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Early Stages of Interchange Reactions in Polymer Blends

Yaroslav V. Kudryavtsev,[1] Alexander V. Chertovich,[2] Darja V. Guseva,[2] Arkady D. Litmanovich[1]*

Summary: Simple models are studied for better understanding of the early stages of interchange reactions in polymer blends. For a homogeneous blend of homopolymers A and B, parameters of copolymer AB formed at the reaction beginning are explicitly calculated. It is shown that the analysis of the copolymer composition can help to establish the prevailing interchange mechanism. For a bilayer blend of immiscible homopolymers A and B, the reactive compatibilization through interchange is studied by continual Monte Carlo modeling. The analysis of the local distribution in block length shows that the interdiffusion of blend components may start only after the formation of rather short copolymer blocks in the course of interchange.

Keywords: blends; compatibilization; interchain exchange; Monte Carlo simulation; theory

Introduction

Interchange reactions in the blends of condensation polymers lead to significant variations in their molar mass, chemical structure, and functionality. The synthesis of multiblock copolymers and blend compatibilization are considered as the main practical applications of those reactions. However, controlled processing is up to date problematic so that the materials with well-defined morphologies in the micro- to nano-scale cannot be easily obtained. Studying simple models could help to solve this problem by finding regularities in the evolution of the local molar mass and block length distributions.

The interchange kinetics was extensively investigated theoretically for homopolymer melts and homogeneous polymer blends.[1,2] It is widely accepted that a rapid (for minutes) relaxation of the molar mass distribution to its most probable form is followed by a much slower (for hours) randomization of the unit distribution in a resultant copolymer. During the early stage, the composition of the copolymer and whole blend can differ considerably, which may be detected in experiments. An approach relating the copolymer composition with the predominant interchange mechanism was elaborated[3,4] and applied to different systems, however, some discrepancies were later found.[5,6] In order to make the situation more clear, we exactly calculate in the next section the initial copolymer composition and discuss its dependence on the reaction mechanism and characteristics of the initial blend.

When the reactive compatibilization is studied, inhomogeneous models are used. For interchange reactions in incompatible polymer blends, no theory is developed so far, and Monte Carlo simulations are limited to describing either quantities averaged over an entire system, like the total conversion, or crude local charactrestics, such as the structure factor, blend and copolymer composition.[7–9] Progress in computing facilities makes it possible to extract more information from numerical

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[1] Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prosp. 29, Moscow 119991, Russia
Fax: (+7495)2302224
E-mail; yar@ips.ac.ru

[2] Physics Department, Moscow State University, Leninskie Gory, Moscow 119992, Russia

experiments, for example, the local distribution in block length can be captured. We report the results of such study in the third section with an emphasis on the outset of the interchange in a bilayer polymer blend. It is worth noting that just the early stages of reactions in inhomogeneous blends are of the most practical interest because interphase boundaries are continuously regenerated by forced mixing in the course of reactive processing.

Copolymer Formation in a Homogeneous Blend

Consider a homogeneous blend of two homopolymers whose molar mass distribution is characterized by the number of chains of type α (A or B) and length i (the number of reactive monomer units), $m_{\alpha i}$. Let n be the total number of reactive units and ϕ the fraction of units A in the blend. An interchange reaction starts at $t = 0$. Our aim is to describe the block distribution in diblocks formed at the very beginning of the reaction. Let us consider two alternative reaction mechanisms,[2] a direct interchange involving two internal units and an end-group interchange taking place when a reactive chain end attacks an internal monomer unit. In both cases we take that the number average lengths of the initial homopolymers, $\overline{N}_{\mathrm{A0}}$, $\overline{N}_{\mathrm{B0}}$, are large, i.e. much more than unity.

