

Lateral Ordering during Self-Organization of Statistical Multiblock Copolymers¹

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Abstract—The self-organization of statistical multiblock and Bernoulli AB copolymers is studied. The initial ensemble is generated via the polymer-analogous reaction $A \rightarrow B$ that proceeds with the accelerating effect of neighboring B units. In a two-dimensional model, the reaction is performed in a rectangle composed of stretched chains. Then, the rectangle is closed into a cylinder, so that ring chains are located on its side surface. The self-organization of the ensemble is simulated via the successive rotation of each upper ring over the lower ring until arrangement with the maximum (in modulus) energy of attraction between chains is attained. Self-organization by energy is accompanied by lateral ordering: the sizes of clusters—accumulations of the one-type units—and mean heights H_A (H_B) of stems—columns consisting of A or B units perpendicular to chains—increase. The ratio between the values of H_A , as well as H_B , for ordered and initial ensembles is independent of the average composition of the system and as a rule increases as the length of blocks increases and the length of chains decreases. Features of generation of the ensemble of short chains and their ordering are revealed. It is shown that, during ordering of multiblock copolymers, the probabilistic properties (the stochastic behavior) of the ensemble are disturbed. The self-organization of statistical multiblock copolymers in a three-dimensional model is investigated via rotation of rings in the torus of the rectangular cross-section. The effects of various factors on self-organization by energy and local ordering in 2D and 3D models are similar; however, the efficiency of ordering in the three-dimensional system is always lower because, in this case, arrangements with the maximum energy of attraction simultaneously to two neighboring chains, rather than to one, are implemented for the majority of chains.

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INTRODUCTION

Regular di- and multiblock AB copolymers easily form ordered structures via microsegregation if interchain contacts of A and B units are unfavorable [1, 2]. In addition, irregular (statistical) copolymers are capable of self-organization, although any disorder in the distribution over block length hampers ordering [3]. The phase behavior of statistical copolymers is intensively studied both from the viewpoint of theory (e.g., in terms of mean-field approaches [4–7]) and with the use of Monte Carlo simulations [8, 9] and dissipative particle dynamics [10, 11]. Theoretical analysis predicts macrophase or microphase separation, depending on the value of the parameter of correlations along chain, $\lambda = P_{A \rightarrow A} + P_{B \rightarrow B} - 1$ (where $P_{A \rightarrow A}$ and $P_{B \rightarrow B}$ are conditional probabilities to find unit A on the right of A and unit B on the right of B, respectively) and the parameter of interaction between A and B units. However, the results of theoretical calculations are in conflict with simulation results [9]. The larger the number of blocks in a chain or the longer the

chain, the higher this discrepancy. These discrepancies indicate that there is a need to analyze ordering in statistical copolymers in more detail.

The ordering of stretched chains in Bernoulli copolymers was investigated both via Monte Carlo simulation and with the use of analytical approaches, methods of the probability theory [12]. The results of these studies are in good agreement, so that a simple Monte Carlo technique, which will be described in the next section, may be recommended for the study of self-organization of copolymers of other classes, for which the analytical approach is extremely complicated (if not impossible).

Recently [13], Monte Carlo simulation was used to examine the self-organization of statistical multiblock copolymers. This class of copolymers, which are of considerable interest for both fundamental science and practical application, has been poorly studied. An efficient method for the synthesis of statistical multiblock copolymers involves the interchain exchange between condensation polymers [14, 15]. However, the interchain-exchange reaction is complex for simulation of self-organization because the reaction event is accompanied by a change in the chain length, so

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that the initial ensemble generated via the exchange reaction is polydisperse. Therefore, the polymer-analogous reaction was selected for simulation.

MODEL AND ORDERING ALGORITHM

The initial ensemble of chains of equal lengths was generated via simulation of the polymer-analogous reaction $A \rightarrow B$ that proceeds with the accelerating effect of neighboring units B. In [16], in the two-dimensional (2D) model, the reaction was performed in a rectangle containing M stretched chains with a length of N units. The values of M and N were varied within 1000–50000 and 20–1000. In this case, the total number of units was kept constant: $M \times N = 1\,000\,000$.

The distribution over the lengths of A and B blocks in a chain averaged over the whole ensemble was determined from rate-constant ratio $k_0 : k_1 : k_2$ for the transformation of A units having 0, 1, and 2 B neighbors, respectively. (In fact, ratios $c_0 : c_1 : c_2 = k_0 : k_1 : k_2$, where $c_0 + c_1 + c_2 = 1$, were changed.) Interchain interaction was set in terms of the energy of pairwise attraction between units: ε_{AA} , ε_{BB} , and ε_{AB} ($\varepsilon_{ij} < 0$).

Self-organization was simulated via transformation of the rectangle into a cylinder through superposition of its parallel sides containing chain ends. In this case, chains were transformed into rings of N units and, then, each upper ring was rotated above each lower ring into the arrangement with the maximum (in modulus) energy of attraction between them.

For the 2D model, the master relation was found for self-organization by energy [13]:

$$\Delta\varepsilon = \chi\Delta\varphi_{AB}, \quad (1)$$

where $\Delta\varepsilon$ is the change in the mean energy of interchain attraction per contact, $\Delta\varphi_{AB}$ is the change in the mean fraction of contacts AB, and $\chi = \varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2$ is the Flory–Huggins parameter. Relationship (1) was fulfilled in all numerical calculations (experiments). Equations relating fractions φ_{AA} , φ_{BB} , and φ_{AB} of interchain contacts AA, BB, and AB were derived as well.

The Monte Carlo technique was used to determine the following values averaged over the whole ensemble:

(i) Parameters of chain structure: the mean lengths of A and B blocks, l_A and l_B ; the probability of the boundary between blocks, R ; and the numbers of A blocks and B blocks of different lengths (i.e., the distribution over block length).

