A MONTE CARLO STUDY OF COPOLYMER CHAIN CONFORMATIONS IN DILUTE SOLUTIONS IN GOOD AND SELECTIVE SOLVENTS

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Conformations of symmetric diblock copolymers AB in dilute solutions in good and selective solvents were studied by Monte Carlo simulations on a simple cubic lattice. Individual chain conformations were created by the self-avoiding walk algorithm. A modified thermal equilibration of the system based on the Metropolis acceptance criteria for energies of the system and the Rosenbluth weights of chain conformations was applied. Interactions of the nearest neighbours ($r = l$), where l is the lattice distance, and interactions for $r = \sqrt{2}l$ and $r = \sqrt{3}l$ were considered. Various structural characteristics of the whole copolymer chain and individual blocks A, B were obtained in the course of computer simulations. It was found that a moderate contraction of the worse soluble block B and a certain segregation of blocks occurs in dilute solutions in selective solvents for the block A, however neither that contraction, nor the segregation of blocks are extensive.

Block and graft copolymers represent very important class of polymeric materials. Their thermodynamic and mechanical properties are quite unique and differ considerably from all other types of men-made polymers. It is the reason why they find rich industrial applications and are intensively studied by many research groups all over the world. They are used in large quantities, e.g., in the rubber industry, but their utilisation grows steeply in many other fields, such as pharmaceutical industry, etc.

Linear di- and triblock copolymers of the type AB, or ABA form spherical multimolecular micelles[1–3] in dilute solutions in selective solvents (a good solvent for block A and a nonsolvent for B). Multimolecular micelles are uniform in mass and size and are in a reversible equilibrium with unimer[4]. Unimer concentration is equal to c.m.c. which is usually very low. It is often below the detection limit of almost all experimental techniques, such as elastic, or quasielastic light scattering, etc. which are currently used for studying micellizing systems.

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Multimolecular micellization of block copolymers in selective solvents has been intensively studied both by experimentalists (see, e.g., the review article[3] and the references therein) and by theoreticians[5–16]. Despite the intense interest of many scientists in micellizing copolymer systems, relatively little is known concerning the detailed structure and properties of the unimer form. It is due in part to the extremely low concentration of this form in micellizing systems and experimental difficulties arising from it, and to the fact that almost all interesting, important and applicable properties of micellizing systems are those of the associated polymer form which is present in a great surplus in the system.

Unimer is assumed to form unimolecular micelles[17], i.e., to create conformations similar to the letter "V" or "C" with partially segregated blocks and slightly collapsed nonsoluble block B. Neither the segregation of blocks, nor the collapse of the block B are extensive since the unfavourable enthalpic contribution to the Gibbs free energy of the system arising from interactions of a low fraction of unimers with solvent molecules is compensated by the positive entropy of mixing of all three components of the mixture (solvent, unimers and multimolecular micelles). Pure unimolecular micelles (with the above described structure) exists only below c.m.c.

Older computer simulation[18–20] roughly confirm the assumed conformation, even though the approximations that had to be used do not meet the standards of the up-to-date studies. So far nobody re-examined in details to what extent the used simplifications might have affected the general reliability of the results.

In this paper we report on the Monte Carlo studies of the fully self-avoiding copolymer chain behaviour on a simple cubic lattice. To describe interactions in the system, we consider not only the nearest neighbour groups (i.e., those separated by the lattice distance, l), but also groups with mutual distances $\sqrt{2}l$ (the surface diagonal), and $\sqrt{3}l$ (the body diagonal). Interaction parameters for corresponding distances were recalculated using the Lennard–Jones (12–6) formula[21].

METHOD

Simulation Technique

Possible conformations of isolated copolymer chains with increasing numbers of segments, N = 40, 60, 80 and 100, and equal lengths of blocks were obtained by the self-avoiding walk on a simple cubic lattice together with the equilibrium procedure described bellow. In this study, a periodic cubic box (i.e. the fundamental box surrounded by its images) containing 23 × 23 × 23 lattice sites with the nearest distance, l, was used.

Periodic boundary conditions secure even interactions for all segments (independently on the distance from walls) and remove external constraints imposed by the small volume of the fundamental box, however they do not remove the bias of the

steadily increasing density (fraction of the occupied lattice sites) during the growth of a chain. For the longest chain, $N = 100$, the fraction of the occupied lattice sites is ca $8.2 \cdot 10^{-3}$. That value is lower than the average segment density in a random coil of the same length. It means that the bias of the steadily growing density is not important in our simulations. All simulated chains start in the centre of the fundamental box. The average ratio of the transitions between different boxes during the growth of a chain to the number of segments was always lower than 1%. Under these conditions, the performed simulations model isolated copolymer chains at the infinite dilution fairly well.

