Macromolecules **1997,** *30,* 4511−4519

Quantitative Theory of Free-Radical Copolymerization Allowing for the Phenomenon of Preferential Sorption

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Received October 3, 1996; Revised Manuscript Received April 22, 1997⊗

ABSTRACT: A number of anomalies, found in studies on the free-radical copolymerizations of a variety of monomers are attributed to the globular state of growing macroradicals, the monomer mixture composition inside and outside of which differ markedly. An account of such partitioning of monomers (the Harwood Bootstrap Effect) is performed within the framework of a new quantitative theory of copolymerization which interprets the dependence of the composition of copolymers obtained at low conversions on their molecular weights, as well as explains the pronounced intramolecular and compositional inhomogeneity of these copolymers. A theoretical approach has been elaborated to describe the copolymerization of an arbitrary number of monomers which is easy to verify experimentally because along with reactivity ratios its only other input parameters are the Flory χ-parameters of pair interactions between monomer units, monomers, and solvent molecules.

1. Introduction

The first, very relevant papers dealing with the kinetics of free-radical copolymerization were published about 50 years ago.[1−4] Essentially two kinetic models were proposed: the first of them takes into account the relative reactivities of growing macroradicals toward the different monomers present. Initially, this model considered only the reactivity of the terminal monomer unit of the chain. Subsequent developments of this approach attributed some relevance also to penultimate[5] and penpenultimate[6] monomer unit effects. The second model implies the formation of a complex between the components of the polymerization mixture and their involvement in subsequent polymerizations. Kinetic equations based on this second approach consider all possible reactions between the growing macroradicals, the complexes and the monomers, as well as the effect of the solvent.[7−11]

Both theories pay almost exclusive attention to the kinetics and mechanism of the propagation step without considering the important role played by physical factors. Proper consideration of the latter has been introduced only recently. In 1978, Plochocka and Harwood[12] published experimental data concerning the copolymerization of styrene and methacrylic acid carried out in carbon tetrachloride and dioxane at low conversions. Their unexpected finding was that copolymers having the same composition had the same microstructure independent of the solvent and of the monomer molar ratio in the feed. In 1987, Harwood published further data on other systems (styrene copolymerized with methacrylic acid and methacrylonitrile in benzene and dimethylformamide).[13] The new results fully confirmed the previous ones. In more recent years, many papers[14−20] provided new evidence about this phenomenon which was named the bootstrap effect by Harwood.[13] This effect has been explained by the assumption that the growing polymer chain controls its own environment in such a way that the local monomer ratio can differ, often significantly, from their ratio in the bulk of the polymerization mixture. This explanation was used to interpret qualitatively not only the fact that copolymerization products of the same composition have the same sequence distribution, even when prepared in different solvents from a variety of monomer mixture compositions, but also other interesting features peculiar to this phenomenon. The main peculiarities have been detected experimentally and explored in detail in a series of papers by Semchikov *et al.* and Smirnova *et al.*,[21−36] who investigated the radical bulk copolymerization of about 30 pairs of the most common vinyl monomers. The above peculiarities can be summarized as follows:

(1) The compositions of many copolymers obtained at low conversions are markedly controlled by their molecular weight, at least in a well-defined range of values. This dependence, for a given temperature and monomer feed composition, is not at all related to the method used for molecular weight control, which can be accomplished by changing the concentration of either the initiator or a chain transfer agent.

(2) Copolymers synthesized in low conversion (i.e., less than 10%) are characterized by an anomalous composition inhomogeneity, exceeding that predicted by the classical theory of free-radical copolymerization. This is due to the considerable polydispersity of these products with respect to the number of their monomer units as described by the Flory exponential distribution. Since the composition of each macromolecule within the sample is unambiguously related to its degree of polymerization, the material composition inhomogeneity can be very substantial if the molecular weight distribution is sufficiently wide.