(ii) Parameters of interchain interaction: the fractions of interchain contacts, φ_{AA} , φ_{BB} , and φ_{AB} ; the mean energy of interchain interaction per contact, ε .

Parameters of interchain interaction were calculated before and after ordering, for example, φ_{AA}^{in} and $\varphi_{AA}^{\text{opt}}$. These data made it possible to analyze the dependence of self-organization coefficient $\Delta\varepsilon/\varepsilon^{\text{in}}$ ($\Delta\varepsilon =$

$\varepsilon^{\text{opt}} - \varepsilon^{\text{in}}$, where ε^{in} and ε^{opt} are the mean attraction energies per contact in the initial and ordered ensembles, respectively) on various parameters and to compare simulation results with theoretical relationships. Self-organization coefficient $\Delta\varepsilon/\varepsilon^{\text{in}}$, which characterizes the efficiency of ordering over energy, is determined by the structure and length of chains and by interchain interactions. Deviations of $\Delta\varphi_{AB}$ and $\Delta\varepsilon/\varepsilon^{\text{in}}$ from purely random values become, as a rule, much more pronounced with an increase in the length of blocks and a decrease in the length of chains.

However, for ensembles of short chains in statistical multiblock copolymers ($N = 20$) generated at a strong accelerating effect of neighboring units ($c_0 : c_1 : c_2 = 1 : 50 : 100$), the value of $\Delta\varepsilon/\varepsilon^{\text{in}}$ sharply decreases owing to two causes. First, this ensemble is strongly heterogeneous with respect to chain composition p (the fraction of units A): It contains many chains of homopolymers, which during self-organization make no contribution to the value of $\Delta\varepsilon/\varepsilon^{\text{in}}$. Second, on short chains there is not enough room for the formation of long blocks that appear during marked acceleration of the reaction. Thus, simulation and theoretical analysis make it possible to reveal the main relationships for self-organization of statistical multiblock copolymers over energy and the features for generation of ensembles of short chains and their ordering [13].

In this study, the simulation program was substantially modified. The new version makes it possible to form images of initial and ordered ensembles.

Figure 1 compares images obtained for ensembles of multiblock copolymer chains ($c_0 : c_1 : c_2 = 1 : 50 : 100$) before and after ordering. Accumulations of one-type units, clusters, are seen. After ordering, their number decreases, while mean size increases. Note that the growth of clusters along the vertical is especially pronounced. Perpendicular to stretched chains, N bands of height M contain columns of A or B units (A stems or B stems), and, after self-organization via rotation of rings, the height of stems increases on average. Hence, in addition to ordering over energy along chains, *lateral* ordering occurs and results in the formation of nanoclusters composed of one-type units in the polymer bulk. In fact, such clusters play the role of interchain physical crosslinks and, as expected, will strongly affect the mechanical properties of the polymer material.

Therefore, the modified program provides for calculations of parameters characterizing lateral ordering: ensemble average heights H_A and H_B of stems A and B; the total numbers of A and B stems; and, more importantly, the number of stems of different heights, that is, distributions over the heights of A and B stems. These values were calculated before and after ordering, for example, H_A^{in} and H_A^{opt} and H_B^{in} and H_B^{opt} .

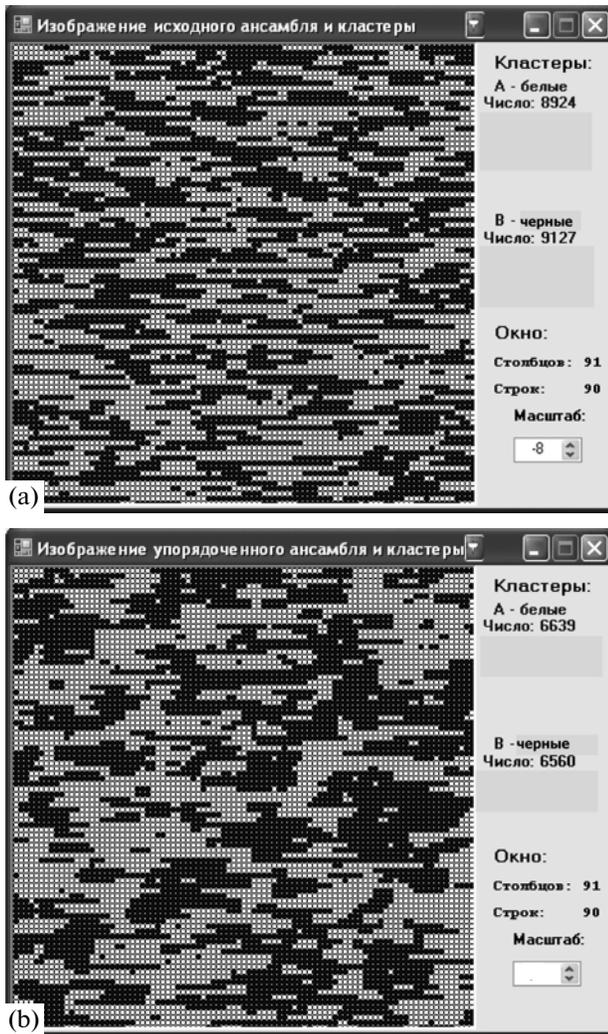


Fig. 1. Images of (a) initial and (b) ordered ensembles of the statistical multiblock copolymer for the 2D model: $N = 100$, $M = 10000$, $p = 0.50$, $c_0 : c_1 : c_2 = 1 : 50 : 100$; $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, and $\varepsilon_{AB} = -0.1$.

