

Monte Carlo Simulation of a Polymer-Analogous Reaction in a Polymer Blend¹

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Abstract—The autocatalytic polymer-analogous reaction $A \rightarrow B$ in a blend composed of two contacting layers of compatible homopolymers A and B is studied by numerical simulation using the dynamic continuum Monte Carlo method. The evolution of the numerical density of units A and units initially belonged to the chains of homopolymer A is investigated in the course of the reaction and interdiffusion. Local characteristics of the distribution of the homopolymer with respect to its composition and blocks A and B with respect to their length are calculated at different times. The dispersions of the above distributions are appreciably higher than the corresponding dispersion of the Bernoullian copolymer of the same average composition, despite the random character of the reaction. This effect can be provided by changes in the composition of the blend on the scale of the reacting chain as well as by the diffusive mixing of the above chains. For the products of the polymer-analogous reaction, the broadening of the compositional distribution is predicted also by the theoretical model, which describes interdiffusion in the reacting system on scales that are markedly greater than the size of a polymer chain.

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INTRODUCTION

Polymer-analogous reactions during which the backbone of a macromolecule remains unchanged but pendant groups are involved in the chemical transformations serve as a convenient object for the development of theoretical models of macromolecular reactions as well as for experimental studies [1, 2]. In recent years, most attention has been focused on the reactions in polymer melts and blends [3]. In this direction, many problems that cannot be studied in laboratory experiments can be analyzed via numerical experiments. The scope of related problems is gradually increasing.

The objective of this study is to demonstrate the applicability of the Monte Carlo method for the simulation of a polymer-analogous reaction in a spatially inhomogeneous polymer blend. We used the continuum version of this method [4, 5], which makes it possible to avoid any artifacts (such as markedly retarded relaxation processes) pertaining to the simulation of the dynamics of random copolymers on a lattice through the algorithm of a bond fluctuation model [6, 7]. Let us mention that the continuum Monte Carlo method has been successfully applied for the simulation of the interchain exchange reaction at the boundary between incompatible polymers [8]. Therefore,

this study widens the set of macromolecular reactions in polymer mixtures that can be studied by the methods of computer-aided experiments.

Along with the academic objective, the problem of calculating the local dispersion of the distribution of chains with respect to their composition and blocks with respect to their lengths is addressed. As was predicted in a recent theoretical study [9], the diffusive mixing of chains of random copolymers can lead to a marked increase in the local dispersion of the compositional inhomogeneity; in turn, this parameter controls the rate of the interdiffusion and, in the reacting system, the kinetics of the chemical reaction. We will revisit the same simple model of a melted polymer blend as in [9]: In the initial bilayer system composed of two compatible homopolymers A and B, autocatalytic reaction $A \rightarrow B$ commences. For the sake of convenience, units A are referred to as reacting units, and units B are referred to as catalytic units; for the chains initially composed of units A, we will use the term *reacting chains*. As was shown in [10], this model can be experimentally verified for a blend of poly(*t*-butyl acrylate-*co*-styrene) and poly(acrylic acid-*co*-styrene). In this system, the units of tert-butylacrylate are transformed into units of acrylic acid, and styrene units serve as an inert diluent, which improves the compatibility of the system.

In order to simplify the study of the diffusion processes, we will take into account the accelerating

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action of only external neighbors of selected unit A (interchain effect), but the effect of the neighboring units along the chain is disregarded. In a homogeneous system, this reaction leads to the formation of Bernoullian copolymer AB, in which the distribution of units in chains is fully random. In addition, let us exclude the polydispersity in the chain length; its effect on the interdiffusion in inhomogeneous mixtures of polymers has been discussed in [11].

Owing to limited computational resources, problems concerning the direct verification of the theoretical results related to space–time scales, which markedly exceed the characteristic scale and time of the diffusion relaxation of an individual macromolecule, are beyond the scope of this study. Using the numerical simulation, we will study the inhomogeneity of the distribution of chains with respect to the composition and blocks with respect to their lengths on small scales, which are beyond the applicability limits of the macroscopic theory. This study will provide important information concerning the evolution of the detailed structure of the reacting polymer blend in the immediate vicinity of the interphase boundary. This information is difficult to obtain experimentally but is crucial for the explanation of the processes of the reaction compatibilization and for control over these processes.

The next section is devoted to the description of the model and to the calculation scheme, which are used in the computer-aided experiments, as well as to the theoretical model [9], which describes its reaction diffusion equations. Below, the results of the numerical simulation and theoretical calculations are described and compared.

MODEL AND CALCULATION METHOD

Computer-Aided Simulation

In terms of the standard off-lattice model [4], a macromolecule is presented as a set of “beads” (units) connected by “springs” (bonds). Each bead corresponds to the group of atoms in the polymer backbone and serves as the center of the application of potentials, whereas the springs stand for the chemical bonds.

