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Monte Carlo Studies of Conformational Characteristics of Block Copolymer Chains in Solution

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ABSTRACT: The behavior of two-block copolymer chains in solution is studied by computer simulation. The effect of heterointeractions on the chain dimensions is examined and the mean numbers of hetero- and homocontacts are determined. It is found that in the case of incompatibility of the chain components each block is in a "segregated state" which is similar to that of the portion of homopolymer chain in good solvent. In regions where the heterocontacts are favorable the mixing of blocks occurs, accompanied by a sharp decrease of the dimensions of the chain and a small decrease of the dimensions of separate blocks. The behavior of a block copolymer chain under temperature changes is analyzed and a nonmonotonic change of the chain dimensions is found to occur. The results are compared with experimental data on the temperature dependence of specific viscosity of block copolymers.

The properties of copolymers composed of different chemical units depend both on the composition and the chemical sequence distribution, i.e., on the primary macromolecule structure. Block copolymers composed of different chemical blocks of some length are of special interest for their structural characteristics and a whole complex of their properties as well.

This paper presents the results of Monte Carlo studies of the block copolymer chain composed of two blocks of equal length in solution. Such a system has been studied by experimental[1-6] and theoretical methods[7,8] in the Gaussian subchain approximation.

The Model

The structure of a copolymer chain in dilute solution (in particular a block copolymer chain) is essentially influenced by the long-range interactions, i.e., by the interactions of segments which are remote in the chain sequence but randomly approach each other in the process of the fluctuating coiling of the chain. In homopolymers these interactions are eliminated (at least on the average) in the theta solvent. As to copolymers, the theta conditions for each component are different, and therefore the volume interactions will not be compensated.

To study these interactions nonintersecting chains were generated on the five choice simple cubic lattice (see for details ref. 9). Chains of 10 to 128 bonds were composed of two blocks of equal length and flexibility and were simulated by random walks on the lattice. Thus it is the flexible chains which are considered, the average length of a segment being approximately equal to its thickness.

To take into account the excluded volume effects, chain self-intersection was not allowed and the interaction energy was attributed to any pair of nonbonded segments separated by one lattice spacing. As distinct from homopolymers where there is only one energy parameter for all pairs in contact, the two-component copolymers require consideration of three different energy parameters: those for two kinds of homocontacts ϵ_{AA} and ϵ_{BB}, and ϵ_{AB} for heterocontacts. In the two-block copolymers ϵ_{XX} (X = A or B) and ϵ_{AB} characterize the intrablock and interblock contacts, respectively. The parameters ϵ_{XY} (X, Y = A, B), which for simplicity will be referred to as contact energies, measured in units of kT, are the free-energy differences for segment–segment (F_{XY}) and segment–solvent (F_{XS}) interactions

$$\epsilon_{XY} = \frac{F_{XY} + F_{SS}}{kT} - \frac{F_{XS} + F_{YS}}{kT} \qquad (1)$$

(F_{SS} is the solvent–solvent interaction free energy.) They characterize the intramolecular contacts with respect to the case where there are no contacts and segments are immersed in solvent (see Figure 1), i.e., they are measures of the quality of solvent. At $\epsilon_{XX} > 0$ the polymer–solvent contacts are more preferred than the intrachain ones and this corresponds to a good solvent. When ϵ_{XX} decreases the solvent becomes poorer for each block and at $\epsilon_{XX} < \epsilon_{\Theta} < 0$ the structure of a given block becomes more compact than at the theta point. The three parameters ϵ_{XY} are similar to χ_A, χ_B, and χ_{AB} in thermodynamic theories of Flory and others.

On the other hand the quantity

$$\Delta\epsilon_{AB} = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) = \frac{F_{AB}}{kT} - \frac{F_{AA} + F_{BB}}{2kT} \qquad (2)$$

characterizes the degree of polymer component compatibility. At $\Delta\epsilon_{AB} > 0$ the heterocontacts are energetically less favorable than homocontacts and this corresponds to increase of the component incompatibility with increasing $\Delta\epsilon_{AB}$. At $\Delta\epsilon_{AB} < 0$ heterocontacts are more favorable than homocontacts; this is usually connected with specific intercomponent interactions (e.g., hydrogen bonding).

