} = \frac{s^{2}(r)}{\langle s^{2}\rangle_{0}} \tag{8}$$

vs r_{red} for the systems investigated. s_{rel}^2 is the relative mean square radius of gyration at a certain intermolecular distance r, $s^2(r)$, normalized to the value of the isolated chain, $\langle s^2\rangle_0$. Starting from infinite separation, s_{rel}^2 decreases for athermal chains, then reaches a minimum[12,14,15] at $r_{\mathrm{red}} \approx 1.9$ and increases for distances smaller than $r_{\mathrm{red}} \approx 1.4$. At zero separation, the chains are more expanded by approximately 20% than isolated athermal chains. Θ-Chains, on the contrary, expand when they establish the first intermolecular contacts (see insert of Figure 4) and s_{rel}^2 reaches a maximum near $r_{\mathrm{red}} \approx 2.4$. When r_{red} falls below 2, the chains are slightly compressed due to dominant repulsive interactions caused by (intermolecular) excluded volume effects. At distances smaller than one root mean square radius of gyration, they again become expanded by up to 10% at zero intermolecular separation.[14,15]

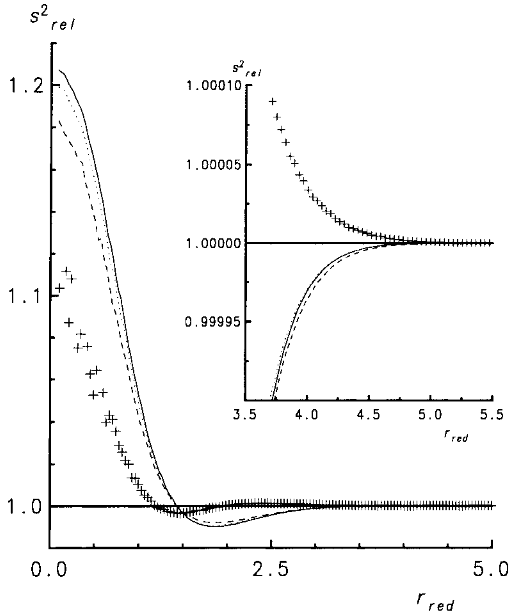

Figure 4. Relative mean square radius of gyration, s_{rel}^2, vs the reduced distance r_{red} (symbols as in Figure 1). The inset shows a closeup for large values of r.

Again, the AB diblock copolymer exhibits behavior similar to the athermal chain although neither compression nor expansion is as pronounced as for AA. The expansion at zero separation of the AB chains is about 18%, which is significantly smaller than that of AA or CC, respectively. This difference can again be ascribed to the interaction between the two B-blocks.

Looking at the expansion of the individual blocks in Figure 5, it can be seen that in the case of an athermal homopolymer the two "blocks" are less than half as expanded as the overall chain at zero intermolecular distance. This, to some extent, can be attributed to the fact that the centers of gravity of the two blocks are not identical to those of the overall chain, and thus no full intermolecular overlap of the two blocks can occur. The poor statistics for Θ-chains makes it impossible to determine the exact expansion of the individual blocks. Furthermore, the relative increase in size amounts to about one half of the expansion of the overall chain at $r = 0$. Surprisingly, the two *different* blocks of the AB system do *not* show different extents of expansion: at $r = 0$ they are about 8% in both cases. The homopolymer CC exhibits behavior intermediate between AB and AA.

The relative mean square end-to-end distance, h_{rel}^2, behaves qualitatively in the same manner as the relative mean square radius of gyration. A quantitative difference arises in the more pronounced expansion of the former quantity at small distances. This difference in expansion is roughly 3% in the case of good or selective solvent. For Θ-solvents the difference is not significant. Details are given in Table 3.