The biased sampling with the Rosenbluth weights[22], $w_i^{(m)}$, in each step, i (in the growth of the m-th chain) was used to avoid the "attrition" problem. Equilibration of the system was performed according to a modified Metropolis criterion[23]. A new chain is accepted if the following relation is satisfied

$$X \leq (W_{m+1}/W_m) \exp [-(U_{m+1} - U_m)/N_t \boldsymbol{k} T] \ , \qquad (1)$$

where $X \in \langle 0, 1 \rangle$ is a random number obtained by a congruent generator of random numbers[24], $W_m = \Pi_{(i)} w_i^{(m)}$ are the Rosenbluth weights of the old, m, and the new chain, $m + 1$, respectively, U_m and U_{m+1} are the corresponding interaction energies, N_t is the total number of segments and solvent molecules (equal to the number of all lattice sites in the fundamental box), $\boldsymbol{k}$ is the Boltzmann constant and T is temperature.

Since individual chain conformations are statistically uncorrelated, all accepted chain conformations may be used for the evaluation of conformational characteristics. However the Metropolis acceptance rule must be used for testing all successive pairs of generated chains, independently of the fact whether they have been accepted, or not. The total number, M, of generated chains was used $M = 1 \cdot 10^6$ which required a successful generation of $1 \cdot 10^8$ segment positions.

Interaction energy of the system (in the m-th generated state) was calculated according to the formula

$$U_m = \sum_{(ij)} N_{ij}^{(m)}(r) \, u_{ij}(r) \ , \qquad (2)$$

where $N_{ij}^{(m)}(r)$ are numbers of individual interacting pairs with mutual distances r: (i) $i = j$ = A: segment A–segment A; (ii) $i = j$ = B: segment B–segment B; (iii) i = A, j = B: segment A–segment B; (iv) i = A, j = S: segment A–solvent S; (v) i = B, j = S: segment B–solvent S; (vi) $i = j$ = S: solvent S–solvent S, and $u_{ij}(r)$ are the corresponding interaction energies depending on the distance r. We have considered not only interactions of the given segment (or solvent molecule) with the nearest

neighbours (6 neighbour sites for each lattice site, i.e., 4 interactions for polymer segments and 5 for end-segments), but also with neighbours at the surface diagonal (12 for each lattice site) and with neighbours at the body diagonal (8 for each lattice site) – see Fig. 1. Interactions between the nearest neighbours of the same type were described by a parameter $\xi_{ii}(r = l) = \varepsilon_{ii}/\boldsymbol{k}T$ (for $i = j$) where ε_{ii} is a depth in the Lennard–Jones (12–6) potential

$$u_{ij}(r) = 4\,\varepsilon_{ij}\,[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}] \qquad (3)$$

and $\sigma_{ij} = l/(2)^{1/6}$, where i, j = A, B, S for segments A, B and solvent molecules, respectively. Values of ξ_{ii} ($r = l$) were varied in the range 0 to 1 in order to model the continuous deterioration of the solvent quality for individual blocks of a studied copolymer. Parameters $\xi_{ij}(r = l)$ for $i \neq j$ were calculated using the following approximate formula $\xi_{ij} = (\xi_{ii}\xi_{jj})^{1/2}$ and all remaining parameters for $r = \sqrt{2}\,l$ and $r = \sqrt{3}\,l$ were recalculated from the Lennard–Jones formula (Eq. (*3*)).

All calculations were performed on a DEC 5000/200 computer using an original simulation program written in FORTRAN 77. The longest calculations took up to several hours of the CPU.

Calculated Functions

The following distribution functions were constructed as histograms during simulations of chain conformations:

a) Distribution function of the end-to-end distances (i.e., the free ends of the block A and the block B), $\rho_{\mathbf{AB}}(r_{\mathbf{AB}})$, and distributions of distances of both ends of the block A

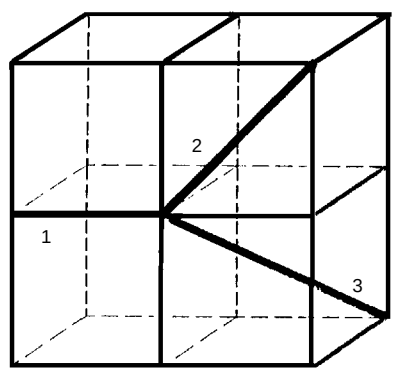

FIG. 1
A schematics showing the considered interactions on a simple cubic lattice

(i.e., distances from the free end of the block A to its connection to the block B), $\rho_{CA}(r_{CA})$, and the corresponding function for the block B, i.e., $\rho_{CB}(r_{CB})$, see Figs 2*a* and 2*b*. Value of this function for a given value of r is calculated as the number of chains with one end fixed in the centre [0,0,0] and the other end located in the narrow spherical layer of the radius r and a constant thickness $\Delta_1 = 1.0l$, normalised by the number of all lattice sites in that layer. The three above defined distribution functions, $\rho_{AB}(r_{AB})$, $\rho_{CA}(r_{CA})$ and $\rho_{CB}(r_{CB})$ are the probability density functions.

b) Distribution functions of the radii of gyration of the whole copolymer chain, $\sigma(\sqrt{\langle s^2 \rangle})$, and individual blocks, $\sigma_A(\sqrt{\langle s_A^2 \rangle})$ and $\sigma_B(\sqrt{\langle s_B^2 \rangle})$, were calculated similarly to the end-to-end distribution functions.