The overall energy of a polymer melt involves two components:

$$U = U_{\text{bond}} + U_{\text{nonbond}},$$

where U_{bond} is the energy of the covalent bonds in macromolecules and U_{nonbond} is the energy of the volume interactions between monomer units.

The energy of bonds reads as

$$U_{\text{bond}} = \sum_{j=1}^m \sum_{i=1}^{N-1} U(l_{ij}).$$

Here, m is the number of bonds (in the monodisperse case under study, each chain involves $N-1$ bonds), l_{ij} is the bond length or the distance between the i th and $(i+1)$ th units on the j th chain expressed in

internal length units. The interaction between neighboring units is described by the truncated potential of the harmonic oscillator:

$$U(l) = k_s(l - l_0)^2, \quad l_{\min} < l < l_{\max}$$

$$U(l) = \infty, \quad l \leq l_{\min}, \quad l \geq l_{\max}$$

$$l_0 = \frac{l_{\min} + l_{\max}}{2},$$

where k_s , l_{\min} , and l_{\max} stand for the rigidity and minimum and maximum admissible lengths of each spring, respectively. The potentials of bond angles and internal rotation angles are not introduced with allowance for the selected level of model coarse-graining.

Volume interactions between units are described in terms of the Morse potential as

$$U_{\text{nonbond}} = \sum_{i < j} U_M(r_{ij})$$

$$U_M(r)/E = \exp[-2\alpha(r - r_{\min})] - 2\exp[-\alpha(r - r_{\min})].$$

Parameter r_{\min} defines the position of the potential minimum, α is the radius of interaction, and E is the characteristic potential in units of $k_B T$.

When the parameters are selected as $E = 0.1-1.0$ and $\alpha = 24$ and the internal length units are selected so that $r_{\min} = 0.9$, it may be expected that $U_M(1) \approx 0$. Hence, the potential truncation radius is equal to unity and comparable to the size of one monomer unit. Hence, it is possible to apply the linked-list algorithm [12] for the tabulation of the interacting units with the linear size of the cell, which is equal to unity; this approach markedly improves the performance of the program. Model parameters can be selected ($l_{\min} = 0.4$, $l_{\max} = 1$, $k_s = 10$) so that the probability of random mixing of units is negligibly small. In this case, no verification is required, a circumstance that markedly improves the computation rate. The problem concerning the correspondence between internal program units and real scales [8, 13] allows the conclusion that the average length of the spring ($l_0 \approx 0.7$) is close to the length of two C–C bonds.

The model by itself, its use for the study of various polymer systems, and comparison with experimental results have been described in detail in [4].

The dynamics of the system as a result of the diffusive motions of the monomer units is modeled through the well-known Metropolis algorithm. Each new position (conformation) of a macromolecule is obtained from the previous one by the displacement of a selected unit (bead) by vector $\Delta \mathbf{r} = \{\Delta x, \Delta y, \Delta z\}$, where $\Delta x, \Delta y, \Delta z$ are random variables that are uniformly distributed within the following interval, -0.25 to $+0.25$. The probability of this transition is controlled by the difference of potential energy, ΔU , in the final and initial states: The conformation changes when $W = \exp(-\Delta U/T)$ (T is the effective dimensionless temperature) exceeds a random number from the

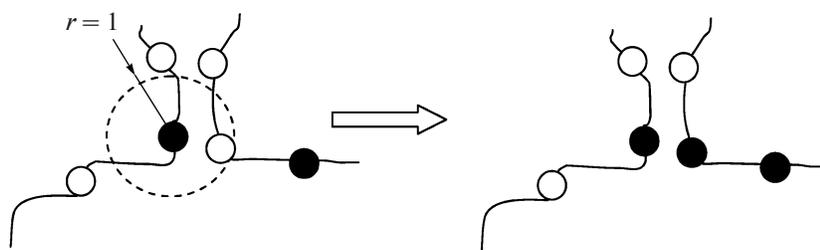


Fig. 1. Schematic representation of autocatalytic polymer-analogous reaction $A \rightarrow B$: (open circles) units A and (closed circles) units B.

interval $(0, -1)$; in the opposite case, a macromolecule preserves its conformation.

After a certain number τ of the above conformational Monte Carlo steps, the step of modeling the autocatalytic polymer-analogous reaction is performed (Fig. 1). The algorithm of this step is as follows: Select a catalytic unit B, and check if there are any units A among the units that are spaced from selected unit B by less than the unit distance and which are not its neighbors along the chain; if such units are detected, one of them is selected at random and its type is changed to type B. In this way, during one reaction step, all catalytic units are sorted out. Low values of τ , which range from 10^2 to 10^6 , correspond to a fast chemical reaction, whereas high values of τ correspond to a slow reaction.