SIMULATION RESULTS

Lateral Ordering in the 2D System

The efficiency of lateral ordering may be quantitatively characterized by ratios $H_A^{\text{opt}}/H_A^{\text{in}}$ and $H_B^{\text{opt}}/H_B^{\text{in}}$ (hereinafter, lateral ordering coefficients). In Table 1, these parameters are compared for fully random (Bernoulli) copolymers and statistical multiblock copolymers of various compositions.

Table 1 shows that the coefficients of lateral ordering are independent of copolymer composition p , unlike coefficient $\Delta\varepsilon/\varepsilon^{\text{in}}$ of self-organization by energy along the direction of chains whose value is maximum at $p = 0.50$ [13]. In all cases, $H_A^{\text{opt}}/H_A^{\text{in}} = H_B^{\text{opt}}/H_B^{\text{in}}$ and the coefficients of ordering for the multiblock copolymer are higher than those for a fully random copoly-

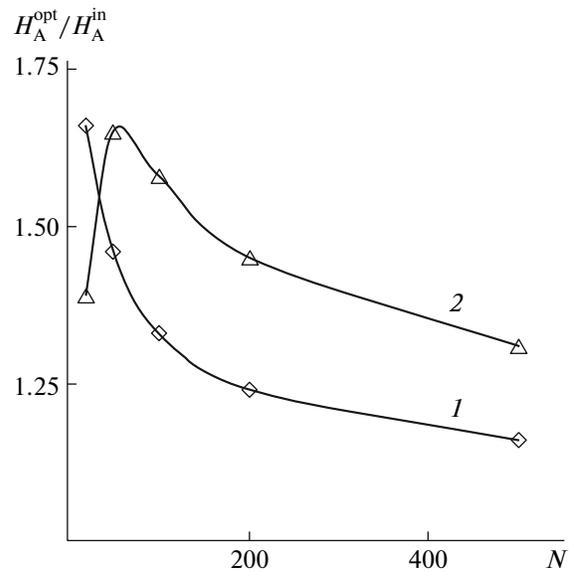


Fig. 2. Coefficient $H_A^{\text{opt}}/H_A^{\text{in}}$ of lateral ordering vs. chain length N for (1) the Bernoulli copolymer and (2) the multiblock copolymer: $c_0 : c_1 : c_2 =$ (1) $1 : 1 : 1$ and (2) $1 : 50 : 100$; $N \times M = 1000000$; $p = 0.50$; $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, $\varepsilon_{AB} = -0.1$.

mer. Thus, the presence of long blocks in chains is favorable for lateral ordering.

As is seen from Fig. 2, for a fully random copolymer, $H_A^{\text{opt}}/H_A^{\text{in}}$ monotonically increases as chain length decreases. For the statistical multiblock copolymer, the coefficient of lateral ordering initially increases and then declines abruptly, so that, at $N = 20$, this ratio is smaller than that for the Bernoulli copolymer of the same length. A sharp reduction in $H_A^{\text{opt}}/H_A^{\text{in}}$ in the interval $50 \geq N \geq 20$ has the same causes as a drop in coefficient $\Delta\varepsilon/\varepsilon^{\text{in}}$ of self-organization by energy [13]: the presence of a considerable amount of homopolymers in the ensemble and an insufficient amount of room on short chains for formation of long blocks favorable for ordering.

With the use of the modified program, the total number of stems A and B and the number of stems of different heights before and after ordering were calculated. The value of this information becomes evident when the theoretical distribution over the stem height is compared with simulation data.

For this purpose, let us estimate probability $P(\text{BA}_i\text{B})$ to find A stems with heights of i units. On the one hand, the number of such stems may be divided by the total number of columns containing A and B units with heights $i + 2$:

$$P(\text{BA}_i\text{B}) = a_i / [(M - i - 1)N], \quad (2)$$

where N is the chain length, M is the number of chains, and a_i is the number of A stems with heights of i units. In fact, the ensemble contains N vertical bands

Table 1. Coefficients of lateral ordering $H_A^{\text{opt}}/H_A^{\text{in}}$ and $H_B^{\text{opt}}/H_B^{\text{in}}$ for the Bernoulli copolymer ($c_0 : c_1 : c_2 = 1 : 1 : 1$) and multi-block copolymer ($c_0 : c_1 : c_2 = 1 : 50 : 100$) at various compositions p ($N = 100$, $M = 10000$, $\epsilon_{AA} = -1.0$, $\epsilon_{BB} = -1.0$, $\epsilon_{AB} = -0.1$, and $\chi = 0.9$)

Experiment	$c_0 : c_1 : c_2$	p	H_A (in/opt)	$H_A^{\text{opt}}/H_A^{\text{in}}$	H_B (in/opt)	$H_B^{\text{opt}}/H_B^{\text{in}}$
1	1 : 1 : 1	0.50	1.998/2.659	1.33	1.998/2.659	1.33
2	1 : 1 : 1	0.80	4.995/6.766	1.35	1.249/1.692	1.35
3	1 : 1 : 1	0.20	1.251/1.693	1.35	5.002/6.769	1.35
4	1 : 50 : 100	0.50	2.005/3.187	1.59	2.005/3.187	1.59
5	1 : 50 : 100	0.80	4.981/7.880	1.58	1.246/1.971	1.58
6	1 : 50 : 100	0.20	1.250/2.019	1.62	4.997/8.074	1.62

with heights of M units. In this band, $M - i - 1$ columns with heights of $i + 2$ units may be chosen and the total number of such columns is $(M - i - 1)N$, among which a_i columns are BA_iB stems.