A direct interchange results in a copolymer formation if units A and B are involved. Let k_{AB} be the corresponding rate constant, then the number of blocks A and B of length i appearing per unit time is $2k_{\mathrm{AB}}(1-\phi)\sum_{j=i}^{\infty} m_{\mathrm{A0}j}$, $\quad 2k_{\mathrm{AB}}\phi\sum_{j=i}^{\infty} m_{\mathrm{B0}j}$, respectively. Using standard definitions, we can calculate the number- and weight-average lengths of blocks α:

$$\overline{N}^{(0)}_{\alpha cop} = \frac{1}{2}\overline{N}_{w\alpha 0},\ \overline{N}^{(0)}_{w\alpha cop} = \frac{2}{3}\overline{N}_{z\alpha 0}, \qquad (1)$$

where $\overline{N}_{w\alpha 0}$, $\overline{N}_{z\alpha 0}$ are the weight- and z- average polymerization degrees of the initial homopolymers, respectively. The polydispersity index for the copolymer blocks reads

$$\gamma^{(0)}_{\alpha cop} = \frac{\overline{N}^{(0)}_{w\alpha cop}}{\overline{N}^{(0)}_{\alpha cop}} = \frac{4}{3}\frac{\overline{N}_{z\alpha 0}}{\overline{N}_{w\alpha 0}} \qquad (2)$$

Thus, if the initial homopolymers A and B have the Flory molar mass distribution, the copolymer formed at the reaction beginning is characterized by the same polydispersity: $\gamma^{(0)}_{\alpha cop} = 2$. In the case of monodisperse initial homopolymers, the interchange increases the polydispersity index: $\gamma^{(0)}_{\alpha cop} = 4/3$.

The initial copolymer composition equals the ratio of the number of units A in the copolymer to that of all copolymer units. Simple calculations lead to the expression

$$\phi^{(0)}_{cop} = \frac{\overline{N}_{w\mathrm{A0}}}{\overline{N}_{w\mathrm{A0}} + \overline{N}_{w\mathrm{B0}}}, \qquad (3)$$

which may considerably differ from the blend composition ϕ.

If the interchange proceeds via the end-group mechanism, then a copolymer can be initially formed as a result of an A end attack on a B chain, or vise versa. Let k_{AB} and k_{BA} be the corresponding rate constants so that the number of A blocks of length i appearing per unit time in this case is $k_{\mathrm{AB}}(1-\phi)m_{\mathrm{A0}i} + k_{\mathrm{BA}}((1-\phi)/\overline{N}_{\mathrm{B0}})\sum_{j=i+1}^{\infty} m_{\mathrm{A0}j}$. For B blocks, we get from analogy $k_{\mathrm{BA}}\phi m_{\mathrm{B0}i} + k_{\mathrm{AB}}(\phi/\overline{N}_{\mathrm{A0}})\sum_{j=i+1}^{\infty} m_{\mathrm{B0}j}$. From this we can derive the average block lengths at the reaction outset:

$$\overline{N}^{(0)}_{\mathrm{A}cop} = \frac{k_{\mathrm{AB}} + k_{\mathrm{BA}}\overline{N}_{w\mathrm{A0}}\overline{N}^{-1}_{\mathrm{B0}}/2}{k_{AB}\overline{N}^{-1}_{\mathrm{A0}} + k_{BA}\overline{N}^{-1}_{\mathrm{B0}}},$$

$$\overline{N}^{(0)}_{\mathrm{B}cop} = \frac{k_{\mathrm{BA}} + k_{\mathrm{AB}}\overline{N}_{w\mathrm{B0}}\overline{N}^{-1}_{\mathrm{A0}}/2}{k_{AB}\overline{N}^{-1}_{\mathrm{A0}} + k_{BA}\overline{N}^{-1}_{\mathrm{B0}}}$$

$$\overline{N}^{(0)}_{w\mathrm{A}cop} = \overline{N}_{w\mathrm{A0}}\frac{k_{\mathrm{AB}} + k_{\mathrm{BA}}\overline{N}_{z\mathrm{A0}}\overline{N}^{-1}_{\mathrm{B0}}/3}{k_{\mathrm{AB}} + k_{\mathrm{BA}}\overline{N}_{w\mathrm{A0}}\overline{N}^{-1}_{\mathrm{B0}}/2},$$