c) Distribution functions of the distances of the free ends, **A**, **B**, of individual blocks A and B from the gravity centre, **T**, of the whole copolymer chain, $\tau_{TA}(t_{TA})$ and $\tau_{TB}(t_{TB})$, and distribution functions of the gravity centres, **X** and **Y**, of both blocks from **T**, $\tau_{TX}(t_{TX})$ and $\tau_{TY}(t_{TY})$, respectively, distribution of the distances of the gravity centre of the whole chain, **T**, from the connection of the blocks, **C**, (**C** is defined as the middle of the bond connecting the both blocks), $\tau_{TC}(t_{TC})$, and distribution function of mutual

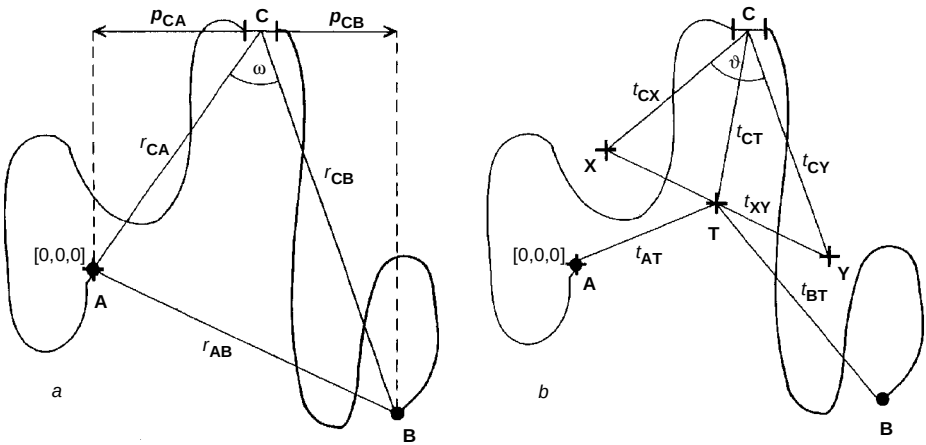

FIG. 2

A schematics explaining the studied conformational characteristics of copolymer chains: **A** and **B** are the free ends of the blocks A and B, respectively, **C** is the connection of both blocks (the middle of the connecting bond), **T** is the centre of gravity of the whole chain and **X** and **Y** are the gravity centres of individual blocks. *a* r_{AB} is the mutual distance of the free ends of both blocks, r_{CA} is the distance of the free end of the block A (point **A**) from its connection to the block B (point **C**) and r_{CB} is the analogical characteristics for the block B, $\boldsymbol{p}_{CA}$ and $\boldsymbol{p}_{CB}$ are projections of **CA** and **CB** vectors into the direction of the bond connecting both blocks and ω is the angle **ACB**; *b* t_{CT}, t_{CX} and t_{CY} are distances of the gravity centres of the whole chain and individual blocks from the connection **C**, t_{AT} and t_{BT} are the distances of the block free ends from the gravity centre, t_{XY} is the mutual distance of the gravity centres of both blocks and ϑ is the angle **XCY**

distances of the gravity centres of both blocks, $\tau_{\mathbf{XY}}(t_{\mathbf{XY}})$ are numbers of chains with particular values $t_{\mathbf{TA}}$, $t_{\mathbf{TB}}$, etc., normalised by the numbers of the lattice sites in the spherical layers of the thickness $\Delta_2 = 0.2l$ (the lower value of the thickness was used, since the values of $t_{\mathbf{TA}}$, etc. are quite low as compared with probable values of $r_{\mathbf{AB}}$.

d) Distribution of the angles defined by the gravity centres of both blocks and the blocks connection, ϑ, $\phi(\vartheta)$, and distribution of the angles defined by the free ends of blocks and their connection, ω, $\psi(\omega)$ are the number fractions of copolymer chains with the angles ϑ and ω in narrow intervals $<\vartheta, \vartheta + \Delta\vartheta)$ and $<\omega, \omega + \Delta\omega)$, respectively, with $\Delta\vartheta = \Delta\omega = 5°$ (i.e., they do not represent the probability density functions).

e) Distributions of the projections of **CA** and **CB** vectors into the direction of the bond connecting the last segment of the block A and the first segment of the block B, $f_A(\boldsymbol{p}_{\mathbf{CA}})$ and $f_B(\boldsymbol{p}_{\mathbf{CB}})$ are the number fractions of chains with particular values of those projections.

