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# Interplay of Chemical and Physical Factors in Reacting Polymer Blends. Theoretical Considerations

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**Summary:** Various effects produced by copolymers in polymer blends are discussed, with an emphasis on the role of interchain interactions. Simple theoretical models are considered to study the following problems: the interplay of diffusion and macromolecular reaction in compatible and incompatible blends, the stabilizing effect of premade diblock copolymer on the system of minor phase particles in incompatible blends, the kinetics of transesterification in a homogeneous blend. The effect of diblock copolymer on the Ostwald ripening in a polymer blend is stated in more details; the possibility of narrowing the size distribution of minor phase particles is predicted.

**Keywords:** blends; block copolymers; compatibilization; interchain interactions; macromolecular reactions

Theory of macromolecular reactions, in its development, passed from the analysis of relatively simple systems to studying more and more complex ones. First these were the reactions of quasi-isolated macromolecules in dilute solutions; then the reactions in melts. The modern stage of the theory is an investigation of peculiarities of the reactions in polymer blends.[1,2]

Recently experimentalists, using simple model systems, revealed a determining role of interchain interactions in the processes taking place in reacting polymer blends. Interchain interactions affect both the reactivity of polymer functional groups and the mobility of macromolecules, hence, such processes as interdiffusion and phase separation. Therefore, an actual task is to describe the evolution of the reacting blend structure under mutual action of different chemical and physical factors.

From this point of view, we have analyzed several theoretical problems. In this paper, we present a review of these studies. Three types of reactions are considered: a polymeranalogous reaction, an end-coupling reaction, and a transesterification whose products are statistical copolymers, diblocks, and multiblocks, respectively.

Let us begin with the polymeranalogous reaction proceeding with interchain chemical effect. Suppose A units transform into B units, the latter accelerating the reaction. Thus, the reactivity of an A group depends on its microenvironment, including both inner (of the same

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chain) and external neighboring units. In a non-homogeneous compatible blend of reacting polymer A and accelerating polymer B, the microenvironment is changed due to the reaction and interdiffusion as well.

The interdiffusion in a reacting polymer blend has some important features. First, these are polymer chains that diffuse but these are units that react, such a divergence affecting both driving forces of the interdiffusion and the reaction kinetics. Then, in the course of the process the initial binary blend becomes essentially multicomponent. The intermixing of random copolymers of different composition should be taken into account along with the interdiffusion of A and B chains.

Thus, the problem of describing the reaction in a heterogeneous blend is rather complicated. For a slow reaction, we have investigated it a few years ago using the methods of linear non-equilibrium thermodynamics.[3] To study the structure of the reacting blend, we have derived and numerically solved the reaction-diffusion equations. The typical illustration is given in Fig. 1.

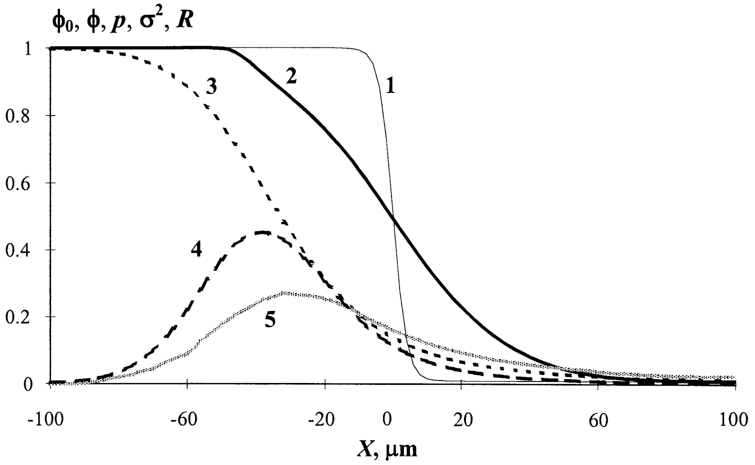

Fig. 1. Structure of the compatible reacting polymer blend. $N_A = 500$, $N_B = 2000$, $\chi = -0.01$, the rate constants $\beta = \gamma = 2\cdot10^{-5}$ s$^{-1}$, time $t = 10^5$ s. Designations – see text.

