Macromolecules **2005,** *38,* 2937−2947

Theory of Interphase Free-Radical Copolymerization at the Oil−Water Boundary

S. I. Kuchanov and A. R. Khokhlov*

Physics Department, Moscow State University, 119992 Moscow, Russia, and Department of Polymer Science, University of Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany

Received July 29, 2004; Revised Manuscript Received January 25, 2005

ABSTRACT: A physicochemical model of the interphase free-radical copolymerization of hydrophilic and hydrophobic monomers at the oil−water interface is put forward for the first time. Such a mode of copolymer synthesis makes possible a conformation-dependent design of the sequences of monomeric units in macromolecules since their chemical structure here is governed along with the kinetic and stoichiometric parameters of a reaction system also by the conformational statistics of polymer chains. In the framework of the model proposed the expressions are derived for the rate of copolymerization as well as for main statistical characteristics of the chemical structure of this process products. Theoretical dependencies of these characteristics on the initial composition of monomers and their conversion are presented for different values of the thermodynamic parameter characterizing the degree of incompatibility of hydrophilic and hydrophobic units in a macromolecule.

Introduction

Many commercial copolymers are synthesized by free-radical mechanism. Under traditional copolymerization conducted in one-stage macromolecules are obtained whose monomeric units are distributed statistically. This result does not depend on whether polymer chains are formed in bulk, in solution, or inside latex particles. An essentially different situation takes place when the growth of a polymer chain occurs in the vicinity of the boundary separating two immiscible liquid phases (e.g., oil and water), each containing molecules of only one type of monomers (see ref 1 and references therein). In this case an active center of a growing polymer radical can cross the interface in both directions, which leads to the formation of polymer chains with each type monomeric units arranged in blocks (Figure 1). Such block copolymer macromolecules showing an extraordinary high surface activity will be disposed exclusively in the vicinity of the interface acting, in essence, as polymer emulgator.

The aforementioned mechanism of the growth of polymer chains will be realized provided a surface active initiator (SAI) is involved. Conversely, if copolymerization is conducted in the presence of a traditional initiator, solvable in either of two phases, the only products of such a process will be homopolymer molecules.[2] It can be attributed to the fact that a homopolymer chain is not a surfactant, and consequently, the probability for the terminal monomeric unit of a growing macroradical to fall on the interface is negligible. In the presence of SAI a polymer chain starting its growth close to this boundary will stay later in its vicinity. This is because a SAI fragment adjoined to the inactive end of a homopolymer radical residing on the interfacial surface acts as an "anchor" which prevents this radical from going deep into the volume of one of the phases. If the surface activity of an initiator is sufficiently pronounced, a macroradical remains in the neighborhood of the interface up to the instant when its reactive end crosses this boundary. Thereafter, the growth of the second block of a macroradical begins, resulting in the transformation of the latter into polymer emulgator virtually incapable of abandoning the interfacial area.

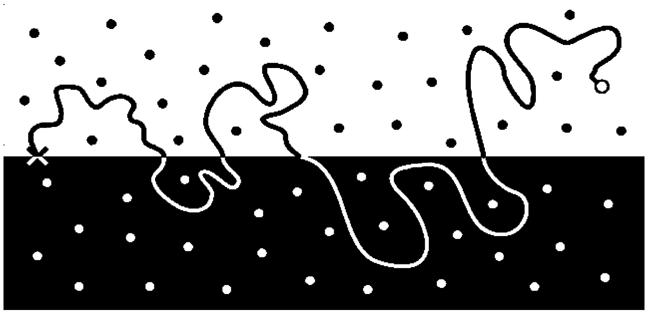


Figure 1. Schematic representation of a polymer chain growing in the vicinity of the interface.

Advantageous implementation of the above-described mechanism of the formation of block copolymer molecules is largely predetermined by an adequate choice of SAI. The role of this latter may be performed by ordinary oligomer surfactants upon introducing in their molecules peroxide or diaso groups, involved in the traditional initiators of the radical polymerization.[3] Synthesizing diblock copolymers which contain on the ends of their macromolecules the above-mentioned labile functional groups, it is possible to obtain polymer SAI showing appreciably greater surface activity compared to that of SAI prepared from traditional surfactants. The main requirement to the initiator chosen is its minor solubility in both phases. This condition should be necessarily met to exclude the formation of homopolymer molecules far from the interphase boundary. When the concentration of an insoluble SAI is not too low, just its small amount will be situated on the above boundary, whereas most of the SAI will be concentrated in the precipitate, where polymerization is impossible.

Some peculiarity of interphase copolymerization whose products are molecules of block structure is worth

---

* To whom correspondence should be addressed: Tel +7-095-9391013; Fax +7-095-9392988; e-mail khokhlov@polly.phys.msu.ru.

10.1021/ma048440o CCC: $30.25

emphasizing. The accumulation of these molecules throughout the synthesis on the interface leads, apparently, to the reduction in the surface tension, and, consequently, to the expansion of the interfacial surface. This effect induces, in turn, the enrichment of this surface by SAI molecules transferred there from the precipitate. These additional molecules initiate on the surface new polymer chains, stimulating thus further decrease of the surface tension. Hence, a specific interplay between physical and chemical factors which is peculiar to this system will necessarily cause the autoacceleration of the copolymerization in hand.

Having discussed the mechanism of the interphase copolymerization, let us proceed to its theoretical description. Considering this process conducted in miniemulsion oil−water, we will proceed from the quasi-homogeneous approach[4] generally employed for the mathematical modeling of chemical transformations in heterophase systems. The essence of this approach consists of invoking for the description of such systems the equations of the homophase kinetics with parameters, allowing for the peculiarities of the macrokinetics in heterophase systems. In the framework of the macrokinetic model of our interest the quasi-homogeneous approach may be viewed as an appropriate approximation for describing the chemical transformations at spatial scales far more large than the size of the miniemulsion particles. This approximation is correct since the rate of the diffusion of monomers toward the interface appreciably exceeds that of their addition to the growing macroradicals. In this case monomer concentration M'_α of the monomer M_α may be thought of as identical all over the α-th phase.

This monomer concentration M_α in the formalism of the quasi-homogeneous approximation, unlike M'_α, refers to the whole volume of the two-phase system. The aforementioned quantities are connected by simple relationship $M_\alpha = y^\alpha M'_\alpha$, where y^α stands for the volume fraction of the α-th phase in miniemulsion. An analogous relation, $R_\alpha = sd_\alpha R'_\alpha$, exists between the concentrations R_α of the α-th type active centers in the entire system and those R'_α in the surface layer of the α-th phase. This layer thickness d_α has the scale of average spatial size of the α-th type block which hereafter is presumed to be small as compared to the average radius of miniemulsion drops. Apparently, in this case the curvature of the interphase surface can be neglected, and thus the propagation of a macroradical can be considered in the vicinity of the plane. In this approximation the volume fraction of a system occupied by the surface layer is equal to the product of its thickness d_α and factor s, equal to the interphase surface area per unit volume of a miniemulsion.

The development of a quantitative theory of free-radical copolymerization implies the derivation of equations for the rate of monomers' depletion and the statistical characteristics of the chemical structure of macromolecules present in the reaction system at given conversion p of monomers. Elaborating such a theory, one should take into account a highly important peculiarity inherent to any free-radical copolymerization. This peculiarity is that the characteristic time of a macroradical life is appreciably less than the time of the process duration. Consequently, its products represent definitely a mixture of macromolecules formed at different moments, i.e., at different monomer mixture compositions. That is why problems of two kinds are generally encountered when developing a quantitative theory of free-radical copolymerization. The first of them are those related to finding instantaneous values of the statistical characteristics of the chemical structure of macromolecules formed at given value of conversion p'. However, of particular practical interest are average values of these characteristics describing copolymerization products which are present in the reactor at conversion p. To calculate such characteristics, it is necessary to average their instantaneous values over all conversions $p' < p$, preliminarily having found the dependence of monomer mixture composition on p'. The realization of such an averaging procedure just belongs to the problems of the second kind.

The paper is organized as follows. First we present a detailed description of the kinetic model of interphase copolymerization underlying the theoretical approach proposed. Then the expression for the rate of the process is found. In the next section an expression is derived for the instantaneous distribution of macromolecules for their chemical size and composition, and formulas are written down for its statistical moments. Next the dependencies are found on conversion p of the monomer mixture composition and the most important statistical characteristics of the copolymerization products. The paper is concluded by a brief discussion of the main results obtained in the framework of our theoretical approach. Besides, in the conclusion some estimates of the values of physicochemical parameters of a reaction system are presented at which this approach can be used for the description of real systems.