It is obvious that for the individual macromolecules in solution the intramolecular contacts compete mainly with the

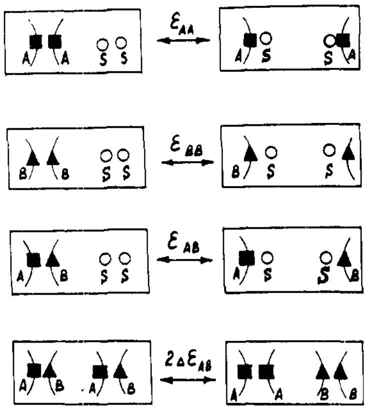

Figure 1. The energy parameters of the copolymer molecule.

polymer–solvent contacts and therefore there are reasonable parameters ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}. At the same time for bulk state the thermodynamic properties of copolymers are determined by the competition between homo- and heterocontacts, so the main parameter is $\Delta\epsilon_{AB}$ (see Figure 1).

The mean-square end-to-end distance $\langle h^2 \rangle$ and the number of contacts $\langle m \rangle$ in the chain were considered as the physical characteristics of the system. Simultaneously, the computer simulation succeeded in distinguishing between the contacts of different kinds and determining not only the characteristics of the molecule as a whole but also those of the chain blocks $\langle h_X{}^2 \rangle$ and $\langle m_{XX} \rangle$.

It should be emphasized that in the experimental study of the copolymer of given chemical composition, any change in conditions (change of T, solvent, etc.) leads to the simultaneous change of all three parameters ϵ_{XY}. Complex dependence of the properties observed on the external conditions must have been caused by this reason (see below). To make the interpretation more clear and to construct a general physical situation we shall mainly analyze the dependence of the chain properties on one of the parameters ϵ_{XY}, two others being fixed.

Results and Discussion

(a) Influence of Heterointeractions on the Physical Characteristics of Block Copolymer. In Figure 2 there are calculated plots of $\langle h^2 \rangle$ and $\langle m_{XY} \rangle$ vs. ϵ_{AB} and simultaneously vs. $\Delta\epsilon_{AB}$ for the chain of 64 segments which may be used to analyze the effect of heterointeractions on the characteristics of a whole polymer chain and each block as well. Values of the homocontact energy ϵ_{AA} and ϵ_{BB} which characterize the quality of solvent for each block are taken to be fixed: Figures 2a and 2b represent the macromolecule with two blocks in good solvent and in precipitant, respectively, and Figures 2c and 2d correspond to that with one block in good solvent and another in precipitant.

Dashed curves in Figure 2 represent the dimension and the number of contacts in separate blocks, i.e., in homopolymer chains of 32 segments with the same homocontact parameters.

Moreover, Figure 2e shows the dimension ratio $\langle h^2 \rangle / \langle h_{\epsilon_{AB}=0}{}^2 \rangle$ and the mean number of heterocontacts $\langle m_{AB} \rangle$ as functions of the heterocontact energy $(-\epsilon_{AB})$ in different solvents; values of the intrablock interactions are given in the legend.