Suppose we initially have two films of homopolymers A and B, to the left and to the right of the boundary $\phi_0$ given by curve 1. The interdiffusion and reaction described above lead to the separation of the concentartion profiles of reacting chains $\phi$ (curve 2) and of their average composition $p$ (curve 3). Other curves give the detailed information on the blend structure, they are the dispersion of compositional heterogeneity of reacting chains $\sigma^2$ (curve 4) and the probability of a boundary between the $A$ and $B$ sequences in a copolymer chain, $R$ (curve 5).

Note that it is extremely difficult to obtain such detailed information in an experiment, whereas it might be very useful for determining the relations between the structure and properties of a blend.

Thus, the theory permits to describe an evolution of the blend structure under mutual influence of the reaction and interdiffusion.

Let us turn to the second reaction type – the diblock copolymer formation. End-coupling is an extremely important reaction used for stabilizing incompatible polymers blends by diblock copolymers.[4] In general, this problem includes various important aspects.

Block copolymer chains are located at interfaces. The size of minor phase particles and the concentration of particles in the blend may change either by coalescence or by diffusion of chains through the continuous phase until the equilibrium is attained. This state is characterized by the minimal free energy so that the effective surface tension becomes zero. The first task is to analyze the thermodynamic equilibrium in such system, in particular, to determine an average particle size.

Leibler[5] was the first to suggest a theoretical solution of the problem for an incompatible blend of homopolymers A and B and diblock copolymer AB. Neglecting the penetration of homopolymers into the copolymer layer at the interface, he concluded that the difference in block lengths affects strongly the equilibrium and that a symmetric copolymer does not stabilize the system of particles at all - in contradiction to experiment.

Govorun et al.[6-8] have reexamined this model taking into account the possibility of homopolymer penetration into the interfacial copolymer layer („wet-brush“ model). Under the assumption of complete copolymer adsorption at the interface, the equilibrium value of the interface area per copolymer chain is calculated. The stabilization of the system of disperse phase particles is attained via the competition between the interfacial tension and "spreading" of the interface caused by the interchain interactions of entropic and enthalpic origin between homopolymer chains and copolymer blocks. The symmetric diblock copolymer can stabilize particles of reasonable size, whereas the diblock copolymer asymmetry $N_{cA}/N_c$ ($N_{cA}$ and $N_c$ are the lengths of block A and copolymer chain, respectively) only slightly influences the equilibrium interfacial area per copolymer chain $\Sigma$ (Fig. 2). The lowest value of $\Sigma$ corresponds to the block length ratio approximately equal to the homopolymer length ratio.

The average particle radius in equilibrium presented in Fig. 3 is consistent with the experimental data by Macosko et al. for the blends prepared in a shear field.[9]

The calculations demonstrate that longer copolymer chains have lower equilibrium interfacial density but, at the same time, higher volume fraction of long copolymer is needed to stabilize the system of particles of given size. Therefore, one should prefer short diblock copolymer as a stabilizer, however, its block lengths must exceed a certain critical value, otherwise, no adsorption would be observed.

Thus, the analysis of the equilibrium properties of polymer blends may help to improve the composite stability by using proper structure and ratios of the components.

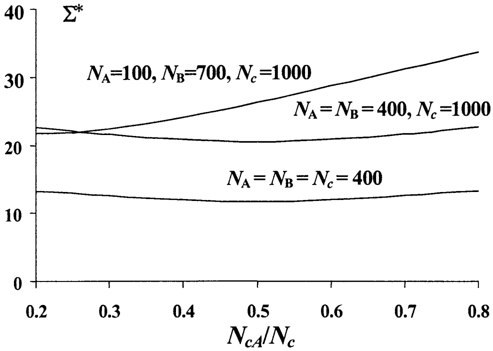

Fig. 2. Equilibrium value of the interface area per copolymer molecule $\Sigma^* = \Sigma/a^2$ ($a$ is the segment size) *vs.* copolymer asymmetry $N_{cA}/N_c$.