Kinetic Model

Let us consider an individual block copolymer chain propagating in the vicinity of the surface separating the organic and water phases, with only one of two monomers, M_1 or M_2, solved in each phase. Upon falling into the α-th phase (α = 1, 2) the active center situated on the end of this macroradical begins to add monomer M_α until going to other phase or terminating. The rate of such an addition $\theta_\alpha = k_{\alpha\alpha} M'_\alpha$ is equal to the product of the rate constant $k_{\alpha\alpha}$ of the reaction of a homopolymer chain propagation and concentration M'_α of monomer M_α in the α-th phase. In a time t_α, elapsed between two successive crossings of the α-th phase boundary by the active end of a macroradical, the latter increases its chemical size by the length $l_\alpha = \theta_\alpha t_\alpha$ of a single block of α-th type units. Because of the proportionality of quantities l_α and t_α, the chemical structure of a macroradical may be exhaustively specified not only by the sequence of the constituent blocks but also by an analogous sequence of the residence times of an active center in different phases.

Thus, the problem on the growth of a block copolymer chain in the course of the interphase radical copolymerization may be formulated in terms of a stochastic process whose regular states correspond to α = 1 and α = 2 types of terminal units (i.e., active centers) of a macroradical. The fact of independent formation of its blocks means in terms of a stochastic process the independence of times t_α of the uninterrupted residence in every α-th stay of any realization of this process. Stochastic processes possessing such a property have been scrutinized in the renewal theory.[5] Invoking the ideas of this theory, it is easy to write down the set of kinetic equations describing the interphase copolymerization.

So, the concentrations of the radicals of length l with type 1 or 2 terminal units are determined from the following expressions:

$$R_1(l) = \int_0^l Q_1(l-\xi) w_1(\xi)\, \mathrm{d}\xi\, \theta_1^{-1}$$

$$R_2(l) = \int_0^l Q_2(l-\xi) w_2(\xi)\, \mathrm{d}\xi\, \theta_2^{-1} \quad (1)$$

Here the functions $Q_\alpha(\xi)$ ($\alpha = 1, 2$) having a meaning of the rate of generating of macroradical with length ξ and α-th type terminal unit are obtained from the solution of two coupled linear equations:

$$Q_1(\xi) = \int_0^\xi Q_2(\xi-\eta) w_2(\eta) V_{21}(\eta)\, \mathrm{d}\eta\, \theta_2^{-1} + I_1 \delta(\xi)$$

$$Q_2(\xi) = \int_0^\xi Q_1(\xi-\eta) w_1(\eta) V_{12}(\eta)\, \mathrm{d}\eta\, \theta_1^{-1} + I_2 \delta(\xi) \quad (2)$$

The kernels of these integral equations which are derived from simple probabilistic considerations represent up to the factor θ_α^{-1} the product of two factors. The first of them, $w_\alpha(\eta)$, is equal to the fraction of α-th type blocks, whose lengths exceed η. The second one, $V_{\alpha\beta}(\eta)$, is the rate with which an active center located on the end of growing block of monomeric units M_α with length η switches from the α-th type to β-th type under the transition of this center from phase α into phase β. The right-hand side of eq 2 comprises items equal to the product of the rate of initiation I_α of α-th type polymer chains and the Dirac delta function $\delta(\xi)$.

The propagation of the α-th type block of a macroradical may be interrupted either as a result of the addition of monomer M_β or owing to the loss of an active center caused by the chain termination reaction. The probabilities of these events within the interval $d\tau_\alpha = dl/\theta_\alpha$ are equal to $V_{\alpha\beta}(l)d\tau_\alpha$ and $T_\alpha d\tau_\alpha = k_{t\alpha} R'_\alpha d\tau_\alpha$, respectively. Hereafter, $k_{t\alpha}$ is the constant of the chain termination reaction while R'_α stands for the concentration of α-th type active centers in the surface layer of the α-th phase. The function $w_\alpha(\eta)$, having the sense of the probability for α-th type terminal block of a macroradical to attain length η, reads as

$$w_\alpha(\eta) = \exp\left\{-\int_0^\eta \frac{V_{\alpha\beta}(\xi)}{\theta_\alpha}\, \mathrm{d}\xi - \frac{T_\alpha}{\theta_\alpha}\eta\right\} \quad (3)$$

where indices $\alpha \neq \beta$ run values 1 and 2.

Having hypothetically assumed that rates $V_{12}(\xi)$ and $V_{21}(\xi)$ of an active center transition through the interface does not depend on length ξ of growing terminal block of a macroradical, one will find the distribution of blocks for length (3) to be exponential. In this case, having nothing to do with reality, the solution of eqs 1 and 2 will formally reduce to the solutions of the traditional equations of radical copolymerization[6] for the concentrations $R_\alpha(l)$ of radicals with length l

$$\theta_1 \frac{\mathrm{d}R_1(l)}{\mathrm{d}l} = -V_{12}R_1(l) + V_{21}R_2(l) - T_1R_1(l) + I_1\delta(l)$$

$$\theta_2 \frac{\mathrm{d}R_2(l)}{\mathrm{d}l} = -V_{21}R_2(l) + V_{12}R_1(l) - T_2R_2(l) + I_2\delta(l) \quad (4)$$

in which $V_{\alpha\beta}$ has the meaning of the rate of the addition of monomer M_β to the α-th type active center. This kinetic parameter equals the product of the rate constant of the chain propagation reaction $k_{\alpha\beta}$ and the concentration of the aforementioned monomer.

For process of the interphase copolymerization, however, the dependence of coefficients $V_{12}(\xi)$ and $V_{21}(\xi)$ of eqs 2 on ξ proves to be rather substantial. It is determined by the following expressions

$$V_{12}(\xi) = p_1(\xi) k_{12} M'_2 \qquad V_{21}(\xi) = p_2(\xi) k_{21} M'_1 \quad (5)$$

where $p_\alpha(\xi)$ represents the probability that an α-th type active center positioned on the end of terminal block of length ξ resides in phase β close to its boundary. Since the time scale of the addition of a monomer to the growing macroradical as a rule appreciably exceeds the time scale of attaining by this macroradical conformational equilibrium, the dependence $p_\alpha(\xi)$ has to be found from an equilibrium theory.

In the framework of this theory the probability $p_\alpha(\xi)$ is equal to the product of two factors. The first of them, $q_\alpha(\xi)$, equals the probability for the growing end of an α-th type block to be situated in the neighborhood of the interphase boundary on the α-th phase side. The second factor, $\kappa_\alpha = \exp\{-\Delta F_{\alpha\beta}/k_B T\}$, is controlled by the loss in free energy $\Delta F_{\alpha\beta}$ of α-th type macroradical under the transition of its terminal unit through the interface from phase α to phase β. The more is the ratio of this quantity to the product of the Boltzmann constant k_B and temperature T, the less the probability for the terminal unit of the macroradical to cross the interface. The problem of finding the dependence $q_\alpha(\xi)$ for Gaussian polymer chain reduces to the consideration of the random walks in half-space over the plane with reflecting boundary. Under such a consideration the unknown function $q_\alpha(\xi)$ will equal the probability to find among all trajectories with length ξ such a trajectory whose both ends are located on the plane. The solution of this problem yields at $\xi \gg 1$ asymptotic dependence $q_\alpha(\xi) = c\xi^{-1/2}$ where the numerical coefficient $c = 2/\sqrt{2\pi}$.[7] As a result, the following expression for function $w_\alpha(\eta)$ (3) is arrived at

$$w_\alpha(\eta) = \exp\{-2\epsilon_\alpha \eta^{1/2} - \epsilon_\alpha^{(0)}\eta\} \quad (\alpha \neq \beta = 1, 2) \quad (6)$$

where the following designations are used:

$$\epsilon_\alpha = \frac{cM'_\beta \kappa_\alpha}{2M'_\alpha r_\alpha} \qquad \epsilon_\alpha^{(0)} = \frac{T_\alpha}{\theta_\alpha} = \frac{k_{t\alpha}R'_\alpha}{k_{\alpha\alpha}M'_\alpha} \quad (7)$$

The values of the reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ involved in the first of formulas (7) are available in the literature for hundreds monomeric pairs which are employed in radical copolymerization.[8]

Substituting expressions 6 for $w_1(\eta)$ and $w_2(\eta)$ into relationships 1 and 2, we get a closed set of kinetic equations describing radical copolymerization in the framework of the simplest model in hand. The values of the rates of initiation in phases 1 and 2 entering in eqs 2 are determined as follows

$$I_1 = k_1^{in}\Theta s \qquad I_2 = k_2^{in}\Theta s \quad (8)$$

where Θ denotes the surface concentration of an initiator molecules. Here the rate constant of the initiation reaction in the α-th phase, k_α^{in}, is proportional to the probability that the decomposition of labile bond of the initiator molecule will happen just in the α-th phase as well as to the rate constant of this bond decomposition and the efficiency of a polymer chain initiation in the α-th phase.

