Dilute Solutions of Block Copolymers. 2. Triblock Copolymers

O. F. Olaj,* B. Neubauer, and G. Zifferer

Institut für Physikalische Chemie, Universität Wien, Währinger Strasse 42, A-1090 Wien, Austria

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

ABSTRACT: Dilute solutions of symmetric triblock copolymers ABA and BAB in a selective solvent, i.e., a solvent good for one type of monomers (A) and poor for the other (B), and of their constituent homopolymers were investigated by exact enumeration of pair configurations of cubic lattice chains generated by a Monte Carlo method. Quantities characterizing the size and the molecular shape were investigated as a function of the intermolecular distance between the chains. In addition, integral quantities of chain properties (related to concentration dependencies) were computed. On the whole, behavior of triblock copolymers was closer to that of athermal chains than to that of Θ-homopolymers. Their architecture, however, significantly influenced the details. The pair distribution function of BAB exceeded unity at large distances as is characteristic for homopolymers in Θ-solvents and poor solvents. Furthermore, behavior characteristic of Θ-systems persisted for all *distance dependent* quantities investigated for BAB at large separations. This was not however sufficiently pronounced as to be reflected in the sign of *integral* quantities which again resembled those of the athermal system.

I. Introduction

The behavior of block copolymers is a field of increasing interest due to their role as surfactants in many technical applications.[1−7] Understanding their behavior by relating it to molecular properties is one of the aims of computer simulation on this subject.[8−15]

In this paper, symmetric triblock copolymers ABA and BAB will be investigated in a selective solvent (which is a good one for type A segments and a Θ-solvent for type B segments) and the results will be compared to the behavior of their constituent homopolymers. (In part 1 of this series,[16] symmetric *diblock* copolymers were studied.) To compare not only the properties not only of entire chains but also those of individual blocks, the homopolymers have been artificially divided into three parts, each corresponding to a block of the copolymers with respect to the block lengths N_X and N_Y, respectively (N_X:N_Y:N_X = 1:2:1; the total chain length $N = 2N_X + N_Y$ comprising 160 segments).

In contrast to infinitely diluted solutions—whose properties are determined by those of *isolated* molecules[17]—intermolecular interactions between *two* molecules in solution will have to be taken into consideration (i.e., the presence of *pairs* of macromolecules[18−26]) in highly diluted solutions (dealt with in the present paper), using simulation methods as described in part 1. Molecular properties of two *approaching* molecules as a function of the intermolecular distance of the chains will be examined and the variation of molecular properties with *concentration* in dilute solutions[21,22] will be estimated. The data presented will be based on 10^6 investigated pairs.

The energetics of a polymer solution in a lattice simulation is determined by interaction parameters φ_{XY} reflecting the energy gain or loss (in multiples of kT) when forming a contact between polymer segments of type X and Y (simultaneously breaking the contacts of these segments with solvent molecules). In the case of homopolymers, a single interaction parameter is sufficient to describe the system[28,29] because only one kind of segment is present. For copolymers, however, three interaction parameters[30−33] are necessary to describe a copolymer comprising two different types of monomers, X and Y. In the present simulation, the letter A stands for athermal conditions which are determined by $\varphi = 0$, while B signifies Θ-conditions characterized by $\varphi_\Theta = -0.27$ (see part 1). Thus homopolymers are given by $\varphi_{XX} = \varphi_{YY} = \varphi_{XY} = 0$ (athermal chain; named AAA) and by $\varphi_{XX} = \varphi_{YY} = \varphi_{XY} = -0.27$ (Θ-chain BBB), respectively. The triblock copolymers are constructed in such a way that the solvent is either an athermal one for the end blocks and a Θ-solvent for the middle block (ABA) or a Θ-solvent for the end blocks and an athermal one for the middle block (BAB). Both cases correspond to $\varphi_{AA} = 0$ and $\varphi_{BB} = -0.27$.

Table 1. Interaction Parameters for the Systems Investigated

system XYX	φ_{XX}	φ_{YY}	φ_{YX}	φ'_{XY}
AAA	0	0	0	0
BBB	−0.270	−0.270	−0.270	0
ABA	0	−0.270	0	+0.270
BAB	−0.270	0	0	+0.270

The interaction between segments of different blocks is best described by another parameter φ'_{XY} representing the energy gain or loss (again in multiples of kT) when forming two XY contacts and simultaneously breaking one XX and one YY contact. A φ'_{AB} value of +0.27 will account for a repulsive interaction between segments of different type (different blocks) as is usually present in real block copolymer systems. Actually, for the parameters chosen, each type of segments acts as a Θ-solvent for the other. In the case of homopolymers where X = Y = A or X = Y = B, respectively, φ'_{XY} clearly equals zero as it is related to φ_{XY} by $\varphi'_{XY} = 2\varphi_{XY} - (\varphi_{XX} + \varphi_{YY})$. For the convenience of the reader, the interaction parameters presented above are summarized in Table 1.

