Monte Carlo Simulation of Polymeranalogous Reaction in Confined Conditions: Effects of Ordering

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Summary: The influence of energetic parameters of the interchain homo- and heterocontacts on a local ordering of Bernoullian copolymers has been studied using Monte Carlo simulations and probabilistic analysis. The results of both methods are in a good agreement. Then simple Monte Carlo procedure was employed to study the ordering in products of a polymeranalogous reaction with accelerating effect of neighboring groups. When the reaction with intra- and interchain acceleration and local ordering proceed simultaneously in confined conditions, the ordering might affect the process so that the formation of certain nano-structures (in particular, not trivial strip-like ones) is possible.

Keywords: Monte Carlo simulation; nanostructures; polymeranalogous reaction; probabilistic analysis; self-assembly

Introduction

Regular di- and multi-block *AB* copolymers easily form ordered structures via microsegregation provided *AB*-contacts are unfavorable.[1] Any disorder in the blocks distribution along the chain hinders an ordering.[2] Just therefore ordering of irregular statistical copolymers sparks the keen interest of theorists. A phase behavior of the copolymers is mainly considered. Recently de Gennes[3] considered the weak segregation of a random *AB* copolymer in a melt using very simple elegant approach. He found that the segregation might proceed at high value of Flory-Huggins parameter $\chi \geq 2$, the result being in accordance with detailed calculations performed earlier[4] using the random phase approximation.[5] Phase behaviour of random copolymers both in melts[6] and in concentrated solutions[7] was studied also by Monte Carlo simulations; a segregation in melts[6] and inhomogeneity of the solutions structure[7] were predicted but again for $\chi \geq 2$.

In the meantime, another aspect is of great interest, namely the local ordering as a component of self-assembly of statistical copolymers leading to a formation of energy-wise advantageous

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structure. Let us consider the simplest model system: two stretched *AB* chains of composition *p* (*p* is a molar fraction of *A* units). Their interaction energy consists of energies of interchain *AA*-, *BB*- and *AB*-contacts. Potential capability of an ensemble of such chains to ordering is determined by their primary structure, namely by units distribution. Among irregular copolymers, Bernoullian ones are most disordered. So it is especially interestingly to elucidate whether Bernoullian copolymers are capable to a local ordering and, if so, how to estimate such a tendency?

To study the problem, a simple Monte Carlo procedure has been suggested recently.[8]

Monte Carlo procedure and Probabilistic analysis

M Bernoullian chains of the length *N* were generated and arranged in the *N*x*M* rectangle. *N* and *M* were varied within 20 – 1000 and 100 – 1000000, respectively. The numbers of interchain *AA*-, *BB*- and *AB*- contacts were calculated. In all cases, an average value of the fraction of the interchain *AB*-contacts, ϕ_{in}, was equal to the pure random value of $2p(1\text{-}p)$. Then the rectangle was closed to a cylinder (with a generatrix *M*) and each upper ring was rotated over the lower ring to attain a position with minimal fraction of unfavorable *AB*-contacts, ϕ_{min}. The values of ϕ_{min} averaged over the whole ensemble deviate noticeably from the pure random value $\phi_{in} = 2p(1\text{-}p)$: 0.286 and 0.500, respectively, for $p = 0.50$ and $N = 20$.

For Bernoullian chains, it is possible to elaborate an analytical approach as well.

Let us enumerate units in each chain from 0 to $N - 1$. Now a Bernoullian chain of the length *N* is represented by a set of independent variables $\{x_k\}$; x_k takes the value *A* with the probability *p* and *B* with the probability $q = 1 - p$. Now join such sequences in an infinite chain, so that $x_{k+N} \equiv x_k$. This is *N*-periodic Bernoullian *AB* chain $\{x_k\}$. Consider two such jointly independent periodic chains $\{x_k\}$ and $\{y_k\}$. Sliding of the chain $\{x_k\}$ along the chain $\{y_k\}$ with a shift, *s*, $0 \le s \le N\text{-}1$ is equivalent to the Monte Carlo rotation procedure for two corresponding cycles of the length *N*.

Let the interaction energy of two units x_k and y_l, $u_{kl} \equiv u(x_k, y_l)$, takes the values ε_{AA}, ε_{AB}, and ε_{BB} with probabilities p^2, $2pq$, and q^2, respectively.