On the other hand, $P(BA_iB)$ may be calculated with the use of conditional probabilities:

$$P(BA_iB) = (1 - p)P_{B \rightarrow A}(P_{A \rightarrow A})^{i-1}P_{A \rightarrow B} \quad (3)$$

In fact, the probability of such a stem is equal to the product of (i) the probability of finding a B unit ($1 - p$), (ii) the conditional probability of finding an A unit over a B unit ($P_{B \rightarrow A}$), (iii) the conditional probability of finding an A unit over an A unit ($P_{A \rightarrow A}$) raised to the power of $i - 1$, and (iv) the conditional probability of finding a B unit over an A unit ($P_{A \rightarrow B}$).

Conditional probabilities are calculated from the fractions of interchain contacts:

$$\begin{aligned} P_{B \rightarrow A} &= \varphi_{BA}/(\varphi_{BA} + \varphi_{BB}), P_{A \rightarrow B} = \varphi_{AB}/(\varphi_{AB} + \varphi_{AA}) \\ P_{A \rightarrow A} &= \varphi_{AA}/(\varphi_{AA} + \varphi_{AB}), P_{B \rightarrow B} = \varphi_{BB}/(\varphi_{BA} + \varphi_{BB}), \end{aligned} \quad (4)$$

and $\varphi_{AB} = \varphi_{BA}$ in this case.

From Eqs. (2) and (3), we have

$$a_i = (M - i - 1)N(1 - p)P_{B \rightarrow A}(P_{A \rightarrow A})^{i-1}P_{A \rightarrow B} \quad (5)$$

The numerical fraction of A stems with heights of i units from the total number of A stems is

$$f^{\text{calc}}(a_i) = a_i / \sum_{i=1}^{M-2} a_i, \quad (6)$$

where a_i is set by expression (5).

In addition, the height distribution of stems may be computed through the direct calculation of a_i from the Monte Carlo simulation:

$$f^{\text{MC}}(a_i) = a_i / \sum_{i=1}^{M-2} a_i \quad (7)$$

Similar dependences $f^{\text{calc}}(b_i)$ and $f^{\text{MC}}(b_i)$ describe distributions over the heights of B stems. For the statistical ensemble, both calculation procedures should be equivalent.

Let us compare distributions over the heights of stems obtained through these methods for Bernoulli and multiblock copolymers. As is seen from Fig. 3, for the Bernoulli copolymer of the composition $p = 0.5$, coincident results were obtained both before and after ordering. (Note that, for an equimolar system, the corresponding distributions of A and B stems are the same.)

For the Bernoulli copolymer of the composition $p = 0.8$ (Fig. 4), the height distributions of A and B stems are different, but the results of calculations via both methods coincide for both initial and ordered ensembles.

Figure 5 compares distributions over stem height for the multiblock copolymer ($c_0 : c_1 : c_2 = 1 : 50 : 100$) of the composition $p = 0.50$ that were likewise derived

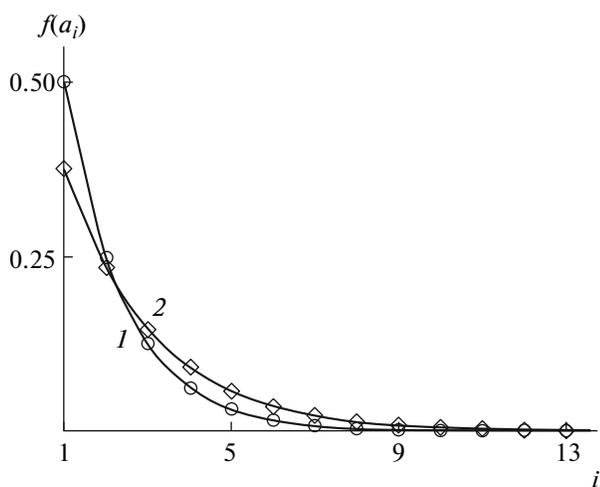


Fig. 3. Distribution $f(a_i)$ over height i of A stems for the Bernoulli copolymer of the composition $p = 0.50$ from (symbols) simulation data and (curves) fractions of contacts φ_{ij} in (1) initial and (2) ordered ensembles.

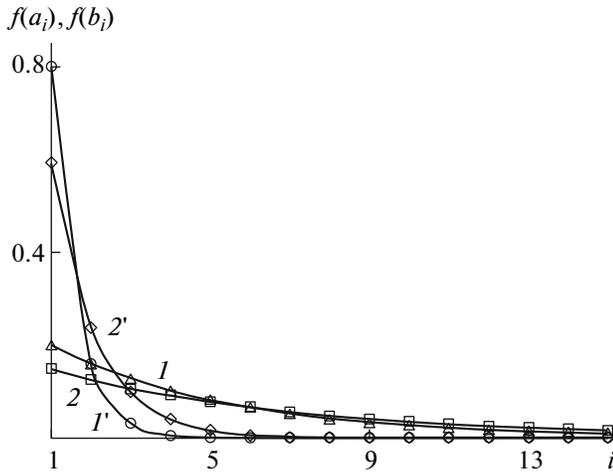


Fig. 4. Distribution over height i of A stems $f(a_i)$ and B stems $f(b_i)$ for the Bernoulli copolymer of the composition $p = 0.80$ from (symbols) simulation data and (curves) fractions of contacts ϕ_{ij} in (I , I') initial and (2 , $2'$) ordered ensembles: (I , 2) A stems and (I' , $2'$) B stems.

through two methods. In the case of the initial ensemble, similar results were obtained, whereas for the ordered ensemble, the fractions of stems with heights of one unit (single stems) were different.

A similar picture is observed for the statistical multiblock copolymer of the composition $p = 0.8$: The fractions of single A and B stems calculated through different methods coincide for the initial ensemble and are different for the ordered ensemble (Fig. 6).

During discussion of the causes of such a discrepancy, above all, a question arises about whether the size of the ensemble is sufficient for its characteristics (in this case, the distribution over stem height) to be calculated in probability terms. Table 2 lists the data on fractions $f^{\text{MC}}(a_1)$ and $f^{\text{calc}}(a_1)$ of single A stems in relation to the number of chains M that are derived through both methods.