II. Results and Discussion

A. Differential Changes. Pair Distribution Function. The pair distribution function $g(r)$ gives the relative probability of finding two polymer chains at a given separation r between their centers of gravity. For two athermal chains this is equivalent to the fraction

S0024-9297(97)01088-7 CCC: $15.00

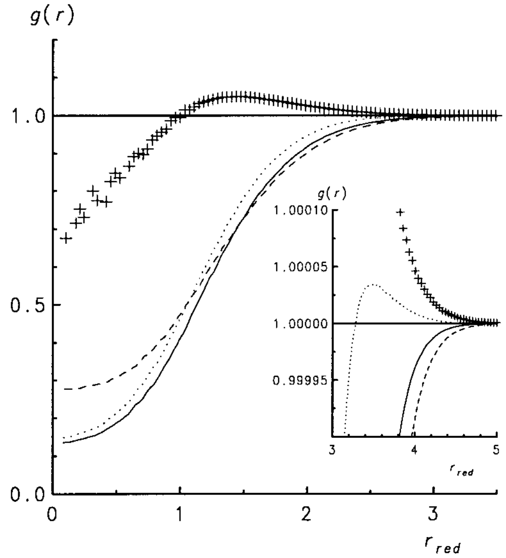

Figure 1. Pair distribution function $g(r)$ vs r_{red} (r_{red} being the distance between the centers of gravity of the two chains normalized by their root-mean-square radius of gyration) for the homopolymers AAA (—) and BBB (+) and the triblock copolymers ABA (– –) and BAB (···). The inset shows $g(r)$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

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

system XYX	$g(r = 0)$
AAA	0.1358/0.1358[a]
BBB	0.6767/0.7967[a]
ABA	0.2776
BAB	0.1491

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

of pairs which are free of mutual intersection. Obviously, the range where $g(r)$ significantly deviates from unity greatly depends on chain dimensions. For this reason, intermolecular separation is normalized by the root-mean-square radius of gyration of the isolated polymer chain $\langle s^2\rangle_0^{1/2}$. In Figure 1, the pair distribution function $g(r)$ is depicted as a function of r_{red} (as defined in part 1) for the systems investigated including homopolymers for comparison.[18,20] At zero concentration, starting from infinite separation, $g(r)$ gradually decreases for athermal conditions to roughly 0.13 while for Θ-conditions $g(r)$ first becomes larger than 1 before diminishing to about 0.70 at $r = 0$ (Table 2).

At first sight, the triblock copolymers seems to behave similarly to the athermal homopolymer, but—due to their attractive B blocks—there are characteristic deviations from $g(r)$ of AAA. The ABA triblock copolymer is slightly less compatible than the athermal homopolymer at larger reduced distances. This means that the repulsive interaction between the athermal end blocks of the two ABA chains appears at larger reduced distances than in the case of AAA. In a previous paper,[27] the mean square radius of gyration of ABA was shown to be particularly small[27,34] due to the concentration of mass in the middle block (and thus near the center of gravity). In terms of reduced distance, this small $\langle s^2\rangle_{ABA}$ is responsible for the fact that repulsive interaction starts at a larger r_{red} in case of ABA than for AAA. At smaller intermolecular separations, ABA chains become more compatible with each other because the attractive middle blocks of the two molecules can come into contact with each other and thus raise the Boltzmann factor (i.e., the statistical weight) of the pair configuration leading to increased values of $g(r)$ at distances r_{red} smaller than 0.5 (at $r_{red} \approx 0.5$, the inner blocks should begin to overlap). At smaller distances, the repulsive forces operative between the inner parts of the molecule are mostly compensated for by the attractive ones caused by intermolecular contacts. As a consequence, $g(r)$ remains approximately constant within a range $0 \leq r_{red} \leq 0.5$. At zero distance, $g(r) = 0.28$.

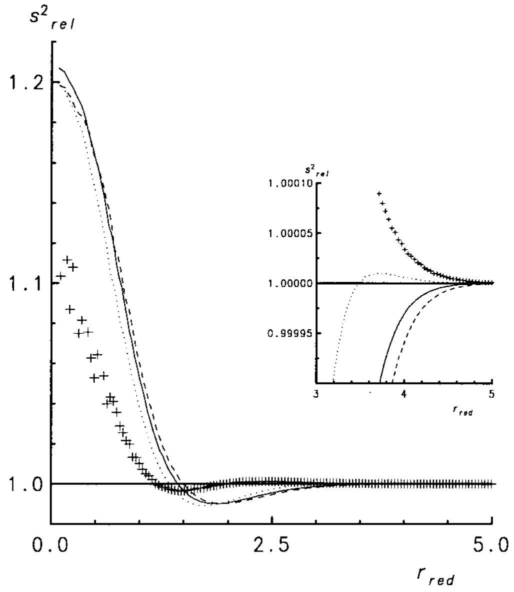

Figure 2. Relative mean square radius of gyration, s_{rel}^2, vs the reduced distance r_{red} (symbols as in Figure 1). The inset gives a close-up of s_{rel}^2 for large values of r.

The pair distribution function of its "inverse" triblock copolymer BAB seems to follow $g(r)$ of AAA, slightly shifted to the left side (smaller r_{red} values). The attractive end blocks, however, give rise to an effect characteristic of Θ-solvents and bad solvents, respectively, which may be seen in the inset of Figure 1: Although the positive deviation of $g(r)$ from 1 at large distances is very small, it is characteristic for this type of copolymer because it is missing in all the other systems investigated (including the diblock copolymer[16] AB) except Θ-homopolymers. At smaller distances, the pair distribution function is dominated by the athermal middle blocks in such a way that the compatibility at zero intermolecular separation is 15% and thus approximately the same as that for athermal homopolymers.