Interaction energy of two *N*-periodic *AB*-chains $\{x_k\}$ and $\{y_k\}$ and at a shift *s* (per one contact), u_s, is given by Eq. (1):

$$u_s = \frac{1}{N}\sum_{k=0}^{N-1} u(x_k, y_{k+s}) = \frac{1}{N}\sum_{k=0}^{N-1} u_{k,k+s}, \quad s = 0,1,\ldots,N-1 \qquad (1)$$

As $N \to \infty$, the distribution of u_s values tends asymptotically to the normal distribution.[8] Hereafter we will consider variables $\{u_s\}$ as normally distributed.

For any shift s, the mean value of the random variable u_s is given by Eq. (2):

$$\langle u_s \rangle = p^2 \varepsilon_{AA} + 2pq\varepsilon_{AB} + q^2 \varepsilon_{BB} = \varepsilon . \tag{2}$$

The normally distributed vector $(u_0, u_1, ..., u_{N-1})$ is completely characterized by its covariation matrix

$$a_{mn} = \langle (u_m - \langle u_m \rangle)(u_n - \langle u_n \rangle) \rangle = \langle u_m u_n \rangle - \langle u_m \rangle \langle u_n \rangle = \langle u_m u_n \rangle - \varepsilon^2 , \tag{3}$$

which may be directly calculated:

$$a_{mn} = N^{-1} \left((pq(\varepsilon_{AA} - 2\varepsilon_{AB} + \varepsilon_{BB}))^2 \delta_{mn} + 2pq(-p\varepsilon_{AA} + (2p-1)\varepsilon_{AB} + (1-p)\varepsilon_{BB})^2 \right) , \tag{4}$$

where δ_{mn} is the Kronecker symbol.

Let us introduce the variables

$$\chi = \varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2 , \qquad r_w = -p\varepsilon_{AA} + (2p-1)\varepsilon_{AB} + (1-p)\varepsilon_{BB} \tag{5}$$

In this notation, elements of the covariation matrix take the form

$$a_{mn} = N^{-1} (\delta_{mn} (1-a)^2 \chi^2 / 4 + (1-a) r_w^2 / 2) . \tag{6}$$

where $a = (1-2p)^2$.

As follows from Eq. (6), the random variables u_s (s = 0, 1, ..., N-1) are independent only at $r_w = 0$. In the general case, we may write

$$u_s = \varepsilon + \nu_s + w , \tag{7}$$

where ε is the constant introduced above, w and ν_s (s = 0, 1, ..., N-1) are mutually independent variables that are distributed normally with the zero mean value $\langle \nu_s \rangle = \langle w \rangle = 0$ and the dispersions

$$\sigma_\nu^2 = (1-a)^2 \chi^2 / (4N) , \qquad \sigma_w^2 = (1-a) r_w^2 / (2N) \tag{8}$$

In order to find the minimum value of the interaction energy

$$u_{\min} = \min_{0 \le n \le N-1} (\varepsilon + \nu_n + w) = \varepsilon + \min_{0 \le n \le N-1} (\nu_n + w) \tag{9}$$

let us calculate the probability that $\nu = \min_{0 \le n \le N-1} (\nu_n + w)$ is not less than θ, $F(\theta)$:

$$F(\theta) = P(\nu \ge \theta) = \int_{-\infty}^{+\infty} d\eta [F_\nu(\theta - \eta)]^N f_w(\eta) \tag{10}$$

where $F_\nu(\theta - \eta) = \int_{\theta-\eta}^{\infty} dy f_\nu(y) = \frac{1}{2}\left(1 - erf\left(\frac{\theta - \eta}{|\chi|(1-a)}\sqrt{2N}\right)\right)$ is the probability that ν_n is not less than $\theta - \eta$, $f_w(\eta) = \frac{1}{\sqrt{2\pi\sigma_w}} \exp\left(-\frac{\eta^2}{2\sigma_w}\right)$, and $erf(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x dy \exp(-y^2)$ is the error function.