Among the major problems challenging a quantitative theory of any copolymerization process is the derivation of the expressions for its rate as well as for the composition and the chemical structure of macromolecules formed. Below the derivation of these equations will be presented on the basis of the above formulated physicochemical model of interphase copolymerization. When choosing this model, we presumed the rate constants of all elementary reactions to be independent of the chemical size and composition of polymer radicals as well as of monomers' conversion. Along with this Flory principle feasibility, generally accepted in the theory of macromolecular reactions,[3,6] we also proceeded for simplicity sake from the assumption that thermodynamic parameters κ_1 and κ_2 remain unchanged in the course of the synthesis. These and other assumptions underlying the above-proposed simplest model of interphase copolymerization may be relaxed in subsequent works devoted to the refinement of the theory of this process.

Kinetics of Interphase Free-Radical Copolymerization

The rate of this process

$$V = -\frac{dM}{dt} = V_1 + V_2 \tag{9}$$

is the sum of the rates of the formation of homopolymer blocks in each phase

$$V_1 = -\frac{dM_1}{dt} = \theta_1 R_1 \qquad V_2 = -\frac{dM_2}{dt} = \theta_2 R_2 \tag{10}$$

Concentrations R_1 and R_2 of the active centers of types 1 and 2 are, obviously, equal to the values of the Laplace transforms $\tilde{R}_1(p)$ and $\tilde{R}_2(p)$ of the distributions of concentrations of macroradicals $R_1(l)$ and $R_2(l)$ for their length

$$\tilde{R}_\alpha(p) \equiv \int_0^\infty R_\alpha(l) \exp(-pl)\, dl \quad (\alpha = 1, 2) \tag{11}$$

taken at the value of variable p equal to zero. Functions $\tilde{R}_\alpha(p)$ are readily obtained from the solution of the set of linear algebraic equations to which the integral equations (1) and (2) are reduced upon undergoing the Laplace transformation. The resulting expressions read

$$\tilde{R}_1(p) = \frac{\tilde{w}_1(p)[I_1 + I_2\tilde{u}_2(p)]}{\theta_1[1 - \tilde{u}_1(p)\tilde{u}_2(p)]} \qquad \tilde{R}_2(p) = \frac{\tilde{w}_2(p)[I_1\tilde{u}_1(p) + I_2]}{\theta_2[1 - \tilde{u}_1(p)\tilde{u}_2(p)]} \tag{12}$$

with $\tilde{w}_\alpha(p)$ being the Laplace transform of function (7)

$$\tilde{w}_\alpha(p) = \frac{1 - \tilde{u}_\alpha(p)}{p + \epsilon_\alpha^{(0)}} \tag{13}$$

The function $\tilde{u}_\alpha(p)$ appearing on the right-hand sides of expressions 12 and 13 is the Laplace transform of the function $u_\alpha(\eta) = w_\alpha(\eta)\epsilon_\alpha/\sqrt{\eta}$. This can be calculated from

$$\tilde{u}_\alpha(p) = H(y_\alpha) = \sqrt{\pi y_\alpha} \exp(y_\alpha) \operatorname{erfc}(\sqrt{y_\alpha}) \tag{14}$$

where the symbol "erfc" denotes the function, referred to as "addition to the probability integral",[9] while the dependence of variable y_α on p looks as

$$y_\alpha = \frac{{\epsilon_\alpha}^2}{p + \epsilon_\alpha^{(0)}} \tag{15}$$

If p in formulas 12 is assigned zero, a set of two equations for the overall concentrations of active centers $R_\alpha = \tilde{R}_\alpha(0)$ will be obtained:

$$R_1 = \frac{(1 - H_1)(I_1 + I_2H_2)}{T_1(1 - H_1H_2)} \qquad R_2 = \frac{(1 - H_2)(I_1H_1 + I_2)}{T_2(1 - H_1H_2)} \tag{16}$$

Here $H_\alpha \equiv \tilde{u}_\alpha(0) = H(b_\alpha)$ is defined by expression 14 with parameter $b_\alpha = {\epsilon_\alpha}^2/\epsilon_\alpha^{(0)}$ instead of y_α.

Depending on parameters b_1 and b_2, it is possible to distinguish three limiting regimes of interphase copolymerization

$$(1)\ b_1 \gg 1, b_2 \gg 1; \quad (2)\ b_1 \ll 1, b_2 \ll 1; \quad (3)\ b_1 \gg 1, b_2 \ll 1 \tag{17}$$

Considering these regimes, one should take into account the behavior of function $H(y)$ (14). When its argument y changes from 0 to ∞, $H(y)$ increases from 0 to 1, the asymptotic expression $H(y) = 1 - (2y)^{-1}$ being true at $y \gg 1$. By virtue of the above reasoning, the important conclusions concerning the architecture of macromolecules formed under different copolymerization regimes (17) may be made. This is because quantity $0 < H_\alpha < 1$ has rather transparent probabilistic meaning. In fact, the growth of the terminal α-th type block of a macroradical may be over either by the active center transition into other phase or by its loss due to the chain termination reaction. The probabilities of these events, coinciding with the probabilities that a block chosen at random will be either internal or external, are equal to H_α and $1 - H_\alpha$, respectively.

In the first of the limiting regimes (17) both quantities $H_1 = H(b_1)$ and $H_2 = H(b_2)$ turn out to be close to unity. This means that the fraction of the internal blocks substantially exceeds the fraction the external ones; i.e., copolymerization products under this regime are multiblock copolymers. A completely different type of situation occurs in the limiting regime II (17) where both quantities, H_1 and H_2, are much less than unity. In this regime almost all blocks are external, and consequently, a mixture of molecules of two homopolymers is formed in the course of copolymerization. As for the third of the regimes (17), here the value of quantity H_1 is very close to unity, while H_2 is small enough. Under this regime the copolymerization products will be homopolymer molecules with the second type units and those of diblock copolymer being formed under the initiation of chains in the second and the first phases, respectively. Obviously, the most promising from practical viewpoint is the regime I that will be addressed in more detail below.

In this regime eqs 16 for finding the concentrations of active centers are

$$R_1 = \frac{Ib_1^{-1}}{T_1(b_1^{-1} + b_2^{-1})} \quad R_2 = \frac{Ib_2^{-1}}{T_2(b_1^{-1} + b_2^{-1})}, \quad \text{where } I = I_1 + I_2 \quad (18)$$

Substituting their solutions into formulas 10, we will get the expression for the rate of monomer M_α depletion

$$V_\alpha = \frac{1}{\epsilon_\alpha^2}\sqrt{\frac{Is}{\Lambda}}\ (\alpha = 1, 2), \quad \text{where } \Lambda = \frac{k_{t1}}{d_1\theta_1^2\epsilon_1^4} + \frac{k_{t2}}{d_2\theta_2^2\epsilon_2^4} \quad (19)$$

which leads in the simplest case $d_1 = d_2 = d$ to the following formula for the interphase copolymerization rate

$$V = (Isd)^{1/2}[\rho_1^2(M'_1)^4 + \rho_2^2(M'_2)^4][\delta_1^2\rho_1^4(M'_1)^6 + \delta_2^2\rho_2^4(M'_2)^6]^{-1/2} \quad (20)$$

Here $\rho_\alpha = r_\alpha/\kappa_\alpha$, while $\delta_\alpha = k_{t\alpha}^{1/2}/k_{\alpha\alpha}$ represents the parameter entering in the traditional expression for homopolymerization rate[6]

$$V_\alpha^{\text{hom}} = \sqrt{I}M_\alpha/\delta_\alpha \quad (21)$$

The values of this parameter are extensively reported in the literature for many monomers.[10] Noteworthy, expression 21 will also describe the rates of monomers' depletion during the process of interphase copolymerization provided it proceeds under regime II (17).

At the first glance it may appear that formula 20 for the rate of the formation of macromolecules containing large number of long blocks may be obtained up to the factor $\sqrt{sd}$ from the expression for the rate of the traditional radical copolymerization upon the replacement of reactivity ratios r_1 and r_2 by their modified values $\hat{r}_1 = \rho_1$ and $\hat{r}_2 = \rho_2$. Indeed, when $r_1 \gg 1$ and $r_2 \gg 1$ the formulas of the traditional copolymerization formally describe the formation of macromolecules of multiblock copolymer with long blocks whose chemical structure is identical to that of macromolecules formed under regime I of interphase copolymerization. However, the comparison of the expression for the rate of copolymerization

$$V = I^{1/2}(r_1M_1^2 + r_2M_2^2)(\delta_1^2r_1^2M_1^2 + \delta_2^2r_2^2M_2^2)^{-1/2} \quad (22)$$

proceeding in homophase solution in case $r_1 \gg 1$, $r_2 \gg 1$ with expression 20 and copolymerization occurring at the surface separating two immiscible phases shows that this guess is really wrong. This is because the formal replacement of reactivity ratios r_1 and r_2 in relationship 22 by their modified values $\hat{r}_1 = \rho_1$, $\hat{r}_2 = \rho_2$ leads to the dependence of V on the concentrations of monomers different from that of formula 20. The comparison of these expressions indicates that the dependencies of the rate V of the depletion of monomers on their overall concentration $M = M_1 + M_2$ and on the initiation rate I are the same for homophase and interphase copolymerization. However, the dependence of V on monomer mixture composition $\mathbf{x}$ is qualitatively different for these two processes.