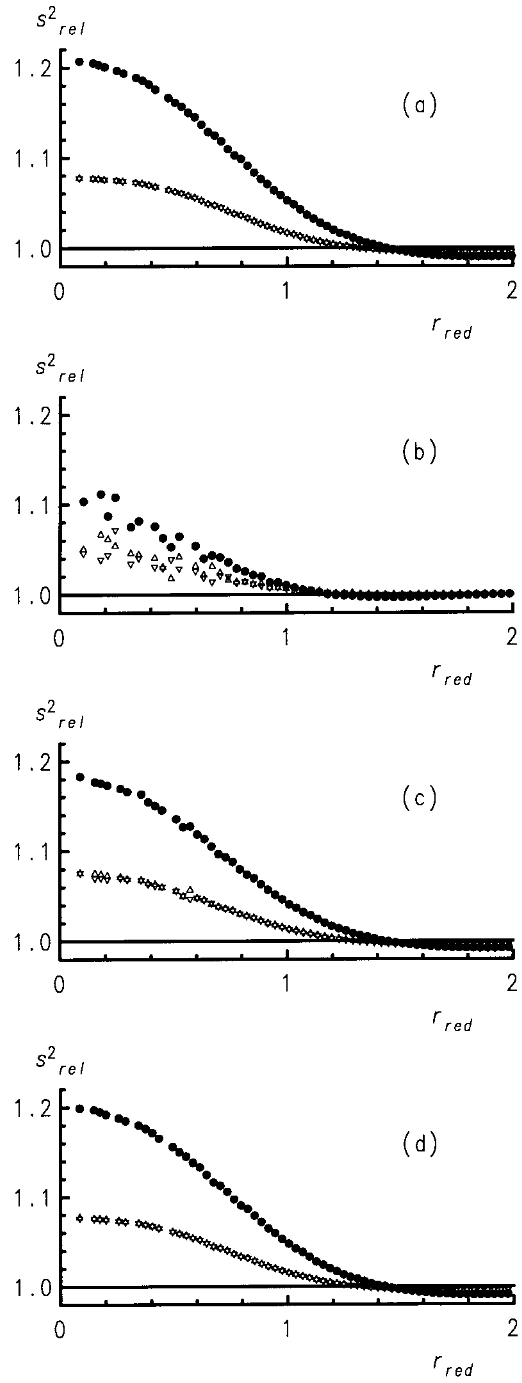

Figure 5. Relative mean square radius of gyration, s_{rel}^2, of blocks (△, ▽) and overall chain (●) vs the reduced intermolecular separation r_{red} for the homopolymers AA (a), BB (b), CC (d) and the diblock copolymer AB (c).

Figure 6 compares the two quantities, s_{rel}^2 and h_{rel}^2, which correspond to the full symbols (circles for s_{rel}^2 and triangles for h_{rel}^2). In addition, the quantity

$$\tau_x = \frac{x_{\mathrm{rel,block}}{}^2(r)}{x_{\mathrm{rel,chain}}{}^2(r)} \quad (x = s,\, h) \tag{9}$$

is shown by the open symbols denoting the contribution of the individual blocks to the expansion of the entire chain. It may be seen that for h_{rel}^2 the blocks contribute more to the expansion of the entire chain than for s_{rel}^2. This is due to the fact that the chains' overlap has a larger effect on the junction points (and thus on the end segments of the blocks), which are likely to be close to the center of gravity, and a smaller effect on the segments in a block as a whole (reflected by s_{rel}^2). It may also be seen in Figure 6 that for intermolecular distances r_{red} smaller than 0.5 (which means that half of each chain, i.e. one block, overlaps with half of the other chain), h_{rel}^2 of the *blocks* expands to the same extent as that of the entire chain while the contribution of the blocks in case of s_{rel}^2 diminishes as intermolecular separation approaches zero. This reflects the fact that the centers of gravity of the entire chain and of the individual blocks do not coincide.

Molecular Shape. There are various ways to describe the shape of a polymer: One of the more convenient measures is the asphericity factor δ (see refs 32−34), which is a combination of the principal components L_i^2 ($L_1^2 \le L_2^2 \le L_3^2$) of the square radius of gyration $s^2 = L_1^2 + L_2^2 + L_3^2$ of individual configurations taken along the principal axes of inertia which represent the chain as an equivalent ellipsoid[35,36]

$$\delta = \frac{\langle (L_2{}^2 - L_1{}^2)^2 + (L_3{}^2 - L_2{}^2)^2 + (L_3{}^2 - L_1{}^2)^2 \rangle}{2\langle (L_1{}^2 + L_2{}^2 + L_3{}^2)^2 \rangle} \tag{10}$$

In this definition δ is 1 for rodlike molecules and zero for spheres. For isolated chains theoretical values for random walks,[33] $\delta = 10/19 \approx 0.5262$, and for self-avoiding walks,[32] $\delta \approx 0.534$ exist.