(3) Each copolymer macromolecule is chemically inhomogeneous along its chain length. It has been demonstrated[34−36] that different segments along the same polymer chain, having the same length and containing a sufficiently large number of monomer units, can have rather different compositions. According to the concepts of the traditional theory of free-radical copolymerization such intramolecular inhomogeneity should be negligible by virtue of the fact that polymer

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

S0024-9297(96)01473-8 CCC: $14.00

radicals grow for such a short term that the monomer feed composition should not change during the formation of a given polymer molecule. This statement does not obviously hold if the phenomenon of preferential sorption manifests itself, i.e., when the local monomer concentration ratio in the vicinity of the growing radical drifts along with the macroradical composition at constant monomer concentration ratio in bulk. Experimentally, intramolecular inhomogeneity of copolymers was qualitatively studied by performing selective scission of the copolymers and analyzing the resulting products.[34−36] The systems in which the peculiarities discussed above are present have been termed *anomalous*[30,35] to differentiate them from *classical* ones, which can be properly described by simply using the traditional theories of free-radical copolymerization. It must be underlined that, among the studied monomer pairs, the *classical* systems constitute only about a third of the total.[21−36] The phenomenon of preferential sorption appears as a fairly general feature of free-radical copolymerization. As a consequence, a proper theory should take into account its role to describe the above process quantitatively. In this paper we present a first attempt to elaborate a new theory on the basis of both the Bootstrap Model (BM)[13] and the current concepts of statistical physics and chemical kinetics related to polymer growth.

2. Background

At the initial stage of a copolymerization reaction, i.e., at low conversion, the concentration of copolymer chains is sufficiently small that each macromolecule can be considered as a separate "microreactor" having boundaries permeable to the monomer molecules. The concentration of these molecules inside the microreactor is governed by thermodynamic equilibria because the reaction of a polymer chain propagation is for the system in question kinetically controlled. This statement is easy to verify having compared characteristic time of the diffusion of the monomer molecule inside the microreactor and that of its addition to the macroradical. The latter is, as a rule, several orders of magnitude higher than the former so that the entry of monomer molecules into the chemical reaction does not virtually affect their equilibrium partitioning between free solvent and domains of growing polymer radicals. Finding of this distribution constitutes one of the two main problems whose solution is indispensable for the elaboration of a copolymerization theory that allows for preferential sorption of monomers. Let us discuss the assumptions that can be made for the solution of the above problem.

It is well-known[37] that a macromolecule in solution can be found in one of two macroscopic states commonly indicated as *coil* and *globule*. According to the interpretation given by Lifshitz,[37,38] a globule is the state in which the polymer molecule has a definite and thermodynamically reliable spatial structure. This means that the fluctuations of the monomer unit density in a globule are less than the density itself or, alternatively, that the range of density correlations is finite when the number of units in a macromolecule l tends toward infinity. On the contrary, the coil state is that in which a macromolecule is characterized by having no definite spatial structure. In a coil, the fluctuations of polymer density are of the same order of the density itself, and the radius of correlation is comparable to the dimension of the coil, i.e., it indefinitely increases when $l \to \infty$.

With an increase in the number of units l of the polymer chain, their density in the microreactor should be expected either to approach zero or to remain nonvanishing, depending on whether this chain is in the coil or globule state. In the first case this density at $l \approx 10^3-10^4$ is so small that any distinction between the concentrations of monomers in the microreactor and their values in bulk can hardly be expected. This conjecture has been convincingly supported by some simple estimates by Smirnova,[36] on the basis of her experimental data for the bulk copolymerization of an equimolar mixture of styrene and methacrylic acid. By two independent methods (equilibrium dialysis and light scattering) it has been established that an increase in the molecular weight of the copolymer from 3×10^4 to 1×10^6 involves a corresponding growth of the coefficient of methacrylic acid preferential sorption by $\Delta\lambda = 0.35$ mL/g and an increase of the content of its units in the macromolecular chain by 10−12 mol %. Such a change in copolymer composition ΔX corresponds to a change in the composition of the monomer feed Δx in the microreactor of 15−17%. This value exceeds by a factor of approximately 10 exceeds the value of $\Delta x \approx 1-2\%$, which results from simple estimates using the value $\Delta\lambda = 0.35$ mL/g on the assumption that a macroradical represents a gaussian coil. Thus, Smirnova[36] proposed that a monomer preferentially sorbed by the macroradical is mainly localized in the vicinity of the polymer chain in a solvating layer whose composition differs from that of the monomer mixture in the whole reactor.

