

MODERN PROBLEMS OF THE THEORY OF MACROMOLECULAR REACTIONS IN POLYMER BLENDS

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Abstract: The main task of the theory of macromolecular reactions in polymer blends is to describe an evolution of the blend structure under the concerted action of the reaction and interdiffusion. For a polymeranalogous reaction proceeding with autoacceleration in a compatible blend, the task has been solved by methods of linear non-equilibrium thermodynamics. The set of reaction-diffusion equations derived permits to describe the blend structure in details, including the parameters characterizing compositional heterogeneity and units' distribution of the reacting chains in any local region of the blend. For incompatible blend of two homopolymers, the competition between a phase separation and the reaction of end-coupling with a formation of diblock-copolymer has been considered. The peculiarities of the processes mentioned as well as the actual problems in this field are discussed.

INTRODUCTION

They began to build the theory of macromolecular reactions having analyzed chemical transformations of quasi-isolated macromolecules. The effect of neighboring units, conformational and electrostatic effects have been considered. The most advanced theory is one elaborated for the neighbor effect. The equations derived connect the rate constants of the reaction and the distribution of reacted and unreacted units along the chain of the product. It permits to calculate any parameters of the units' distribution including ones that are difficult or even impossible to estimate experimentally. Such an information may be used both for elucidating the

reaction mechanism and for studying "structure - properties" relations. Theoretical results related to these problems as well as numerous examples of their application to experimental data have been published recently (Refs. 1, 2).

The results mentioned are used to describe the reactions in diluted solutions. Meanwhile the chemical processes in a polymer bulk state - in melts, in glasses and especially in blends - attain more and more practical importance.

Some reactions used purposely to improve a compatibility of polymer blends may be pointed out.

(a) Interchain exchange, in particular, transesterification. Tanaka a.o. (Ref. 3) studied a competition between phase separation and transesterification occurring in blends of polycarbonate and poly(ethylene terephthalate) or polycarbonate and polyarylate.

(b) Formation of block copolymers *in situ*. Macosko and co-workers studied the reaction between chain ends in a blend of carboxylic acid terminal polystyrene and epoxy terminal poly(methyl methacrylate) (PMMA) (Ref. 4). The formation of di-block copolymer prevents a growth of the particles of a dispersed phase and stabilizes the blend morphology.

(c) Polymeranalogous reaction. Jayabalan (Ref. 5) foamed a mixture of PVC and PMMA at 200°C and obtained an impact-resistant foam possessing only one glass temperature. An explanation is that a partial dehydrochlorination of PVC occurs and the mobile allylic H atoms generated form hydrogen bonds with carbonyl groups of PMMA thus promoting the blend homogenization.

In general, a realization of chemical reactions directly during the mixing is used widely to modify the blends properties: RIM process, reactive extrusion (Ref. 6)

It is obvious that an information about the reaction kinetics and the blend structure is necessary to control such processes and to interpret the properties of the composites produced.

However the studying the detailed structure of blends is an extremely difficult task. Meanwhile till recently there was not any theory that would permit to describe quantitatively the change of polymer blends structure during their chemical transformations.

Our objective is to consider the problem and the first attempts of the theoretical analysis of macromolecular reactions in polymer blends.

PECULIARITIES OF REACTIONS IN BLENDS

Consider some essential peculiarities of the reactions in polymer blends.

First of all, for reactions in a polymer bulk state, one needs to take account of the chemical interchain effect, i.e., a direct influence of the interchain interactions on the reactivity of polymer functional groups.

Let, in a polymer *A* melt, *A* units transform irreversibly into *B* ones. According to the theory of interchain effect (Ref.7), the *A* group reactivity depends upon its microenvironment; these are inner neighbors (two nearest neighboring *A* and *B* units of the same chain) and external ones (units belonging to the other chains). This effect has been studied using thermal decomposition of pendant groups of poly(*t*-butyl acrylate) (PTBA).

The reaction proceeds with pronounced acceleration caused by an interaction of the ester group with two carboxylic groups, one or two of the latter being external neighbors; i.e., just interchain interaction is an inalienable component of the acceleration (Ref. 8). Such an interaction manifests itself strikingly during the PTBA decomposition in blends. Thus the reaction rate increases in PTBA blends with poly(acrylic acid) (PAA) containing carboxylic groups and, conversely, decreases in blends with polyethyleneimine binding carboxylic groups that are formed as a result of ester groups decomposition (Refs 9, 10).

The blend initial structure affects essentially the reaction kinetics. Ermakov a.o. (Refs. 11, 12) prepared two PTBA - PAA blends of the same composition by one and the same procedure (freeze drying) but from different solvents: *tert*-butanol - water (7:1) and dioxane - water (50:1). More effective interpenetration of the components for the blend prepared from *tert*-butanol - water has been proved by physical methods. Just in that blend, a more pronounced interchain acceleration was realized.