Using expressions 8, it is easy to note that overall number of moles of monomers being polymerized in unit time in a reaction system is proportional to interphase surface area in the miniemulsion.

Distribution of Macromolecules for Size and Composition

Each copolymer chain is characterized by vector $\mathbf{l}$ with components l_1 and l_2 equal to the numbers of the first and the second type monomeric units. A pair of these numbers unambiguously characterizes chemical size ($l = l_1 + l_2$) and composition ($\zeta_1 = l_1/l$, $\zeta_2 = l_2/l$) of a macromolecule. Among the main problems of the statistical chemistry of copolymers is the determination of the probability $f_N(\mathbf{l})$ for a randomly chosen molecule to have vector $\mathbf{l}$. To solve this problem, let us resort to the superposition principle,[11] which permits to reduce the problem of finding the Laplace transform $G_N(\mathbf{p})$ of the size−composition distribution (SCD) $f_N(\mathbf{l})$ of copolymer chains

$$G_N(\mathbf{p}) \equiv \int_0^\infty\int_0^\infty f_N(\mathbf{l}) \exp(-p_1l_1 - p_2l_2)\, dl_1\, dl_2 \quad (23)$$

to the solution of two subsidiary problems. The first of them consists of the derivation of the expression for the generation function

$$U(\mathbf{z}^{\text{in}},\mathbf{z}^{\text{ex}}) \equiv \sum_{\mathbf{n}}\sum_{\mathbf{m}} P(\mathbf{n},\mathbf{m})(z_1^{\text{in}})^{n_1}(z_2^{\text{in}})^{n_2}(z_1^{\text{ex}})^{m_1}(z_2^{\text{ex}})^{m_2} \quad (24)$$

of the probability distribution $P(\mathbf{n},\mathbf{m})$ of macromolecules for number of constituent blocks. Vectors $\mathbf{n}$ and $\mathbf{m}$ have components n_1, n_2 and m_1, m_2, equal to the numbers of internal (n_1, n_2) and external (m_1, m_2) blocks, consisting of units of types 1 or 2. To solve the second subsidiary problem, it is necessary to derive the expressions for the Laplace transforms

$$g_\alpha^{\text{in}}(p_\alpha) \equiv \int_0^\infty \varphi_\alpha^{\text{in}}(l_\alpha) \exp(-p_\alpha l_\alpha)\, dl_\alpha$$
$$g_\alpha^{\text{ex}}(p_\alpha) \equiv \int_0^\infty \varphi_\alpha^{\text{ex}}(l_\alpha) \exp(-p_\alpha l_\alpha)\, dl_\alpha \quad (25)$$

of distributions $\varphi_\alpha^{\text{in}}(l_\alpha)$ and $\varphi_\alpha^{\text{ex}}(l_\alpha)$ of internal and external blocks, respectively, for number l_α of monomeric units involved. Further recourse to the superposition principle[11] leads to the important expression for the Laplace transform of SCD

$$G_N(\mathbf{p}) = U(\mathbf{g}^{\text{in}}(\mathbf{p}),\mathbf{g}^{\text{ex}}(\mathbf{p})) \quad (26)$$

To employ this formula, one should find analytical expressions for the generating function (24) and substitute in it for arguments $\mathbf{z}^{\text{in}}$ and $\mathbf{z}^{\text{ex}}$ the Laplace transforms (25) of the MWD of the internal and external blocks of different types.

The first subsidiary problem may be most conveniently solved by virtue of the statistical method,[12] bearing in mind that the succession of blocks in the chains under examination is described by the absorbing Markov chain with the transition matrix $\mathbf{Q}^{ab}$ and the vector of initial states $\mathbf{v}$

$$\mathbf{Q}^{ab} = \begin{pmatrix} 1 & 0 & 0 \\ \nu_{10} & 0 & \nu_{12} \\ \nu_{20} & \nu_{21} & 0 \end{pmatrix} \qquad \begin{aligned} &v_1 = I_1/I,\ v_2 = I_2/I \\ &\nu_{12} = 1 - \nu_{10} = H_1 \\ &\nu_{21} = 1 - \nu_{20} = H_2 \end{aligned} \quad (27)$$

Here $H_\alpha \equiv H(b_\alpha)$, where $b_\alpha = {\epsilon_\alpha}^2/\epsilon_\alpha^{(0)}$ while parameters ϵ_α and $\epsilon_\alpha^{(0)}$ (7) and function $H(y)$ (14) have been defined above. The mathematical apparatus of the theory of the Markov chains[13] enables one to write down immediately the expression for generating function (24)

$$U(\mathbf{z}^{\text{in}},\mathbf{z}^{\text{ex}}) = \frac{(v_1 + v_2\nu_{21}z_2^{\text{in}})z_1^{\text{ex}}\nu_{10} + (v_1\nu_{12}z_1^{\text{in}} + v_2)z_2^{\text{ex}}\nu_{20}}{1 - \nu_{12}\nu_{21}z_1^{\text{in}}\, z_2^{\text{in}}} \tag{28}$$

Expanding the right-hand part of this function by formula of the geometric progression, it is possible to get the expression for the distribution of molecules $P(\mathbf{n},\mathbf{m})$ for numbers of constituent blocks. Their average values are readily found as corresponding derivatives of function (28) at point $\mathbf{z}^{\text{in}} = \mathbf{z}^{\text{ex}} = \mathbf{1}$

$$\bar{n}_1 = \frac{(v_1 + v_2\nu_{21})\nu_{12}}{1 - \nu_{12}\nu_{21}} \qquad \bar{n}_2 = \frac{(v_1\nu_{12} + v_2)\nu_{21}}{1 - \nu_{12}\nu_{21}}$$

$$\bar{m}_1 = \frac{(v_1 + v_2\nu_{21})\nu_{10}}{1 - \nu_{12}\nu_{21}} \qquad \bar{m}_2 = \frac{(v_1\nu_{12} + v_2)\nu_{20}}{1 - \nu_{12}\nu_{21}} \tag{29}$$

For the most important regime I (17) we will obtain

$$\bar{n}_1 = \bar{n}_2 = \frac{2b_1b_2}{b_1 + b_2} \qquad \bar{m}_1 = \frac{b_2}{b_1 + b_2} \qquad \bar{m}_2 = \frac{b_1}{b_1 + b_2} \tag{30}$$

where parameters $b_\alpha = {\epsilon_\alpha}^2/\epsilon_\alpha^{(0)}$ are expressed through the parameters of the reaction system (7).

Going to the solution of the second subsidiary problem indispensable in finding the Laplace transform of the SCD (23), it is pertinent to stress that the distributions of the internal and external blocks for their length η follow from simple probabilistic reasoning. These distributions have the following appearance

$$\varphi_\alpha^{\text{in}}(\eta) = \frac{u_\alpha(\eta)}{H_\alpha} = \frac{w_\alpha(\eta)\epsilon_\alpha}{\sqrt{\eta}H_\alpha} \tag{31}$$

$$\varphi_\alpha^{\text{ex}}(\eta) = \frac{\epsilon_\alpha^{(0)}w_\alpha(\eta)}{1 - H_\alpha} \tag{32}$$

where function $w_\alpha(\eta)$ has been introduced earlier (3). The Laplace transformations of expressions 31 and 32 yield

$$g_\alpha^{\text{in}}(p) = \frac{\tilde{u}_\alpha(p)}{\tilde{u}_\alpha(0)} = \frac{H(y_\alpha)}{H_\alpha}, \quad H_\alpha \equiv H(b_\alpha) \tag{33}$$

$$g_\alpha^{\text{ex}}(p) = \frac{\epsilon_\alpha^{(0)}\tilde{w}_\alpha(p)}{1 - H_\alpha} = \frac{\epsilon_\alpha^{(0)}}{p + \epsilon_\alpha^{(0)}}\,\frac{1 - H(y_\alpha)}{1 - H_\alpha} \tag{34}$$