Mean Square Chain Dimensions. Figure 2 shows the relative mean square radius of gyration, $s_{rel}^2 = s^2(r)/\langle s^2\rangle_0$ vs the reduced intermolecular distance, r_{red}, for the systems investigated. (To investigate the *changes* caused by the presence of another molecule and to compare molecules of different dimensions, the mean square chain dimensions at an intermolecular distance r, $x^2(r)$ ($x = s, h$), were normalized to their value at infinite separation, $\langle x^2\rangle_0$.) Starting from infinite separation, s_{rel}^2 of the athermal chain is first diminished, then exhibits a minimum level near $r_{red} \approx 2$ and after that increases to ≈1.21 at zero distance.[21,22,25] Furthermore, Θ-chains are first slightly expanded, then a little compressed, and finally expanded again. At zero intermolecular separation[21,22] (see Table 3) s_{rel}^2 is ≈1.10.

Table 3. Values of Chain Data at Zero Intermolecular Separation

system XYX	s_{rel}^2	h_{rel}^2	δ_{rel}	λ_{rel}	κ_{rel}
AAA[a]	1.2070/1.2070	1.2349/1.2349	1.0701/1.0701	1.0091	1.0403
BBB[a]	1.1035/1.0902	1.1020/1.0583	1.0296/1.0178		
ABA	1.1983	1.2632	1.1008	1.0051	1.0567
BAB	1.2001	1.2273	1.0557	1.0097	1.0343

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

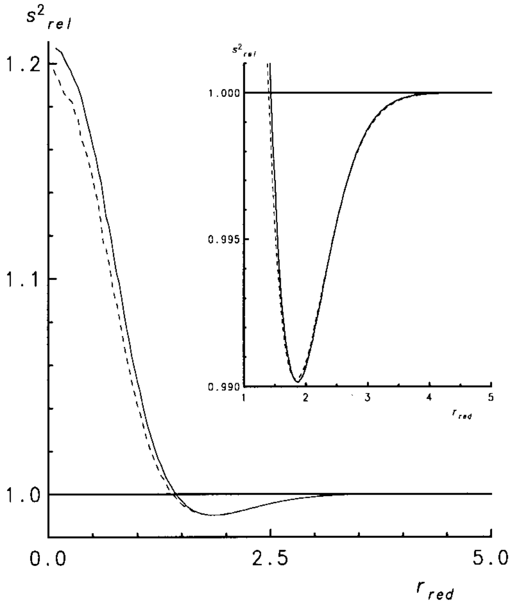

Figure 3. Comparison of the relative mean square radius of gyration, s_{rel}^2, of the triblock copolymer ABA (– –), which is shifted by $\Delta r_{\mathrm{red}} = 0.1$ to smaller values of the relative intermolecular distance r_{red}, to that (nonshifted) of the homopolymer AAA (—).

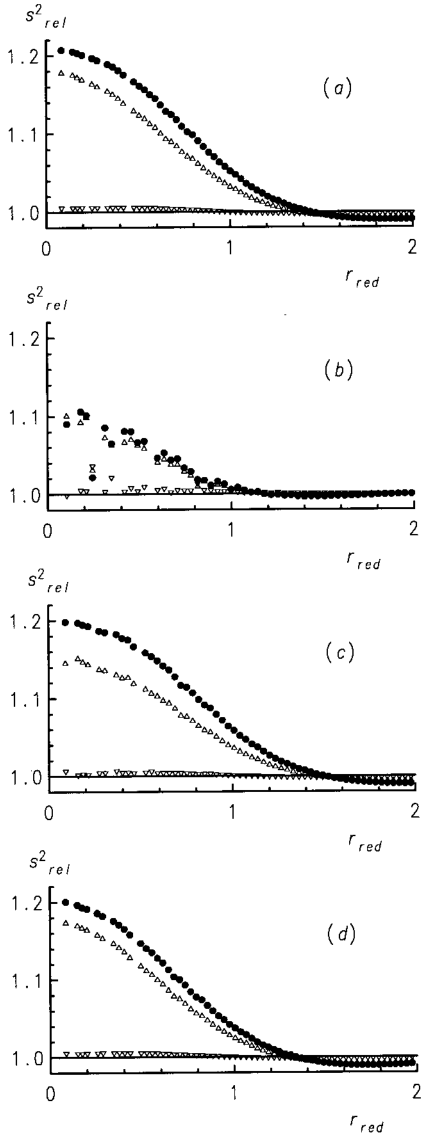

Figure 4. Relative mean square radius of gyration, s_{rel}^2, of blocks (▽ for end blocks, △ for middle blocks) and overall chain (●) vs the reduced distance r_{red} for the homopolymers AAA (a) and BBB (b) and the triblock copolymers ABA (c) and BAB (d).