The first mathematical models for the reaction in PTBA - PAA blends (Ref.11) involved the contributions of both the interchain effect and the blend initial structure but failed to describe experimental data quantitatively. The necessity became clear to take account of a change of the blend structure as a result of interdiffusion. Thus the new problem arose: theoretical description of interdiffusion in reacting polymer blends.

Interdiffusion in blends without a reaction is studied intensively by both theoretical and experimental methods (Refs. 13, 14). A binary blend of compatible flexible polymers *A* and *B* is mainly considered, an evolution of its structure being described by a time-depending profile of the volume fraction of *A* chains ϕ .

Let now a reaction proceed in such a blend: *A* units transform into *B* ones; in that case some new factors are involved into the problem.

a) First, in polymer systems these are chains that diffuse but these are units that react. Therefore the concentration profile of reacting chains (ϕ) and that of transforming units *A* (ρ) do not coincide and such a divergence may affect both the driving forces of interdiffusion and the reaction kinetics.

b) Second, the products of macromolecular reaction are heterogeneous in composition, so that a binary initial blend becomes essentially multicomponent during the process. As a consequence, a new type of diffusive movement arises in the system, that will be discussed below.

Thus the problem is significantly complicated and, to create a theory, one must begin from some relatively simple models (however reflecting peculiarities of the process).

REACTION AND INTERDIFFUSION IN COMPATIBLE BLEND

Consider spatially inhomogeneous blend of compatible homopolymers A and B with chain length N_A and N_B respectively. Let irreversible reaction $A \rightarrow B$ proceed in the blend, B units accelerating the reaction, so that A units transform by three independent pathways:

1. spontaneously, in any microenvironment, with the rate constant α ;
2. having one inner neighbor B , with the rate constant β
(neighbor effect, the influence of the two inner B neighbors is additive);
3. in a contact with an external B unit, with the rate constant γ
(interchain effect).

The task is to describe an evolution of the blend structure under concerted action of the interdiffusion and the reaction (Refs. 15 -17).

Consider a region, small but containing many polymer chains, a size of the region being of the order of a coil size R_0 .

Now let us take the two assumptions:

- a) during the time of a single unit A transformation τ_{react} , a reacting chain diffuses on the distance L_{diff} of the order of its own size R_0

$$\frac{L_{diff}}{R_0} \approx \left(\frac{D_s \tau_{react}}{R_0^2} \right)^{1/2} \geq 1 \quad (1)$$

where D_s is the self-diffusion coefficient of the chain; in other words, the reaction is slow enough so that the diffusion is able to restore the local thermodynamic equilibrium in the system;

- b) the blend is weakly inhomogeneous so that, within the region, a change of the volume fraction of the reacting chains is small in comparison with its value ϕ

$$\left| \frac{\delta \phi}{\phi} \right|_{R_0} \ll 1. \quad (2)$$

Now the methods of linear non-equilibrium thermodynamics may be applied to describe the model.

To solve the task formulated above, it is necessary: first, to derive an expression of the free energy density for the locally equilibrium blend of homopolymer *B* and heterogeneous in composition random copolymer *AB*; second, to calculate the kinetic coefficients which control diffusive movements of various components in such a reacting blend.

The following expression for the free energy density has been derived (Ref. 16):

$$\begin{aligned} \frac{F(\phi, \rho_1, \rho_2)}{k_B T} = & \frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \\ & \rho_2 \ln \rho_2 + 2(\rho_1 - \rho_2) \ln(\rho_1 - \rho_2) + (\phi - 2\rho_1 + \rho_2) \ln(\phi - 2\rho_1 + \rho_2) \\ & \rho_1 \ln \rho_1 - (\phi - \rho_1) \ln(\phi - \rho_1) + \chi \rho_1 (1 - \rho_1) \end{aligned} \quad (3)$$

The first two terms in the right-hand side of (3) are the entropy of mixing S_{tr} of reacting and non-reacting (*B*) chains, the last term is the interaction energy of units; these are the ordinary constituents of the Flory free energy of mixing. The remaining terms, however, present an essentially new constituent, namely, this is a structural contribution into entropy S_{str} originated from the irregularity of the reacting chains structure. Here ρ_1 and ρ_2 are the volume fractions of *A* units and *AA* diads.

The kinetic coefficients may be expressed in the matrix form (Ref. 17)

$$\Lambda = \Lambda_{inter} \begin{pmatrix} 1 & \rho_1 & \rho_2 \\ \rho_1 & \rho_1^2 & \rho_1 \rho_2 \\ \rho_2 & \rho_1 \rho_2 & \rho_2^2 \end{pmatrix} + \Lambda_A \begin{pmatrix} 0 & 0 & 0 \\ 0 & \sigma_{11}^2 & \sigma_{12}^2 \\ 0 & \sigma_{12}^2 & \sigma_{22}^2 \end{pmatrix} \quad (4)$$

The first term corresponds to the contribution of interdiffusion of the homopolymer *B* and the copolymer *AB*, the process being controlled by coefficient Λ_{inter} and structural parameters - units *A* and diads *AA* fractions in the reacting chains, ρ_1 and ρ_2 respectively. In turn, within framework of the fast-mode diffusion theory (Ref. 13),

$$\Lambda_{inter}^{(fast)} = (1-\phi)^2 \Lambda_A + \phi^2 \Lambda_B \quad (5)$$

where

$$\Lambda_A = \phi N_A D_A$$

$$\Lambda_B = (1-\phi) N_B D_B$$

D_A и D_B are self-diffusion coefficients of the reacting *AB* and non-reacting *B* chains respectively.