In a previous article,[37] we investigated the asphericity of isolated diblock copolymers and have found the asphericity for diblock copolymers in a selective solvent to be higher than for homopolymers, which is also the case for a random-walk model of diblock copolymer molecules.[38] This effect is seen in Figure 7 for large intermolecular distances. The systems AA, CC, and AB qualitatively show the same dependence of δ on r. Starting from infinite separation, δ first decreases, passes through a minimum, and then increases. The deviation of δ from δ_0 (the value of an isolated chain) is largest for system AA. In case of homopolymers in a good solvent, the interaction between the two chains is always *repulsive*, and thus, a uniform longitudinal deformation (perpendicular to the axis between the centers of gravity) is supposed to take place. In the case of the AB diblock copolymers the increase of δ at small intermolecular distances is negatively affected by *attractive* interactions between the two B blocks. The features observed in the systems AA, AB, and CC are also found for BB, albeit to a much lesser degree. It should be mentioned that for system BB an additional range of slightly increased asphericity at large separations appears, in agreement with the findings reported in ref 15.

The *relative* change in δ

$$\delta_{\mathrm{rel}} = \frac{\delta(r)}{\delta_0} \tag{11}$$

i.e., $\delta(r)$, normalized by the asphericity of the isolated molecule, is listed in Table 3 at zero separation.

A comparison of the asphericities of the two blocks of AB (Figure 8) reveals that δ_{rel} is slightly larger in the case of the B block for small distances. This is a result of repulsive interaction with the A block of the other molecule which occurred in half of the cases and caused

Table 3. Values of Chain Data at Vanishing Separation

system XY	$s_{\rm rel}^2$	$h_{\rm rel}^2$	$\delta_{\rm rel}$	$\lambda_{\rm rel}$	$\kappa_{\rm rel}$
AA[a]	1.2070/1.2070	1.2349/1.2349	1.0701/1.0701	1.0210	1.0662
BB[a]	1.1035/1.0902	1.1020/1.0583	1.0296/1.0178	0.9994	1.0024
AB	1.1830	1.2045	1.0552	1.0202	1.0526
CC	1.1989	1.2262	1.0665	1.0212	1.0632

[a] The two values correspond to two independent ensembles.