In this study, we used a $16 \times 16 \times 16$ (internal length units) XYZ cubic cell; into this cell, 256 regularly positioned homopolymer chains composed of 16 units (128 homopolymer chains A in one-half of the cell at $0 \leq z \leq 8$ and 128 chains of homopolymer B at $8 \leq z \leq 16$) are placed. All in all, the system contains 4096 monomer units, a case that corresponds to a volume fraction of a polymer equal to ≈ 0.27 . Along the X and Y axes, the periodic boundary conditions are applied; along the Z axis, the existence of an impermeable wall at the cell boundaries is assumed.

Above all, it seems necessary to define the initial state of the blend: contacting layers of homopolymers A and B. To this end, the dynamics of the system is modeled according to the Metropolis algorithm at a far more favorable attraction interaction of similar units ($E_{AA} = E_{BB} = 10E_{AB}$). The equilibrium state of the system is evaluated from the calculation of the mean-square displacement of a monomer unit, d , with respect to its initial position. The time for the formation of the initial separated system is assumed to be equal to the number of conformational Monte Carlo steps that, having been doubled, practically does not change the density profiles of various units. The calculations show that, during this time interval, each monomer unit is shifted by a distance of approximately the layer size ($4 < d < 8$). To reduce this time for the formation of the initial state, the mobility of chains

is increased by an increase in the effective temperature.

THEORY

Let us consider the model of a melt containing homopolymers A and B with degrees of polymerization of N_A and N_B , respectively. Assume that the polymers are compatible (the Flory–Huggins parameter $\chi \leq 0$) and initially separated by an interfacial layer with the characteristic width $2\Delta \gg R_A, R_B$, where R_A and R_B are the mean-square radii of chain A and chain B, respectively. This condition corresponds to the selection of the initial profile of the molar fraction of units A as $\rho(z, t = 0) = \rho_0(z) = (1 - \tanh(z/\Delta))/2$, where the z coordinate is scaled along the axis perpendicular to the boundary between polymers A and B. For the sake of simplicity, units A and B are assumed to occupy the same volume so that there is no need to distinguish between molar and volume fractions of all units.

Let us assume that, at time $t = 0$, the reaction of the transformation $A \rightarrow B$ commences; this reaction proceeds with the accelerating interchain effect. The probability of the transformation of each selected unit A per time unit is defined by the product of reaction-rate constant γ and local fraction $(1 - \rho)$ of units B. The local fraction of units in the reacting chains is defined as ϕ , and their average composition is $p = \rho/\phi$. The reaction in the blend of compatible polymers is accompanied by their interdiffusion, and the mobility of each chain in the melt is described by the Rouse model with the self-diffusion coefficients $D_A \sim 1/N_A$ and $D_B \sim 1/N_B$.

It seems convenient to describe the macroscopic dynamics of the systems in terms of collective variables $\{\phi_i(z)\}$, where ϕ_i is the local fraction of units in the reacting chains containing i units of type A [9, 14]. Local moments μ_k of the composition distribution of chains are defined as

$$\mu_k = \sum_{j=1}^{N_A} (j/N_A)^k \phi_j, \quad k = 0, 1, 2, \dots,$$

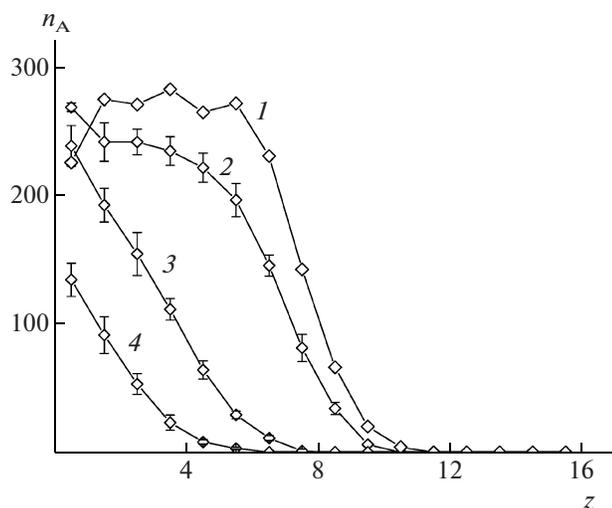


Fig. 2. Numerical density of the reacting units, n_A , along the z coordinate. Profiles are constructed at $\tau = 10^2$ and at $t_{MC} \times 10^{-3} = (1) 0, (2) 2.6, (3) 6.1, \text{ and } (4) 8.2$. The mean-square deviation after averaging over 50 realizations of the process is shown.

and $\mu_0 = \phi$ and $\mu_1 = \rho$. The dispersion of the compositional inhomogeneity of reacting chains can be expressed through the introduced moments as

$$\sigma^2 = \frac{\sum_{i=0}^{N_A} \frac{i^2}{N_A^2} \phi_i}{\sum_{i=0}^{N_A} \phi_i} - \left(\frac{\sum_{i=0}^{N_A} \frac{i}{N_A} \phi_i}{\sum_{i=0}^{N_A} \phi_i} \right)^2 = \mu_2/\mu_0 - \mu_1^2/\mu_0^2$$