The second term reflects a diffusive intermixing of the reacting chains of different composition. This process is controlled by coefficient Λ_A and covariations characterizing a heterogeneity of the reacting chains in composition, in particular, by the dispersion of compositional distribution σ_{11}^2 .

Using expressions for free energy and kinetic coefficients presented, the general balance equations have been solved; the latter included, beside the flows of

macromolecules, also the chemical transformations of A units according to the reaction pathways shown above. In this way the reaction-diffusion equations have been derived (Ref. 16) describing an evolution of the polymer blend structure under concerted influence of a macromolecular reaction and interdiffusion.

The equations are written below in general

$$\frac{\partial \rho_i(\vec{r}, t)}{\partial t} = \vec{\nabla} \left\{ \sum_{j,k} \Lambda_{ij} \frac{\partial^2 F(\{\rho\})/k_B T}{\partial \rho_j \partial \rho_k} \frac{\partial \rho_k}{\partial \vec{r}} \right\} + f_i \quad (6)$$

and in extended form

$$\begin{aligned} \frac{\partial \phi}{\partial t} &= \vec{\nabla} \left\{ D_{coop} \vec{\nabla} \phi - 2 \chi \rho_1 \phi \Lambda_{inter} \vec{\nabla} \rho_1 \right\} \\ \frac{\partial (\rho_1 \phi)}{\partial t} &= \vec{\nabla} \left\{ \rho_1 (D_{coop} - 2 \chi \sigma_{11}^2 \Lambda_A) \vec{\nabla} \phi + \phi (D_A - 2 \chi (\rho_1^2 \Lambda_{inter} + \sigma_{11}^2 \Lambda_A)) \vec{\nabla} \rho_1 \right\} + f_1 \\ \frac{\partial (\rho_2 \phi)}{\partial t} &= \\ \vec{\nabla} \left\{ (\rho_2 D_{coop} - 2 \chi \rho_1 \sigma_{12}^2 \Lambda_A) \vec{\nabla} \phi - 2 \chi (\rho_1 \rho_2 \Lambda_{inter} + \sigma_{12}^2 \Lambda_A) \phi \vec{\nabla} \rho_1 + \phi D_A \vec{\nabla} \rho_2 \right\} + f_2 \end{aligned} \quad (7)$$

where

$$D_{coop} = \Lambda_{inter} \left(\frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} - 2 \chi \rho_1^2 \right)$$

is the coefficient of a cooperative diffusion,

$$\begin{aligned} f_1 &= - \left(\alpha + 2 \beta \left(1 - \frac{\rho_2}{\rho_1} \right) + \gamma (1 - \phi \rho_1) \right) \phi \rho_1 \\ f_2 &= - 2 \left(\alpha + \beta \left(1 - \frac{\rho_2}{\rho_1} \right) + \gamma (1 - \phi \rho_1) \right) \phi \rho_2 \end{aligned}$$

f_1 and f_2 are the rates of a decay of A units and AA diads respectively.

Using these equations, an influence of various factors on the evolution of a reacting polymer blend has been studied (Ref. 18).

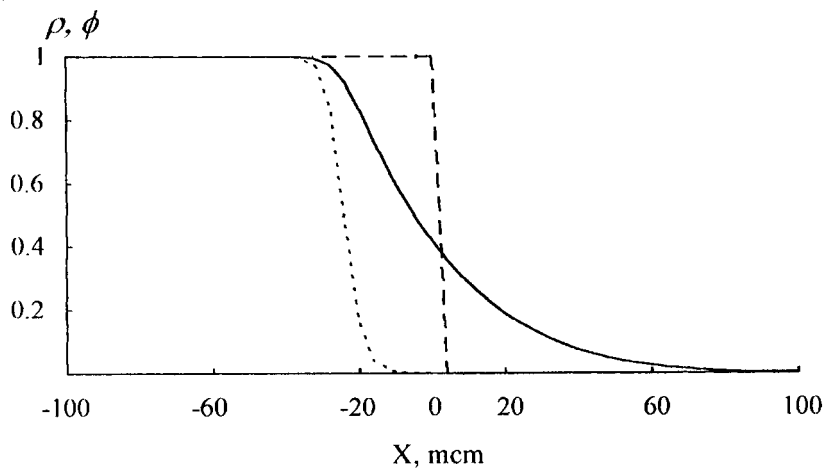
The effects observed were especially pronounced for a strong interchain acceleration, i.e., for the values of the rate constants $\alpha = \beta = 0$; $\gamma \neq 0$.