Besides the described functions, the following average structural characteristics of chains were obtained: (i) the mean square distance of the ends of the whole chain, $<r^2_{\mathbf{AB}}>$, (ii) the mean square distances of the ends of the block A, $<r^2_{\mathbf{AA}}>$ and the block B, $<r^2_{\mathbf{BB}}>$, respectively, (iii) the mean numbers of the closest (non-bonding) interactions, $N^{(1)}_{AA}$, $N^{(1)}_{BB}$ and $N^{(1)}_{AB}$, numbers of interactions for the distance $\sqrt{2}\,l$: $N^{(2)}_{AA}$, $N^{(2)}_{BB}$ and $N^{(2)}_{AB}$ and those for the distance $\sqrt{3}\,l$: $N^{(3)}_{AA}$, $N^{(3)}_{BB}$ and $N^{(3)}_{AB}$ and the mean numbers of interactions: segment–solvent, $N^{(i)}_{AS}$ and $N^{(i)}_{BS}$, where i = 1, 2 and 3, for the same distances as before. The further calculated characteristics were: (iv) the total radius of gyration of the chain, $<s^2>$ and radii of gyration of individual blocks, $<s^2_A>$ and $<s^2_B>$, respectively, and (v) the mean values of the angles ϑ, ω. The last group of the calculated characteristics (vi) concerns the distances the gravity centre of the whole chain and individual blocks from the connection of blocks, $<t_{\mathbf{TC}}>$, $<t_{\mathbf{XC}}>$, and $<t_{\mathbf{YC}}>$, respectively, and from each other, $<t_{\mathbf{XY}}>$.

RESULTS AND DISCUSSION

In this communication, we report on the computer simulations of the behaviour of dilute solutions containing symmetric self-avoiding copolymer chains (i.e., chains with equal lengths of blocks A and B, and the following numbers of all segments, $N_A + N_B = 40$, 60, 80 and 100) in solvents which are extremely good (athermal) for the block A, $\xi_{AA} = 0$, and their quality continuously worsens for the block B, $\xi_{BB} \in <0, 1>$, $\xi_{AS} = \xi_{BS} = \xi_{SS} = 0$. The cross-interaction parameters, $\xi_{AB} = (\xi_{AA}\,\xi_{BB})^{1/2}$ equal zero in all studied systems. It means that the decrease in the solvent quality for the block B is modelled by the same deterioration of interactions $u_{BS}(r)$ and $u_{AB}(r)$ with respect to $u_{BB}(r)$. In contrast to some earlier studies of other authors[18–20,25], we do not use a constant and negative value of the parameter ξ_{AB} to strengthen the incompatibility of blocks A and B. A certain and quite important incompatibility arises in selective solvents for the block A automatically due to the fact that $(\xi_{BB} - \xi_{AB}) > 0$, even though $(\xi_{AA} - \xi_{AB}) = 0$.

Systems with all $\xi_{ij} = 0$ model homopolymers in a good solvent (or a hypothetical "copolymer" with fully compatible blocks in a solvent which is equally good for both blocks). The results are necessary for comparison with realistic copolymers. Systems with $\xi_{BB} = 1$ and all other $\xi_{ij} = 0$ model copolymers with fairly incompatible blocks in a strong selective solvent for A. Results of simulations for other sets of interactions parameters will be presented in the near future (mainly those for systems with significant repulsion between segments A and B).

To check the program correctness, the behaviour of a homopolymer in solvents with continuously changing quality was also simulated. Since we discuss in the following part the behaviour of copolymer chains in solvents with changing quality for the block B, now we consider that the whole chain behaves as the homopolymer B and the test simulations are therefore performed for the following interaction parameters: $\xi_{SS} = 0$ and $\xi_{AA} = \xi_{BB} = \xi \in \langle 0, 1 \rangle$. It should be mentioned that in our systems where not only the nearest neighbour interactions (for $r = l$), but also interactions for longer distances, $r = \sqrt{2}l$ and $r = \sqrt{3}l$ are considered (the strength of which is recalculated according to the Lennard–Jones formula), the Θ-conditions are defined for $\xi = 0.295$.

A large collection of various distribution functions and average structural characteristics gives a detailed description of the system behaviour. Not all calculated functions will be presented here since it would exceed the reasonable size of a comprehensive paper.

Structural and thermodynamic characteristics for the chain with $N = 100$ segments, and for several equidistant values of $\xi = 0.0$, 0.25, 0.5, 0.75 and 1.0 are given in Tables I and II. Values of the end-to-end dimensions, $\langle r^2 \rangle$, show a continuous decrease in the

TABLE I

The average conformational characteristics of an isolated homopolymer chain B ($N = 100$) in solvents with decreasing thermodynamic quality (i.e. with increasing value of ξ). Symbols **X** and **X′** stand for the gravity centres (and the ends) of two different halves of a chain; $\xi_{SS} = 0$

Characteristic	$\xi_{AA} = \xi_{BB}$				
	0	0.25	0.50	0.75	1.00
$\langle r^2 \rangle$	178.05	174.72	151.75	150.02	150.02
$\langle s^2 \rangle$	29.26	28.83	25.50	25.24	25.23
$\langle t_{\mathbf{TC}} \rangle$	3.46	3.45	3.33	3.33	3.32
$\langle t_{\mathbf{XX'}} \rangle$	7.30	7.23	6.64	6.59	6.60
$\langle \vartheta \rangle$	96.90	96.48	93.45	93.16	93.27

chain dimensions with increasing ξ and the same behaviour of both "blocks" (i.e., halves of the chain). The diminution of the chain dimensions is steep close to the Θ-state and flat in the regions $\xi \in \langle 0.0, 0.25\rangle$ and $\xi \in \langle 0.5, 1.0\rangle$. The simulated conformational behaviour agrees with the known behaviour of homopolymers[26].