In [9], the reaction-diffusion equations for moments μ_k have been derived in terms of the linear nonequilibrium thermodynamics as

$$\begin{aligned} \frac{\partial \mu_k}{\partial t} = & \frac{\partial}{\partial z} \left(D_A \frac{\partial \mu_k}{\partial z} + \frac{\mu_k}{\phi} (D_{\text{int}} - D_A) \frac{\partial \phi}{\partial z} \right) \\ & - 2\chi \left(\frac{\rho}{\phi} \left(\frac{\Lambda_{\text{int}}}{\phi} - N_A D_A \right) \mu_k + N_A D_A \mu_{k+1} \right) \frac{\partial \rho}{\partial z} \\ & - \gamma (1 - \rho) \sum_{l=1}^k C_k^{l-1} \mu_l (-1)^{k-l} N_A^{l-k}, \end{aligned} \quad (1)$$

where $C_k^{l-1} = \frac{k!}{(l-1)!(k-l+1)!}$ is the binomial coefficient,

$D_{\text{int}} = \Lambda_{\text{int}} \left(\frac{1}{\phi N_A} + \frac{1}{(1-\phi) N_B} \right)$, and $\Lambda_{\text{int}} = \phi(1-\phi) \left((1-\phi) N_A D_A + \phi N_B D_B \right)$.

In the equation for the zero moment $\mu_0 = \phi$, the reaction term is missing.

It is easy to show that, in a general case, set of equations (1) is not closed, because the equation for μ_k involves μ_{k+1} . In [9], various methods for the closure of

this system have been considered, and these methods make it possible to approximately calculate the profiles $\phi(z)$, $\rho(z)$, and $\sigma^2(z)$ at different times. Here, we will consider the particular case $\chi = 0$, in which Eqs. (1) can be solved numerically without any additional assumptions.

RESULTS AND DISCUSSION

After the formation of the initial state of the polymer blends, we studied the concomitant processes of self-diffusion and chemical reaction. Simulation was performed at $E_{AA} = E_{BB} = E_{AB}$, a case corresponds to the assumption $\chi = 0$ in the theoretical model. In addition, we assumed that $N_A = N_B = N = 16$ and $T = 1$.

In the course of the computer-aided experiment, initial information, such as coordinates (x, y, z) and the type of each monomer unit and its parent chain, made it possible to calculate (i) the spatial distribution of units in the reacting chains and homopolymer chains B and of various units and (ii) the averaged local characteristics of the distribution of the reacting chains with respect to the composition and of blocks A and B with respect to their lengths for different effective times t_{MC} (the number of conformational Monte Carlo steps).

For each set of the parameters of the system, simulation is performed 50 times from the defined initial state. Averaging of the results makes it possible to obtain sufficiently smooth dependences. Figure 2 shows the front advance of the chemical reaction: At different times, the profile of the numerical density of the reacting units, $n_A(z)$, is constructed, where z is the coordinate along the direction perpendicular to the initial boundary between the layers of polymers A and B. For each point on curves 2–4, the root-mean-square deviation is presented; it is seen that, with time, the accuracy of the calculations does not decrease.

Figure 3 shows the dependences $n_A(z)$ and the numerical density of units in the reacting chains, $n_{\text{react}}(z)$, or the front of the interdiffusion at various τ , which controls the relative diffusion rate and the reaction rate in the system. Note that an almost similar conversion of units A, which in all cases is $\approx 90\%$, is attained within different times t_{MC} .

As follows from Figs. 3b and 3c, the chemical conversion of reacting chains and their diffusion-controlled mixing with chains of homopolymer B proceed simultaneously; at the same time, the profile n_{react} for the fast reaction in Fig. 3a is similar to the initial profile: During the time of almost complete conversion of units A, the interdiffusion of reacting and catalytic chains is negligible. In this case, the reaction front travels inside the layer of polymer A owing to the contacts between units A and B of the reacting chains. The mean distance between the neighboring units in the system is equal to unity, and this is the maximum dis-