Thus, two kinds of diffusive movements proceed in a reacting polymer blend: 1) interdiffusion (opposite flows) of the reacting and non-reacting chains resulting in a penetration of B chains into A region which is described by a change of ϕ profile; 2) diffusive intermixing of the reacting chains of different structure. The second kind of the movements is caused by compositional heterogeneity of the reaction products; its contribution is shown on Fig. 1.

If the intermixing is neglected (Ref. 15), the reaction proceeds only in the regions where the B chains have penetrated (Fig. 1a). However correct calculations show that due to intermixing, the reaction for the same time interval extends throughout all

the region occupied by reacting chains (Fig. 1b). So the degree of conversion increases markedly (the fraction of unreacted units A corresponds to the area under a curve ρ).

a)



b)

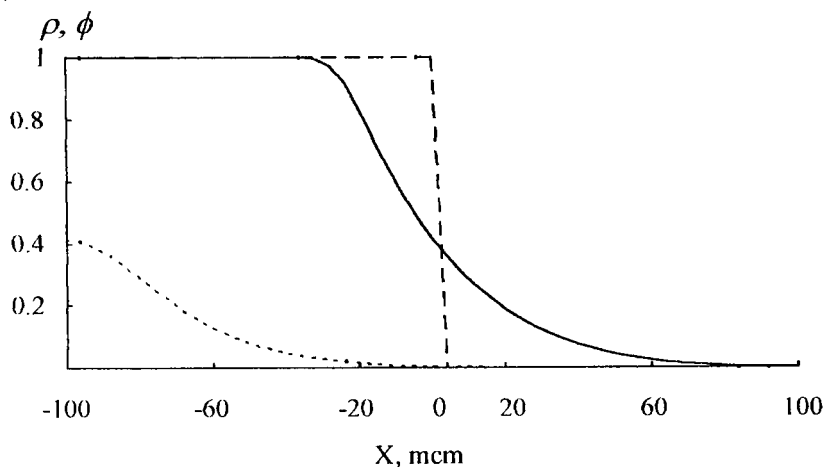
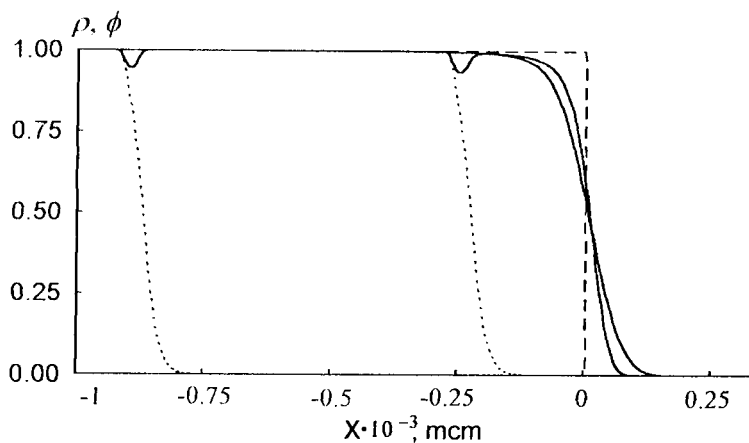


Fig 1. Influence of diffusive intermixing of reacting chains on the reaction kinetics. Volume fractions' profiles of the A groups (ρ , dotted line) and that of reacting chains (ϕ , solid line) are given: with consideration of intermixing (b) and without it (a). The initial profile of ϕ is denoted by the dashed line.

$N_A/N_B = 1/4$, $\alpha = \beta = 0$, $\gamma = 5 \cdot 10^{-5} \text{ s}^{-1}$, $\chi = 0$, time $17,5 \cdot 10^4 \text{ s}$.

Thus the diffusive intermixing may affect significantly the reaction kinetics. The separation of ϕ and ρ profiles is seen clearly in Fig. 1.

a)



b)

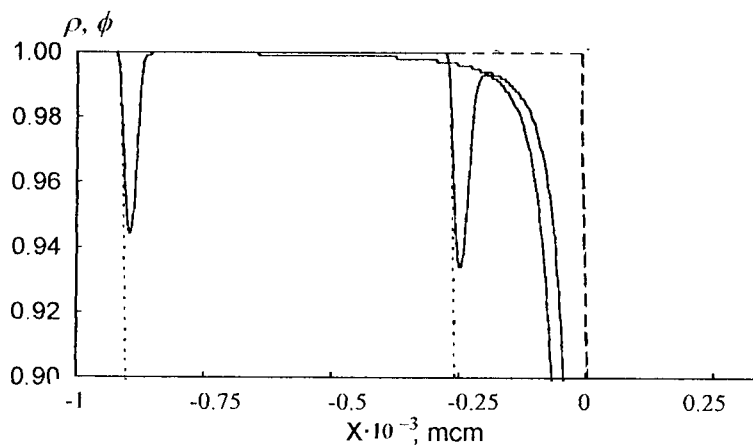


Fig. 2. Auto-wave regime of the macromolecular reaction. Chains mobilities are equal. Two moments of time: $3 \cdot 10^5$ s and $1.2 \cdot 10^6$ s are presented. Magnified upper part of Fig. a) is shown on Fig. b).