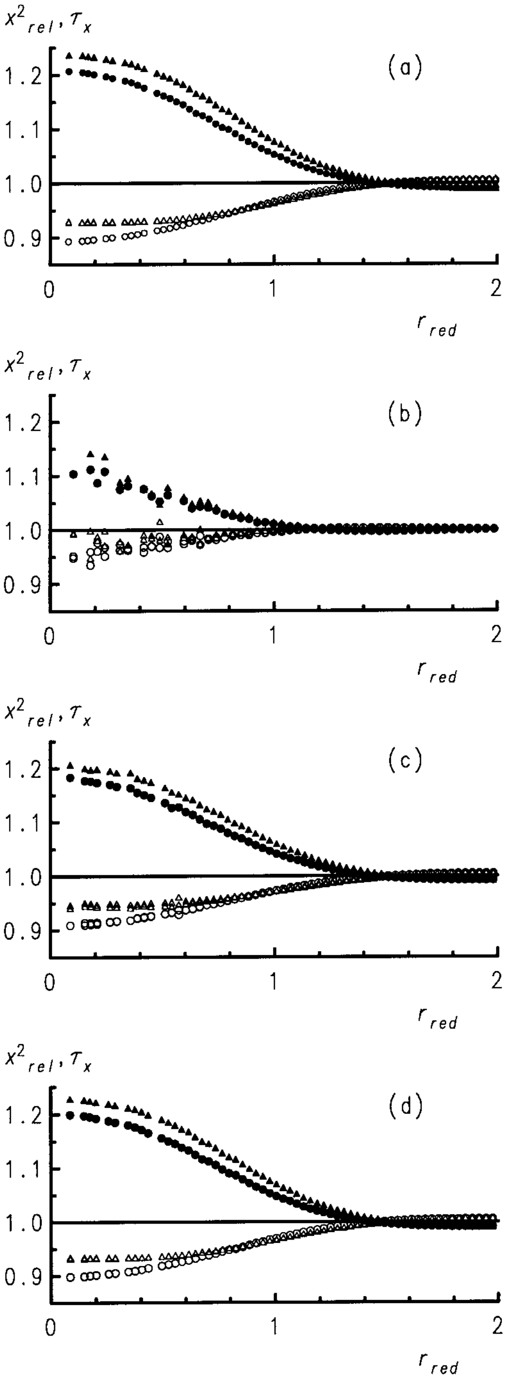

Figure 6. Relative mean square radius of gyration $s_{\rm rel}^2$ (●), relative mean square end-to-end distance $h_{\rm rel}^2$ (▲) as well as the quantities τ_s (○) and τ_h (△) as defined by eq 9 vs the reduced intermolecular separation $r_{\rm red}$ for the homopolymers AA (a), BB (b), and CC (d) and the diblock copolymer AB (c).

a relatively high deformation of this block (compared to the small asphericity of the B block).

In order to investigate the extent of segregation, the relative orientation of blocks was evaluated. One measure is the angle λ between the longest axes of

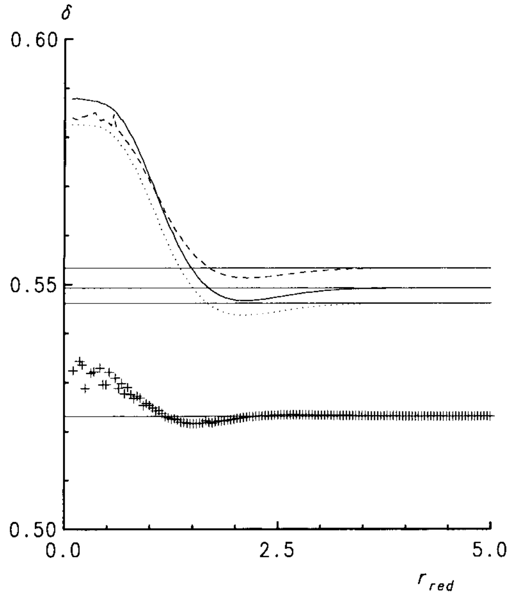

Figure 7. Asphericity, δ, vs the reduced distance $r_{\rm red}$ (symbols as in Figure 1).

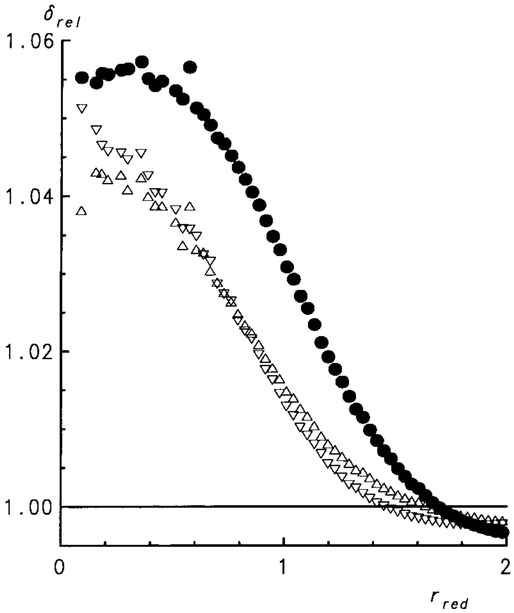

Figure 8. Relative asphericity, $\delta_{\rm rel}$, of the diblock copolymer AB vs the reduced intermolecular separation $r_{\rm red}$ for the entire chain (●) and the blocks (△ for A, ▽ for B), respectively.