TABLE II

The average numbers, N, of closest $N^{(1)}$ (along the cube edge), face-diagonal $N^{(2)}$, and body-diagonal $N^{(3)}$ non-bonding interactions in the same homopolymer–solvent system as in Table I; subscripts BB and BB′ stand for interactions of segments belonging to the same and different halfs of a chain, respectively, BS stands for segment–solvent interactions; $\xi_{SS} = 0$

$\langle N\rangle$	$\xi_{AA} = \xi_{BB}$				
	0	0.25	0.50	0.75	1.00
$\langle N_{BB}^{(1)}\rangle$	14.24	14.46	16.06	16.18	16.20
$\langle N_{BB'}^{(1)}\rangle$	4.20	4.31	5.52	5.60	5.61
$\langle N_{BB}^{(2)}\rangle$	68.50	68.98	72.81	73.11	73.16
$\langle N_{BB'}^{(2)}\rangle$	13.33	13.64	16.94	17.17	17.19
$\langle N_{BB}^{(3)}\rangle$	32.65	32.90	35.18	35.35	35.39
$\langle N_{BB'}^{(3)}\rangle$	9.42	9.64	11.95	12.11	12.13
$\langle N_{BS}^{(1)}\rangle$	168.32	167.78	163.38	163.04	163.00
$\langle N_{BS}^{(2)}\rangle$	449.66	448.41	437.46	436.62	436.50
$\langle N_{BS}^{(3)}\rangle$	325.29	324.56	317.70	317.20	317.10

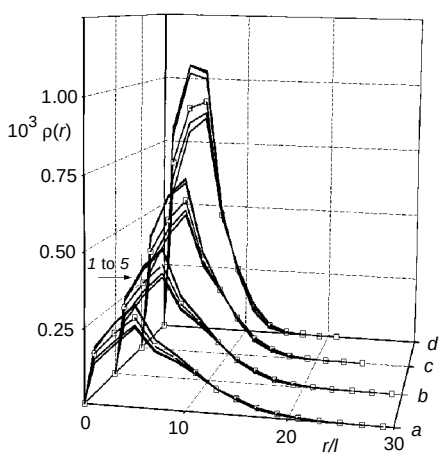

FIG. 3

Distribution functions, $\rho(r)$, of the end-to-end distances for homopolymer chains with the following numbers of segments N: 100 (*a*), 80 (*b*), 60 (*c*), 40 (*d*) for the following values of ξ: 0.0 (*1*), 0.25 (*2*), 0.5 (*3*), 0.75 (*4*) and 1.0 (*5*) indicated by the arrow. The curve for $\xi = 0.295$ (corresponding to the Θ-conditions) is indicated by ❒

Distribution functions of the end-to-end distances of homopolymer chains with increasing length, $\rho(r)$, in solvents with decreasing solvent quality are shown in Fig. 3 for the same equidistant values of ξ as in Tables I and II and for the Θ-state ($\xi = 0.295$), values of the last curve are indicated by squares. The simulated shape of $\rho(r)$ corresponds well to that for the self-avoiding chain[26]. The magnitudes of $\rho(r)$ generally decrease with increasing N which is the result of the normalisation of that function:

$$\int_0^\infty \rho(r)\, 4\pi r^2\, \mathrm{d}r = 1 \quad . \tag{4}$$

Simulated data show that the effective average volumes occupied by chains increase with increasing N faster than $V^{ef} = \text{const}\, N$. We have found for the athermal systems the following value of the scaling exponent, $\nu = 0.54$, in the relation

$$\langle r^2 \rangle = \text{const}\, N^{2\nu} \quad . \tag{5}$$

TABLE III

The average conformational characteristics of an isolated copolymer chain ($N_A = N_B = 50$) in solvents with decreasing quality for the block B (i.e., with increasing value of ξ_{BB}); $\xi_{AA} = \xi_{SS} = 0$

Characteristic	ξ_{BB}				
	0	0.25	0.50	0.75	1.00
$\langle r^2_{AB} \rangle$	178.05	182.83	178.19	173.51	170.31
$\langle r^2_{CA} \rangle$	86.06	91.92	91.96	90.64	89.51
$\langle r^2_{CB} \rangle$	86.06	81.77	76.94	74.20	72.94
$\langle s^2 \rangle$	29.26	30.02	29.34	28.67	28.22
$\langle s^2_A \rangle$	14.06	14.79	14.80	14.62	14.48
$\langle s^2_B \rangle$	14.06	13.40	12.73	12.37	12.20
$\langle t_{AT} \rangle$	7.12	7.36	7.34	7.28	7.22
$\langle t_{BT} \rangle$	7.12	7.04	6.86	6.74	6.68
$\langle t_{CT} \rangle$	3.46	3.44	3.40	3.37	3.35
$\langle t_{XY} \rangle$	7.30	7.51	7.42	7.32	7.24
$\langle \vartheta \rangle$	96.90	99.21	99.40	99.08	102.32
$\langle \omega \rangle$	94.39	95.63	95.80	95.58	95.30

This value is lower than the theoretical value, $\nu = 0.6$, for the self-avoiding chain[26], probably due to the relatively short lengths of the studied chains. A similar value was found by Fried and Binder[16] in lattice simulations for the self-avoiding chains of the finite length.