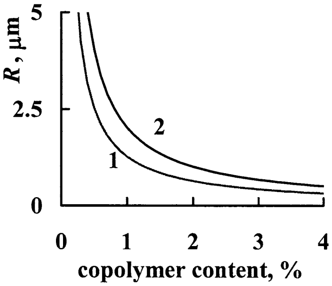

Fig. 3. Equilibrium radius of disperse phase particles $R$ *vs.* diblock copolymer contents $\phi_c \cdot 100\%$. $N_{cA} = N_{cB} = 400$; $N_A = N_B = 100$ (curve 1), $N_A = N_B = 400$ (2).

The next problem is to elucidate the effect of diblock copolymer additives on the late stages of phase separation. Consider a quasi-homogeneous blend of incompatible polymers A and B and diblock copolymer AB. If the content of polymer A is relatively small and the mobility of A chains is high enough then Ostwald ripening is the most important mechanism of phase separation.[10] The theory of Ostwald ripening[11,12] has been applied to describe phase separation in a blend of two homopolymers.[13] In the theoretical model, the blend contains a bulk phase and a minor phase. In the former, both polymers A and B are present, the concentration of component A being higher than at the thermodynamic equilibrium. The minor phase consists of spherical particles A of different size. The growth of a particle A is thermodynamically favorable only if particle's radius exceeds the certain critical value $r_{cr}$. Smaller particles dissolve and enrich the bulk phase with chains A that diffuse to larger particles providing their growth.

Our aim is to study the influence of the diblock copolymer AB on the process. It is supposed that a part of copolymer chains covers particles A and the rest is distributed throughout the continuous phase. The surface density of the copolymer is assumed to be proportional to the particle radius. Properties of the interfacial layer are described using the “wet-brush” model considered above, which enables one to find the copolymer volume fraction in the interfacial layer, $\phi_l$, and the surface tension, $\sigma_c$, for a particle of radius $r$.

The effect of a diblock copolymer on the Ostwald ripening may be attributed to two factors. The thermodynamic factor is the decrease of the surface tension. This, first, diminishes the critical radius $r_{cr}$ allowing the greater fraction of particles to grow. Second, for sufficiently large particles, $\sigma_c = 0$, so that these particles would never dissolve, they keep on growing but may lose the spherical form. The kinetic factor is the overcrowding of the particles surfaces by diblock copolymer chains. It makes the surfaces less permeable for chains A diffusing from the bulk phase thus retarding the particle growth. To take account of the kinetic factor, the permeability of a particle, $\alpha(r) = 1 - \phi_l(r)$, is introduced.

The evolution of the blend is determined by the set of equations

$$\frac{\partial f(r,t)}{\partial t} + \frac{\partial}{\partial r}\left( f(r,t)\frac{dr}{dt} \right) = 0 \tag{1}$$

$$\frac{dr}{dt} = D\left(1 + r\sqrt{4\pi N(t) r_{av}(t)}\right)\alpha(r)\frac{(\phi_A(t) - \phi_{eq})r - \sigma^*(r)}{r^2}; \quad \sigma^*(r) = \frac{2\sigma_c(r) N_{\mathrm{A}} v \phi_{eq}}{k_B T}; \tag{2}$$

$$\phi_A(t) + \frac{4\pi}{3}\int r^3 (f(r,0) - f(r,t))dr = \phi_A(0) \tag{3}$$

which includes the continuity equation for the function $f(r,t)$ describing the particle size distribution (1), the rate equation for the diffusive growth (or dissolution) of particles (2), and the conservation law for the component A (3).