The mean value of minimum interaction energy of two chains (per one contact) is

$$\langle u_{\min} \rangle = \varepsilon + \langle v \rangle = \varepsilon - \int_{-\infty}^{+\infty} d\theta \cdot \theta \frac{dF(\theta)}{d\theta}. \quad (11)$$

Since $f_w(\eta)$ differs noticeably from zero only in the narrow region of width ~ $N^{-1/2}$ near $\eta = 0$, it is possible to use the approximation[8] $F(\theta) \approx [F_v(\theta)]^N$, $F_v(\theta - \eta) \approx F_v(\theta)$, whence

$$\langle u_{\min} \rangle = \varepsilon + \langle v \rangle = \varepsilon - \int_{-\infty}^{+\infty} d\theta \cdot \theta \frac{d[F_v(\theta)]^N}{d\theta}. \quad (12)$$

For equal energies $\varepsilon_{AA} = \varepsilon_{BB}$, the interaction energy of two chains (per one contact) is related identically to the fraction of *AB*-contacts between those chains, ϕ_{AB}:

$$\phi_{AB} = \frac{u - \varepsilon_{AA}}{\varepsilon_{AB} - \varepsilon_{AA}} \quad (13)$$

Therefore the fraction of *AB*-contacts corresponding to the mean minimum value of the interaction energy for those chains is given by Eq. (14)

$$\langle \phi_{AB\min} \rangle = \frac{\langle u_{\min} \rangle - \varepsilon_{AA}}{\varepsilon_{AB} - \varepsilon_{AA}}. \quad (14)$$

Dependencies of $\langle \phi_{AB\min} \rangle$ on the logarithm of chain length *N* for unfavorable and favorable *AB*-interaction were calculated using both a set of equations given above and Monte Carlo simulations. It is seen in the Figure 1 that the results of both methods are in a good agreement. Deviations of $\langle \phi_{AB\min} \rangle$ from the pure random value might serve as a measure of the capability of Bernoullian chains to ordering. These deviations decrease when *N* increases, however they are significant even for long chains: ~25-30 % and ~10 % for *N* = 100 and 1000, respectively (Figure 1).

Note that estimations of a capability to an ordering given by the rotation procedure are good for a sliding not only of periodic but also for that of true Bernoullian chains.[8] Therefore the simple Monte Carlo procedure seems to be suitable for estimating ordering in copolymers of other classes when an analytical approach is more complicated.

Using this procedure, ordering of *AB* copolymers formed during a polymeranalogous reaction *A*→*B* with accelerating effect of the neighboring *B* units has been studied. The ratios of the rate constants for central *A* units in triads *AAA*, *AAB* (*BAA*), *BAB* were k_0: k_1: k_2 = 0.02: 0.245: 0.490. An ensemble of *M A*-chains of the length *N* was generated. Then *A* units transformed into *B* ones with probabilities proportional to corresponding rate constants till the mean value over the whole ensemble for the prescribed the product composition, *p*, was attained.