$$\overline{N}^{(0)}_{w\mathrm{B}cop} = \overline{N}_{w\mathrm{B0}}\frac{k_{\mathrm{BA}} + k_{\mathrm{AB}}\overline{N}_{z\mathrm{B0}}\overline{N}^{-1}_{\mathrm{A0}}/3}{k_{\mathrm{BA}} + k_{\mathrm{AB}}\overline{N}_{w\mathrm{B0}}\overline{N}^{-1}_{\mathrm{A0}}/2} \qquad (4)$$

and the polydispersity index for each block type

$$\gamma_{\mathrm{A}cop}^{(0)}=\frac{\overline{N}_{w\mathrm{A}cop}^{(0)}}{\overline{N}_{\mathrm{A}cop}^{(0)}}=\overline{N}_{w\mathrm{A0}}\frac{(k_{\mathrm{AB}}+k_{\mathrm{BA}}\overline{N}_{z\mathrm{A0}}\overline{N}_{\mathrm{B0}}^{-1}/3)(k_{AB}\overline{N}_{\mathrm{A0}}^{-1}+k_{BA}\overline{N}_{\mathrm{B0}}^{-1})}{(k_{\mathrm{AB}}+k_{\mathrm{BA}}\overline{N}_{w\mathrm{A0}}\overline{N}_{\mathrm{B0}}^{-1}/2)^2},$$
$$\gamma_{\mathrm{B}cop}^{(0)}=\frac{\overline{N}_{w\mathrm{B}cop}^{(0)}}{\overline{N}_{\mathrm{B}cop}^{(0)}}=\overline{N}_{w\mathrm{B0}}\frac{(k_{\mathrm{BA}}+k_{\mathrm{AB}}\overline{N}_{z\mathrm{B0}}\overline{N}_{\mathrm{A0}}^{-1}/3)(k_{AB}\overline{N}_{\mathrm{A0}}^{-1}+k_{BA}\overline{N}_{\mathrm{B0}}^{-1})}{(k_{\mathrm{BA}}+k_{\mathrm{AB}}\overline{N}_{w\mathrm{B0}}\overline{N}_{\mathrm{A0}}^{-1}/2)^2}. \tag{5}$$

Again, if the initial homopolymers have the Flory distribution, then at the early stage of the reaction we get the same for copolymer blocks: $\gamma_{\mathrm{A}cop}^{(0)}=\gamma_{\mathrm{B}cop}^{(0)}=2$, whereas in the case of initially monodisperse polymers at $k_{\mathrm{AB}}=k_{\mathrm{BA}}$ the polydispersity index is slightly more than unity: $\gamma_{\mathrm{A}cop}^{(0)}=\gamma_{\mathrm{B}cop}^{(0)}=32/27$. Now let one type of end-attack dominate say the end of an A chain on an internal B unit, which can be realized for $\overline{N}_{\mathrm{A0}}\ll\overline{N}_{\mathrm{B0}}$ or $k_{\mathrm{AB}}\gg k_{\mathrm{BA}}$. It is easy to find from Eq. (5) that copolymer blocks A will be as polydisperse as the initial homopolymer A ($\gamma_{\mathrm{A}cop}^{(0)}=\overline{N}_{w\mathrm{A0}}/\overline{N}_{\mathrm{A0}}$), while for blocks B the polydispersity index will obey Eq. (2) $\gamma_{\mathrm{B}cop}^{(0)}=4\overline{N}_{z\mathrm{B0}}/(3\overline{N}_{w\mathrm{B0}})$, as for the direct interchange.

The initial copolymer composition for the end-group interchange reads

$$\phi_{cop}^{(0)}\approx\frac{k_{\mathrm{AB}}+k_{\mathrm{BA}}\overline{N}_{w\mathrm{A0}}\overline{N}_{\mathrm{B0}}^{-1}/2}{k_{\mathrm{AB}}(1+\overline{N}_{w\mathrm{B0}}\overline{N}_{\mathrm{A0}}^{-1}/2)+k_{\mathrm{BA}}(1+\overline{N}_{w\mathrm{A0}}\overline{N}_{\mathrm{B0}}^{-1}/2)}, \tag{6}$$

which is, as well as Eq. (3), completely independent of the average blend composition ϕ.