These relationships combined with expressions 14 and 15 represent the exact solution of the second subsidiary problem. They are conducive, in particular, to the following formulas for average lengths of blocks:

$$\bar{\eta}_\alpha^{\text{in}} = -\frac{\mathrm{d}g_\alpha^{\text{in}}(p)}{\mathrm{d}p}\Big|_{p=0} = \frac{1}{\epsilon_\alpha^{(0)}}\left[\frac{1}{2} - \frac{b_\alpha(1 - H_\alpha)}{H_\alpha}\right] \tag{35}$$

$$\bar{\eta}_\alpha^{\text{ex}} = -\frac{\mathrm{d}g_\alpha^{\text{ex}}(p)}{\mathrm{d}p}\Big|_{p=0} = \frac{1}{\epsilon_\alpha^{(0)}}\left[1 + b_\alpha - \frac{H_\alpha}{2(1 - H_\alpha)}\right] \tag{36}$$

which under the regime I (17) are simplified to

$$\bar{\eta}_\alpha^{\text{in}} = \frac{1}{2{\epsilon_\alpha}^2} = \pi\left[\frac{x_\alpha r_\alpha}{(1 - x_\alpha)\kappa_\alpha}\right]^2 \qquad \bar{\eta}_\alpha^{\text{ex}} = 3\bar{\eta}_\alpha^{\text{in}} \tag{37}$$

As it ensues from this expression, the average length of blocks of the α-th type monomeric units increases with the growth of molar fraction x_α of monomer M_α and radical R_α reactivity ratio r_α. Both of these factors, enlarging the probability of the addition to the propagating radical R_α of monomer M_α rather than monomer M_β, are inherent in homophase copolymerization. However, in parallel with two aforementioned factors there is one more peculiar to the interphase mechanism of the copolymer synthesis responsible for the formation of long blocks. This factor is minor thermodynamic affinity between hydrophilic and hydrophobic monomers as well as between their units in macromolecules. The less pronounced is this affinity, the smaller the thermodynamic parameter κ_α and, thus, the higher, according to formula 37, the average length of blocks in copolymer chains.

Substituting functions 33 and 34 into formula 28 yields, in accordance with expression 26, the exact expression of the Laplace transform of the copolymer SCD (23). Obtained in such a way, the function $G_N(\mathbf{p})$ is of utmost importance for building up the phase diagram of a melt or solution of the interphase copolymerization products since it enters in the equations for the cloud points curve.[14] Besides, the statistical moments of the SCD may be found by differentiating function $G_N(\mathbf{p})$ with respect to its arguments p_1 and p_2. For instance, the average number of α-th type units in a macromolecule is calculated by formula

$$\bar{l}_\alpha = -\frac{\partial G_N}{\partial p_\alpha}\Big|_{\mathbf{p}=\mathbf{0}} = \bar{n}_\alpha\bar{\eta}_\alpha^{\text{in}} + \bar{m}_\alpha\bar{\eta}_\alpha^{\text{ex}} \tag{38}$$

complemented by relationships (29), (35), and (36). It is also an easy matter to find average values of chemical size $\bar{l} = \bar{l}_1 + \bar{l}_2$ and composition $X_\alpha = \bar{l}_\alpha/\bar{l}$ of a copolymer, the expressions for which in terms of the parameters (7) have a simple form for regime I (17)

$$\bar{l} = \frac{1}{\epsilon_1^{(0)}X_1 + \epsilon_2^{(0)}X_2} \qquad X_\alpha = \frac{{\epsilon_\alpha}^{-2}}{{\epsilon_1}^{-2} + {\epsilon_2}^{-2}} \tag{39}$$

In this regime macromolecules of the ergodic copolymer[12] are formed whose SCD has exactly the same appearance as in the case of traditional free-radical copolymerization.[15,16] This SCD represents the product of two functions. The first of them is the distribution of macromolecules for their degree of polymerization l, whereas the second one is fractional distribution $W(l|\zeta)$ of macromolecules with fixed number of units l for their composition $\zeta \equiv \zeta_1 = l_1/l$. The function $W(l|\zeta)$ is described by the Gauss formula with the average value $\bar{\zeta} = X_1$ (39) and dispersion ${\sigma_l}^2 = D/l$. The parameter D as well as X_1 is independent of l and may be found by the methods of the statistical chemistry of polymers.[17] However, for real polymer chains with large values of l the dispersion ${\sigma_l}^2$ of the distribution $W(l|\zeta)$, being reciprocal to l, is so small that the composition inhomogeneity of macromolecules formed at fixed monomer mixture composition may be neglected. It is a very good approximation because this instantaneous composition inhomogeneity is normally far more less pronounced as compared to the conversional composition inhomogeneity originated by monomer composition drift in the course of copolymerization. Only at its initial stages when such an evolution can be ignored one may use the above-presented theoretical formulas. To extend the quantitative theory of interphase copolymerization to the whole range of monomers' conversions, it is necessary to consider this process dynamics just along the same lines as it is commonly made under the theoretical description of the traditional homophase copolymerization.[16]

Conversional Evolution of a Copolymer Composition Distribution

Under the quasi-homogeneous approach, the monomer mixture composition is characterized by vector $\mathbf{x}$ with components $x_1 = M_1/M$ and $x_2 = M_2/M$, whose drift with conversion is described by equations

$$(1-p)\frac{\mathrm{d}x_\alpha}{\mathrm{d}p} = x_\alpha - X_\alpha(\mathbf{x}), \quad x_\alpha(0) = x_\alpha^0 \quad (\alpha = 1, 2) \qquad (40)$$

where $X_\alpha(\mathbf{x})$ represents molar fraction of the α-th type units in a copolymer macromolecules being formed at the monomer composition $\mathbf{x}$. Components $X_1(\mathbf{x})$ and $X_2(\mathbf{x})$ (39) of vector $\mathbf{X}(\mathbf{x})$ of the instantaneous composition of a copolymer, which is formed under the regime I in the proximity of the interface at fixed $\mathbf{x}$, can be calculated in accordance with expression 19 using the following expression:

$$X_\alpha(\mathbf{x}) \equiv \frac{\mathrm{d}M_\alpha}{\mathrm{d}M} \equiv \frac{V_\alpha}{V} = \frac{{\epsilon_\alpha}^{-2}}{{\epsilon_1}^{-2} + {\epsilon_2}^{-2}} = \frac{{\hat\rho_\alpha}^2 {x_\alpha}^4}{{\hat\rho_1}^2 {x_1}^4 + {\hat\rho_2}^2 {x_2}^4}, \quad \text{where } \hat\rho_\alpha = \frac{\rho_\alpha}{(y_\alpha)^2} \qquad (41)$$

By virtue of the conditions $x_1 + x_2 = 1$ and $X_1 + X_2 = 1$ only one of two equations (40) (e.g., the first one) is independent. This equation can be integrated in an explicit form. However, before presenting the explicit appearance of the solutions of eq 40 for the processes of homophase and interphase copolymerization, important qualitative conclusions on the behavior of these solutions may be made on the basis of the theory of dynamic systems. General ideas of the methods of this theory as applied to the description of the dynamics of radical copolymerization are expounded in the review article.[16] The analysis of the dynamic equations of interphase copolymerization (40) and (41) carried out by means of the approaches outlined[16] has revealed that the mode of the drift with conversion p of monomer mixture composition $\mathbf{x}$ and the instantaneous copolymer composition $\mathbf{X}$ qualitatively differs from that taking place in the processes of homophase copolymerization. Such an analysis showed that at any values of parameters $\hat\rho_1$ and $\hat\rho_2$ and the initial composition $\mathbf{x}^0$ both vectors, $\mathbf{x}$ and $\mathbf{X}$, will tend with increasing conversion to the same limit $\mathbf{x}^* = \mathbf{X}^*$ known in the copolymerization theory as "azeotrop". Naturally, its value for homophase (a)[16,18] and interphase (b) copolymerization differ

$$\text{(a)}\ x_1^* = \frac{1-r_2}{2-r_1-r_2}, \quad x_2^* = \frac{1-r_1}{2-r_1-r_2}$$
$$\text{(b)}\ x_1^* = \frac{{\hat\rho_2}^{2/3}}{{\hat\rho_1}^{2/3} + {\hat\rho_2}^{2/3}} \equiv a_2, \quad x_2^* = \frac{{\hat\rho_1}^{2/3}}{{\hat\rho_1}^{2/3} + {\hat\rho_2}^{2/3}} \equiv a_1 \qquad (42)$$