Here, $\Delta f(a_1) = f^{\text{MC}}(a_1) - f^{\text{calc}}(a_1)$ and the discrepancy is expressed as a percentage of the value estimated from the amount of single stems a_1 . It is clear that, for initial ensembles, this value is below 1%. For the ordered ensemble of a fully random copolymer, the discrepancy is of the same order of magnitude, whereas for the ordered ensemble of the multiblock copolymer, this parameter is $\sim 8.5\%$ and does not decrease as the number of chains is increased by two orders of magnitude from 1000 to 100 000. Hence, the cause of the discrepancy between the two methods used to estimate the fraction of single stems is not related to a small size of the ensemble.

The observed disturbance of the probabilistic, stochastic character of the ensemble of the statistical multiblock copolymer seems to be a substantial consequence of ordering. Note that, in the case of Bernoulli copolymers, ordering does not entail such conse-

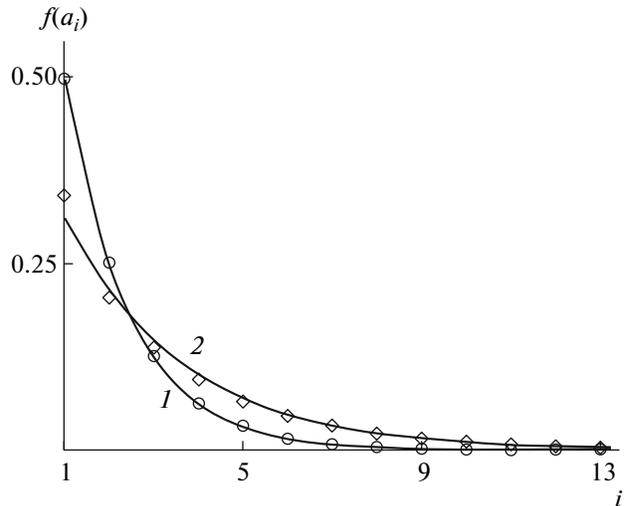


Fig. 5. Distribution $f(a_i)$ over height i of A stems for the multiblock copolymer ($c_0 : c_1 : c_2 = 1 : 50 : 100$) of the composition $p = 0.50$ from (symbols) simulation data and (curves) fractions of contacts ϕ_{ij} in (I) initial and (2) ordered ensembles.

quences. It may be suggested that the disturbance of the stochastic behavior will manifest itself also in the study of other properties of multiblock copolymers. In this situation, adequate information about the ensemble structure is provided only by the direct calculation of structure parameters from the results of the Monte Carlo simulation that should be used for comparison with the experiment.

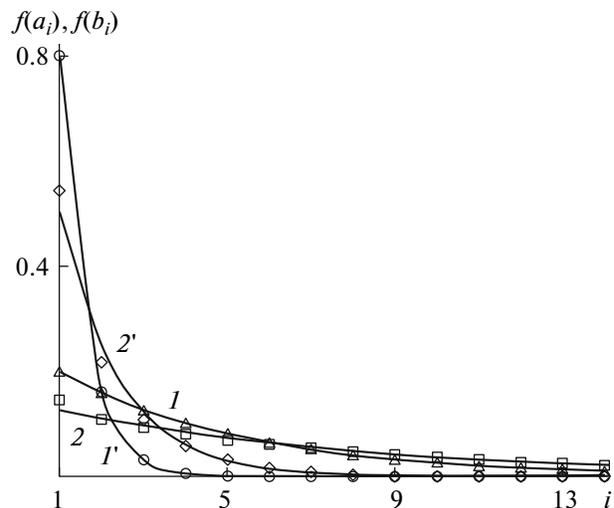


Fig. 6. Distributions over heights i of A stems, $f(a_i)$, and of B stems, $f(b_i)$, for the multiblock copolymer ($c_0 : c_1 : c_2 = 1 : 50 : 100$) of the composition $p = 0.80$ from (symbols) simulation data and (curves) fractions of contacts ϕ_{ij} in (I , I') initial and (2 , $2'$) ordered ensembles: (I , 2) A stems and (I' , $2'$) B stems.

Table 2. Effect of number of chains M on lateral ordering ($N = 100$, $p = 0.50$, $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, and $\varepsilon_{AB} = -0.1$)

Fraction of single A stems	$c_0 : c_1 : c_2$	Values of f for different M^*		
		10^3	10^4	10^5
$f^{MC}(a_1)$	1 : 1 : 1	0.502/0.379	0.500/0.376	0.500/0.376
	1 : 50 : 100	0.502/0.338	0.501/0.345	0.500/0.344
$f^{calc}(a_1)$	1 : 1 : 1	0.500/0.375	0.500/0.375	0.500/0.376
	1 : 50 : 100	0.502/0.311	0.500/0.314	0.500/0.314
$\frac{\Delta f(a_1)}{f^{MC}(a_1)} \times 100\%$	1 : 1 : 1	0.4/1.0	0.0/0.3	0/0
	1 : 50 : 100	0.1/8.0	0.2/9.0	0.0/8.7

* Here, the first number refers to the initial ensemble and the second number refers to the ordered ensemble.

Self-Organization of Statistical Copolymers in the 3D System

In the three-dimensional model, the initial statistical ensemble of the multiblock copolymer was formed as a rectangular parallelepiped. Initially, M chains of homopolymer A composed of N units of each chain were put in the horizontal layer, and, in total, K such layers were constructed. In most experiments, it was assumed that $N \times M \times K = 1000000$. Then, as in the 2D case, reaction $A \rightarrow B$ was performed until the desired value of p , the molar fraction of A units in copolymer chain, averaged over the ensemble was attained.