Comparing Eqs. (3) and (6), we may conclude that the mechanism of interchange in fact has a pronounced effect on the initial copolymer composition. For instance, in the case of monodisperse initial homopolymers of equal length ($\overline{N}_{\mathrm{A0}}=\overline{N}_{\mathrm{B0}}$) we get $\phi_{cop}^{(0)}\approx 1/2$ for the direct interchange and $\phi_{cop}^{(0)}\approx(2k_{\mathrm{AB}}+k_{\mathrm{BA}})/(3(k_{\mathrm{AB}}+k_{\mathrm{BA}}))$ for the end-group reaction. If end groups B are inactive ($k_{\mathrm{BA}}=0$), then $\phi_{cop}^{(0)}\approx 2/3$ so that the resultant copolymer is enriched with units A, whereas in the opposite situation ($k_{\mathrm{AB}}=0$) it contains more units B as $\phi_{cop}^{(0)}\approx 1/3$, and, finally, in the case of equal reactivity ($k_{\mathrm{AB}}=k_{\mathrm{BA}}$) $\phi_{cop}^{(0)}\approx 1/2$. However, for the blends of homopolymers having the Flory distribution, which is the most probable one for linear chains of condensation polymers, both interchange mechanisms lead to the same initial copolymer composition. In fact, we get from either Eq. (3) or Eq. (6) the value of $\phi_{cop}^{(0)}\approx\overline{N}_{\mathrm{A0}}/(\overline{N}_{\mathrm{A0}}+\overline{N}_{\mathrm{B0}})$, which is determined by the average homopolymer lengths $\overline{N}_{\mathrm{A0}}$, $\overline{N}_{\mathrm{B0}}$ independently of the rate constant values and composition of the whole blend.

The simple calculations carried out in this section may be useful for analysing experimental data on copolymer structure in the course of early stages of interchange reactions in polymer blends. It is shown that the conclusion whether the initial copolymer composition is indicative of the interchange mechanism depends on the characteristics of the initial polymer blend. Information on the subsequent evolution of the unit distribution can be obtained through numerical solution of the kinetic equations derived in refs.[5,6]

Interchange at a Polymer/Polymer Interface

The computer simulation of an interchange reaction in a heterogeneous polymer blend was carried out using the continual dynamic Monte Carlo method[10] that avoids appearance of lattice-induced artefacts. To start with, a cubic cell XYZ $16\times16\times16$ was filled with 256 homopolymer chains of 16 reactive units each (128 chains A were placed at $0\le z\le 8$ and 128 chains B at $8\le z\le 16$). Along axes X and Y the periodic boundary conditions were imposed, whereas no diffusive flux was allowed through cell boundaries perpendicular to Z-axis. Chains were represented using the bead-spring model, with inter-chain interactions described by Morse potentials.[11] The volume fraction of polymer units was about 0.27. The dynamics was modeled through the standard Metropolis algorithm. After every τ Monte Carlo conformational movements, the reaction step was carried out so that any end-group could break one of neighboring bonds (springs) and attach to one of the newborn ends, while another end became a reactive end group. Small values of τ, which was varied from 10^3 to 10^6, corresponded to the fast reaction, while large to the slow one.

First of all, an equilibration of the bilayer homopolymer system was performed at a considerably stronger attraction of similar units (the characteristic energy $E_{AA} = E_{BB} = 10E_{AB}$) and interchange only between them (A and A, B and B). Since monomers A and B remained compatible in all considered cases, the formation of short chains was hindered by prohibiting reactions that involve internal units situated in less than l units to a chain end (normally, $l = 4$ was taken). This restriction got the model system properties closer to those of a real polymer blend, where the role of short chains is usually negligible. A stationary state of the initial bilayer system is shown at Figure 1. The molar mass distribution of both components is of the Flory type.