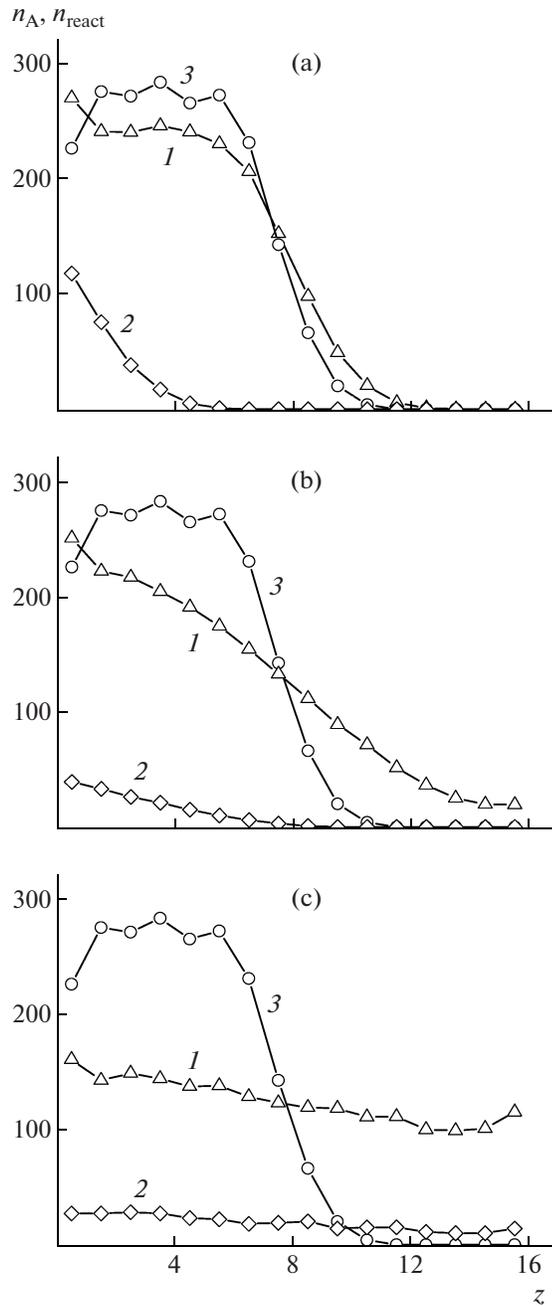


Fig. 3. Numerical density of (1) the units of the reacting chains, n_{react} , and (2) units A, n_A , along the z coordinate; $\tau =$ (a) 10^2 , (b) 10^4 , and (c) 10^6 ; $t_{\text{MC}} =$ (a) 8.7×10^3 , (b) 9.8×10^4 , and (c) 5.2×10^5 . In all cases, the conversion is $\approx 90\%$. (3) The initial profile $n_{\text{react}}(z, t_{\text{MC}} = 0) = n_A(z, t_{\text{MC}} = 0)$.

tance at which, upon its contact with unit B, unit A can be transformed; hence, the reaction can proceed to high conversions even in the systems containing totally immobile chains according to the mechanism of the “chemical relay race” [3]. The conformational

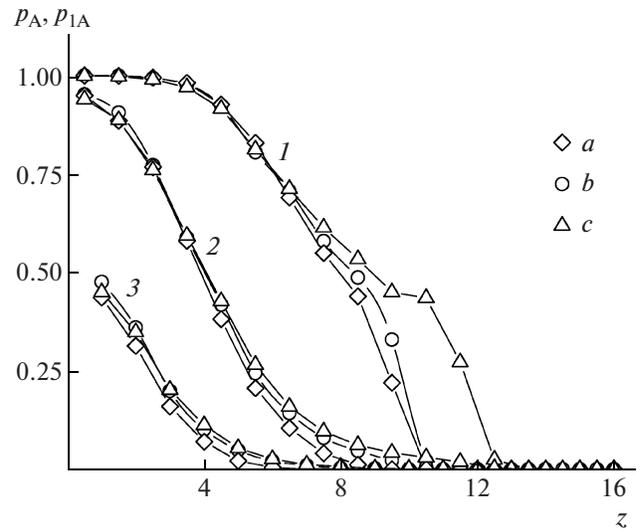


Fig. 4. (a) Local composition of the blend $p_A(z) = n_A(z)/n_{\text{react}}(z)$ and (b, c) average composition of the reacting chain $p_{1A}(z)$, where averaging is performed for the chains whose (b) center of mass or (c) any unit lies within the interval $z - 0.5$ to $z + 0.5$. The profiles are constructed at $\tau = 10^2$ and at $t_{\text{MC}} \times 10^{-3} =$ (1) 2.6, (2) 5.6, and (3) 8.7.

mobility of the formed copolymers AB allows them to react fully and to be transformed into homopolymer B.

Figures 4 and 5 show the characteristics of the compositional distribution of the reacting chains: the average chain composition, $p_{1A}(z)$, and the compositional dispersion, $\sigma^2(z)$. The above parameters depend on the local averaging over the distribution of units in the reacting chains.

First, there are several options how to select the chains with the same z coordinate, because the step along the z coordinate (unity) is lower than the mean-square size of the chain, which is four. One option is to select the chain during the local averaging in the layer with the z coordinate (in other words, within the interval $z - 0.5$ to $z + 0.5$) if this layer contains at least one unit of a given chain. Another option is to distinguish the chains between the layers according to the positions of their centers of mass.