$N_A = N_B = 1000$, $\gamma = 5 \cdot 10^{-5} \text{ s}^{-1}$, $\chi = -0.05$, other designations -- see Fig. 1

It is interesting to note that a front of the reaction is formed in time and moves with the constant speed, the ρ profile keeping its form, i.e., the reaction proceeds in an auto-wave regime (Fig.2a). For certain values of $\chi < 0$ and the ratios of the chain lengths of the components, a pronounced minimum on the ϕ profile arises and moves with the speed equal to that of the ρ profile over a long period of time (Fig.2b); due to diffusion, the minimum scatters gradually and finally disappears.

The origin of the minimum may be understood as follows. At $\chi < 0$, it is more preferable thermodynamically for the B units to be surrounded by the A units. At the very beginning of the process, a small portion of B chains is absorbed into the A region and stimulate the reaction $A \rightarrow B$; in such a way the reaction front is formed. The reacting chains are enriched with A units from the left side and with B units from the right side of the front. As a result the first portion of B chains moves with the speed of the front, whereas the others B chains move more and more behind the front.

The theory permits to calculate not only the ϕ and ρ profiles but also fine local parameters of the blend structure.

Fig.3 presents the blend structures for the reactions proceeding with and without the accelerating effect of the neighboring units. It is seen that the ϕ and ρ profiles are almost identical qualitatively, however the dispersion of the compositional distribution of the reacting chains σ^2 increases significantly due to the accelerating neighbor effect. This is in accordance with the theory of the neighbor effect (Ref.1). Thus not only the mean values of the composition of the reaction product $p_1 = \rho/\phi$ but also its local compositional heterogeneity may be calculated.

Moreover it is possible also to calculate the local mean value of the probability of the boundary between the A and B sequences $R=2P(AB)$. This parameter characterizes the units distribution along the reacting chains, i.e., their primary structure. Fig.4 shows an example of calculations of a detailed structure of the blend. Local values of the reacting chains concentration ϕ , their mean composition p_1 , a dispersion of the compositional heterogeneity σ^2 and the probability of a boundary R are presented in the Figure.

It is worth to note that we have not tried to describe any concrete experiment. It would be a premature task. Our goal was to find out how to describe the diffusive processes in a blend containing the chains of an irregular structure, the parameters characterizing this irregularity being changed both in time and in space. An analysis of the simple model considered above demonstrated an importance of the processes of a diffusive intermixing of the reacting chains. It refers especially to the polymeranalogous reactions proceeding with an autoacceleration.