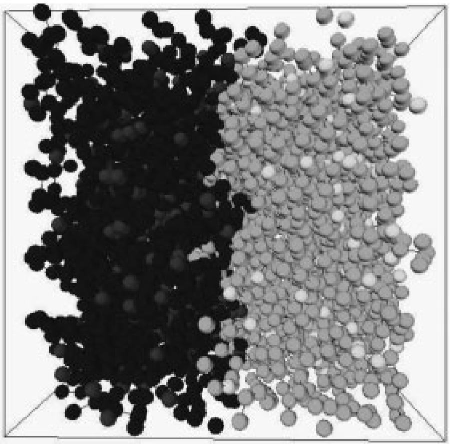

Figure 1.
Snapshot of the initial bilayer blend of homopolymers A and B. End groups are shown in lighter shades.

Then, the interchange between A and B chains was allowed in order to observe the reactive compatibilization. Two parameters were varied, the "effective temperature" T, which enters the Metropolis criterion and governs the diffusion rate only, and τ, which determines the ratio of diffusion and reaction rates. For simplicity, T and τ were treated as independent parameters.

Simulations demonstrate that the interchange proceeds differently from that process in a homogeneous blend, even in terms of the most crude characteristics. As is seen from Figure 2, the dependence of the blend-average length of block A, L_A, on time is far from exponential, which should be a straight line in the chosen coordinates, and its large-time limit $L_{A\ min}$ considerably exceeds the value of 2 characterizing a completely random (Bernoullian) copolymer of an equimolar composition. It is found that $L_{A\ min}$ decreases if T or τ are increased. Thus, in the course of reactive compatibilization, inhomogeneities do not completely disappear, which may be explained by a strong attraction of similar units.

Local averages, such as the number density of units (n_A, n_B) and dyads (n_{AB}) along Z-axis, contain more information

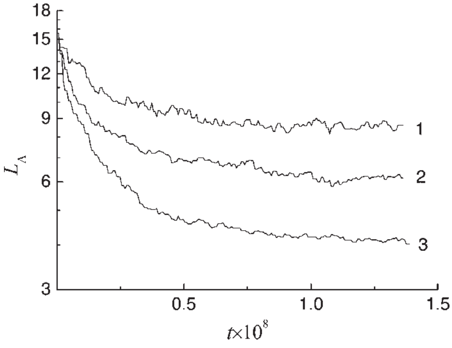

Figure 2.
Dependence of the average length of block A, L_A, on time t (in MC steps) at $T = 0.6$ (curve 1), 0.8 (2), and 1.0 (3) for $\tau = 1.0 \times 10^6$.

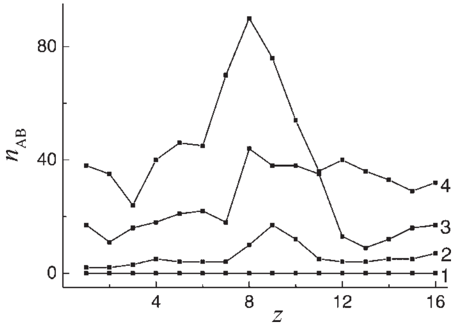

Figure 3.
The number density of dyads AB, n_{AB}, vs. coordinate z at $T = 1.0$ for the moments of time $t = 5.9 \times 10^5$ (curve 1), 5.2×10^6 (2), 2.0×10^7 (3) и 1.15×10^8 (4) for $\tau = 1.0 \times 10^6$.

about the structure of a reacting polymer blend. At high temperature ($T = 2.0$) the blend is macroscopically compatible and the initial system is not really a bilayer one so that the interchange proceeds in the bulk almost from the beginning. For $T = 1.0$, one can see at Figure 3 that at early stages the copolymer is formed at the interface, then its degree of blockiness increases with time and, simultaneously, the content of AB dyads in the initial phases grows due to the interdiffusion. Finally, an inhomogeneous equilibrium state is formed, with characteristics to be described elsewhere. In the case of low temperature $T < 1.0$, only a slight relaxation of the initial inhomogeneity is observed since the copolymer formed by the interchange is localized within the interfacial layer.