Second, by itself, the local averaging over the selected reacting chains can be number-based (random selection of a chain), mass-based (selection of a unit), etc. The calculations show that, at any mode of averaging, no qualitative disagreement in the behavior of profiles $p_{1A}(z)$ is observed, while the quantitative difference is most pronounced at the initial stage of the reaction in the region initially occupied by polymer B, into which penetration of separate units of the reacting chains is easier than that of their centers of mass (Fig. 4). As follows from Fig. 4, the difference between $p_{1A}(z)$ and the local composition $p_A(z) = n_A(z)/n_{\text{react}}(z)$ is small.

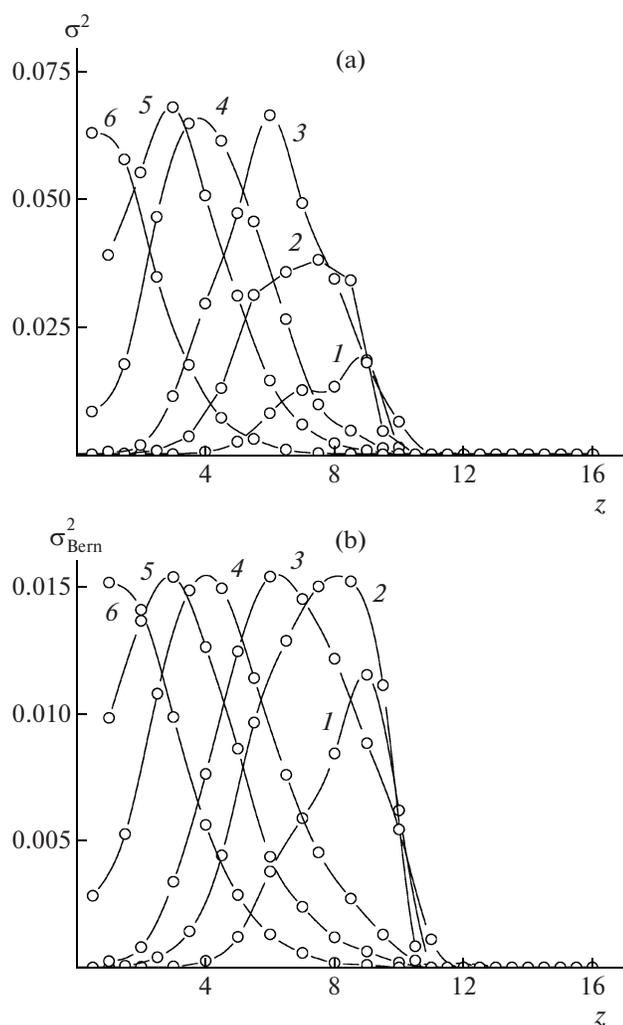


Fig. 5. (a) Local compositional dispersion of the reacting chains, $\sigma^2(z)$ (averaging is performed for the chains whose center of mass lies within the interval $z - 0.5$ to $z + 0.5$), and (b) dispersion $\sigma_{\text{Bern}}^2(z)$ of the Bernoullian copolymer of same average chain composition $p_{1A}(z)$. The profiles are constructed at $\tau = 10^2$ and at $t_{\text{MC}} \times 10^{-3} = (1) 1.5, (2) 2.6, (3) 4.1, (4) 5.6, (5) 7.2, \text{ and } (6) 8.7$.

In addition, evolution of the local compositional dispersion slightly depends on the mode of averaging. At the same time, in the region of the reaction front, even shortly after the reaction outset, $\sigma^2(z)$ is much higher than the dispersion of the Bernoullian copolymer, $\sigma_{\text{Bern}}^2(z) = p_{1A}(z)(1 - p_{1A}(z))/N$, with same average composition $p_{1A}(z)$ (compare Figs. 5a and 5b). Note that, owing to the fully random mechanism of the reaction, no correlations between the types of the neighboring units are observed. At the same time, various fragments of the same reacting chain can be located in regions with different average composition $p_A(z)$; hence, on the whole, formed copolymer AB is not the Bernoullian copolymer. Another factor

responsible for an increase in the compositional dispersion of the reacting chains is their diffusion-controlled mixing; as a result, the composition of the chains in the same layer (with the same z coordinate) can be appreciably different.

The broadening of the compositional distribution of the reaction products observed in the computer-aided experiments qualitatively agrees with the theoretical predictions [9]. Figure 6 presents the average local composition of the blend, p , and the compositional dispersion, σ^2 , plotted against dimensionless coordinate $z/(12R_0)$ for various values of dimensionless time t/τ_0 ; the dependences are constructed according to Eqs. (1) at $\chi = 0$ and $N_A = N_B = N = 16$. Here, R_0 and τ_0 stand for the mean-square radius of the chain and the time of diffusion of its center of mass by distance R_0 , respectively; these values are assumed to be the same over the entire system.