In the present paper we suggest an alternative explanation that is able to eliminate the above contradiction without necessarily assuming preferential adsorption of monomers on coiled polymer chains. We believe that in order to have the phenomenon of preferential sorption be sufficient to markedly change the monomer composition in a microreactor, the macroradical should be in a globular state. Indeed, in this state the density of a polymer, depending on the thermodynamic affinity of the latter toward the solvent, may have a wide range of values and these substantially exceed the value which a high molecular weight macroradical in a coil state would have.

A considerable body of experimental data regarding preferential sorption of binary solvent molecules by different homopolymers shows a dramatic intensification of this effect in the proximity of the Θ-point.[39,40] At the Θ-point, by its definition,[37] a macromolecule of infinite molecular weight undergoes a transition from the coil to the globular state. If the thermodynamic affinity between polymer and solvent decreases, such a transition occurs when a macromolecule has finite length. As one moves away from the Θ-point, the increase in polymer density inside the core of a globule is accompanied by a narrowing of the thickness of the surface layer on its boundary. The free-energy difference between a globule and a coil is due to both volume and surface contributions, which have different signs for a thermodynamically poor solvent. When these contributions become equal in absolute value, the coil-to-globule transition takes place. This generally happens by changing the temperature and/or the thermodynamic quality of the solvent. On the contrary, in our case these parameters remain constant, and the above transition is induced by only increasing the degree of polymerization of the macromolecule. According to our interpretation, the following explanation may be suggested for the peculiarities normally observed during the initial stage of a free-radical copolymerization that is influenced by the phenomenon of preferential sorption. Such peculiarities are thought to show up to an appreciable extent only when monomer mixture or, more precisely, the reaction medium is a moderately poor solvent for the copolymer chain being formed. If the solvent medium exhibits lower affinity to the polymer, it will behave as a precipitating agent, thus conditioning the heterophase regime of copolymerization, whereas when higher affinity is shown, i.e., when the monomer mixture is a good solvent, strongly pronounced anomalies are not likely to arise. Thus, depending on thermodynamic affinity of the monomer mixture (which also could contain solvent molecules) to the copolymer being formed, one could expect three different regimes of copolymerization.

All three regimes indicated above have been experimentally observed[22] in the bulk copolymerization of styrene and methacrylic acid for some specific ranges of composition values of the monomer mixture, whose thermodynamic affinity toward the copolymer was found to decrease by increasing the acid fraction. In this system, the dependence of the composition of a copolymer on its molecular weight is the most strongly pronounced in the boundary area around the region of heterophase regime of copolymerization. This behavior, which also characterizes other *anomalous* copolymerization systems,[22,36] agrees with our hypothesis concerning the role of globular state of macroradicals, inasmuch as in diluted solutions, due to the worsening of the affinity between polymer and solvent, the coil-to-globule transition immediately precedes polymer precipitation as a separate macrophase.[37] The temperature difference under which these two thermodynamic transitions occur is due to the translational entropy of macromolecules.

By adding to the monomer mixture a low molecular weight component, one can either increase or decrease its solvent power. This way of controlled alteration of thermodynamic affinity between solvent and polymer provides a possibility to verify our globular state hypothesis using the experimental data already obtained by Smirnova *et al.* and Semchikov *et al.*[22,36] They chose a typical representative of both *classical* (styrene + methyl methacrylate) and *anomalous* (styrene + methacrylic acid) systems and copolymerized the first of these monomer pairs in the presence of the precipitating agent (cyclohexane or methyl alcohol), while the copolymerization of the second pair has been carried out in the presence of a "good" solvent such as dimethylformamide. It was found that in the first system the addition of the precipitating agent, in an amount not sufficient to cause phase separation, results in a considerable dependence of copolymer composition on molecular weight. Conversely, in the second system, the addition of the solvent was found to lead to the disappearance of this effect. Consequently, its appearance is a signal that all copolymer macromolecules have been formed in a moderately poor solvent medium.