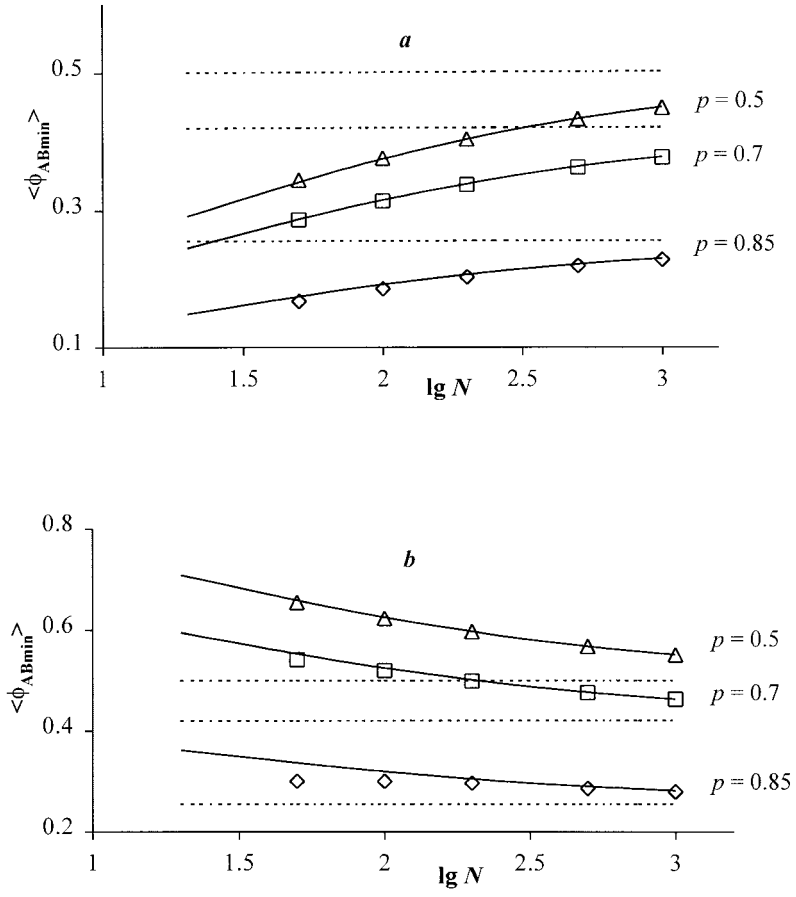

Figure 1. Minimized fraction of interchain *AB*-contacts $\langle \phi_{AB\,\min} \rangle$ *vs* chain length. (a) unfavorable *AB*-contacts: $\varepsilon_{AB} = -0.1$, $\varepsilon_{AA} = \varepsilon_{BB} = -1$; (b) favorable *AB*-contacts: $\varepsilon_{AB} = -1$, $\varepsilon_{AA} = \varepsilon_{BB} = -0.1$; dashed lines – pure random values for corresponding average composition *p*.

For such copolymers, the deviations $\langle \phi_{AB\,\min} \rangle$ from ϕ_{in} are also significant. Moreover, the deviations turn out to be greater than the ones for Bernoullian copolymers (see Figure 2). This is due to a tendency to the block distribution typical for the products of reactions with accelerating neighbor effect.[9]

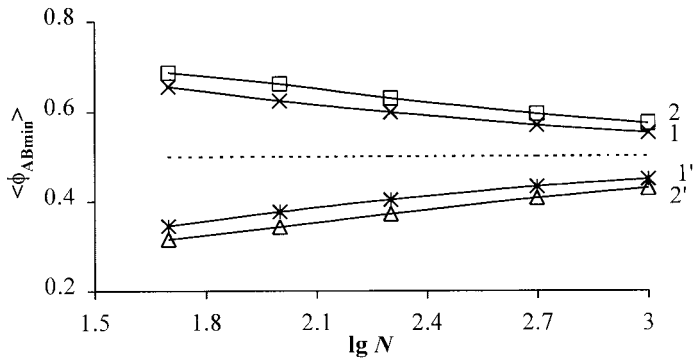

Figure 2. Effect of the chain structure on the ordering: $\langle \phi_{AB\,\min} \rangle$ *vs* chain length for mean chain composition $p = 0.5$; Bernoullian chains (1,1′) and reaction products (2,2′), rate constant ratios k_0: k_1: $k_2 = 0.02$: 0.245: 0.490; favorable (1,2) and unfavorable (1′,2′) *AB* contacts; interchain contact energies like in Fig. 1; dashed line – no ordering.

Ordering during Reaction

It is reasonable to assume that a tendency to ordering might affect both reaction kinetics and structure of the product if ordering and a polymeranalogous transformation proceed simultaneously.

Let us consider a two-dimensional system composed of M stretched chains A of the length N where $A \rightarrow B$ reaction with accelerating effect of both inner and external neighboring B units takes place. It might be viewed as a very thin layer on a surface or within a narrow slit, so that the chains may slide one along the other while the transversal displacements are hindered. This is an already familiar rectangle, so the effects of ordering were studied using the Monte Carlo procedure – rotation of rings. Let accelerating effects of the internal and external neighbors be equal so that the ratios of the rate constants for A units having 0, 1, 2, 3 и 4 B neighbors are k_0: k_1: k_2 : k_3: k_4 = 0.020: 0.265: 0.510: 0.755: 1.000. Each Monte Carlo test consists of the following successive operations: a random choice of a unit; testing whether the unit reacts or not (provided the chosen unit is A); displacement of the chain containing the unit in accordance with the model studied.

The following reaction models were studied.

Local Ordering - after each Monte Carlo test for $A \rightarrow B$ reaction, the tested chain is shifted to a position with minimal energy of interchain contacts with two neighboring chains. Two cases are considered: favorable and unfavorable AB-contacts, **Local Ordering AB$_f$** and **Local Ordering AB$_{unf}$**, respectively.

For the purpose of comparison, the other models were studied as well.

Immobile chains - the reaction in a system of immobile chains;

Ideal Mixing - random sliding in a system with equal energies of interchain contacts;

No Interchain Effects - the reaction without interchain acceleration and ordering.

The product structure was characterized by composition p – fraction of units A, probability of a boundary between A and B sequencies, R, and a dispersion of compositional distribution, D. The fraction of interchain AB-contacts, $\phi_{ABtransv}$, was also calculated.