For ordering by energy, the ends of each chain were connected and the parallelepiped was transformed into the torus of the rectangular cross section. Each ring chain of length N was rotated until attainment of the position in which the absolute value of the energy of its attraction to previously "stacked" chains was maximum. The position of the first chain in the first layer of the parallelepiped was initially fixed. The second and subsequent chains of this layer were succes-

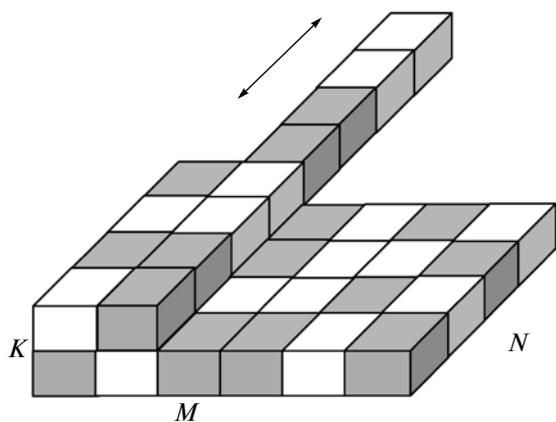


Fig. 7. Algorithm of ordering of periodic chains in the 3D model; N is the chain length, M is the number of chains in a layer, and K is the number of layers. Arrows show the possible directions of motion of the incorporated chain.

sively ordered, and, each time, the bond energy of only two adjacent chains was taken into account. The first chain of the second layer and the first chain of each subsequent layer were ordered relative to the first chain of the preceding layer. All other chains, which represented the absolute majority, were ordered relative to two chains: the preceding chain of its layer and the corresponding (having the same number) chain of the preceding layer.

As was mentioned in [12], the rotation of rings during ordering is equivalent to the sliding of periodic chains. Hence, the initial ensemble in the form of the torus is equivalent to the rectangular parallelepiped with periodic boundary conditions along the direction of stretched chains. This analogy makes it possible to visually illustrate the self-organization process. Figure 7 shows embedding of the second chain of the second layer into the ordered structure being formed. Because of periodicity, this structure is composed of two identical chains of lengths $N = 4$, and the position with the maximum (in modulus) energy of attraction to two neighboring chains that have been already stacked was found with the use of sliding: the first chain of the second layer and the second chain of the first layer. This process simulates the formation of ordered structures through the successive adjustment of copolymer chains, for example, via formation of crystallites from melt under equilibrium conditions.

Let us consider the effects of various factors on the efficiency of copolymer ordering in the three-dimensional model system relative to those in the two-dimensional model.

Figure 8 shows that, in the 3D system, the efficiency of ordering monotonically increases with a decrease in N for the fully random copolymer but sharply decreases in the region of short chains ($N = 20$) for the multiblock copolymer, as in the 2D system [13].

Note that, at all N values, the corresponding values of $\Delta\varepsilon/\varepsilon^{in}$ obtained for the 3D system are smaller than those for the 2D system. This phenomenon is due to the fact that the position with the maximum (with

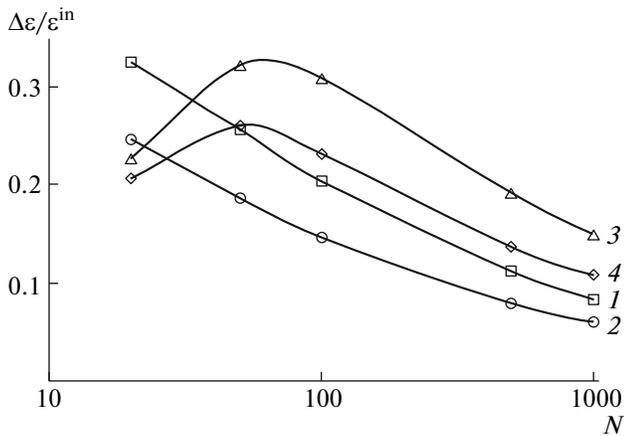


Fig. 8. Effect of chain length N on ordering efficiency $\Delta\varepsilon/\varepsilon^{\text{in}}$ for (1, 2) the Bernoulli copolymer and (3, 4) the multiblock copolymers for (1, 3) 2D and (2, 4) 3D systems: $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, $\varepsilon_{AB} = -0.1$; $p = 0.50$; $\chi = 0.9$, and (2D) $M \times N = 1000000$ and (3D) $M \times N = 10000$, $K = 100$.

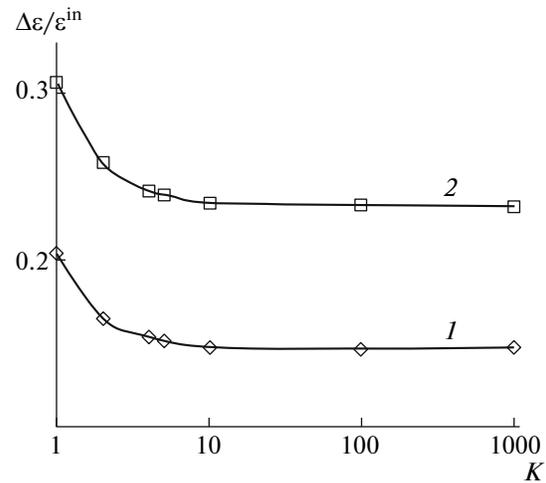


Fig. 9. Effect of number of layers K on ordering efficiency $\Delta\varepsilon/\varepsilon^{\text{in}}$ for (1) Bernoulli and (2) multiblock copolymers in the 3D system: $N = 100$, $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, $\varepsilon_{AB} = -0.1$; $p = 0.50$, and $M \times K = 10\,000$.

respect to the modulus) energy of attraction of the tested chain to two neighboring chains (a “two-contact” chain) in general does not coincide with positions corresponding to the maxima of attraction between chain pairs separately. In addition, these features become apparent when 2D and 3D systems are compared.