Conformational characteristics of the copolymer with $N_A = N_B = 50$ are given in Tables III and IV for several increasing values of $\xi_{BB} = 0.0$, 0.25, 0.5, 0.75 and 1.0. Behaviour of the copolymer is fairly complex. It is interesting to compare dependences of various structural characteristics on ξ_{BB} for a homopolymer B (in that case, $\xi_{BB} = \xi$) and for a copolymer AB. The deterioration of the solvent quality for segments B is accompanied by a slight contraction of the block B and by a certain segregation of both blocks. Neither the contraction of the block B, nor the blocks segregation are extensive up to quite large and positive values ξ_{BB}.

Figure 4 shows dependences of $\langle r^2_{\mathbf{AB}} \rangle$, $\langle r^2_{\mathbf{CA}} \rangle$ and $\langle r^2_{\mathbf{CB}} \rangle$ on ξ_{BB}. For comparison, $\langle r^2 \rangle$ vs ξ for a homopolymer of the same length is also shown. The decrease in $\langle r^2_{\mathbf{CB}} \rangle$ is similar to that of a homopolymer. Solvent quality for segments A remains constant,

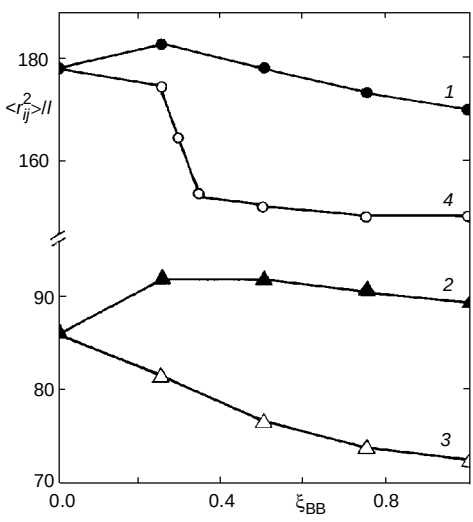

FIG. 4

Dependences of the mutual mean square distances $\langle r^2_{\mathbf{AB}} \rangle$, $\langle r^2_{\mathbf{CA}} \rangle$ and $\langle r^2_{\mathbf{CB}} \rangle$ (curves *1*, *2* and *3*, respectively) for a diblock copolymer chain with $N_A = N_B = 50$. For a comparison, the dependence of the mean square end-to-end distance, $\langle r^2 \rangle$, on ξ_{BB} for a homopolymer B with $N = 100$ is also shown (curve *4*), $\xi_{AA} = \xi_{SS} = 0$

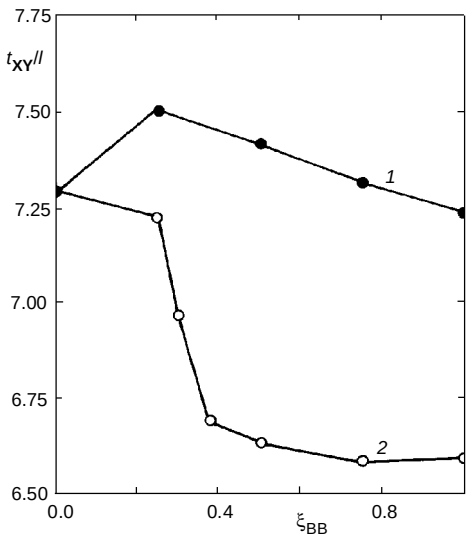

FIG. 5

Dependence of the average mutual distance, $\langle t_{\mathbf{XY}} \rangle$, of the gravity centres, **X** and **Y**, of individual blocks on increasing ξ_{BB} for a copolymer with $N_A = N_B = 50$ (*1*) and the analogical dependence of the average distances of the gravity centres of the two halves of a homopolymer chain B with $N = 100$ (*2*); $\xi_{AA} = \xi_{SS} = 0.0$

however the conformational behaviour of the block A is indirectly influenced by the diminution of the block B and the dimensions of that block pass through a maximum. Dimensions of the whole chain pass also through an insignificant maximum, however they change only little, since effect of changing block dimensions is partially compensated by the effect of the blocks segregation.

The average mutual distance of the gravity centres of both blocks, $\langle t_{\mathbf{XY}} \rangle$, is shown in Fig. 5 as a function of ξ_{BB}. For comparison, the distance of the gravity centres of the two halves of a homopolymer B is also shown. The shape with a maximum value for $\xi_{BB} = 0.25$ is a result of a combination of the segregation of blocks and the decrease in dimensions of the block B.