As is seen from Figure 4, the reaction rate is the most important factor at early stages (Figure 4a), whereas later the temperature begins to play a major role (Figure 4b), T determines the width of the interfacial copolymer layer and its degree of blockiness in the equilibrium state (Figure 4c) as well.

At Figures 5 and 6 the dependence of the number density of blocks of different length on the coordinate z is shown in two-

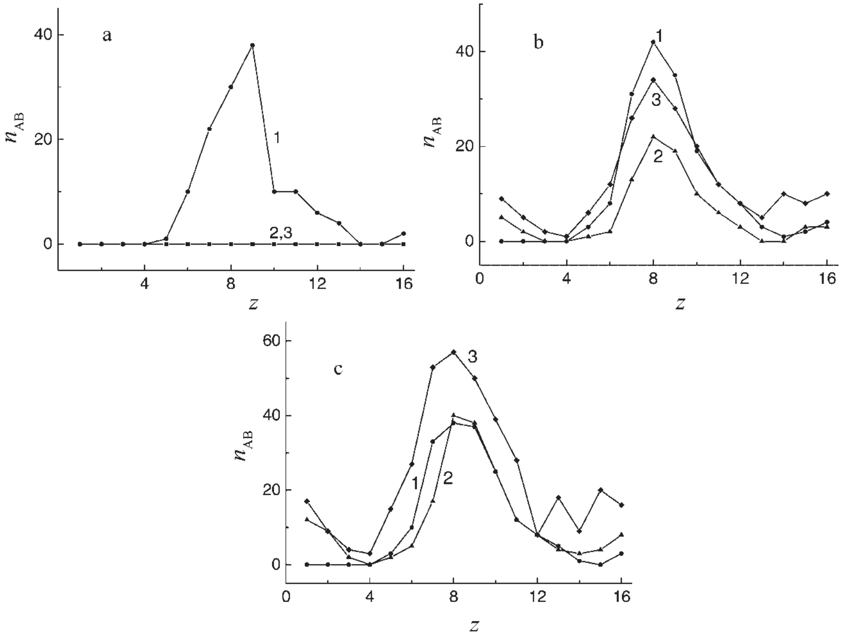

Figure 4.
The number density of dyads AB, n_{AB}, vs. coordinate z for the fast reaction ($\tau = 4.1 \times 10^3$) at $T = 0.6$ (curve 1) and slow one ($\tau = 1.0 \times 10^6$) at $T = 0.6$ (2) and 0.8 (3). The profiles are plotted for the moments of time $t = 5.9 \times 10^5$ (a), 2.0×10^7 (b), and 1.4×10^8 (c, the equilibrium state).