Under such conditions, a polymer chain begins growing in a coil state and then, once a critical value of l^* units is attained, it changes into a globular state, continuing its growth up to the moment when the chain is terminated by interaction with either another radical or with a chain transfer agent. The most interesting case will now be discussed, when l^* is much less than the average degree of polymerization, i.e., when for most of its lifetime the macroradical grows in a globular state. In this case the most pronounced anomalies should be expected as compared to the classical picture of radical copolymerization. The reason for such anomalies lies in the fact that the monomer mixture composition in a globule, because of the phenomenon of preferential sorption, differs—generally speaking—from its value in bulk. Moreover, thermodynamic equilibrium values of the monomer concentrations in a globule are not likely to be constant during the process of macroradical growth, but will change as a consequence of the alteration of the propagating copolymer chain composition. Since the latter by itself depends on the monomer mixture composition in the microreactor, close interactions of physical and chemical factors are the dominating factors by virtue of which the propagating copolymer radical can control its own environment.

Let us discuss a copolymerization of an arbitrary number m of monomers $M_1, ..., M_\alpha, ..., M_m$, whose molar fractions in the initial mixture $x_1^0, ..., x_\alpha^0, ..., x_m^0$ represent the components of vector $\mathbf{x}^0$. At the initial stage of the process to be considered below, the composition of the monomer mixture in bulk may be thought of as unaltered and equal to $\mathbf{x}^0$ unlike its value $\mathbf{x}$ in a globule, which changes during the growth of the polymer chain. The evolution of its composition $\mathbf{X}$ with the increase of the number l of monomer units of this chain is described by the following equation:

$$\frac{\mathrm{d}\mathbf{X}_\alpha}{\mathrm{d}\xi} = \pi_\alpha(\mathbf{x}) - X_\alpha \qquad \text{where } \xi = \ln l \qquad (\alpha = 1, ..., m) \tag{1}$$

where $\pi_\alpha(\mathbf{x})$ is the αth component of the vector $\pi\ (\mathbf{x})$ of the instantaneous composition of the copolymer, formed at the fixed monomer mixture composition $\mathbf{x}$. Equation 1, resulting from the material balance conditions when dealing with nonstationary growth of polymer chains,[41] does not depend on the kinetic model chosen, which imposes only a particular appearance of the dependence of π on $\mathbf{x}$. For the Mayo-Lewis terminal model π is a stationary vector of the Markov chain with the matrix of transition probabilities, whose elements

$$\nu_{\alpha\beta} = r_{\alpha\beta}^{-1} x_\beta \Big(\sum_{\gamma=1}^{m} r_{\alpha\gamma}^{-1} x_\gamma\Big)^{-1} \tag{2}$$

are governed along with $\mathbf{x}$ only by the values of monomer reactivity ratios $r_{\alpha\beta}$, which have been tabulated for many hundreds of monomer pairs ($M_\alpha + M_\beta$). By their definition, the components π_β of the vector $\boldsymbol{\pi}$ represent the solution of a set of linear equations

$$\pi_\beta = \sum_{\alpha=1}^{m} \pi_\alpha \nu_{\alpha\beta} \qquad (\beta = 1, ..., m) \qquad \sum_{\alpha=1}^{m} \pi_\alpha = 1 \tag{3}$$

In the particular case of a binary copolymerization they have the familiar appearance

$$\pi_1 = \frac{\nu_{21}}{\nu_{12} + \nu_{21}}, \quad \pi_2 = \frac{\nu_{12}}{\nu_{12} + \nu_{21}};$$
$$\nu_{12} = \frac{x_2}{r x_1 + x_2}, \quad \nu_{21} = \frac{x_1}{x_1 + r_2 x_2} \tag{4}$$

where the traditionally adopted designations $r_1 \equiv r_{12}$, $r_2 \equiv r_{21}$ are used.

The set of differential equations (1), describing the alteration of molar fractions X_α of monomer units of different types $\alpha = 1, ..., m$ in the propagating copolymer chain, is nonclosed because the right-hand parts of these equations include, apart from X_α, also unknown components x_α of the vector $\mathbf{x}$ of the monomer mixture composition in the microreactor. To have this set truncated, one should determine the dependence between vectors $\mathbf{x}$ and $\mathbf{X}$ in the state of thermodynamic equilibrium, i.e., one has to solve the problem of equilibrium partitioning of monomers between globules and their environment.