Analysis of the diffusion reaction equations in terms of the selected model [9, 15] makes it possible to conclude that, starting at a certain moment of time, the advance of profile $p_A(z)$ becomes autowavelike and can be described with the well-known Fisher equation [16]; in this case, the profile's rate $c_0 = 2(D_A\gamma)^{1/2}$ and characteristic width $L_0 = 4c_0/\gamma = 8(D_A/\gamma)^{1/2}$ remain constant. The numerical calculations show that the development of the autowave regime can be expected at any $\chi \leq 0$ [9]; in this case, dispersion profile $\sigma^2(z)$ advances with the same rate as $p_A(z)$ (Fig. 6). The attained dispersion is several times higher than that of the Bernoullian copolymer of the same average composition. This difference increases with an increase in chain length N because $\sigma_{\text{Bern}}^2 \propto N^{-1}$ and $\sigma^2 \propto N^0$ [9].

Note that the dispersion estimated in the theoretical calculations is two times lower than that obtained by the numerical simulation at the same system parameters. The origin of the above discrepancy requires further analysis. In particular, this behavior can be explained by a marked difference between the models of polymer melts, which are used in the Flory theory and in the continuum simulation via the Monte Carlo method. Moreover, in the large-scale theoretical model, the compositional gradient on the scale of one chain is negligibly small; therefore, an increase in the compositional inhomogeneity is provided only by the interdiffusion of the reacting chains of different compositions. Note that, in the simulation, both factors are crucial.

Figures 7 and 8 present the results of the calculations of the distribution with respect to the length of block A in reacting chains. Even though, as follows from Fig. 3a, the interdiffusion of the reacting chains and chains of homopolymer B at $\tau = 10^2$ is slow, the average length L_A of the block dramatically decreases; initially, this decrease is observed throughout the layer (Fig. 7). Note that the first, different-from-the-initial

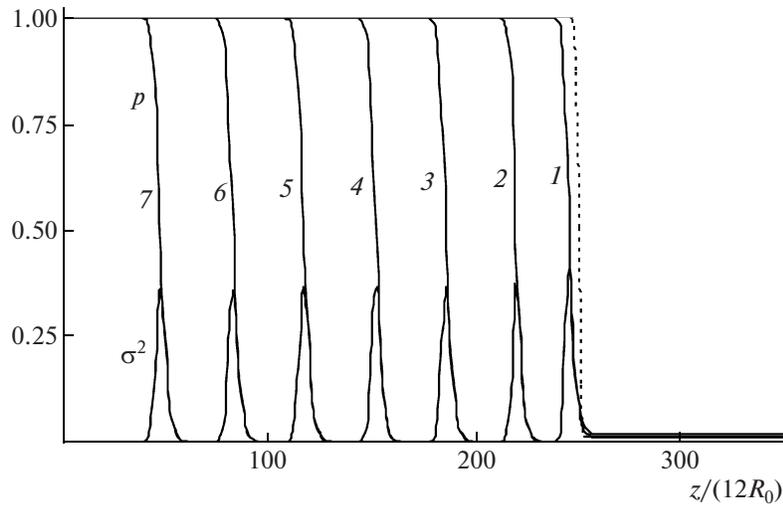


Fig. 6. Local average composition of the blend, $p(z)$, and compositional dispersion $\sigma^2(z) \times 10$: theoretical calculation through Eqs. (1) at $\chi = 0$ and $\gamma\tau_0 = 0.01$. The profiles are constructed at time $(t/\tau_0) \times 10^{-3} = (1) 0.4, (2) 2, (3) 4, (4) 6, (5) 8, (6) 10,$ and $(7) 12$. The initial boundary between units A and B, $\rho(z, t = 0)$, is shown by the dotted line.

profile $L_A(z)$ (curve 2) corresponds to time $t_{MC} = 10^3$ or to ten reaction steps. Within this period of time, the reaction spans over the entire layer of initial polymer A exclusively because of the chemical-relay-race mechanism. The width of the region where $L_A(z) = \text{const}$ is nearly equal to the width of the region where $p_A(z) \approx p_{1A}(z) \approx 1$ (compare curve 4 in Fig. 7 and curve 1 in Fig. 4 at the same time). This behavior corresponds to the case when, at the early reaction stages, the transformed units form thin filaments, which pass through the entire layer of the reacting chains, and the reaction

front (profile $n_A(z)$) starts to advance from the boundary inside this layer somewhat later.