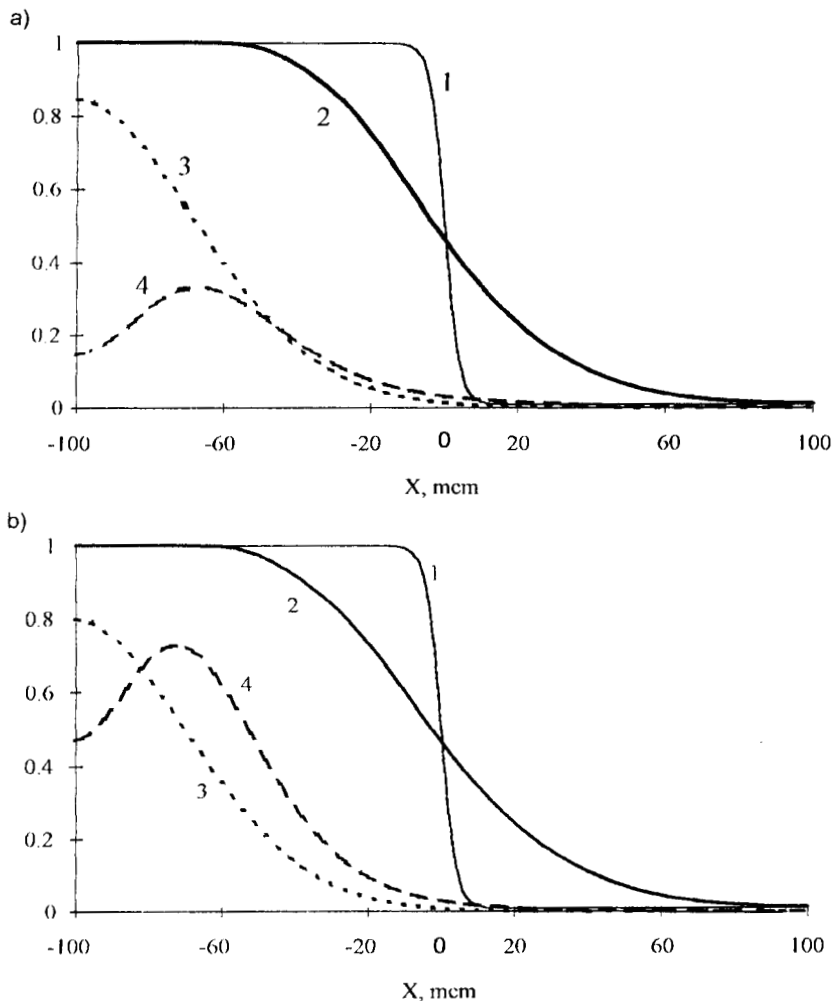


Fig. 3. The blend structure for reaction with external catalytic effect only (a) ($\alpha = \beta = 0$, $\gamma = 4 \cdot 10^{-5} \text{ s}^{-1}$) and with neighbor effect (b) ($\alpha = 0$, $\beta = \gamma = 2 \cdot 10^{-5} \text{ s}^{-1}$). Moments of time on figures a) and b) are different ($1.5 \cdot 10^5 \text{ s}$ and $1.6 \cdot 10^5 \text{ s}$) in order to provide the same degree of reacting chains' conversion (0.7). 1 -- the initial profile of $\phi(x)$; 2 -- $\phi(x)$ -- volume fraction of reacting chains; 3 -- $\rho(x)$, volume fraction of A units; 4 -- σ^2 the dispersion in composition of reacting chains. $N_A/N_B = 1/4$, $\chi = -0.01$.

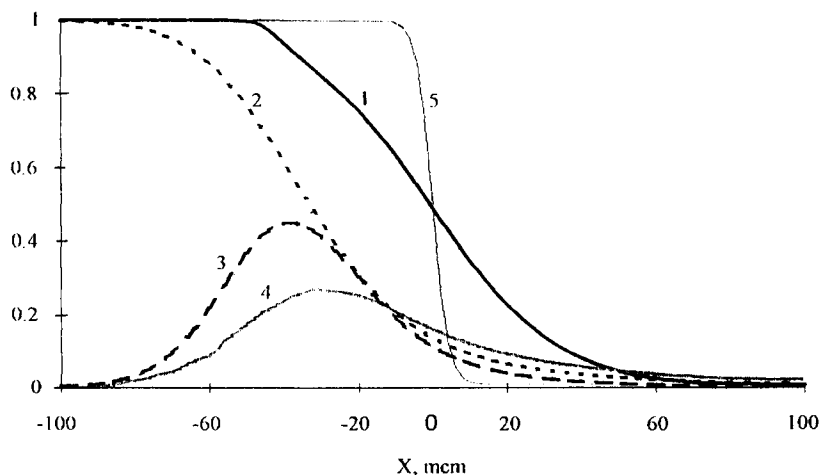


Fig 4. The detailed structure of the reacting blend.

1. $\phi(x)$, 2. - the probability to find a unit A in a reacting chain $p(x)$, 3. - the dispersion of reacting chains in composition σ^2 , 4. - the probability of a boundary between A and B sequences $R = 2 P(AB)$, 5 - the initial profile of $\phi(x)$.

$N_A = 500$, $N_B = 2000$, $\chi = -0.01$, $\alpha = 0$, $\beta = \gamma = 2 \cdot 10^{-5} \text{ s}^{-1}$, time 10^5 s .

Note that the methods elaborated may be applied easily to describe some more general schemes of the macromolecular reactions. The simplest example is the reaction $A \rightarrow B$ in a blend of homopolymers A and C resulting in the formation of an irregular copolymer AB, units C being capable to catalyze the reaction.

It is more difficult to build a theory for reacting blends of incompatible polymers. A significant advance in a dynamic theory of the polymer blends is necessary to solve the problem. A description of diffusive movements close by narrow interfaces is especially needed.

FORMATION OF BLOCK-COPOLYMER IN INCOMPATIBLE BLEND

The following model is convenient to begin with theoretical efforts in this direction. Consider artificially prepared homogeneous incompressible blend of homopolymers A and B having polymerization degrees N_1 and N_2 respectively. Take that each A- and B-chain bears one active end-group, so that a formation of diblock-copolymer AB may proceed by end-coupling. Let at $t = 0$ the interaction parameter χ is instantly increased, for example, as a result of a temperature jump. Now two competitive processes are going on, namely the phase separation and the formation of diblock-

copolymer, the third component of the blend. After that, in general case, either segregation might take place or the blend may remain compatible. Our goal is to analyze how the reaction affects the initial stage of the possible spinodal decomposition.

Let $\varphi_1(\vec{r})$ and $\varphi_2(\vec{r})$ denote the local volume fraction of homopolymers A and B, $\varphi_3(\vec{r})$ and $\varphi_4(\vec{r})$ denote the local volume fractions of A and B units belonging to diblock-copolymer AB chains respectively.

The fluctuations of the blend composition are:

$$\delta\varphi_i(\vec{r}) = \varphi_i(\vec{r}) - \bar{\varphi}_i, \quad \bar{\varphi}_i = \frac{1}{V} \int d\vec{r} \varphi_i(\vec{r}),$$

here V is the volume of the blend. The reaction is assumed to be slow (a kinetically controlled regime) so that the fluctuations are small due to diffusive movements.