3. Thermodynamics of Preferential Sorption

Let us turn to the general case, where the initial reaction system in parallel with m types of monomers contains n types of solvent. Let us denote by N_α the number of molecules of these low-molecular components in a globule. Here the subscript $\alpha = 1, ..., m$ for monomers and $\alpha = m + 1, ..., m + n$ for solvents. In addition to $N^M = N_1 + ... + N_m$ monomer molecules and $N^S = N_{m+1} + ... + N_{m+n}$ solvent molecules, a globule involves units $\bar{M}_1, ..., \bar{M}_m$ of the high molecular weight component, the numbers $l_1, ..., l_m$ of which add up to the value l of the degree of polymerization of the macroradical and characterize its molar composition $X_\alpha = l_\alpha/l$ ($\alpha = 1, ..., m$). In order to find the specific dependence on it of the monomer mixture composition in a globule $x_\alpha = N_\alpha/N^M$ ($\alpha = 1, ..., m$), it is necessary to consider the thermodynamics of swelling of the latter in the presence of monomers and solvents.

According to the thermodynamic theory,[37,38] most of the globule is occupied by a spatially homogeneous core, where the volume fraction of each of the low molecular weight components φ_α (monomers and solvents) and quasi-components Φ_α (monomer units) has a definite value, identical in all points of the core. Only within a rather narrow surface layer of the globule the change of volume fractions from φ_α and Φ_α in the globule core up to φ^0_α and 0 in the surrounding solution occurs. Examination of this layer, necessary for finding the surface tension at the globule boundary, constitutes a complicated problem in comparison with the description of the globule core and thus it will be considered elsewhere. The reason of these difficulties, arising for the calculation of concentration distributions of the components and quasi-components within the surface layer, has to do with the fact that these distributions are prescribed by the type of arrangement of monomer units in a macromolecule, whereas the values of these concentrations in the globule core are not influenced by such an arrangement.

Volume approximation under which they neglect the surface contribution to the free energy of a globule works better the farther the system is from the point of the coil-to-globule transition. The latter coincides under volume approximation with the Θ-point, but actually with the allowance made for the surface layer the difference between these two points is the more pronounced it is the less is the length of polymer chain l. Hence, the condition, imposed on the thermodynamic and stoichiometric parameters of the system by the equation of the Θ-point, controls the position of the boundary in the region of alterations of these parameters, separating that part of the above region, where marked manifestation of the bootstrap effect should be expected.

Explicit thermodynamic consideration of the role of the one-component solvent in the theory of homopolymer globules has been carried out by Lifshitz and Grosberg.[42] By extending their approach to the case under discussion, it is possible, within the framework of the simplest Flory-Huggins lattice model, to write down the following expression

$$\frac{\Delta G}{NT} = \sum_{\alpha=1}^{m+n} \varphi_\alpha \ln \varphi_\alpha + h(\varphi,\Phi) - \sum_{\alpha=1}^{m+n} \varphi_\alpha \frac{\mu^0_\alpha}{T} - \Phi\eta^0 \quad (5)$$

for the difference of the Gibbs free energy ΔG of a heteropolymer globule and a coil in a multicomponent solvent. The first term in the right-hand part of the expression 5 corresponds to the translational entropy of low molecular weight components, whereas the second one involves three contributions

$$h(\varphi,\Phi) = h^{\mathrm{LL}} + h^{\mathrm{LP}} + h^{\mathrm{PP}}, \quad h^{\mathrm{LP}} = h^{\mathrm{PL}} = \Phi \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m+n} \chi^{\mathrm{PL}}_{\alpha\beta} X_\alpha \varphi_\beta$$