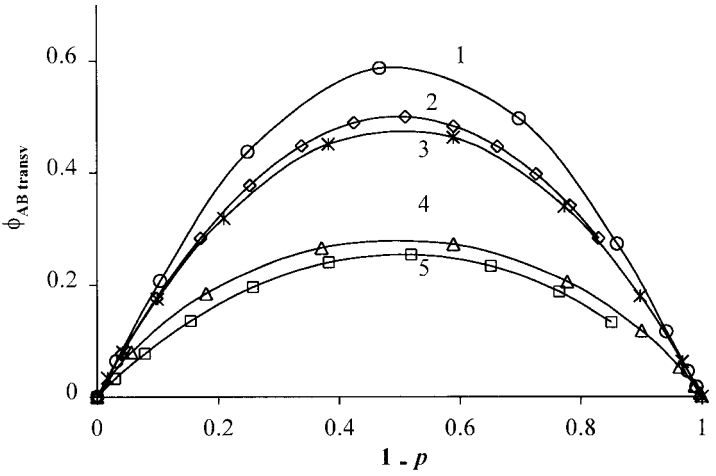

Figure 3. The fraction of interchain AB-contacts, $\phi_{ABtransv}$, vs conversion, $1 - p$. Curves correspond to the different reaction models: **Local Ordering AB$_f$** (1), **No Interchain Effects** (2), **Ideal Mixing** (3), **Immobile chains** (4), **Local Ordering AB$_{unf}$** (5).

For the model **No Interchain Effects**, the values of $\phi_{ABtransv}$ are equal to the pure random values $2p(1\text{-}p)$ (see Figure 3). For **Ideal Mixing**, the values of $\phi_{ABtransv}$ were found to be close to the latter as well. Ordering significantly affects this quantity. For **Local Ordering AB$_f$**, the value of $\phi_{ABtransv}$ is considerably greater than $2p(1\text{-}p)$, while for **Local Ordering AB$_{unf}$** it is markedly less than the random values. This kind of data is quite informative. So, $\phi_{ABtransv}$ for **Local Ordering AB$_{unf}$** and for **Immobile chains** are close to one another. Accordingly, the other characteristics of those systems are quite similar.

During the reaction with an accelerating effect of inner neighbors, relatively long blocks are formed; consequently, the probability of a boundary between A and B sequences, R, is relatively small (Figure 4). Due to interchain acceleration, the rate of generation of new blocks increases and the probability of a boundary increases as well. Naturally, the increase of R is minimal for **Local Ordering AB$_{unf}$** and maximal for **Local Ordering AB$_f$**.

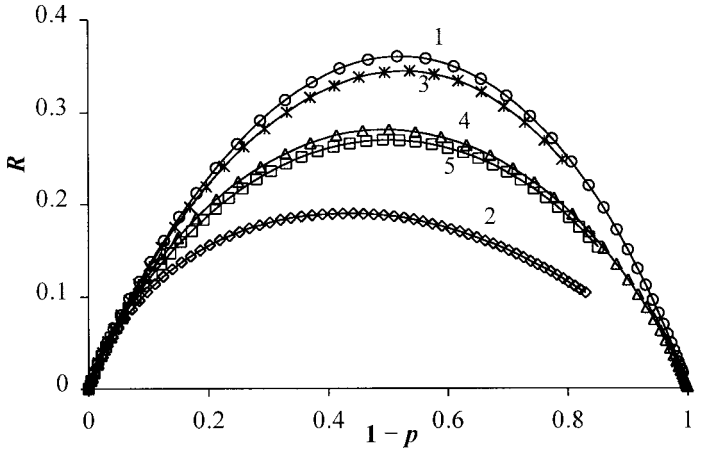

Figure 4. The probability of an AB-boundary, R, vs conversion, $1 - p$. Curve numbers are as in Fig. 3.

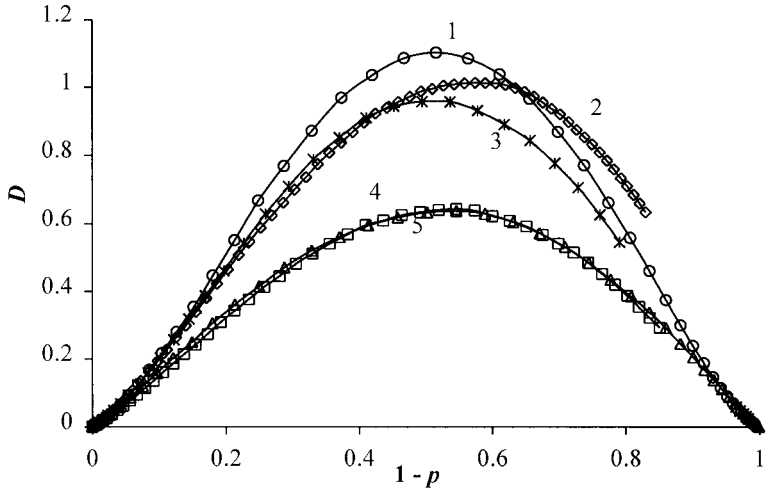

Figure 5. The dispersion of compositional distribution, R, vs conversion, $1 - p$. Curve numbers are as in Fig. 3.