As previously seen for $g(r)$, the triblock copolymers correspond fairly well with the behavior of a polymer in a good solvent. s_{rel}^2 of the ABA triblock copolymer exhibits the same general appearance as the athermal homopolymer, only shifted to slightly larger distances. To demonstrate this behavior more clearly, s_{rel}^2 of ABA is displaced by $\Delta r_{\mathrm{red}} = 0.1$ in Figure 3. The two functions coincide fairly well for $r_{\mathrm{red}} > 2$. For smaller separations, the influence of the compact middle block of ABA becomes visible. At zero separation, due to the attractive units of the middle block, the expansion of ABA is slightly smaller than the expansion of AAA (see Table 3). This effect is small, however. The triblock copolymer BAB exhibits features characteristic of Θ-chains, as already found for the pair distribution function. For s_{rel}^2, this translates into a slight expansion of the chains when they first come into contact. This effect is shown in the inset of Figure 2. Due to its relatively large $\langle s^2\rangle_0$, compression and expansion of the chain occur at reduced distances slightly smaller than those for the athermal homopolymer. At zero separation, the relative deviation from $\langle s^2\rangle_0$ is about 0.20 and thus the same as for ABA.

Regarding the behavior of the individual blocks, as shown in Figure 4, it is obvious that the end blocks are not greatly influenced by the presence of another molecule even at small intermolecular separations. This is certainly due to the fact that they are not forced to overlap with each other at these distances. The inner block, on the contrary, behaves like the entire chain and is expanded. Interestingly, the relative expansion of the inner block is always smaller than that of the entire chain except for the Θ-chain where they are of equal degree within statistical error. This might be explained by the fact that the center of gravity of this block and that of the entire chain do not perfectly coincide. The large expansion of the entire chain is also caused by a reorientation of the individual blocks, influencing their relative position to each other. Further investigation shows that the angle between the longest axes of inertia of the blocks increases with decreasing distance between the chains. This means that the molecule as a whole becomes more expanded compared with the expansion of the blocks (see following section). Due to its Θ-middle block, the expansion of the inner block of ABA is much

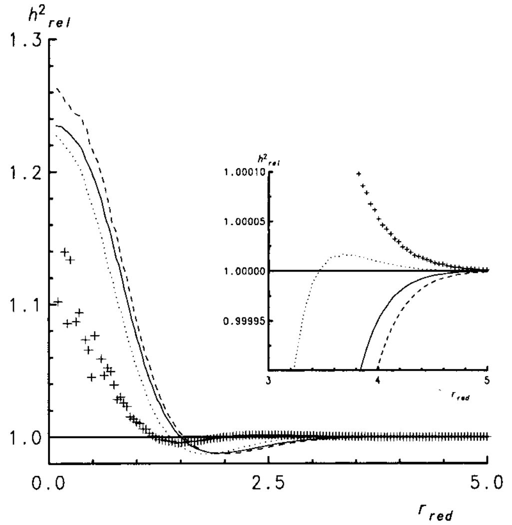

Figure 5. Relative mean square end-to-end distance, h_{rel}^2, vs the reduced distance r_{red} (symbols as in Figure 1). The inset gives a close-up of h_{rel}^2 for large values of r.

smaller than that of the inner block of AAA or BAB, respectively, which are of roughly the same degree.

Figure 5 shows the relative mean square end-to-end distance, h_{rel}^2, for the systems investigated. In contrast to s_{rel}^2, it is not the athermal chain which exhibits the largest expansion at zero intermolecular distance, but the triblock copolymer ABA (Table 3). It is the attractive middle block of ABA which is responsible for this behavior. To enable an overlap of the two B blocks without being disturbed by the athermal end blocks, the molecule becomes stretched to a more rodlike shape (see also the increase of the parameter asphericity discussed in the following section). This expansion favors a larger separation of the two chain ends and results in a larger h_{rel}^2. The BAB copolymers behave as if in a bad solvent at large distances (see inset of Figure 5) and behave similar to an athermal polymer at small separations.

In Figure 6 the increase of s_{rel}^2 is compared to that of h_{rel}^2 of the entire chain. As already mentioned in part 1, the increase of h^2 at small intermolecular separations is larger than that of s^2. This is due to chain stretching which affects h^2 more than s^2. An exception is the Θ-chain where the attractive interaction keeps the molecule compact.

As already mentioned, h_{rel}^2 increases to a much greater extent at small distances in the case of ABA than for AAA or BAB, respectively. This may also be seen in Table 3, where the values for zero distance are given (23% for AAA and BAB and 26% for ABA).

The quantity $\tau_x = x^2_{\text{rel,block}}(r)/x^2_{\text{rel,chain}}(r)$ reflects the contribution of the blocks to dimensional changes of the entire chain. Figure 6 shows that the end blocks do not participate much in the expansion of the entire chain at small intermolecular separation ($\tau_x < 1$), τ_s and τ_h forming a "mirror image" in comparison to s_{rel}^2 and h_{rel}^2. The quantities $s^2_{\text{rel,block}}$ and $h^2_{\text{rel,block}}$, respectively, are approximately the same for all systems in a good or a selective solvent. For ABA, τ_h of the end blocks is slightly smaller than for AAA and BAB. This might be caused by the large value of $h^2_{\text{rel,chain}}$ of ABA. τ_x of the inner block is much closer to unity, indicating that the relative changes are approximately the same as for the chain as a whole. For h_{rel}^2, it is even greater than 1 at small distances ($r_{red} \le 0.5$). Within this range, AAA and BAB behave quite similarly due to their inner athermal block. The contribution of the inner block of ABA is small in comparison due to the *attractive* interaction between the inner Θ blocks of this copolymer.