"equivalent ellipsoids" representing the blocks, where λ was calculated from the scalar product of these vectors. On average a value 1 rad $\approx$ 57.3° would be expected for uncorrelated vectors (random orientation). End-to-end vectors are usually closely correlated[39,40] with the largest principle axis and end segments tend to be farthest from the center of gravity. Thus another measure is the angle κ between the two end-to-end vectors of the blocks (which rather are center-to-end vectors regarding the whole chain). Contrary to λ which

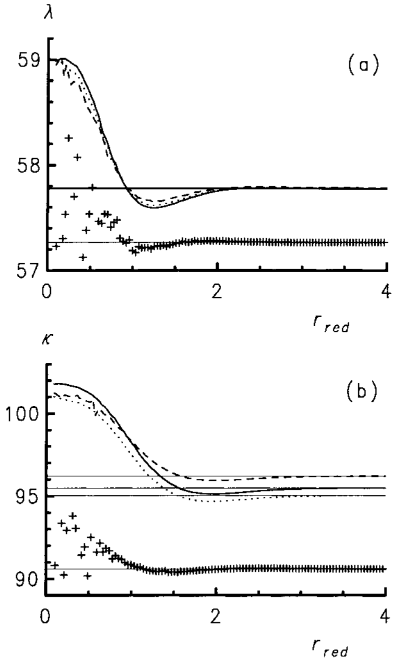

Figure 9. Angles λ (a) and κ (b) between the blocks vs the reduced distance r_{red} (symbols as in Figure 1).

exhibits values between 0 and 90°, κ covers a range of angles [0,180°]. Therefore, in absence of any correlation an average value 90° is expected for κ.

Figure 9 shows the behavior of these vectors with respect to intermolecular separation. For polymers in good and selective solvent, both first of all slightly decrease (κ at larger intermolecular separations than λ, because the chain ends which contribute to κ come into contact at larger separations than inner segments contributing to λ) and then increase to $\lambda(0) = 59°$ and $\kappa(0) \approx 101-102°$, whereas the changes in κ are much more pronounced than those of λ (for the relative increase see Table 3). For $r \rightarrow \infty$, λ's value is near the value for two uncorrelated vectors for the systems investigated. κ, on the other hand, is a good indicator of the degree of (repulsive) interaction between the blocks within the limits of infinite separation. As separation decreases, it is the athermal chains in which the blocks show the strongest tendency to occupy positions “opposite” to each other (κ exhibits the largest increase) which is congruent with the findings concerning the asphericity δ. Due to attractive interactions between segments of CC chains and between the two B blocks, changes in κ of these systems are less pronounced; comparable values (which are smaller than κ of the athermal system) are obtained at zero separation.

B. Integral Effects. This section is dedicated to integral changes that occur when two molecules approach each other. These integral changes are represented by the volume integrals of the separation dependent quantities, as treated in the previous section, and allow a prediction of the behavior of macromolecules in more concentrated systems by use of virial developments. The most prominent integral quantity in this context is the excluded volume u. It is defined as the volume integral of the fraction of forbidden pair configurations by eq 1 and thus associated with the pair distribution function $g(r)$. (In this paper, however, the integral effects were directly calculated by exact enumeration and not computed by means of eq 1.) Furthermore, u is related to the experimentally accessible second osmotic virial coefficient A_2 by

$$A_2 = \frac{N_A u}{2M^2} \tag{12}$$

where N_A signifies the Avogadro number and M the molecular mass. The energetic aspect of pair data will be treated in detail elsewhere. The excluded volume u is shown in Table 4 for the systems investigated. Table 4 additionally contains the excluded volume for purely repulsive interaction due to forbidden double occupancy, u_{rep}, which measures the compatibility if no attractive interaction is operative between two chains. It is evident that the excluded volume of the BB system is slightly negative, however this negative value corresponds to only 6% compared to the athermal value. u_{CC} is considerably larger than u_{AB} and lies approximately between the values for the athermal chain and the copolymer, respectively.