Under homophase synthesis in real systems the azeotrop (a) exists only provided $r_1 < 1$ and $r_2 < 1$. In this case, however, it is a repeller, unlike in the case of interphase copolymerization where the azeotrop (b) is an attractor. This means that at the final stage of homophase copolymerization a homopolymer molecules are primarily formed in all real systems whereas under the interphase synthesis the majority of copolymer chains formed at $p \to 1$ have the azeotropic composition $\mathbf{x}^*$. The above-formulated inferences stem immediately from the theory of homophase copolymerization[16] with allowance for the expression

$$1 - p = h(\mathbf{x})/h(\mathbf{x}^0)$$

where

$$h(\mathbf{x}) = |x_1 - x_1^*|^{1/3}(x_1x_2)^{-1}({a_1}^2{x_1}^2 + {a_2}^2{x_2}^2 + a_1a_2x_1x_2)^{-1/3} \qquad (43)$$

connecting monomer composition $\mathbf{x}$ with conversion p. This expression, resulting from the integration of eq 40 together with formula 41 permit determining the dependence of instantaneous copolymer composition $\mathbf{X}$ on conversion. Given this dependence, it is possible resorting to the general algorithm[16] to derive an expression for the fraction of monomeric units $f_{\mathrm{W}}^{\mathrm{c}}(\zeta;p)$ involved in molecules with composition ζ, which are formed during the interphase copolymerization under all conversions p' preceding p

$$f_{\mathrm{W}}^{\mathrm{c}}(\zeta;p) = \langle\delta(\zeta - \mathbf{X})\rangle \equiv \frac{1}{p}\int_0^p \delta(\zeta - \mathbf{X}(p'))\,\mathrm{d}p'$$
$$= \frac{1}{p}\frac{[(a_1\zeta_1)^{1/4} - (a_2\zeta_2)^{1/4}]^{-2/3}}{h(\mathbf{x}^0)4(a_1a_2)^{1/4}(\zeta_1\zeta_2)^{5/4}} \left[\frac{({a_2}^3\zeta_1)^{1/4} + ({a_1}^3\zeta_2)^{1/4}}{(a_1\zeta_1)^{1/2} + (a_2\zeta_2)^{1/2} + (a_1a_2\zeta_1\zeta_2)^{1/4}}\right]^{4/3} \qquad (44)$$

When deriving this expression for the weight composition distribution, we entirely neglected its instantaneous constituent, having taken (as is customary in the quantitative theory of radical copolymerization[16]) the Dirac delta function $\delta(\zeta - \mathbf{X})$ as the instantaneous composition distribution. Its averaging over conversions, denoted hereinafter by angular brackets, leads to formula 44. Note, this formula describes the composition distribution only provided copolymer composition ζ lies in the interval between $\mathbf{X}(0)$ and $\mathbf{X}(p)$. Otherwise, this function of the distribution vanishes at all values of composition ζ lying outside the above-mentioned interval.

The form of the distribution (44), as shown in Figure 2, qualitatively differs from that exhibited by this distribution for the products of homophase copolymer-

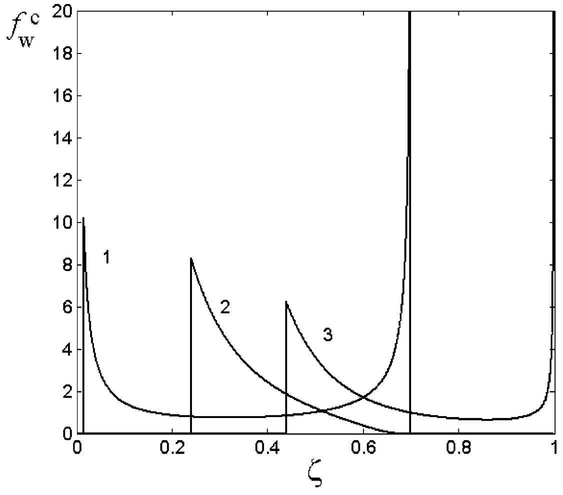


Figure 2. Appearance of the composition distribution function $f^c_W(\zeta;1)$ typical of the products of interphase (1) as well as hypothetical (2) and real (3) homophase copolymerization at complete conversion of monomers.

ization This distinction takes place both in real systems ($r_1 < 1, r_2 < 1$), where statistical copolymers are formed and in hypothetical systems ($r_1 \gg 1, r_2 \gg 1$), where the formation of multiblock copolymers is expected. Essentially, the composition distribution in the latter systems lacks a mode whose maximum corresponds to macromolecules of azeotropic composition. This mode, however, is present in the composition distribution of the interphase copolymerization products. As it can be seen from Figure 2, the composition distribution of final products of traditional homophase copolymerization can be bimodal as well. However, this distribution (curve 3) qualitatively differs from that of composition distribution of the products of interphase copolymerization (curve 1) by the position of the mode with infinite height. In the first case this mode corresponds to homopolymer whereas in the second case it corresponds to azeotropic block copolymer. As for another mode, whose amplitude is finite, it for all curves depicted in Figure 2 corresponds to copolymer formed in the very beginning of the process. This will be either multiblock copolymer (curves 1 and 2) or statistical copolymer (curve 3).

Among important characteristics of composition distribution (44) are its statistical moments of the first and the second order

$$\int_0^1 \zeta_1 f^c_W(\zeta;p)\,d\zeta_1 = \langle X_1\rangle = \frac{1}{p}\int_0^p X_1(p')\,dp' = \frac{1}{p}[x_1^0 - (1-p)x_1] \quad (45)$$

$$\int_0^1 (\zeta_1 - \langle X_1\rangle)^2 f^c_W(\zeta;p)\,d\zeta_1 \equiv \sigma^2(p) = \frac{1}{p}\int_0^p X_1^{\,2}(p')\,dp' - \langle X_1\rangle^2 \quad (46)$$

Formulas 45 and 46 in combination with expressions 41 and 43 enable one to calculate readily the dependence on conversion of principal statistical characteristics of the composition distribution (44). The results of such calculations at fixed value of parameter $a_1 = 1 - a_2$ (42) are depicted in Figure 3.

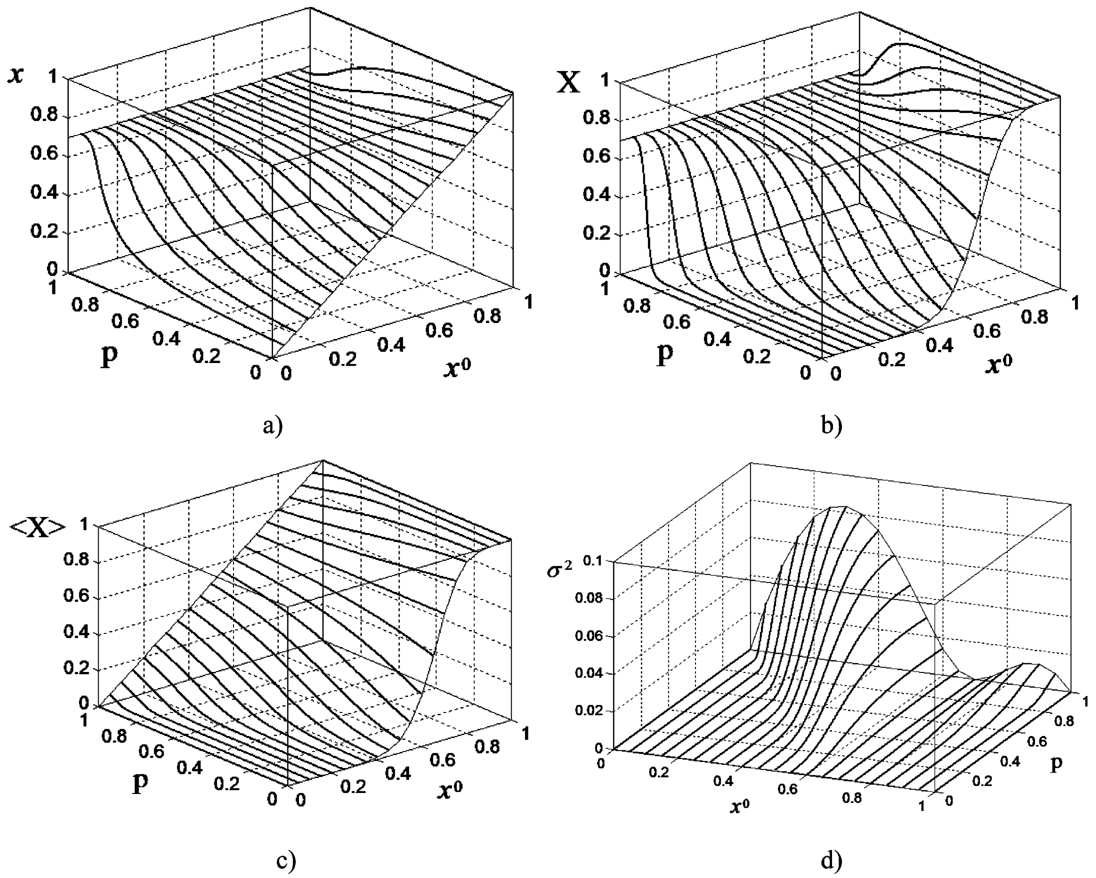
It can be seen from Figure 3a the monomer mixture composition x either increases or decreases with conversion p provided its initial value x^0 is respectively either less or more than azeotropic composition $x^* = 0.7$. An analogous behavior is demonstrated with increasing p by instantaneous X (Figure 3b) and average $\langle X\rangle$ (Figure 3c) copolymer compositions. Both curves characterizing these compositions have value $X(x^0)$ as their starting point. However, the first of them ends at azeotrop $X^* = x^*$ whereas the second one does at point x^0. Figure 3d presents the dispersion σ^2 of the composition distribution (46) which is the qualitative characteristic of composition inhomogeneity of copolymerization products. This dispersion monotonically increases with conversion, changing from $\sigma^2(0) = 0$ up to $\sigma^2(1) = \sigma_{\max}{}^2$. The quantity $\sigma_{\max}{}^2$ is essentially controlled by the initial composition of monomers x^0. It vanishes at points $x^0 = 0$, $x^0 = 1$, and $x^0 = x^* = 0.7$, taking on the larger value the more x^0 is spaced from these three points. As it follows from Figure 3d for the majority of initial compositions x^0 the value of $\sigma_{\max}{}^2$ lies within the range 10^{-2}–10^{-1}. This value is 1 order of magnitude larger than that, which is typical of homophase copolymerization.[16] The aforementioned conclusions are of general significance since the qualitative appearance of the curves presented in Figure 3 remains the same at arbitrary values of parameter a_1.