Figure 9 illustrates the effect of the number of layers, K , on the efficiency of ordering in the 3D system for Bernoulli and multiblock copolymers. It is seen that, with a change in K from 1 to 2 (the transition from 2D to 3D), ordering efficiency $\Delta\varepsilon/\varepsilon^{\text{in}}$ significantly decreases (by 19 and 15.6% for random and multiblock copolymers). With a further increase in K , this effect decrease abruptly and, in the range $10 < K < 1000$, the value of $\Delta\varepsilon/\varepsilon^{\text{in}}$ remains almost unchanged. This phenomenon may be explained by the fact that, as K increases (at the fixed value of $K \times M = 10000$), the fraction of “two-contact” chains first increases, while in the range $10 < K < 1000$, it remains practically invariable. For the multiblock copolymer, the values of $\Delta\varepsilon/\varepsilon^{\text{in}}$ are higher (by 24%) and their reduction is

smaller (by 27.5%) than those for the Bernoulli copolymer.

Calculations showed that the dependence of $\Delta\varepsilon/\varepsilon^{\text{in}}$ on copolymer composition passes through a maximum at $p = 0.50$. It is noteworthy that the efficiency of ordering for the multiblock copolymer is always higher than that for the Bernoulli copolymer. Note that similar dependences were described for the 2D system [13], and the corresponding efficiencies of ordering $\Delta\varepsilon/\varepsilon^{\text{in}}$ turn out to be higher than those for the 3D system.

Table 3 lists the values of $\Delta\varepsilon/\varepsilon^{\text{in}}$ for different combinations of energy parameters ε_{ij} at $N = 100$, $M = 100$, $K = 100$, and $p = 0.50$. In experiments 1 and 2, the Flory–Huggins parameter was taken to be the same ($\chi = 0.05$); however, one combination of ε_{ij} led to the energy per contact $\varepsilon^{\text{in}} = -0.825$ (experiment 1), while another combination led to $\varepsilon^{\text{in}} = -0.125$ (experiment 2). Since, in experiments 1 and 2, the values of $\Delta\varphi_{AB}$ and, in accordance with master relation of ordering (1), the values of $\Delta\varepsilon = \chi\Delta\varphi_{AB}$ are the same, the value of $\Delta\varepsilon/\varepsilon^{\text{in}}$ is much higher in experiment 2. The same relations were observed for experiments 3

Table 3. Effect of combination of energy parameters ε_{ij} on the efficiency of ordering $\Delta\varepsilon/\varepsilon^{\text{in}}$ in the 3D system ($N = 100$, $M = 100$, $K = 100$, and $p = 0.50$)

Experiment	$c_0 : c_1 : c_2$	$\varepsilon_{AA}, \varepsilon_{BB}, \varepsilon_{AB}$	χ	$\Delta\varphi_{AB}$	ε^{in}	$\Delta\varepsilon$	$\Delta\varepsilon/\varepsilon^{\text{in}}$
1	1 : 50 : 100	-1.0; -0.7; -0.8	0.05	0.141	-0.825	0.0070	0.009
2	1 : 50 : 100	-0.2; -0.1; -0.1	0.05	0.141	-0.125	0.0070	0.056
3	1 : 50 : 100	-0.6; -0.5; -0.1	0.45	0.140	-0.325	0.0630	0.194
4	1 : 50 : 100	-1.0; -1.0; -0.55	0.45	0.141	-0.775	0.0633	0.082
5	1 : 1 : 1	-0.1; -0.5; -0.3	0	0.002	-0.300	0	0
6	1 : 50 : 100	-0.1; -0.5; -0.3	0	-0.001	-0.300	0	0

Table 4. Coefficients of horizontal lateral ordering $H_{Ah}^{\text{opt}}/H_{Ah}^{\text{in}}$ and $H_{Bh}^{\text{opt}}/H_{Bh}^{\text{in}}$ for Bernoulli and multiblock copolymers of various compositions p ($N = 100$, $M = 100$, $K = 100$, $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, $\varepsilon_{AB} = -0.1$, and $\chi = 0.9$)

Experiment	$c_0 : c_1 : c_2$	p	H_{Ah} (in/opt)	$H_{Ah}^{\text{opt}}/H_{Ah}^{\text{in}}$	H_{Bh} (in/opt)	$H_{Ah}^{\text{opt}}/H_{Ah}^{\text{in}}$
1	1 : 1 : 1	0.20	1.246/1.528	1.23	4.807/5.848	1.22
2	1 : 1 : 1	0.50	1.980/2.397	1.21	1.981/2.398	1.21
3	1 : 1 : 1	0.80	4.817/5.851	1.21	1.249/1.530	1.22
4	1 : 50 : 100	0.20	1.244/1.770	1.42	4.801/6.733	1.40
5	1 : 50 : 100	0.50	1.973/2.737	1.39	1.971/2.734	1.39
6	1 : 50 : 100	0.80	4.796/6.493	1.35	1.245/1.709	1.37

Table 5. Effect of number of layers K on the ratios of the mean heights of horizontal and vertical stems, H_{Ah}/H_{Av} and H_{Bh}/H_{Bv} , in the ordered ensemble ($N = 100$, $M = 100$; $c_0 : c_1 : c_2 = 1 : 50 : 100$, $p = 0.5$, $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, and $\varepsilon_{AB} = -0.1$)