Dispersion of the distribution with respect to the length of block A, σ_A^2 (Fig. 8), is appreciably different from the values that are characteristic of the Bernoullian copolymer with same average composition p_{1A} . Indeed, at $p_{1A} < 1 - 1/N$, we have $\sigma_{A\text{Bern}}^2 = p_{1A}/(1 - p_{1A})^2 + O(1/N)$. Let us consider $p_{1A} = 0.5$, which is attained at the following points: $z \approx 9$ at $t_{MC} = 2.6 \times 10^3$, $z \approx 4$ at $t_{MC} = 5.6 \times 10^3$, and $z \approx 1$ at $t_{MC} = 8.7 \times 10^3$ (Fig. 4). At these points (Fig. 8, curves 4, 6, 8), the val-

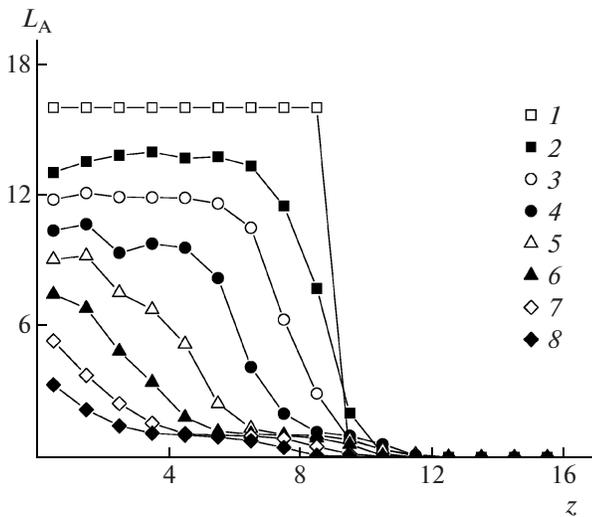


Fig. 7. Local average length of the block composed of units A, $L_A(z)$. Here and in Fig. 8, the profiles are constructed at $\tau = 10^2$ and at $t_{MC} \times 10^{-3} = (1) 0, (2) 1.0, (3) 1.5, (4) 2.6, (5) 4.1, (6) 5.6, (7) 7.2,$ and $(8) 8.7$.

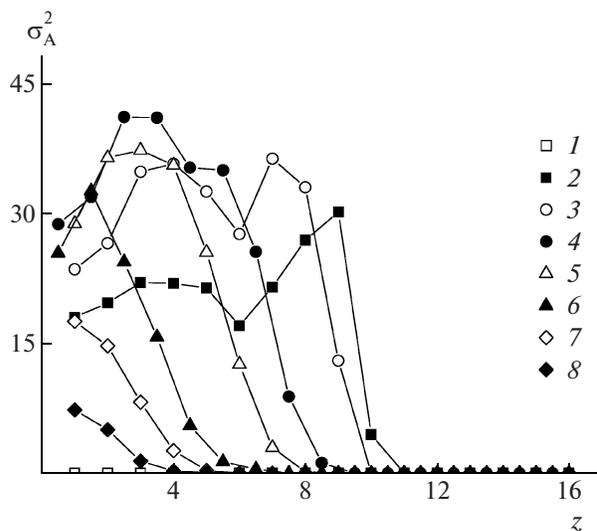


Fig. 8. Dispersion of the distribution with respect to the length of blocks A, σ_A^2 .

ues of σ_A^2 are ≈ 1 , 12, and 7; at the same time, $\sigma_{\text{ABern}}^2 \approx 2$. Let $p_{1A} = 0.75$, a case that corresponds to $z \approx 6.5$ at $t_{\text{MC}} = 2.6 \times 10^3$ and $z \approx 2.5$ at $t_{\text{MC}} = 5.6 \times 10^3$ (Fig. 4). In this case, at both points, $\sigma_A^2 \approx 30$ (Fig. 8, curves 4, 6) and $\sigma_{\text{ABern}}^2 \approx 12$. Detailed analysis shows that, in most cases, σ_A^2 is much higher than σ_{ABern}^2 ; in other words, the length distribution of blocks \bar{A} becomes broader as the reaction advances through the layer of the reacting chains.

CONCLUSIONS

A polymer-analogous reaction with the interchain effect in an inhomogeneous polymer blends is simulated via the Monte Carlo method. The use of the continuum model with the realistic interaction potentials of units makes it possible to analyze the evolution of the local structural characteristics of the reacting polymer system and to compare the contributions of the reaction and diffusion to the dynamics of the entire process.

For the model system under study, inhomogeneity of the system with respect to the composition and the length of the block of the reacting chains in the polymer blend increases on scales that are comparable to the chain size. This circumstance is related to (i) the fact that the reaction proceeds in the inhomogeneous system and (ii) the diffusion-controlled mobility of the reacting chains. The evolution of the parameters of the compositional distribution of chains qualitatively agrees with the theoretical predictions [9] on higher scales.

It may be expected [9, 15] that, in turn, the local inhomogeneity of the polymer mixture should control the reaction kinetics and the rate of the reaction-front motion. This problem was beyond the scope of this study, but, in the future, it will be of interest to study the role of these effects at the early stages when the reaction front is formed.

The importance of the numerical-simulation results is related to the fact that the local structure of the reacting polymer chains is difficult to describe in real experiments [1, 3]. Our further studies on the computer-aided simulation will address the polymer-analogous reactions in incompatible mixtures of poly-

mers; the knowledge thus gained will be important for controlling the reaction compatibilization and development of new multicomponent and multifunctional materials.

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