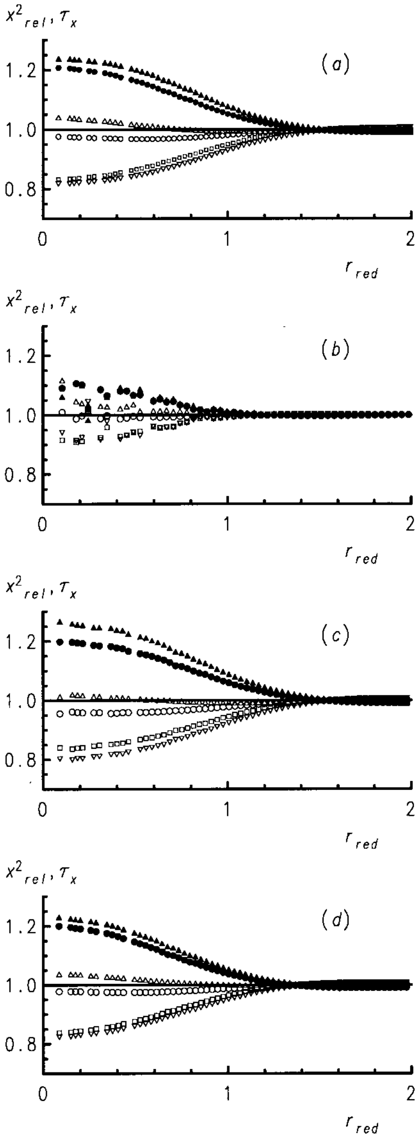

Figure 6. Relative mean square radius of gyration s_{rel}^2 (●), relative mean square end-to-end distance h_{rel}^2 (▲) as well as the quantities τ_s (□ for end blocks; ○ for middle blocks) and τ_h (▽ for end blocks, △ for middle blocks) vs the reduced distance r_{red} for the homopolymers AAA (a) and BBB (b) and the triblock copolymers ABA (c) and BAB (d).

Molecular Shape. The asphericity factor[35,36] δ defined in part 1 is a combination of the principal components of the square radius of gyration of individual configurations taken along the principal axes of inertia[37,38] and represents a measure of molecular shape. In a previous paper,[27] it was seen that the isolated triblock copolymers had asphericities larger (BAB) and smaller (ABA) than their constituent homopolymers which confirms Wei's earlier theoretical finding.[39] The extent of the effects connected with the mutual approach of two molecules may be quite different, as can be seen in Figure 7. While the increase of δ_{ABA} ($\Delta\delta = \delta(0) - \delta_0 \approx 0.0482$) is larger than that of δ_{AAA} ($\Delta\delta \approx 0.0385$), the increase of δ_{BAB} ($\Delta\delta \approx 0.0315$) is smaller than this reference value of AAA where $\delta(r)$ signifies the asphericity at a distance r and δ_0 that of an isolated chain. The shape of Θ-chains is not signifi-

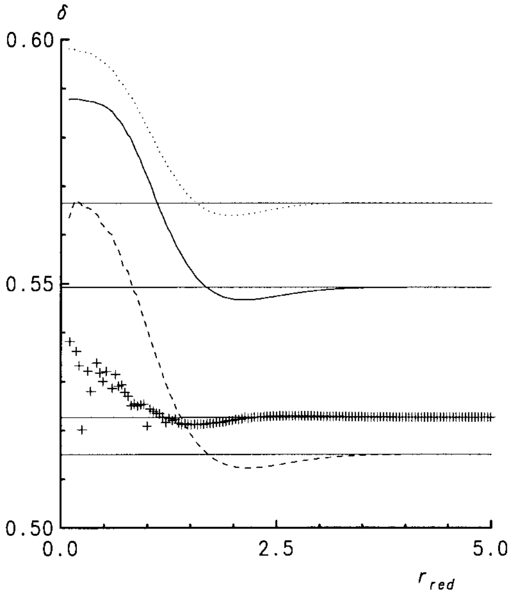

Figure 7. Asphericity, δ, vs the reduced distance r_{red} (symbols as in Figure 1).

cantly modified by the presence of another molecule. (For the relative increase of δ at zero distance see Table 3.)

In Figure 8, the relative change in shape, $\delta_{\mathrm{rel}} = \delta(r)/\delta_0$, is depicted as a function of r_{red}. In the case of a good solvent and a selective solvent, respectively, the shape of the end blocks is not significantly modified (it remains approximately constant for $r_{\mathrm{red}} \leq 0.5$), while the asphericity of the inner block increases sharply for $0 \leq r_{\mathrm{red}} \leq 1.5$. For athermal chains, the asphericity of this block increases slightly less than δ_{rel} of the entire chain at intermediate distances, where reorientation of the blocks might occur. At smaller distances, the asphericity of this block increases more than that of the entire chain. Similar behavior is exhibited by the middle block of the BAB copolymer at small r_{red}. (Only δ_{rel} of the entire BAB chain is smaller than that for AAA.) To keep in contact, the attractive end blocks are not oriented away from the center of the molecule as in case of ABA, which produces a small increase in asphericity of the overall chain. For ABA, δ_{rel} of the entire chain increases more than δ_{rel} of the inner block (even at zero distance). Apparently the chains expand in order to maximize the number of contacts between the attractive inner blocks and to keep the repulsive end blocks away from each other.