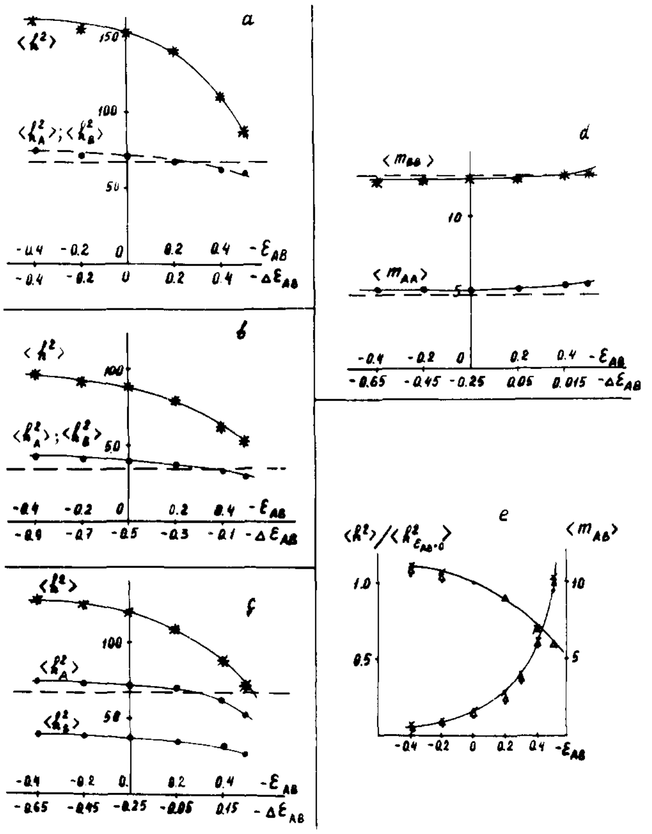

Figure 2. Dimensions and the number of contacts vs. the heterocontact energy ϵ_{AB} and the compatibility parameter $\Delta\epsilon_{AB}$ of the chain of 64 segments. Dashed curves represent the characteristics of the separate block of 32 segments at the same homocontact parameters: (a) each block is in good solvent ($-\epsilon_{AA} = -\epsilon_{BB} = 0$); (b) each block is in precipitant ($-\epsilon_{AA} = -\epsilon_{BB} = 0.5$); (c) and (d) A block is in good solvent and B block in precipitant ($-\epsilon_{AA} = 0$ and $-\epsilon_{BB} = 0.5$); (e) the dimension ratio and the mean number of heterocontacts in block copolymer: (●) $-\epsilon_{AA} = -\epsilon_{BB} = 0$; (△) $-\epsilon_{AA} = 0$ and $-\epsilon_{BB} = 0.5$; (×) $-\epsilon_{AA} = -\epsilon_{BB} = 0.5$.

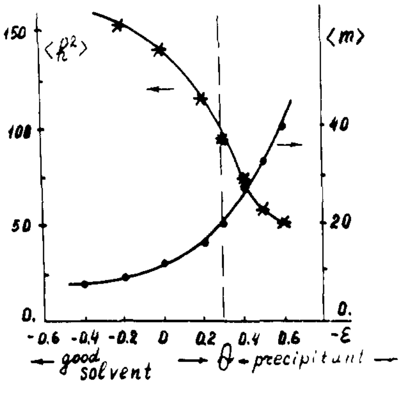

Figure 3. Dimensions and the mean number of contacts in the homopolymer of 64 segments. The dashed line indicates the theta region.

For comparison Figure 3 shows $\langle h^2 \rangle$ and $\langle m \rangle$ vs. the contact energy in a homopolymer of 64 segments.[10] As has been shown,[9,11] the theta conditions for our model correspond to the small attraction between segments drawn together $-\epsilon = -\epsilon_0 = 0.3$, which merely compensates the effect of the inherent volume of the segments. On the left of the theta point, where $(-\epsilon) < (-\epsilon_0)$, the expanded chain is in a good solvent; on the right, where $(-\epsilon) > (-\epsilon_0)$, the chain, being more compact than the unperturbed one, is in a poorer solvent than the theta solvent (i.e., in precipitant).

Let us turn to the data on copolymers. The copolymer characteristics which depend on the heterocontact energy are shown in Figures 2a–e; they reveal the general regularities depending on ϵ_{AB} (cf. Figures 2e and 3). It should be noted that these regularities do not depend on the compatibility parameter of components $\Delta\epsilon_{AB}$. Thus, as has been pointed out,

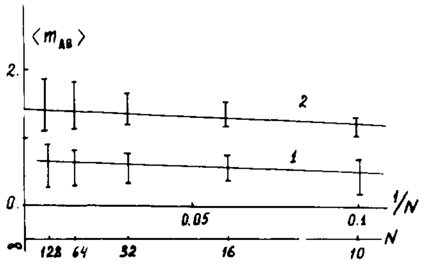

Figure 4. The mean number of heterocontacts in chains of different lengths. Heterocontacts are (1) energetically unfavorable ($-\epsilon_{AB} = -0.5$) and (2) indifferent ($-\epsilon_{AB} = 0$). The homointeraction parameter $-\epsilon_{XX}$ in each block varies between the limits -0.5 and $+0.5$.