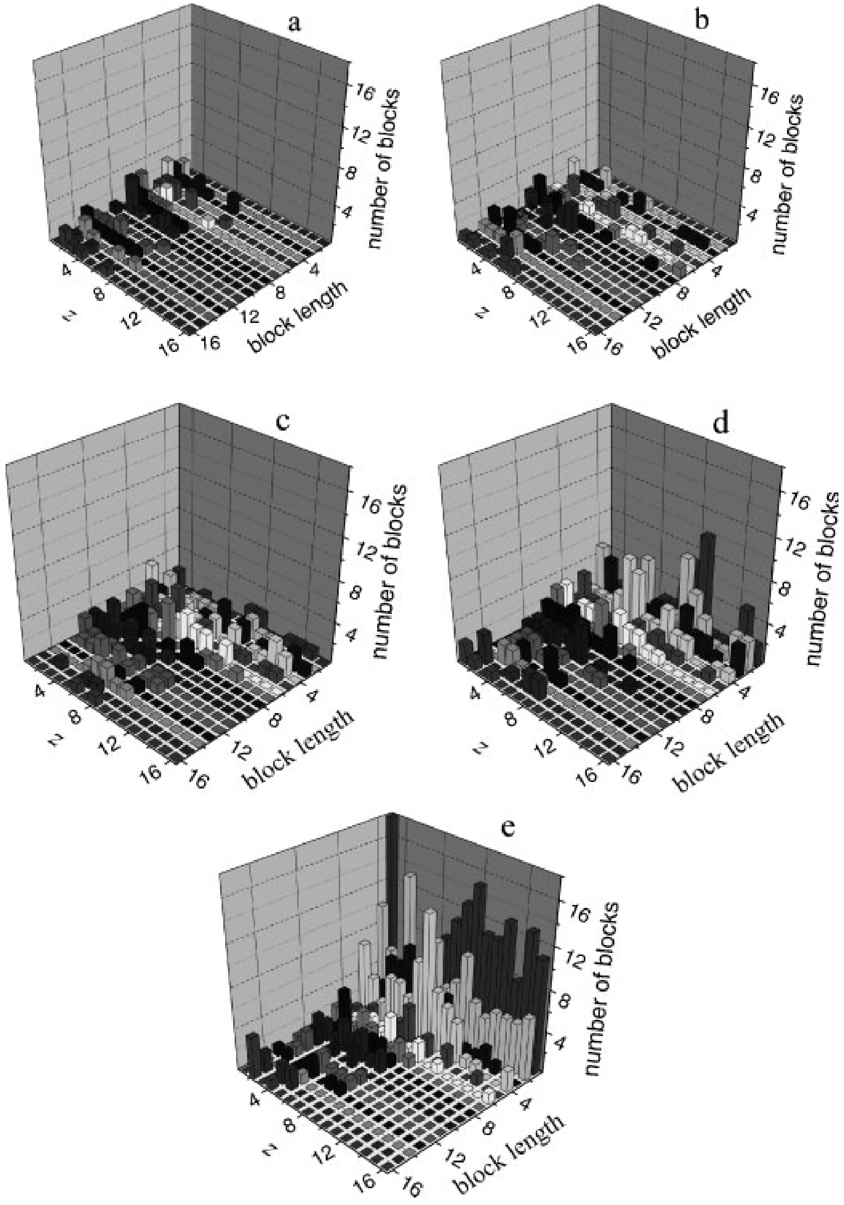

Figure 5.

The evolution of the local block length distribution in a reacting polymer blend. Histograms represent the number of blocks A of different length per unit interval along Z-axis at $T = 0.6$, $\tau = 1.0 \times 10^6$ for the moments of time: $t = 0$ (a), 5.9×10^5 (b), 5.2×10^6 (c), 2.0×10^7 (d), and 1.15×10^8 (e). Blocks longer than 16 units are not shown.

dimensional histograms. A detailed picture of the reactive compatibilization at $T = 1.0$ is presented at Figure 5. Initially, all units A are situated on the farther side of the simulation cell (the layer of homopolymer A). The early stage is characterized by the diffusion of short chains A into phase B due to their thermodynamic compatibility at $T = 1.0$ without any reaction, which is proved by the absence of dyads AB at the