Here $D$ is the diffusion coefficient of a chain A in the bulk phase, $N(t) = \int dr f(r,t)$ is the total number of particles per unit volume, $r_{av}(t) = N^{-1}(t)\int dr f(r,t) r$ is the average particle radius, $N_{\mathrm{A}}$ is the polymerization degree of a chain A, $v$ is the volume of a unit taken to be the same for units A and B, $\phi_{eq}$ is the equilibrium value of the volume fraction of homopolymer A in the bulk phase near a flat interface, $\phi_{\mathrm{A}}(t)$ is the volume fraction of homopolymer A in the bulk phase at time $t$, $k_B$ is the Boltzmann constant, $T$ is temperature. The critical radius is given by the relation $r_{cr}(t) = \sigma^*/(\phi_{\mathrm{A}}(t) - \phi_{eq})$.

The numerical solution of this set of equations was performed for the parameters (homopolymer lengths $N_{\mathrm{A}} = N_{\mathrm{B}} = 20$, block lengths $N_{\mathrm{cA}} = N_{\mathrm{cB}} = 40$, $D = 4.4\cdot 10^{-8}$ cm$^2$/s, the final volume of particles 4%) matching the blend PS/PB where Ostwald ripening from homogeneous state was studied experimentally.[14]

It appears that the effect of block copolymer is most pronounced for systems with $r_{av} \sim 1$ μm. Until phase separation proceeds, the usual power law $r_{av} \sim t^{1/3}$ holds (see Fig. 4), however, several percents of diblock copolymer are enough to stop coarsening of the blend structure (3% in Fig. 4-6 but in real systems this amount may be greater since a part of copolymer chains can form micelles thus being ineffective against phase separation). Smaller amounts of diblock copolymer (1% in Fig. 4-6) may cause essential narrowing of the particles size

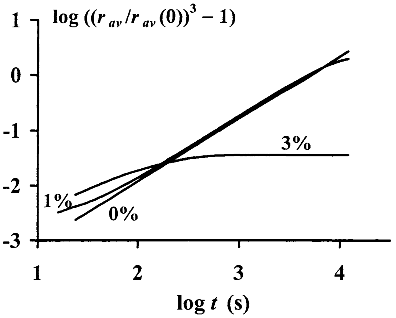

Fig. 4. The effect of diblock copolymer on the growth of the average particle radius in the course of Ostwald ripening. The volume fraction of diblock copolymer is denoted near the curves.

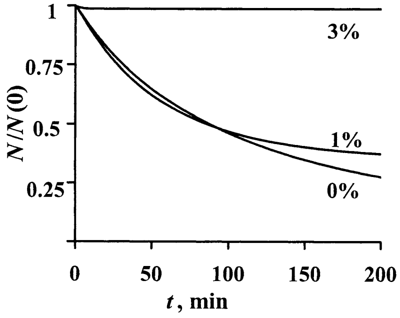

Fig. 5. The effect of diblock copolymer on the number of particles in the course of Ostwald ripening.

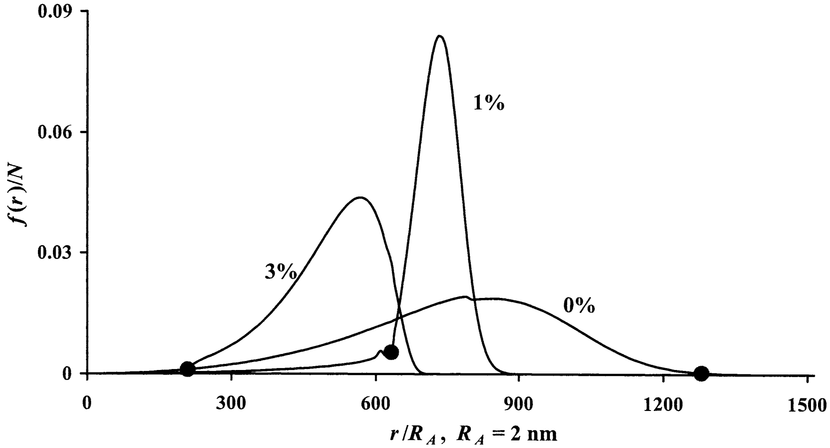

Fig. 6. The particle size distribution for the different copolymer contents at time $t = 200$ min. The initial distribution (not shown) almost coincides with curve 3%. Black circles on the curves mark the radius at which $\sigma_c = 0$. Larger particles will never dissolve.