TABLE IV

The average numbers, $\langle N \rangle$, of various types of non-bonding interactions in the same copolymer–solvent system as in Table III; superscripts (1), (2) and (3) stand for the interactions along the edge, face-diagonal and body-diagonal of the lattice cube, respectively; subscripts A and B stand for the respective types of segments and S for the solvent; $\xi_{AA} = \xi_{SS} = 0$

$\langle N \rangle$	ξ_{BB}				
	0	0.25	0.50	0.75	1.00
$\langle N_{AA}^{(1)} \rangle$	14.24	13.20	13.21	13.46	13.65
$\langle N_{BB}^{(1)} \rangle$	14.24	15.30	16.34	16.88	17.10
$\langle N_{AB}^{(1)} \rangle$	4.20	3.56	3.62	3.78	3.92
$\langle N_{AA}^{(2)} \rangle$	68.50	66.02	66.06	66.64	67.10
$\langle N_{BB}^{(2)} \rangle$	68.50	70.98	73.44	74.70	75.26
$\langle N_{AB}^{(2)} \rangle$	13.33	11.62	11.79	12.26	12.66
$\langle N_{AA}^{(3)} \rangle$	32.65	31.18	31.20	31.53	31.81
$\langle N_{BB}^{(3)} \rangle$	32.65	34.06	35.50	36.24	36.57
$\langle N_{AB}^{(3)} \rangle$	9.42	8.27	8.40	8.74	9.03
$\langle N_{AS}^{(1)} \rangle$	168.32	171.05	170.96	170.30	169.78
$\langle N_{BS}^{(1)} \rangle$	168.32	166.84	164.72	163.48	162.87
$\langle N_{AS}^{(2)} \rangle$	449.66	456.32	456.10	454.46	453.13
$\langle N_{BS}^{(2)} \rangle$	449.66	446.41	441.34	438.34	436.83
$\langle N_{AS}^{(3)} \rangle$	325.29	329.37	329.22	328.20	327.36
$\langle N_{BS}^{(3)} \rangle$	325.29	323.61	320.61	318.78	317.84

Changes in the average numbers of interactions, $N_{AA}^{(1)}$, $N_{BB}^{(1)}$ and $N_{AB}^{(1)}$ with increasing value of ξ_{BB} are shown in Fig. 6 (the corresponding numbers of interactions for distances $\sqrt{2}l$ and $\sqrt{3}l$ are given in Table IV). Average densities of segments A and B are low, the numbers $N_{ij}^{(1)}$ are generally small and do not change much. Changes in $N_{ij}^{(1)}$ do not indicate any strong segregation of blocks.

Similar conclusions may be drawn from the distribution functions of the mutual distances of the gravity centres of both blocks, $\tau_{\mathbf{XY}}(t_{\mathbf{XY}})$, see Fig. 7. Distribution functions for relatively flexible chains with $N_A = N_B = 50$ (see Fig. 7*a*) are very broad and show significant values both for small and large values of $t_{\mathbf{XY}}$ (as compared with the average chain dimensions) – broad distributions of various structures differing significantly in the extent of the blocks segregation exist in good as well as in selective solvents.

Distribution function of the projections of the ends of the block B into the direction of the connection of blocks A and B, $f_B(\boldsymbol{p}_{\mathbf{CB}})$, (Fig. 8) is almost symmetrical and

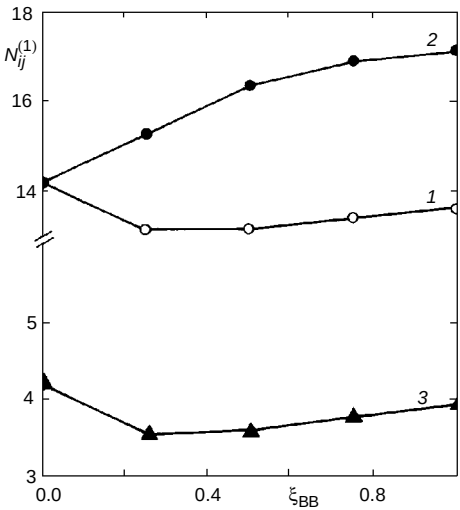

FIG. 6
Changes in the average numbers of the closest non-bonding interactions, $N_{AA}^{(1)}$ (*1*), $N_{BB}^{(1)}$ (*2*) and $N_{AB}^{(1)}$ (*3*) with increasing ξ_{BB} for a copolymer chain with $N_A = N_B = 50$, $\xi_{AA} = \xi_{SS} = 0.0$

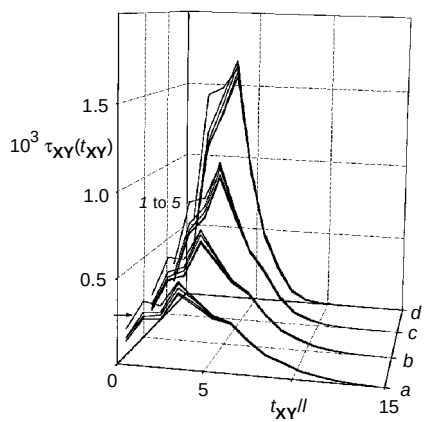

FIG. 7
Distribution functions of the mutual distances of the gravity centres, **X** and **Y**, of individual blocks, $\tau_{\mathbf{XY}}(t_{\mathbf{XY}})$ for $\xi_{AA} = \xi_{SS} = 0.0$, for copolymer chains with $N_A = N_B$ equal to: 50 (plane *a*), 40 (*b*), 30 (*c*) and 20 (*d*), respectively, and changing parameters $\xi_{BB} = 0.0$, 1.0, 0.75, 0.5 and 0.25 (the sequence of ξ_{BB} values, which is not monotonous, is indicated by the arrow)