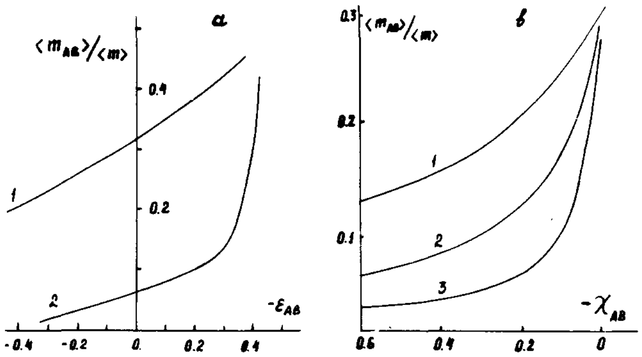

Figure 5. The fraction of heterocontacts vs. the heterointeraction parameter in block copolymers of different lengths, with two blocks being under theta conditions: (a) Monte Carlo calculations ($-\epsilon_{AA} = -\epsilon_{BB} = 0.3$), (1) $N = 16$ and (2) $N = 128$; (b) analytical theory[8] ($\chi_A = \chi_B = 0.5$), (1) $N = 20$, (2) $N = 200$, and (3) $N = 2000$.

it is the competition between the polymer–polymer and polymer–solvent contacts which determines the conformational characteristics of a copolymer in solution but not the competition between contacts of segments of different kinds.

In this section we shall turn to the region $(-\epsilon_{AB}) < (-\epsilon_\Theta)$ where the heterointeractions are just the repulsion of segments (because of the inherent volume of segments at $0 < -\epsilon_{AB} < -\epsilon_\Theta$ or the additional repulsion energy at $(-\epsilon_{AB}) < 0$). The value of ϵ_{AB} in this region is seen in Figure 2 to be ineffective with respect to the intrablock characteristics $\langle h_X{}^2\rangle$ and $\langle m_{XX}\rangle$ (X = A, B). The numbers of the intrablock contacts are practically determined only by the homointeraction energy and in fact are equal to the numbers of contacts in separate blocks (see Figure 2d).

Comparison of values of $\langle h^2\rangle$ of the block itself and the copolymer chain (Figures 2a–c) reveals that the presence of the second block (B block) at any value of $(-\epsilon_{BB})$ and at $(-\epsilon_{AB}) < (-\epsilon_\Theta)$ slightly extends the A-block dimensions. A similar effect occurs in the homopolymer chains immersed in good solvent ($-\epsilon < -\epsilon_\Theta$); in this case the increase of the contour length of the chain leads to a disproportionate growth of the mean dimensions caused by the increase of volume interactions.

The effect of $(-\epsilon_{AB})$ on $\langle h^2\rangle$ and $\langle m\rangle$ of a whole chain is also similar to that of the solvent quality on the characteristics of a homopolymer chain (cf. Figures 2 and 3). Moreover, the dependence of $\langle m\rangle$ on ϵ for a homopolymer is much stronger than that of $\langle m\rangle = \langle m_{AA}\rangle + \langle m_{BB}\rangle + \langle m_{AB}\rangle$ on ϵ_{AB} for the case of copolymer with ϵ_{AA} and ϵ_{BB} fixed, since in the latter (as distinct from a homopolymer) only the number of heterocontacts changes, the number of homocontacts being constant.

It is seen in Figure 2 that the number of heterocontacts is small even at $(-\epsilon_{AB}) = (-\epsilon_\Theta)$. This means that in the whole region $(-\epsilon_{AB}) \leqslant (-\epsilon_\Theta)$ the blocks interpenetrate each other only slightly.

Figure 4 shows that the number of heterocontacts in fact does not depend on the block lengths and the block–solvent interactions (in the region $-0.5 \leqslant -\epsilon_{XX} \leqslant 0.5$) and is determined only by the heterointeraction energy $(-\epsilon_{AB})$, at least at $(-\epsilon_{AB}) \leqslant (-\epsilon_\Theta)$.