One measure for the relative orientation of blocks (and thus the molecular shape) is the average angle λ between the longest axes of "equivalent ellipsoids" representing the blocks and ranging from 0 to 90°, λ to be evaluated from the scalar product of these vectors. For random orientation, a value of 1 rad $\approx$ 57.3° is expected for uncorrelated vectors. Another measure is the angle κ between the two end-to-end vectors of the blocks, being between 0 and 180° at an average value of 90°. As the end-to-end vectors of the blocks are connected by the junction points, a third angle ν can be defined giving the dihedral angle of the three end-to-end vectors, $\vec{h}_i$ (i = 1, 2, 3), in the chain by eq 1.

$$\nu = \frac{\pi}{2} - \arccos\left(\frac{|\vec{h}_3(\vec{h}_1 \times \vec{h}_2)|}{|\vec{h}_3||\vec{h}_1||\vec{h}_2|}\right) \tag{1}$$

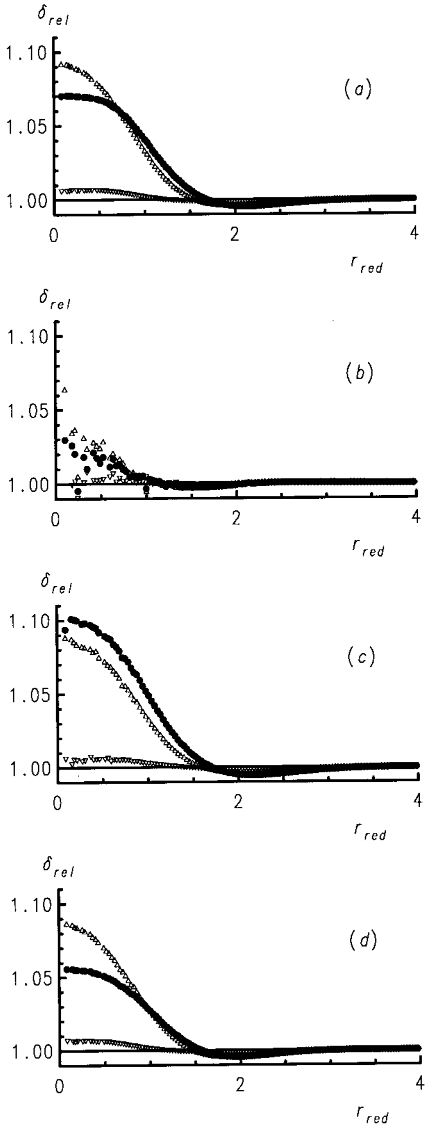

Figure 8. Relative asphericity, δ_{rel}, vs the reduced distance r_{red} for the entire chain (●) and the blocks (▽ for end blocks, △ for middle blocks), respectively, of the homopolymers AAA (a) and BBB (b) and the triblock copolymers ABA (c) and BAB (d).

λ, κ, and ν are depicted in Figure 9. For λ, Figure 9a, all systems show qualitatively the same behavior. Starting from infinite separation, λ first decreases and then increases to a maximum value at zero separation. (This value is given in Table 3 for $\lambda_{\mathrm{rel}} = \lambda(r)/\lambda_0$.) Parts b and c of Figure 9 show κ and ν. As already seen for the asphericity, the ABA molecule becomes most stretched of all systems at small intermolecular separations, as reflected by the angle κ. The dihedral angle ν of ABA remains at more or less the same value at zero distance as at infinite separation (apart from fluctuations arising from the poor statistics due to the compact middle blocks) while that of BAB increases rather sharply compared to the athermal homopolymer. The changes in ν are not very pronounced however.

B. Integral Changes. The integral changes of a macromolecular property in the presence of another molecule may be interpreted as the changes in this property within the limits of zero concentration within the concept of virial development of chain properties as a function of concentration. In this context, the excluded volume u related to the pair distribution function

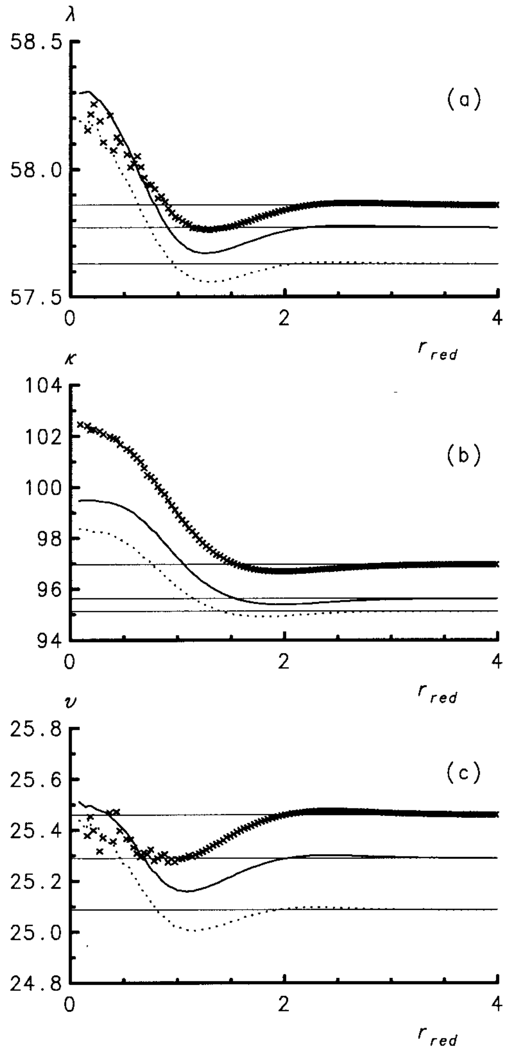

Figure 9. Angles λ (a), κ (b) and ν (c) between the blocks vs the reduced distance r_{red} for the homopolymer AAA (—) and the triblock copolymers ABA (×) and BAB (···). Apart from ABA (where scattering is considerable) lines are used instead of symbols (indicating discrete values) for the purpose of better resolution.