distribution although $r_{av}$ and $N$ may be almost insensitive to such amount of the additive. This is a result of the superposition of two effects mentioned above. First, the diblock copolymer layer impedes the growth of large particles while average particles keep on growing and small ones continue dissolving. Second, the most of particles cannot dissolve due to zero surface tension (see black circle on curve 1% in Fig. 6). Since the enrichment of the bulk phase with chains A ceases, the blend coarsening should be expected to stop thus preserving the narrow particles distribution formed.

Thus, the diblock copolymer can substantially affect the kinetics of phase separation.

The efficiency of premade copolymer additives is often lowered by the formation of copolymer micelles. Therefore, the formation of copolymer *in situ*, or more generally, the reactive compatibilization, is considered as a perspective alternative approach to the improvement of blends structure. In this paper, we discuss the effect of diblock copolymer formation via end-coupling on the initial stages of phase separation.

Consider artificially prepared quasi-homogeneous blend of incompatible polymers $A$ and $B$. Let the spinodal decomposition proceed after a proper temperature jump. It is convenient to describe the evolution of blend morphology in terms of the dynamic structure factor $\hat{S} = \langle \delta\rho_i(-\vec{k},t)\delta\rho_k(\vec{k},t)\rangle$, where $\delta\rho_i$ denotes the fluctuation of the volume fraction of units of type $i$, since the components of $\hat{S}$ may be measured experimentally using light or neutron scattering. The dependence of $S_{AA}$ on the wave vector $k$ contains the information on the distribution of non-homogeneities in the system. Permanent growth of the structure factor with time corresponds to the progressive phase separation.

If each $A$- and $B$-chain bears one active end-group, then the diblock-copolymer $AB$ is formed via end-coupling. The reaction competes with phase separation since the diblock-copolymer is a compatibilizing agent. For the slow reaction, we have described the evolution of $\hat{S}$ in the frame of linear non-equilibrium thermodynamics.[15]

Fig. 7 demonstrates the typical course of the process. At the early stage, while the copolymer volume fraction $\phi_c$ is small, the structure factor component, $S_{AA}$, (divided by its initial value $S_0$) grows thus indicating about the formation of A-rich domains. In the course of the reaction, the copolymer contents increases improving compatibility of the blend. The structure factor begins to decrease, the maximum of the curve being shifted towards the small $k$. It means that the scale of inhomogeneities increases while their amplitude decreases like it should be in a compatible blend due to the interdiffusion. Thus, at this stage the reaction dominates restoring the homogeneity of the blend.

In this paper, several separate problems related to the stabilizing effect of a diblock copolymer were considered. The topical problem is to tie them in the unified description of the process, which includes the end-coupling reaction and phase separation with account of the various mechanisms of particles growth.

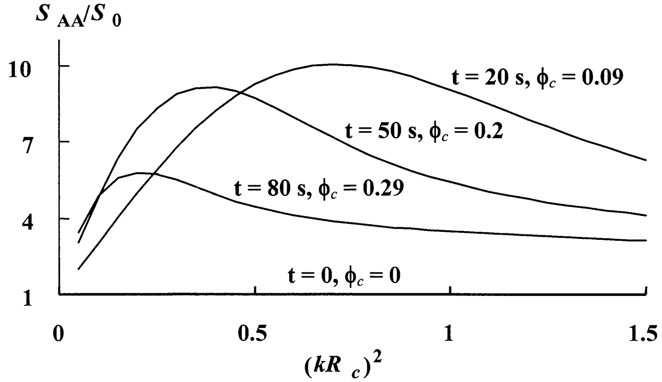

Fig. 7. Time evolution of the reduced structure factor in the reacting blend. $N_A = N_B = 500$, $N_c = 1000$, $\chi_{AB} = 0.005$, $D_A = D_B = D = 2 \cdot 10^{-13}$ cm$^2$/s, the reaction rate constant $\alpha^* = 0.005$ s$^{-1}$.