The heterocontact fraction $\langle m_{AB}\rangle/\langle m\rangle$ vs. the heterointeraction parameter in block copolymers of different lengths is shown in Figure 5a for the case when there are theta conditions for each block ($-\epsilon_{AA} = -\epsilon_{BB} = -\epsilon_\Theta = 0.3$). For comparison Figure 5b represents the same dependence given by the approximate analytical theory[8] for the similar case $\chi_A = \chi_B = 0.5$.

The fraction of heterocontacts (heterointeractions being unfavorable) proves to be small and decreases with the lengthening of blocks. Hence, the interactions between blocks occur in small boundary regions between two components and the heterocontacts mainly arise from the segments belonging to the block joint. This effect (which occurs in homopolymers, too) is caused by the small probability of large loops (cf. ref 12). Thus, the unfavorableness of heterocontacts called forth by the mutual incompatibility of the block copolymer components leads to weak mixing of such blocks in the boundary region. This state of the macromolecule, often called a "segregated state", does not differ in fact from that of half of the homopolymer chain in a good solvent. In both cases the perturbations caused by a second block (or a second half of the chain) are small and occur mainly in the joint.

In the limiting case of absolute incompatibility of blocks when $\epsilon_{AB} \rightarrow \infty$ the heterocontacts are eliminated completely. Generally speaking, a similar situation can be realized in homopolymers as $\epsilon \rightarrow \infty$, too. Indeed, for homopolymers the region $(-\epsilon) \leqslant (-\epsilon_\Theta)$ may be in principle divided into two intervals corresponding to the different signs of interaction energy of the segments drawn together. At $0 < (-\epsilon) < (-\epsilon_\Theta)$ the segment–segment contacts are more favorable energetically than the segment–solvent contacts (eq 1) and this leads to the partial compensation of the segment inherent volume effect. The effective excluded volume of segments is positive and increases from zero at $(-\epsilon) = (-\epsilon_\Theta)$ to the value of the inherent volume of noninteracting segments (cubes in the chain lattice model) at $(-\epsilon) = 0$. At $(-\epsilon) < 0$ the polymer–polymer contacts are found to be less favorable than the polymer–solvent ones. The change of sign of the interaction energy leads only to the further growth of the effective excluded volume. The limiting case $\epsilon \rightarrow \infty$ requires elimination of the segment–segment contacts, and therefore the chain is entirely solvated due to the strong binding with solvent. The segment of such a chain is a segment surrounded with solvent molecules, i.e., a segment of double the initial thickness, and the chain expansion is determined by the inherent volume of such more bulky noninteracting segments.

In the same way in copolymers, with the heterocontacts prohibited, segments behave as those of double thickness (in respect to heterointeractions). Thus, the complete incompatibility of blocks does not yield any peculiarities in the block copolymer chain behavior as compared to the excluded volume effects in homopolymers.

(b) Block Mixing in the Block Copolymer Chain. Consider now the case of $(-\epsilon_{AB}) > (-\epsilon_\Theta)$ when the heterocontacts are energetically favorable. As can be seen in Figure 2e, with increasing $(-\epsilon_{AB})$ the number of heterocontacts sharply grows both with intrablock repulsion and attraction.

With increasing $\langle m_{AB}\rangle$ simultaneous sharp decrease of the block copolymer chain dimensions is observed; the chain dimensions approach those of a separate block (Figures 2a–c). This shows that block mixing occurred and that heterocon-

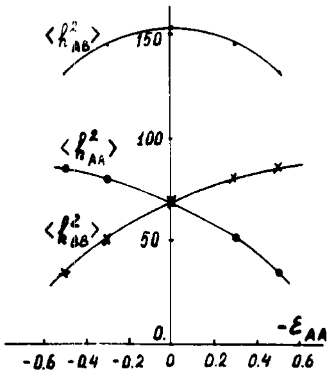

Figure 6. Dimensions of the block copolymer chain of 64 segments and those of its blocks vs. the homocontact energy at $\epsilon_{AA} = -\epsilon_{BB}$ and $-\epsilon_{AB} = 0$.

tacts between segments which are remote in the chain sequence appeared.

The reciprocal bonding of heterosegments, i.e., formation of the interblock complex, affects also the properties of each block. Though the number of the intrablock contacts changes slightly, the decrease of the dimensions of each block is observed. Hence, formation of the complex of two coiled molecules leads both to the decrease of the dimensions of a whole chain and of blocks.