The average volume fractions are changed by the reaction only, according to the following equations:

$$\begin{aligned} \dot{\bar{\varphi}}_1 &= -\frac{\alpha}{N_2 v_0} \bar{\varphi}_1 \bar{\varphi}_2, & \dot{\bar{\varphi}}_2 &= -\frac{\alpha}{N_1 v_0} \bar{\varphi}_1 \bar{\varphi}_2 \\ \dot{\bar{\varphi}}_3 &= -\dot{\bar{\varphi}}_1, & \dot{\bar{\varphi}}_4 &= -\dot{\bar{\varphi}}_2, \end{aligned} \quad (8)$$

here α is the rate constants of the end-coupling, v_0 is the volume per chain unit.

The dynamics of phase separation in blends is examined using scattering methods (Ref. 13). The light scattering intensity $I(\vec{k})$ (\vec{k} is the wave vector) is proportional to the structural factor $S_{AA}(\vec{k})$ corresponding to correlations of fluctuations of the A-units volume fraction $\varphi_A(\vec{r}) = \varphi_1(\vec{r}) + \varphi_3(\vec{r})$. So we derived equations for the matrix \hat{S} of structural factors:

$$S_{ij}(\vec{k}) = \langle \delta\varphi_i(-\vec{k}) \delta\varphi_j(\vec{k}) \rangle,$$

where $\varphi_i(\vec{k}) = \int d\vec{r} e^{i\vec{k}\vec{r}} \varphi_i(\vec{r})$ is the Fourier transform of $\delta\varphi_i(\vec{r})$ (Ref. 19). Such equation might be useful for comparison of the theory with experiment.

The evolution of structural factors matrix is described by the equation (Ref. 20)

$$\frac{d\hat{S}}{dt} = -(\hat{H}\hat{S} + \hat{S}\hat{H}^T) + \hat{\xi}, \quad (9)$$

Here $\hat{H} = \hat{D} + \hat{R}$, \hat{D} and \hat{R} describing the evolution of \hat{S} due to interdiffusion and reaction respectively. \hat{R} may be calculated using linearization of Eqn. (8). $\hat{D} = \hat{\lambda}\hat{G}^{-1}$, $\hat{\lambda}$ is the kinetic coefficients matrix, \hat{G} is the matrix of static correlation functions. The noise correlations are described by the matrix $\hat{\xi} = 2\hat{\lambda}$ while the reaction noise can be neglected for slow reaction.

Thus to describe evolution of \hat{S} it is necessary to derive expressions for free energy and kinetic coefficients.

The specific free energy can be expanded in series of $\{\delta\varphi_{ij}\}$ using the random phase approximation method (Ref. 21)

$$f(\{\varphi_i\}) = f_0(\{\bar{\varphi}_i\}) + \frac{k_B T}{2V^2} \sum_{i,j} \sum_{\vec{k}} \delta\varphi_i(-\vec{k}) G_{ij}^{-1}(\vec{k}) \delta\varphi_j(\vec{k}) + \dots \quad i, j = 1, 2, 3, \quad (10)$$

where $f_0(\{\bar{\varphi}_i\})$ is the specific free energy of the homogeneous state. f_0 and \hat{G} depend on χ in the ordinary form. The phase diagram of such blends was analyzed recently (Refs. 22, 23). If the fraction of the block-copolymer $\bar{\varphi}_c = (\bar{\varphi}_3 + \bar{\varphi}_4) < 0.4$ and $N_1 = N_2$, $\bar{\varphi}_1 = \bar{\varphi}_2$ then the blend has a tendency to macrophase separation rather than to microphase one.

For the incompressible blend $\hat{\lambda}$ may be easily calculated using single chain kinetic coefficients $\Lambda_{nm}^{(0)}$ in accordance with "fast-mode" theory (Ref. 24):

$$\Lambda_{ij}(\vec{k}) = \sum_{n,m=1}^4 (\delta_{in} - \bar{\varphi}_i) \Lambda_{nm}^{(0)}(\vec{k}) (\delta_{jm} - \bar{\varphi}_j). \quad (11)$$

The equations (9) were solved numerically for the initial conditions

$$\hat{S}(k) \Big|_{t=0} = \hat{G}(k) \Big|_{\chi=0}$$

corresponding to the initially compatible blend with $\chi = 0$. We calculated the structural factor $S_{AA}(\vec{k}) = S_{11}(\vec{k}) + 2S_{13}(\vec{k}) + S_{33}(\vec{k})$ for $\bar{\varphi}_1 = \bar{\varphi}_2 = \bar{\varphi}$, $N_1 = N_2 = N = 500$, $N_c = 1000$ (N_c is the diblock-copolymer chain length), $D = 4D_c = 2 \cdot 10^{-13}$ cm²/s (D and D_c are self-diffusion coefficients of homopolymers and diblock-copolymer respectively), $a = 5 \cdot 10^{-8}$ cm, $\chi = 0.0045$. The scaled structural factor $S_{AA}(\vec{k}, t)/S_{AA}(\vec{k}, 0)$ versus $k^2 R_c^2$ (R_c is the diblock-copolymer radius of gyration) for various moments of time are shown in Fig. 5.