Experiment	K	H_{Ah}	H_{Av}	H_{Ah}/H_{Av}	H_{Bh}	H_{Bv}	H_{Bh}/H_{Bv}
1	10	2.783	2.379	1.17	2.786	2.383	1.17
2	20	2.738	2.562	1.15	2.735	2.535	1.08
3	30	2.759	2.629	1.05	2.757	2.627	1.05
4	50	2.743	2.681	1.02	2.745	2.685	1.02
5	75	2.735	2.713	1.01	2.736	2.713	1.01
6	100	2.397	2.402	1.00	2.398	2.402	1.00

and 4. However, as parameter χ is increased to 0.45, the corresponding values of $\Delta\varepsilon$ and $\Delta\varepsilon/\varepsilon^{\text{in}}$ tend to increase. Note that ordering in experiments 1–4 yielded practically the same values of $\Delta\varphi_{AB}$, regardless of the value of χ (at $\chi > 0$). Experiments 5 and 6 were performed with χ set exactly equal to zero. For the fully random copolymer and multiblock copolymer, $\Delta\varphi_{AB} \neq 0$, whereas, in accordance with master relation (1), $\Delta\varepsilon = 0$. This result implies that there are at least two configurations of the examined ensemble that have the same energy per contact, for which $\varepsilon^{\text{opt}} = \varepsilon^{\text{in}}$. Similar relationships were fulfilled for the 2D system [13].

It should be emphasized that master relation of ordering (1) holds true for all simulation experiments in the 3D system. Moreover, relations derived for the 2D system [13] for fractions of contacts φ_{AA} , φ_{AB} , and φ_{BB} are valid.

Lateral Ordering in the 3D System

Lateral ordering in the 3D system can be described in terms of mean heights of horizontal and vertical stems that are calculated before and after self-organization of the ensemble by energy. Then, the results of 3D simulation are compared for Bernoulli and multiblock copolymers and are correlated with the data obtained for the 2D system.

Table 4 presents the results of simulation at $M = K = 100$, when the number of chains in a layer is equal

to the number of layers. In this “symmetric” case, the coefficients of horizontal and vertical lateral ordering are the same. As in the case of the 2D system, the coefficients of lateral ordering are independent of the copolymer composition; for the statistical multiblock copolymer, these parameters are higher than those for the random copolymer. Moreover, for the 3D system, they are smaller than those for the 2D system.

The effect of number of layers K on the ratio between heights of horizontal and vertical stems is exemplified by the ordered ensemble of the statistical multiblock copolymer (Table 5). Naturally, at fixed chain length N and number of chains M in a layer, the difference between the mean heights of horizontal and vertical stems decreases with an increase in number of layers K ; it is important that, beginning from $K = 0.5M$, this difference does not exceed 2% for the ordered ensemble.

Table 6 summarizes the data on the effect of the number of chains in the model system on the number of single horizontal A stems. The discrepancy between the values of a_{1h}^{MC} and a_{1h}^{calc} calculated directly from the simulation data and with the use of the fractions of interchain contacts, respectively, decreases with an increase in number of chains $M \times K$. However, even at $M \times K = 10^6$, for the ordered ensemble of the multiblock copolymer, the discrepancy is 5%. This result implies that the disturbance of the stochastic character of the ensemble as a result of ordering, a phenomenon

Table 6. Effect of number of chains $M \times K$ on the number of horizontal single A stems calculated directly from the simulation data (a_{1h}^{MC}) and with the use of fraction of interchain contacts (a_{1h}^{calc}) for initial and ordered ensembles (3D system, $N = 100$, $p = 0.50$, $\varepsilon_{AA} = -1.0$, $\varepsilon_{BB} = -1.0$, and $\varepsilon_{AB} = -0.1$)

Number of A stems	$c_0 : c_1 : c_2$	Value a_{sh} at different $M \times K$		
		100	330	1000
a_{1h}^{MC}	1 : 1 : 1	1.279/0.867	1.370/0.927	1.253/0.847
	1 : 50 : 100	1.266/0.705	1.369/0.749	1.253/0.681
a_{1h}^{calc}	1 : 1 : 1	1.225/0.824	1.353/0.913	1.248/0.839
	1 : 50 : 100	1.225/0.635	1.353/0.701	1.248/0.647
$\frac{\Delta a_{1h}}{a_{1h}^{MC}} \times 100\%$	1 : 1 : 1	4.2/5.0	1.2/1.5	0.4/0.9
	1 : 50 : 100	3.2/9.9	1.2/6.4	0.4/5.0

* The first number refers to the initial ensemble, and the second number refers to the ordered ensemble.

that was previously described for the 2D system, is also observed for the 3D system.

CONCLUSIONS

It has been shown that the self-organization of stretched statistical copolymers by the energy of interchain contacts is accompanied by lateral ordering. The efficiency of such ordering is independent of chain composition and, as a rule, increases as the length of blocks increases and the length of chains decreases. This relationship is, however, violated in the case of short chains of multiblock copolymers. Lateral ordering is accompanied by formation of the system of interchain nanoclusters that play the role of cooperative physical crosslinks and hence can strongly affect the mechanical properties of the polymer material. This subject requires further investigation.

It has been shown that, during the self-organization of multiblock copolymers, the probabilistic properties (stochastic behavior) of the ensemble are violated. In this situation, adequate information about the ensemble structure may be provided only by the Monte Carlo simulation of structure parameters.

The effect of various factors on the efficiency of ordering for the 3D system is similar to that for the 2D system. However, in all cases, the efficiency of ordering for the 3D system is lower than that for the 2D system.

Thus, the simulation algorithms and programs developed in this study, in combination with theoretical analysis, make it possible to examine in detail the effect of various factors on the ordering of statistical multiblock copolymers.

The above-described data should be taken into account during the synthesis of multiblock copolymers via polymer analogous reactions with accelera-

tion and for estimation of their self-organization ability, especially in the case of relatively short chains.

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