(c) Behavior of the Block Copolymer Chain under Variation of External Conditions. Up to this point the behavior of the copolymer chain with variation of one of the parameters has been discussed. As has been pointed out, with changing external conditions all three parameters ϵ_{XY} usually vary. This can yield some peculiarities in behavior of the block copolymer in comparison with the homopolymer. The situation appears to be possible even in the region of the reciprocal repulsion of blocks where characteristics of the blocks are close to those for individual homopolymer chains. For example, Figure 6 shows the characteristics of the macromolecule at $\epsilon_{AA} = -\epsilon_{BB}$; when the repulsion energy within one block increases (i.e., solvent quality increases), the attraction energy within another block increases (i.e., solvent quality decreases) and $\epsilon_{AB} = 0$. Though dimensions of each block change monotonically, the dimensions of the chain have a maximum. Due to the symmetry of the system these changes are symmetric with respect to the axis of ordinates.

Styrene–α-methylstyrene block copolymers in toluene and cyclohexane,[4] styrene–isoprene copolymers in cyclohexane,[5] and styrene–methyl methacrylate copolymers in benzene[3] have been found to demonstrate nonmonotonic dependence of $[\eta]$, the specific viscosity, on temperature (see Figure 7a). Since cyclohexane is a good solvent for polystyrene ($\theta = 34.5°$) and poly-α-methylstyrene ($\theta = 37$–$38°$), the first growth of $[\eta]$ with increasing T^4 seems to be connected with the expansion of each block. The decrease of viscosity at further increase of T is probably connected with the block mixing, since the incompatibility of polymers decreases with increasing T. The further growth of $[\eta]$ is similar to the increase of the homopolymer dimensions with improving solvent.

The possibility of such a situation was considered in the lattice model. The temperature dependence of $\epsilon_{AA} = \epsilon_{BB}$ and ϵ_{AB} being given by the plots of Figure 7b, the temperature dependence of the chain dimensions obtained is shown in Figure 7c. It can be seen that the results calculated are close to those experimentally obtained. Therefore, the model suggested treats qualitatively the observed behavior of the block copolymer chains in solution.

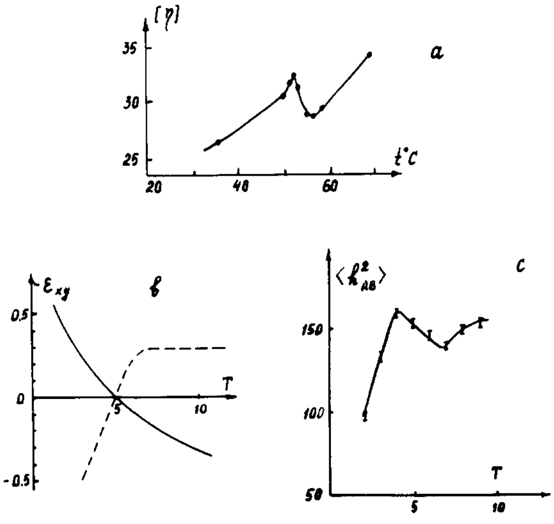

Figure 7. (a) Temperature dependence of the specific viscosity for the two-block copolymer of styrene–α-methylstyrene in cyclohexane. (b) Suggested temperature dependence of the parameters of homointeractions $-\epsilon_{AA} = -\epsilon_{BB}$ (solid curves) and heterointeractions (dashed curves). (c) Temperature dependence of the mean-square end-to-end distance of the two-block copolymer of 64 segments obtained by Monte Carlo calculations (I is the calculation error).

In conclusion the problem of the block copolymer chain transition from the "segregated" state where blocks are practically independent to the mixing state is of interest. The phase nature of this transition was proposed by Froelich and Benoit.[7] If it were really a phase transition then the distribution function of the number of heterocontacts m_{AB} would be represented by a two-humped curve as the parameter ϵ_{AB} changes. In our case when the flexible chain of about 100 segments is considered, such an effect is never observed; with increasing $(-\epsilon_{AB})$ the distribution function on m_{AB} is displaced toward greater values of the number of contacts but there is no phase separation.

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