The last item is the reaction of transesterification, which is also used for the reactive compatibilization. In the course of this reaction, homopolymers transform gradually into block copolymers, multi-block copolymers and eventually into random copolymers. The efficiency of transesterification against phase separation has been demonstrated experimentally.[16] The structure of expanding interface layer determines the blend properties. The theory of transesterification in non-homogeneous systems is still unavailable.

However, the transesterification itself is characterized by rather complicated kinetics so it is reasonable first to elucidate the pecularities of the pure reaction, i.e., to start with the homogeneous system. Recently, this problem has been investigated by Kudryavtsev who derived and solved the equations for the evolution of the molecular-weight distribution (MWD)[17] and block-weight distribution (BWD).[18]

The reaction in an initial blend of homopolymers A and B may be divided into fast and slow stages. The former takes up a few cleavages per average chain. In the course of the fast stage, the homopolymer chains almost disappear, at the same time the MWD and the BWD of units A and B becomes close to the Flory distribution. Then and much slower, the average block lengths tend to the values typical of a completely random (Bernoullian) copolymer. Provided the initial polymers have the most probable MWD, the reaction product has the most probable BWD at any conversion, with the average value decreasing with time. To verify the theory, the Monte Carlo program has been elaborated that permits to simulate both MWD and BWD of the reaction products. It is worth to emphasize (see Fig. 8) that the theoretical curves are in a good agreement with Monte Carlo results.[19]

The present approach elaborated for a homogeneous system might be a starting-point for analysing the transesterification kinetics at the interfaces of real heterogeneous blends.

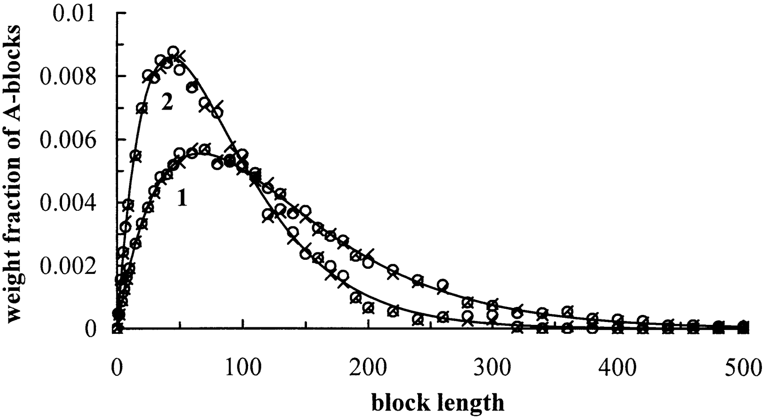

Fig. 8. Block-weight distribution of units A in the transesterifying 50/50 A/B blend at one cleavage per average chain. Initially both polymers A and B have the Flory distribution with average chain length $N_A = N_B = 100$ (1) and $N_A = 50$, $N_B = 550$ (2). Curves: theory (the Flory distribution), points – Monte Carlo simulation of the BWD of units A in the copolymer (circles) and in the blend as a whole (crosses).

To describe the interface broadening in that case, one should account for the mobility of polymer chains. Putting it in other words, it is necessary to elucidate the role of interchain interactions in the system where the transesterification is accompanied by the interdiffusion.

We conclude with several general remarks. Theoretical methods discussed above permit to describe the dynamics of the reacting polymer blends, in particular, an interplay between the chemical reaction and interdiffusion or phase separation. Influence of block copolymers both on equilibrium and on particle growth in incompatible blends has been described as well. Application of the methods to concrete systems might be useful for improving the stability of polymer composites using proper structure and components ratio. Topical problem is a description of reactions in heterogeneous systems, in particular, end-coupling reaction and transesterification.

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