Of considerable theoretical and practical interest is the answer to the question how the composition distribution of the products of interphase copolymerization changes throughout this process. One may get an idea about the peculiarities of such a change turning to Figure 4. The inspection of the curves presented shows how with the rise of conversion the broadening of the composition distribution occurs. This is accompanied by simultaneous formation of its mode whose maximum corresponds at given conversion to a copolymer composition which is the closest to the azeotropic one. Under complete conversion ($p = 1$) such a maximum coincides with azeotrop $x^* = X^*$ and has an infinite height. It can be readily seen in Figure 5 that with decreased fraction of any monomer in the initial mixture, the second mode with the maximum corresponding to the initial copolymer composition emerges on the curve of the composition distribution of the copolymerization final products. The height of this maximum grows to diverge at point $x^0 = 0$ or $x^0 = 1$.

Conclusions

In-depth examination of the mechanism of chain formation in the course of the interphase radical copolymerization undertaken in the paper points to the possibility in the course of the one-stage process the macromolecules consisting of large number of long blocks. This peculiarity is responsible for a dramatic distinction between the way of the synthesis under consideration and that of the interphase copolycondensation[19] whose products are statistical copolymers (see ref 20 and references therein). The reason for such a difference lies in a qualitative distinction in the mechanism of the formation of macromolecules located close to the interface.

In fact, an irreversible propagation of a polymer chain in the vicinity of the interphase boundary is controlled along with the stoichiometric and kinetic factors also by other ones. Under the interphase copolycondensation among the latter are diffusion factors, whereas under the interphase copolymerization are thermodynamic ones. In our kinetic model these factors are



a)

b)

c)

d)

Figure 3. Dependencies on conversion p of monomer mixture composition x (a), instantaneous X (b), and average $\langle X\rangle$ (c) copolymer composition as well as dispersion σ^2 (d) of the composition distribution calculated at different values of the initial compositions of monomers x^0. The calculations have been carried out at values of parameters a_1 and $a_2 = 1 - a_1$ (42) equal to 0.3 and 0.7, respectively.

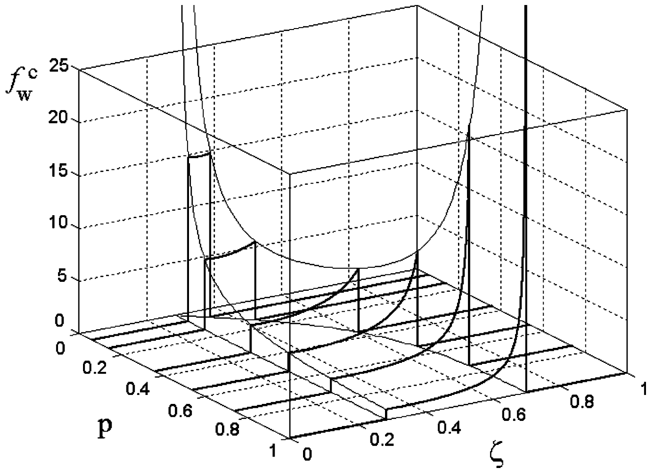


Figure 4. Evolution with conversion p of composition distribution of the products of interphase copolymerization calculated at the initial monomer mixture composition $x^0 = 0.6$ and parameter a_1 (42) equal to 0.3.

characterized by parameters κ_1 and κ_2, where $\kappa_\alpha = \exp(-\Delta F_{\alpha\beta}/k_BT)$ is predetermined by the loss ΔF_α of the free energy of an α-th type macroradical under the transition of its terminal unit through the interface from phase α to phase β. The rest of the parameters of this model are the concentrations of monomers M_1, M_2, the initiation rates I_1, I_2 in both phases close to their boundary, and the rate constants of the elementary chain propagation (k_{11}, k_{22}) and termination (k_{t1}, k_{t2}) reactions under the homopolymerization of these monomers.

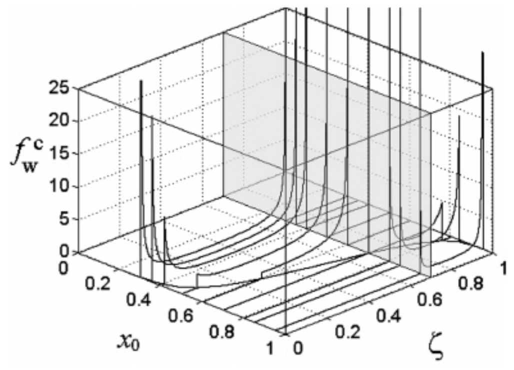


Figure 5. Dependence of the composition distribution of a copolymer formed under complete conversion of monomers $p = 1$ on their initial composition x^0. The diagrams are presented here for interphase copolymerization when parameter a_1 is equal to 0.3.

Of considerable significance for the outlined theory are the dimensionless parameters (7) whose values enable an exhaustive description of the chemical structure of multiblock copolymers with the long blocks being formed during the interphase copolymerization. In particular, resorting to formulas 37, 30, and 39 it is possible to find respectively average lengths of different type blocks, their average numbers in macromolecules, and its average chemical size and composition. When calculating these statistical characteristics, one may use the following expressions for parameters (7)

$$\epsilon_{\alpha} = \frac{1}{\sqrt{2\pi}} \frac{M'_{\beta}}{M'_{\alpha}\rho_{\alpha}} \quad (\alpha \neq \beta = 1, 2)$$

$$\epsilon_{\alpha}^{(0)} = \frac{(\delta_{\alpha}\rho_{\alpha}M'_{\alpha})^2}{d_{\alpha}}[(k_1^{\text{in}} + k_2^{\text{in}})\Theta]^{1/2}\left[\frac{\delta_1^{\,2}}{d_1}\rho_1^{\,4}(M'_1)^6 + \frac{\delta_2^{\,2}}{d_2}\rho_2^{\,4}(M'_2)^6\right]^{-1/2} \quad (47)$$

Here the following designations are employed

$$\rho_{\alpha} = \frac{r_{\alpha}}{\kappa_{\alpha}} \qquad \delta_{\alpha} = \frac{\sqrt{k_{\text{t}\alpha}}}{k_{\alpha\alpha}} \quad (\alpha = 1, 2) \qquad (48)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the reactivity ratios of the first and the second type macroradicals, k_1^{in} and k_2^{in} stand for the rate constants of initiation reaction inside the first and the second phases, Θ denotes surface concentration of initiator at the interface, and d_{α} represents the thickness of surface layer in the α-th phase, while M'_{α} is monomer concentration within it. In order for the products of interphase copolymerization to consist of macromolecules containing large number of long blocks, the following conditions should be met:

$$\epsilon_{\alpha} \ll 1 \quad \epsilon_{\alpha}^{(0)} \ll 1 \quad b_{\alpha} = \epsilon_{\alpha}^{\,2}/\epsilon_{\alpha}^{(0)} \gg 1 \quad (\alpha = 1, 2) \quad (49)$$

Widely used monomers are suitable for the performance of the interphase copolymerization at the oil–water boundary. As hydrophobic ones, it is advisable to choose styrene or some of acrylates or methacrylates. The best studied among hydrophilic monomers are acrylic acid and acrylamide. Concluding this paper, we would like to discuss main assumptions underlying the proposed theory and to estimate expected values of the statistic characteristics of the chemical structure of block copolymers predicted by our original theory.