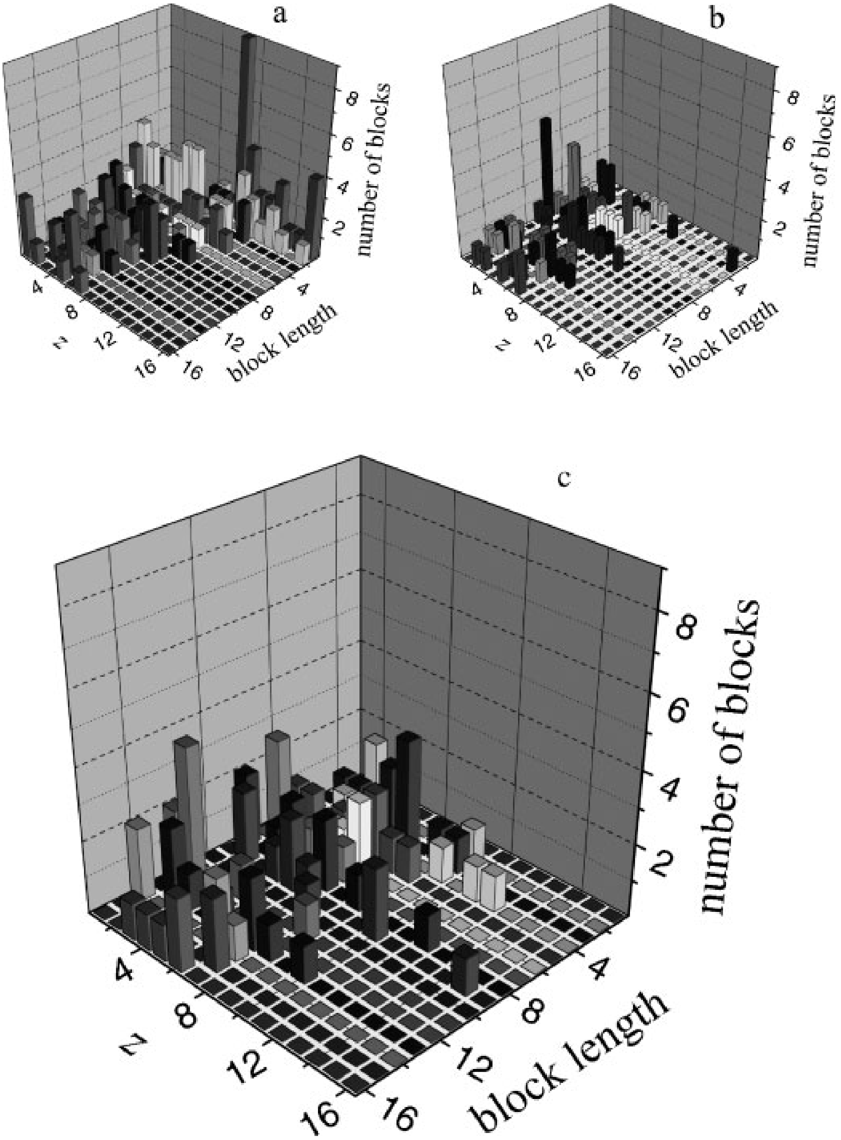

Figure 6.

The early stage of reactive compatibilization in a polymer blend. The number density of blocks A plotted vs. their length and spatial coordinate z at $t = 5.9 \times 10^5$ for the fast reaction ($\tau = 4.1 \times 10^3$) at $T = 0.6$ (a) and slow one ($\tau = 1.0 \times 10^6$) one at $T = 0.6$ (b) and 0.8 (c). Blocks longer than 16 units are not shown.

corresponding moment of time (curve 1 in Figure 4). Later the reaction reveals itself through decreasing the number of long blocks in the phase A and forming many short blocks that diffuse into the phase B and, with the system equilibration, appear to be distributed almost uniformly, while longer blocks are localized mostly in their own phase.

In the equilibrium state, if a long block A is formed in the phase B due to the interchange, then it is pushed into the phase A, where it decays with time into short blocks that can again diffuse into the phase B, and so on. The similar picture is found at other temperatures but with the different content of chains compatible without any reaction. For example, at $T = 0.6$ only very short chains A and B of 1–3 reactive units are compatible but they are absent in the initial model system due to the restrictions imposed on their formation. Therefore, the compatibilization starts only after copolymer AB chains with short enough blocks are formed in the course of interchange. One may expect existence of the similar latent period in real polymer blends deprived of short chains.

The reaction rate has a great influence on the early stage of the process. It is seen from Figure 6 that in the case of fast reaction at $T = 0.6$ blocks of 1–2 units are formed and penetrate the phase B earlier than at $T = 0.8$ the interdiffusion of existing compatible chains of 1–5 units takes place (and much less than at $T = 0.6$). Correspondingly, the equilibration time for the fast reaction is considerably less than for the slow one. The described picture explains in more detail the evolution of AB-dyads density shown in Figure 4.

Thus, Monte Carlo simulations allow us to visualize processes that take place at the interphase boundaries of molten polymers undergoing interchange reactions. As far as we are aware, the evolution of the local block length distribution was monitored in this paper for the first time.

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