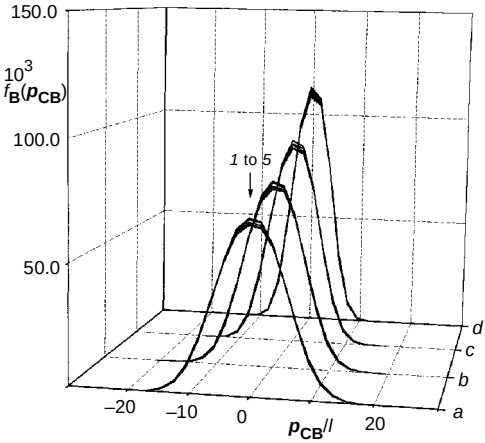

FIG. 8
Distribution functions of the projections of the vector **CB** into the direction of the bond connecting the blocks A and B, $f_B(\boldsymbol{p}_{CB})$, for the same systems as in Fig. 7. The sequence of ξ_{BB} values indicated by the arrow is the following: 0.25, 0.0, 0.5, 0.75 and 1.0

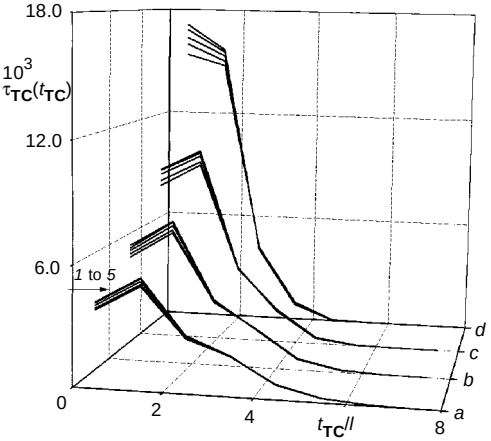

FIG. 9
Distribution functions of the distances of gravity centres, **T**, from the connection of both blocks, **C**, $\tau_{CT}(t_{CT})$, for the same systems as in Fig. 7. The sequence of ξ_{BB} values indicated by the arrow is the following: 0.0, 1.0, 0.25, 0.5 and 0.75

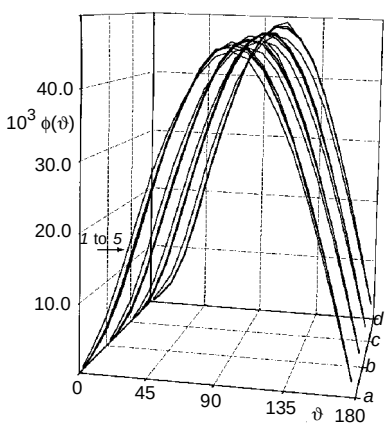

FIG. 10
Distribution functions of the angles ϑ, $\phi(\vartheta)$, for the same systems as in Fig. 7. The sequence of ξ_{BB} values indicated by the arrow is the following: 0.0, 1.0, 0.25, 0.5 and 0.75

indicate that there is no orientation effect of the bond between blocks that would promote the segregation of blocks.

Distribution function of distances of the gravity centre, **T**, of the whole chain from the connection of blocks, **C**, (the middle of the AB connection), $\tau_{\mathbf{TC}}(t_{\mathbf{TC}})$, see Fig. 9, and the distribution function of angles, ϑ, $\phi(\vartheta)$, see Fig. 10, indicate that the gravity centre of the whole flexible chain, **T**, does not coincide with the block connection, **C**. It means that the average shape of a chain reminds the letter "C". The average angle $<\vartheta>$ increases slightly with increasing ξ_{BB}.

The fact that the blocks in a copolymer form a contour similar to the letter "C", or "V" is often mentioned in the literature[18]. However the conformational characteristics for a copolymer are very similar to those for a homopolymer in a good solvent which means that the "C" shape is a result of a general conformational behaviour of flexible chains[26].

CONCLUSIONS

A) Conformational characteristics of block copolymer chains AB were studied by Monte Carlo simulations in selective solvents (very good for the block A and worsening for B) on a simple cubic lattice.

B) Simulations were performed for fully self-avoiding copolymer chains and the interactions of the first, second and third nearest neighbours were considered and their strength were recalculated according to the Lennard–Jones formula.

C) Dimensions of the block B decrease with increasing ξ_{BB} and a certain segregation of blocks A and B occurs, however neither the contraction of the block B, nor the blocks segregation are significant. Various chain structures similar to the letter "C" with a broad distribution in the extent of the blocks segregation exist in solutions.

D) The average "C" shape of the copolymer chain is a result of the general behaviour of flexible chains.

E) We believe that our model describes well the behaviour of realistic chains in selective solvents. The obtained results of Monte Carlo simulations agree with conclusions of several other authors[18–20,27] that the changes in copolymer chain conformations with deteriorating quality of the solvent for the block B are smooth and continuous and that the formation of unimolecular micelles with strongly segregated blocks in dilute solutions is improbable.

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