The most promising from the practical standpoint seems to be a copolymer with macromolecules in which average lengths $\bar{\eta}_1$ and $\bar{\eta}_2$ of both type blocks are identical. To obtain such a block copolymer of equimolar composition $X_1 = X_2 = 1/2$, the ratio M'_1/M'_2 of concentrations of monomers in the first and the second phases are supposed to have, according to formula 37, the definite value $\sqrt{\rho_2/\rho_1}$. In this case the following expressions are valid:

$$\epsilon_1 = \epsilon_2 = \frac{1}{\sqrt{\rho_1\rho_2}} \equiv \epsilon \qquad \bar{\eta}_1 = \bar{\eta}_2 = \frac{1}{2\epsilon^2} = \frac{\rho_1\rho_2}{2} \equiv \bar{\eta} \quad (50)$$

$$\bar{l} = \frac{2}{\epsilon_1^{(0)} + \epsilon_2^{(0)}} = \frac{2}{\sqrt{\mu_1^{\,2} + \mu_2^{\,2}}}, \quad \text{where } \mu_{\alpha} = \left(\frac{k^{\text{in}}\Theta k_{\text{t}\alpha}}{d}\right)^{1/2}\frac{1}{k_{\alpha\alpha}M'_{\alpha}} \quad (51)$$

Formulas 51 ensue immediately from eqs 37 and 47 provided $d_1 = d_2 \equiv d$. Hence, it is rigorously shown that the average length of blocks $\bar{\eta}$ of the equimolar multiblock copolymer does not depend on the parameters of initiation and termination reactions whereas average number of units in a macromolecule $\bar{l}$ is independent of thermodynamic parameters κ_1 and κ_2. As for the average number $\bar{n}$ of blocks in a macromolecule, its value in line with (30) can be found by the formula

$$\frac{1}{\bar{n}} = \frac{\bar{\eta}}{\bar{l}} = \frac{1}{4}\left(\frac{1}{b_1} + \frac{1}{b_2}\right), \quad \text{where } b_{\alpha} = \frac{\epsilon^2}{\epsilon_{\alpha}^{(0)}} \quad (52)$$

The condition $\bar{n} \gg 1$ is, evidently, valid if the smallest of two parameters b_1 and b_2 is large enough.

To roughly evaluate parameter ϵ, let us suppose that the value of quantity κ_{α} coincides with molar solubility of monomer M_{α} in phase $\beta \neq \alpha$. Setting $\kappa_1 = \kappa_2 = 5 \times 10^{-2}$ and $r_1r_2 = 0.25$ in formulas 50, we will have $\epsilon = 10^{-1}$ and $\bar{\eta} = 50$. To assess the characteristic scale of the number of units $\bar{l}$ in a macromolecule for the rate constants of elementary reactions of initiation ($k^{\text{in}} = k_1^{\text{in}} + k_2^{\text{in}}$), propagation ($k_{\alpha\alpha}$) and termination ($k_{\text{t}\alpha}$) of polymer chains the following values can be taken

$$k^{\text{in}} = 10^{-5}\ \text{s}, \quad k_{\alpha\alpha} = 10^2\ \text{L/(mol s)}, \quad k_{\text{t}\alpha} = 10^3\ \text{L/(mol s)} \quad (53)$$

The first two values are typical for homophase free-radical polymerization,[10] whereas the constant k_{t} is approximately 4 orders of magnitude less than that describing the chain termination under traditional homophase polymerization in bulk or solution. Such a decrease of $k_{\text{t}\alpha}$ results from limited mobility of a macroradical due to its "anchoring" on the interphase surface.[21] This circumstance is, naturally, responsible for the retardation of the diffusion-controlled reaction of the chain termination. Upon choosing for the rest of quantities entering in expression for μ_{α} (51), the following values

$$\Theta = 10^{-10}\ \text{mol/cm}^2, \quad M'_{\alpha} = 1\ \text{mol/L}, \quad d = 10^{-7}\ \text{cm} \quad (54)$$

we will get $\epsilon_{\alpha}^{(0)} = 10^{-3}$, which at $\epsilon_1^{(0)} = \epsilon_2^{(0)}$ yields $\bar{l} = 10^3$. Thus, typical products of interphase copolymerization described by the proposed model with parameters (53) and (54) are macromolecules consisting of 20 blocks, each having chemical length of 50 units. Naturally, conditions (49) hold therewith since $\epsilon_1 = 10^{-1}$ and $\epsilon_{\alpha}^{(0)} = 10^{-3}$, whereas $b_{\alpha} = 10$.

The physicochemical model of interphase copolymerization put forward in this paper originates from the assumption that during the time interval between two successive additions of monomers to the growing polymer chain its terminal block wittingly reaches conformational equilibrium. To estimate the relaxation time τ of this block, it is possible to use the Zimm equation[22] $\tau \sim \eta_{\text{s}}R_0^{\,3}/T$, where η_{s} is the solvent viscosity, while R_0 denotes the radius of the Gaussian coil of polymer chain with number of units equal to $\bar{\eta}$. For values $\eta_{\text{s}} \sim 10^2$ P and $\bar{\eta} \sim 10^2$, the maximal relaxation time of this chain $\tau \sim 10^{-6}$ s, which is markedly less than the characteristic scale of time $(k_{\alpha\alpha}M'_{\alpha})^{-1} \sim 10^{-2}$ s of the addition of a monomer to macroradical.

Thus, the above theoretical approach permitted us to specify the conditions for conducting a one-stage process of interphase copolymerization, ensuring the formation of molecules of multiblock copolymers with hydrophilic and hydrophobic monomeric units. Such amphiphilic macromolecules represent polymer emulgators which are capable of stabilizing the colloid particles in miniemulsions, preventing their coagulation. The use of a surface-active initiator enables one to carry out the interphase copolymerization in such colloid systems with sufficiently high rate, which is essential for practical realization of this process. The real possibility of such a realization is supported by experimental evidence reported in a highly interesting publication.[1]

Acknowledgment. The financial support of the Alexander-von-Humboldt Foundation, Program for Investment in the Future (ZIP), is highly appreciated. Authors are also indebted to K. Tarasevich for his kind assistance in preparing the manuscript for publication.

References and Notes

(1) Willert, M.; Landfester, K. *Macromol. Chem. Phys.* **2002**, *203*, 825−836.

(2) In this paper we excluded from consideration the precipitation polymerization when a homopolymer radical during its growth loses the solubility and precipitates on the interphase surface.

(3) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon Press: New York, 1995.

(4) Aris, R. *Introduction to the Analysis of Chemical Reactors*; Prentice Hall, Inc.: Englewood Cliffs, NJ, 1965.

(5) Cox, D. R. *Renewal Theory*; John Wiley & Sons: New York, 1961.

(6) Dotson, N. A.; Galvan, R.; Laurence, R. L.; Tirrell, M. *Polymerization Process Modeling*; VCH: Cambridge, UK, 1996.

(7) Feller, W. *An Introduction to Probability Theory and Its Applications*; John Wiley & Sons: New York, 1966.

(8) Greenley, R. Z. J. *Macromol. Sci., A* **1980**, *14*, 427, 445.

(9) Korn, G. A.; Korn, T. M. *Mathematical Handbook for Scientists and Engineers*; McGraw-Hill Book Co., Inc.: New York, 1961.

(10) Bagdasaryan, Kh. S. *Theory of Radical Polymerization*; Nauka Publ.: Moscow, 1966.

(11) Kuchanov, S. I. In *Comprehensive Polymer Science*, 1st Suppl.; Allen, G., Ed.; Pergamon Press: New York, 1992; Chapter 2, p 23.

(12) Kuchanov, S. I. *Adv. Polym. Sci.* **2000**, *152*, 157.

(13) Kemeny, J. G.; Snell, J. L. *Finite Markov Chains*; Van Nostrand: Princeton, 1960.

(14) Kuchanov, S. I.; Panyukov, S. V. In *Comprehensive Polymer Science*, 2nd Suppl.; Allen, G., Ed.; Pergamon Press: New York, 1996; Chapter 13, p 441.

(15) Stockmayer, W. H. *J. Chem. Phys.* **1945**, *13*, 199.

(16) Kuchanov, S. I. *Adv. Polym. Sci.* **1992**, *103*, 1.

(17) Kuchanov, S. I. In *Mathematical Methods in Contemporary Chemistry*; Kuchanov, S. I., Ed.; Gordon & Breach: Langhorne, PA, 1996; Chapter 5, p 267.

(18) Odian, G. *Principles of Polymerization*; John Wiley & Sons: New York, 1991.

(19) Morgan, P. W. *Condensation Polymers by Interfacial and Solution Methods*; Interscience Publ.: New York, 1965.

(20) Vasnev, V. A.; Kuchanov, S. I. In *Advances in Polymer Chemistry*; Korshak, V. V., Ed.; MIR Publishers: Moscow, 1986; Chapter 4, p 117.

(21) Brook, M. A.; Pavlov, S. A. *Polymerization at Surface of Solids*; Khimia Publ.: Moscow, 1990.

(22) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1988; eq 4.63 in p 100.

MA048440O