Table 4. Excluded Volume

system XYX	u	u_{rep}
AAA	7475.5	7475.5
BBB	−495.7	5303.1
ABA	5655.5	6590.2
BAB	5330.2	6845.0

by $u = \int[1 - g(r)]4\pi r^2\, dr$ is proportional to the second osmotic virial coefficient A_2. The excluded volumes of the systems investigated are listed in Table 4. The excluded volumes of the two triblock copolymers amount to about $^3/_4$ of the athermal value which corresponds to the fact (discussed in part 1) that roughly one-fourth of all intermolecular contacts are B—B contacts which contribute Boltzmann factors larger than unity to u, i.e., diminishing u. The excluded volume of the ABA system is slightly larger than that of BAB. This more Θ-like behavior of BAB is due to the positive deviation of its $g(r)$ from 1 at large separations which, because of being weighted with r^2, contribute heavily to u. On the other hand, u_{rep}, which is the excluded volume in the case of purely repulsive interaction (equivalent to a hard-sphere volume) due to forbidden double occupancy, is *larger* for BAB than for ABA. Taking into account the larger dimensions of BAB by relating u_{rep} to u_s, the excluded volume of a hard sphere

$$u_s = \frac{4\pi}{3}(2\sqrt{\langle s^2\rangle})^3 \qquad (2)$$

with radius $\langle s^2\rangle^{1/2}$ it is clear that u_{rep}/u_s is smaller for BAB ($\approx$ 0.36) than for ABA ($\approx$ 0.43).

Table 5. Coefficients K_s, K_h, and K_δ As Defined by Eq 14 of Part 1

K_x	system XYX	XYX	*X*YX	X*Y*X
K_s	AAA	−1.273	−0.396	−0.898
	BBB	+0.393	+0.149	+0.294
	ABA	−0.861	−0.371	−0.585
	BAB	−0.896	−0.199	−0.776
K_h	AAA	−1.601	−0.603	−1.411
	BBB	+0.471	+0.216	+0.445
	ABA	−1.142	−0.536	−0.957
	BAB	−1.042	−0.311	−1.111
K_δ	AAA	−0.489	−0.197	−0.458
	BBB	+0.071	+0.060	+0.078
	ABA	−0.406	−0.177	−0.330
	BAB	−0.335	−0.111	−0.361

Table 6. Coefficients K_λ, K_κ, and K_ν As Defined by Eq 14 of Part 1

system XYX	K_λ	K_κ	K_ν
AAA	−0.038	−0.289	−0.045
BBB	+0.012	+0.071	+0.014
ABA	−0.026	−0.207	−0.029
BAB	−0.018	−0.135	−0.023

The concentration dependence of molecular dimensions and shape parameters evaluated by use of the procedure developed in ref 21 and outlined in part 1 are given in Tables 5 and 6 for the systems investigated. As already seen in part 1 for the AB diblock copolymer, triblock copolymers also change their size and shape similarly to polymers in a good solvent. Neither ABA nor BAB exhibits sufficient intermolecular attraction to become expanded and more rodlike with increasing concentration as is observed for the Θ-homopolymer. Although BAB behaves slightly more "Θ-like" with respect to K_h and K_δ (which would mean positive values of K_X) than ABA, its (large) $\langle s^2\rangle_0$ is more compressed as concentration increases than in the case of ABA. Concerning the blocks—outer block (second column in Table 5 marked *X*YX) and inner block (third column marked X*Y*X)—it may be seen that the effect of compression (compared with the respective block of the athermal chain) is slightly reduced if the block is an athermal one and is considerably reduced if the block is in a Θ-solvent.

III. Conclusions

Block copolymers whose outer and inner parts are subject to different solvent conditions have different length scales in terms of intermolecular separation. At larger distances, the solvent quality of the outer parts dominates the distance dependent quantities. Thus, BAB may exhibit features such as the positive deviation from unity in the pair distribution function which are characteristic only for bad and Θ-solvents, respectively. No such effect has been found for AB diblock copolymers. At small distances, the solvent quality of the inner block dominates. This, among other things, is the reason for the high values of the pair distribution function of ABA at zero distance. Between these two regimes, an intermediate regime is present which is determined by the energy of A–B contacts. As these contacts are repulsive, the triblock copolymers in a selective solvent behave more like homopolymers in a good solvent than like Θ-chains. Reorientation of the individual blocks (or chain parts in case of homopolymers) takes place especially in this intermediate region where repulsive interaction may be avoided by dodging. At small distances, the dodging persists, albeit on a small scale, i.e., inside the inner block. However if the inner block is in a poor solvent and thus is attractive, the reorientation of repulsive parts continues and segregation of inner and outer blocks takes place in order to maximize the number of intermolecular contacts between the inner blocks of the two chains. This segregation affects not only the molecular shape, e.g., the asphericity, but also the chain dimensions such as the end-to-end distance. On the whole, the concentration dependence of characteristic properties expressed by integral quantities is in good agreement with data from the direct simulation of multichain systems.[40]