Fig.5b illustrates the fact that diblock-copolymer formation can lead to compatibilization of blend components. Indeed, at the early stage of the process the volume fraction of copolymer is small and decomposition proceeds similarly in both cases (curves 1 on Figs. 5a and 5b), note that the scales of S_{AA} axes are different. Further, the formation of copolymer leads to retardation of phase separation (compare curves 2 on Fig. 5a and 5b). The retardation is caused, firstly, by improvement of blend miscibility by diblock-copolymer chains and, secondly, by lesser self-diffusion coefficient of long copolymer chains.

Later on as the content of diblock-copolymer increases gradually the structural factor reaches its maximal value and begins to decrease (curves 2-4 on Fig. 5b). The critical value of $\bar{\varphi}_c$ corresponding to the maximal structural factor is equal to 0.135 for parameters mentioned above. At the same time in the blend without reaction the structural factor increases gradually (curves 3,4 on Fig. 5a).

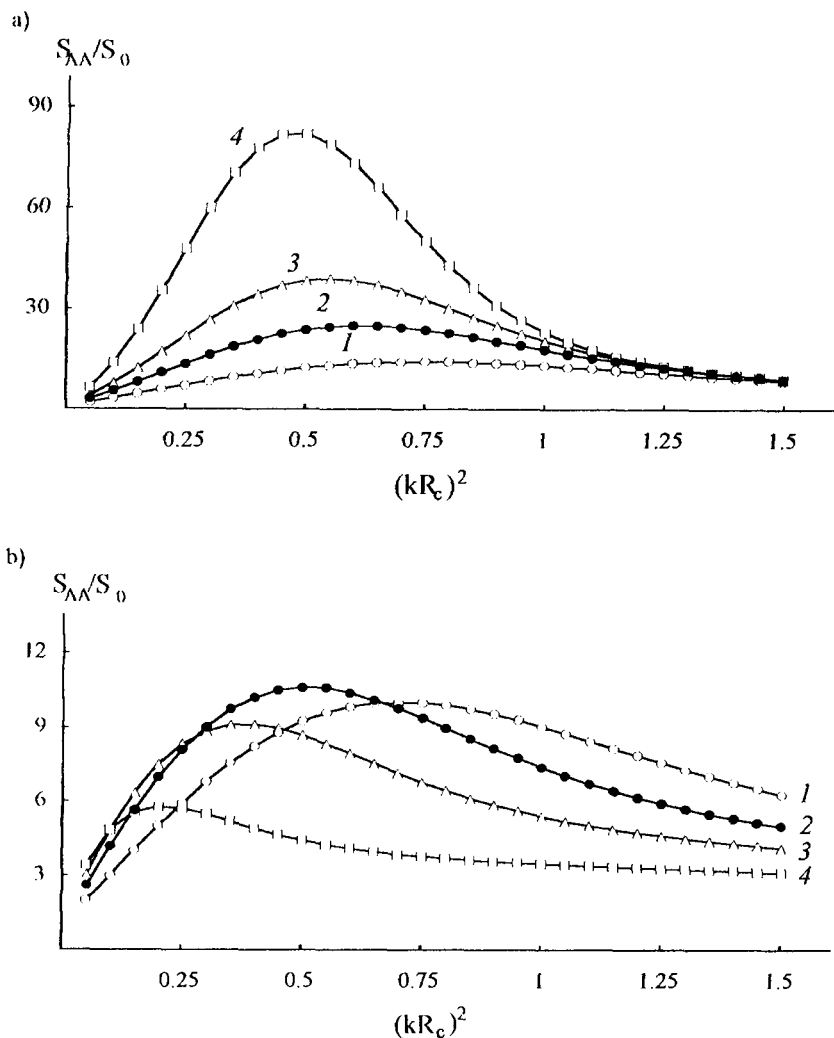


Fig.5. The scaled structure factor for the blend of two incompatible homopolymers without the reaction (a) and with the reaction of diblock-copolymer formation (b) for the moments of time: $t = 20$ s (1); $t = 35$ s (2); $t = 50$ s (3); $t = 80$ s (4). The reaction rate constant $\alpha/\nu_0 = 0.005$ s $^{-1}$. $S_0 = S_{AA}$ ($t = 0$).

It is worth to note that an advance in the theoretical study of such systems depends significantly on the possibilities to verify the theoretical predictions by experiment. So carrying out of some special experiments is extremely needed.

Thus the theoretical approaches suggested permit to describe an evolution of the polymer blend structure under influence of macromolecular reaction and interdiffusion. The results obtained for the simple model systems indicate that it is possible to build the theory of macromolecular reactions in polymer blends basing on methods of linear non-equilibrium thermodynamics.

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