For a reaction with an accelerating effect of inner neighbors only, the dispersion of compositional distribution D is significant and its dependence on conversion is asymmetrical (the maximum is shifted to the right).[9] **Ideal mixing** shifts the maximum to the center, the D value decreases slightly at high conversions (Figure 5). The dispersion decreases greatly for

Local Ordering AB_{unf} and **Immobile chains**. In general, the more R the less D. Therefore it is worthy to notice that for **Local Ordering AB_f** the simultaneous maximum values for both R and D are observed in the results of simulations. It indicates a specific effect of ordering on evolution of the reacting system in two dimensions.

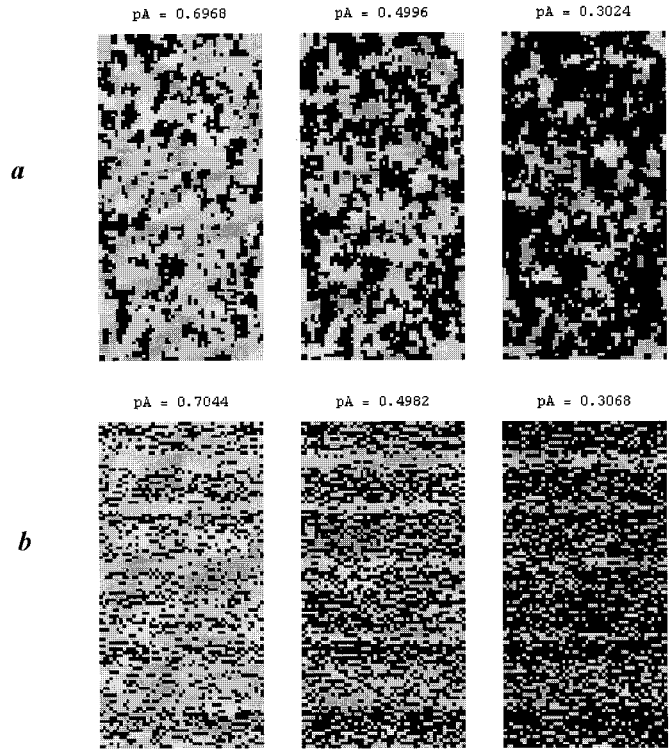

Figure 6. Snap-shots of the system structure for the reaction models **Local Ordering AB_{unf}** (a) and **Local Ordering AB_f** (b). Ensemble consists of M = 150 chains of N = 75 units. Chains are settled along abscissa.

Evolution of the system structure for different models is shown on snap-shots (Figure 6). Chains are settled along abscissa. In case of **Local Ordering AB_{unf}**, the B-blocks, which propagate along a chain, involve the neighboring chains into the reaction; the reaction spreads both in the horizontal and vertical directions, so that black "islands" are formed and grow being distributed relatively uniformly in the white "sea". This is due to the fact that the interchain BB-contacts formed during the reaction are favorable, therefore the chains behave as immobile (for **Immobile chains** similar snapshots "islands in the sea" were obtained). On the contrary, the fraction of favorable AB-contacts increases in the course of ordering in the

Local Ordering AB_f model. As a result, the reaction spreads noticeably along the horizontal axis. This leads to formation of the observed black and white strips, in which the chains significantly differ in the degree of conversion. It corresponds to the greater values of dispersion *D*.

Thus, local ordering might affect the reaction in a two-dimensional system (under confined conditions) and a formation of certain nano-structures is possible in such systems.

Conclusions

The influence of energetic parameters of the interchain homo- and heterocontacts on a local ordering of both Bernoullian copolymers and products of a polymeranalogous reaction with accelerating neighbor effect proceeding in confined conditions has been studied using Monte Carlo simulations and probabilistic analysis. When the reaction with intra- and interchain acceleration and local ordering proceed simultaneously, the ordering might affect the process so that the formation of certain nano-structures (in particular, not trivial strip-like ones) is possible.

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