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

References and Notes

(1) Glatter, O. *J. Phys. IV* **1993**, *3*, 27.
(2) Schillén, K.; Glatter, O.; Brown, W. *Prog. Colloid Polym. Sci.* **1993**, *93*, 66.
(3) Mortensen, K.; Brown, W. *Macromolecules* **1993**, *26*, 4128.
(4) Bass, H. E.; Tan, J. *J. Acoust. Soc. Am.* **1993**, *93*, 283.
(5) Glatter, O.; Scherf, G.; Schillén, K.; Brown, W. *Macromolecules* **1994**, *27*, 6046.
(6) Schillén, K.; Brown, W.; Johnsen, R. M. *Macromolecules* **1994**, *27*, 4825.
(7) Mortensen, K.; Brown, W.; Jørgensen, E. *Macromolecules* **1994**, *27*, 5654.
(8) Rodrigues, K.; Mattice, W. L. *J. Chem. Phys.* **1991**, *95*, 5341.
(9) Larson, R. G. *J. Chem. Phys.* **1992**, *96*, 7904.
(10) Zhan, Y.; Mattice, W. L.; Napper, D. H. *J. Chem. Phys.* **1993**, *98*, 7502.
(11) Larson, R. G. *Macromolecules* **1994**, *27*, 4198.
(12) Haliloglu, T.; Balaji, R.; Mattice, W. L. *Macromolecules* **1994**, *27*, 1473.
(13) Adriani, P.; Wang, Y.; Mattice, W. L. *J. Chem. Phys.* **1994**, *100*, 7718.
(14) Haliloglu, T.; Mattice, W. L. In *Solvents and Self-Organization of Polymers*; Webber, S. E., Munk, P., Tuzar, Z., Eds.; NATO ASI: Series E, Applied Sciences 327; Kluwer: Dordrecht, The Netherlands, 1996.
(15) Haliloglu, T.; Stephenson, D. C.; Mattice, W. L. *J. Chem. Phys.* **1997**, *106*, 3365.
(16) Part 1: Olaj, O. F.; Neubauer, B.; Zifferer, G. *Macromolecules* **1998**, *31*, 4342.
(17) Binder, K. *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*; Oxford University Press: New York, Oxford, England, 1995.
(18) Olaj, O. F.; Pelinka, K. H. *Makromol. Chem.* **1976**, *177*, 3413.
(19) Janssens, M.; Bellemans, A. *Macromolecules* **1976**, *9*, 303.
(20) Olaj, O. F.; Lantschbauer, W. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 985.
(21) Olaj, O. F.; Lantschbauer, W.; Pelinka, K. H. *Macromolecules* **1980**, *13*, 299.
(22) Olaj, O. F.; Zifferer, G. *Macromol. Chem.* **1983**, *184*, 2619.
(23) Barrett, A. J. *Macromolecules* **1985**, *18*, 196.
(24) Yethiraj, A.; Honnell, K. G.; Hall, C. K. *Macromolecules* **1992**, *25*, 3979.
(25) Dautenhahn, J.; Hall, C. K. *Macromolecules* **1994**, *27*, 5399.
(26) Bruns, W. *Macromolecules* **1996**, *29*, 2641.
(27) Olaj, O. F.; Neubauer, B.; Zifferer, G. *Macromol. Theory Simul.* **1998**, *7*, 181.
(28) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*; Reinhold Publishing Corporation: New York, 1950.
(29) Tompa, H. *Polymer Solutions*; Butterworth Scientific Publications: London, 1956.
(30) Froehlich, D.; Benoît, H. *Makromol. Chem.* **1966**, *92*, 224.
(31) Birshtein, T. M.; Skvortsov, A. M.; Sariban, A. A. *Macromolecules* **1976**, *9*, 888.
(32) Sariban, A. A.; Birshtein, T. M.; Skvortsov, A. M. *Vysokomol. Soyed.* **1977**, *A19*, 1728.
(33) Sariban, A. A.; Birshtein, T. M.; Skvortsov, A. M. *Vysokomol. Soyed.* **1977**, *A19*, 2582.
(34) Tanaka, T.; Kotaka, T.; Ban, K.; Hattori, M.; Inagaki, H. *Macromolecules* **1977**, *10*, 960.
(35) Aronovitz, J. A.; Nelson, D. R. *J. Phys. (Paris)* **1986**, *47*, 1445.
(36) Rudnik, J.; Gaspari, G. *J. Phys. A: Math. Gen.* **1986**, *19*, L191.
(37) Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756.
(38) Šolc, K. *J. Chem. Phys.* **1971**, *55*, 335.
(39) Wei, G. Y. IUPAC International Symposium on Macromolecular Condensed State. Beijing, China, 1996; Preprints p 93.
(40) Olaj, O. F.; Neubauer, B.; Zifferer, G. Manuscript in preparation.

MA971088C