Table 4. Excluded Volume u and u_{rep}

system XY	u	u_{rep}
AA	7475.5	7475.5
BB	−495.7	5303.1
AB	5323.8	6616.1
CC	6233.0	7078.8

Table 5. Coefficients K_s, K_h, and K_δ As Defined by Eq 14

	system	$N = 160$			$N = 80$	$N = 40$
K_x	XY	XY	*X*Y	X*Y*	XY	XY
K_s	AA	−1.273	−0.786	×	−0.729	−0.400
	BB	+0.393	×	+0.270	+0.260	+0.167
	AB	−0.821	−0.721	−0.424	×	×
	CC	−1.046	−0.649	×	×	×
K_h	AA	−1.601	−1.142	×	−0.937	−0.532
	BB	+0.471	×	+0.374	+0.323	+0.219
	AB	−1.036	−0.982	−0.617	×	×
	CC	−1.308	−0.938	×	×	×
K_δ	AA	−0.489	−0.348	×	−0.296	−0.180
	BB	+0.071	×	+0.084	+0.056	+0.047
	AB	−0.287	−0.297	−0.201	×	×
	CC	−0.397	−0.281	×	×	×

Integral changes of molecular dimensions and shape may be determined using a concept developed in ref 14. Again the starting point is the expansion of a molecular property X as a function of the concentration ϕ

$$\langle X \rangle_\phi = \langle X \rangle_0 + \langle X \rangle_0 K_X \phi \tag{13}$$

where the subscript 0 indicates zero concentration and the brackets denote ensemble average values. K_X, the slope of the tangent of the relative change of X, $\langle X \rangle_\phi / \langle X \rangle_0$, at zero concentration, may be determined from pair data according to

$$K_X = \frac{1}{N} \int_0^\infty g(r) \frac{X(r) - \langle X \rangle_0}{\langle X \rangle_0} 4\pi r^2 \, \mathrm{d}r \tag{14}$$

where N indicates the chain length, $g(r)$ is the pair distribution function, and $X(r)$ is the value of X when the two chains are at a distance r of their centers of gravity. (Similar to u, these integral changes are also directly obtained by the enumeration method.)

This concept allows the calculation of K_X for properties not only of the entire chain, but also of the individual blocks. The values of K_X ($X = s^2$, h^2, δ, λ, κ) for the systems investigated ($N = 160$) are given in Tables 5 and 6. (In addition, Table 5 comprises values for shorter

Table 6. Coefficients K_λ and K_κ As Defined by Eq 14

system XY	K_λ	K_κ
AA	−0.056	−0.350
BB	+0.018	+0.081
AB	−0.026	−0.155
CC	−0.044	−0.282

chains, $N = 40$ and $N = 80$, for AA and BB in order to demonstrate the chain length dependence of these quantities and for $N = 160$ K_X values referring to block X (second column) and block Y (third column), the respective block marked by italics.) It should be noted that K_X of the AB copolymer has the same sign as K_X of homopolymers in good solvents (AA and CC, respectively). Even the B block of AB shows negative K_X ($X = s^2$, h^2, δ, λ, κ). (This means that it will be compressed with increasing concentration and assume a more globule-like shape.) While the K_X values of the A block of AB are also quantitatively similar to those of the athermal homopolymer AA, those of the B block are only about half as large. The K_X values of the individual blocks of the homopolymers are quite similar to those of homopolymers of equal length ($N = 80$).

IV. Conclusions

The behavior of AB diblock copolymer pairs—as a preliminary approximation—is similar to that of homopolymers in a solvent whose quality is defined by a φ parameter which amounts to one fourth of that necessary to define Θ-conditions (this would be energetically equal to the situation where only one quarter of the intermolecular contacts contributes to the Boltzmann factor of the pair configuration). Deviations are largest at small intermolecular distances where the two B blocks can overlap and contribute to the statistical weight of the pair configuration. At large distances, the influence of these attractive blocks is weakened by the surrounding A blocks which favor repulsive interaction.

The individual blocks of AB behave in the same way, whether they are athermal or Θ-blocks. Slight deviations only arise at intermolecular distances ranging between one and two molecular diameters ($2 - 4\langle s^2\rangle^{1/2}$), i.e., where first intermolecular contacts are established. Obviously these contacts are too few in number to influence the behavior of the overall chain. The concentration dependence of chain properties obtained in the limit of zero concentration corresponds fairly well with simulation data of multibody systems as will be reported in due course.

Acknowledgment. Calculations were performed using the workstation cluster of the Vienna University Computer Center, which is gratefully acknowledged.

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MA971087K