$$h^{\mathrm{LL}} = \frac{1}{2} \sum_{\alpha=1}^{m+n} \sum_{\beta=1}^{m+n} \chi^{\mathrm{LL}}_{\alpha\beta} \varphi_\alpha \varphi_\beta, \quad h^{\mathrm{PP}} = \frac{\Phi^2}{2} \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} \chi^{\mathrm{PP}}_{\alpha\beta} X_\alpha X_\beta = \frac{\Phi^2}{2} \sigma^{\mathrm{PP}} \quad (6)$$

which describe the enthalpy of mixing (per site of lattice) of these components, one with the other (h^{LL}), with monomer units of a macromolecule (h^{LP}) as well as that of the units between themselves (h^{PP}). Along with the Flory-Huggins parameters $\chi_{\alpha\beta}$ the expression 5 includes also the absolute temperature T (expressed in energetic units), the number of sites $N = l + N^M + N^S$ contained in a polymer globule volume, the fraction $\Phi = l/N$ of this volume occupied by the polymer, as well as the quantities μ^0_α and η^0. The first of them represents the chemical potential of the αth component in absence of a polymer, i.e., in the solution outside a globule. As for the second one, this has not such meaning since monomer units, being joined in polymer chains, are not true thermodynamic components. That is why the finding of the expression for η^0 deserves special consideration.[42] With this in mind we arrived at the expressions:

$$\frac{\mu^0_\alpha}{T} = \ln y^0_\alpha + \sigma^{\mathrm{LL}}_\alpha - \frac{1}{2}\sigma^{\mathrm{LL}} \qquad \eta^0 = \sigma^{\mathrm{LP}} - \frac{1}{2}\sigma^{\mathrm{LL}} - 1 \quad (7)$$

where the following designations are applied:

$$\sigma^{\mathrm{LL}} = \sum_{\alpha\beta} \chi^{\mathrm{LL}}_{\alpha\beta} y^0_\alpha y^0_\beta, \quad \sigma^{\mathrm{LP}} = \sum_{\alpha\beta} \chi^{\mathrm{LP}}_{\alpha\beta} y^0_\alpha X_\beta, \quad \sigma^{\mathrm{LL}}_\alpha = \sum_{\beta} \chi^{\mathrm{LL}}_{\alpha\beta} y^0_\beta \quad (8)$$

while y^0_α stands for the αth component of the vector $\mathbf{y}^0$, defining the composition of the low molecular weight solvent in the bulk system.

Equilibrium values of the numbers N_α of molecules of the low molecular weight components in a globule can obviously be found from the condition of minimum free energy ΔG for the system consisting of a globule and the surrounding solution. The fulfillment of this condition assumes the chemical potential of each αth of these $r = m + n$ components to have the same values inside (μ_α) and outside (μ^0_α) the globule:

$$\frac{\partial \Delta G}{\partial N_\alpha} = \Delta\mu_\alpha \equiv \mu_\alpha - \mu^0_\alpha = 0 \qquad (\alpha = 1, ..., r) \quad (9)$$

Differentiating the expression 5 with respect to N_α yields, in terms of the thermodynamic model under discussion, the following expression for the chemical potential of the αth component:

$$\frac{\mu_\alpha}{T} = \ln \varphi_\alpha + h_\alpha - h + \Phi \tag{10}$$

where

$$h_\alpha \equiv h_\alpha^{\mathrm{LL}} + h_\alpha^{\mathrm{LP}} \qquad h_\alpha^{\mathrm{LL}} \equiv \frac{\partial h^{\mathrm{LL}}}{\partial \varphi_\alpha} = \sum_{\beta=1}^{r} \chi_{\alpha\beta}^{\mathrm{LL}} \varphi_\beta$$

$$h_\alpha^{\mathrm{LP}} \equiv \frac{\partial h^{\mathrm{LP}}}{\partial \varphi_\alpha} = \Phi \sigma_\alpha^{\mathrm{LP}} \qquad \sigma_\alpha^{\mathrm{LP}} = \sum_{\beta=1}^{m} \chi_{\alpha\beta}^{\mathrm{LP}} X_\beta \tag{11}$$

Equation 9, complemented by the apparent stoichiometric relationships

$$\varphi + \Phi = 1 \qquad \varphi = \varphi^M + \varphi^S = \frac{N^M + N^S}{N} \tag{12}$$

form a closed set, whose solution permits one to find αth components φ_α of the vector $\boldsymbol{\varphi}$ at given values φ^0 as well as at the polymer chain composition **X**. By knowing the solution of the problem on the partitioning of low molecular weight components between the globule and a surrounding solution, it is easy to find the composition **x** of the monomer mixture in the microreactor

$$x_\alpha = \frac{\varphi_\alpha}{\varphi^M} \quad (\alpha = 1, ..., m) \quad \text{where } \varphi^M = \sum_{\alpha=1}^{m} \varphi_\alpha \tag{13}$$

Such a procedure provides the possibility of establishing an equilibrium correlation between vectors **x** and **X** which, in conjunction with kinetic eq 1, enables one—in terms of the model chosen—to describe macroradical growth with allowance for preferential sorption of monomers in its domain.

Among the solutions of eq 9 only those that correspond to the minimum of free energy G for which the matrix with elements

$$\mu_{\alpha\beta} \equiv N \frac{\partial^2 \Delta G}{\partial N_\alpha \partial N_\beta} = \frac{\partial \mu_\alpha}{\partial \varphi_\beta} - \sum_{\gamma=1}^{r} \varphi_\gamma \frac{\partial \mu_\alpha}{\partial \varphi_\gamma} \tag{14}$$

equal to the second derivatives with respect to the numbers of particles of different kinds in a globule is positive definite, i.e., all its eigen values λ_r are positive. Once ΔG has been calculated for all such solutions, it becomes possible to indicate which of them corresponds to the absolute minimum of free energy. Only this solution will be globally thermodynamically stable, whereas the other free-energy local minima correspond to metastable states. In terms of our model, where the αth component chemical potential is characterized by the expression 10, the matrix elements (14) are

$$\mu_{\alpha\beta} = \varphi_\beta^{-1} \delta_{\alpha\beta} + \chi_{\alpha\beta}^{\mathrm{LL}} - h_\alpha - h_\beta + 2h - 1 - \Phi \tag{15}$$

Among the solutions to eq 9 a special role is played by the trivial one $\varphi = \varphi^0$, which corresponds to the coil state of a macromolecule. The unlimited swelling of a globule $N^{\mathrm{L}} = l/\Phi \to \infty$ formally corresponds to this solution for the model of interest; thus, in order to avoid sophisticated mathematics due to the involvement of infinite quantities, one can find it sometimes more convenient to go from the variables (φ_1, ..., φ_r) to (y_1, ..., y_r; Φ), where among the r components

$$y_\alpha = \frac{\varphi_\alpha}{\varphi} \quad (\alpha = 1, ..., r) \qquad \sum_{\alpha=1}^{r} y_r = 1 \tag{16}$$

of the vector **y** defining the low molecular weight mixture composition, only $r - 1$ are independent. The quantity Φ (11), specifying the degree of a globule expansion describes *total* sorption, while *preferential* sorption is characterized by the difference in composition of a mixture of low molecular weight components inside, **y**, and outside, $\mathbf{y}^0 = \boldsymbol{\varphi}^0$, the globule.[43] The coefficient of preferential sorption

$$\kappa_\alpha(\Phi) \equiv \frac{N_\alpha - N_\alpha^0}{l} = \frac{N_\alpha - \varphi_\alpha^0 N^{\mathrm{L}}}{l} = \frac{1 - \Phi}{\Phi}(y_\alpha - y_\alpha^0) \tag{17}$$

is proportional to the above difference. This coefficient is defined here as the number of molecules of the αth component additionally sorbed by the globule, reduced to the number of monomer units in a macromolecule. The coefficients (16), obeying the stoichiometric condition $\kappa_1 + ... + \kappa_r = 0$, may be either positive or negative, and they correspond to the enrichment or impoverishment of a globule by the molecules of particular solvents and monomers, respectively. The values of the quantities κ_α, on one hand, are experimentally measurable by the method of equilibrium dialysis or by light-scattering measurements.[44] On the other hand, they can be calculated in terms of the suggested approach (via the solution of the set of eq 9 at arbitrary numbers r and m of the components and quasi-components, respectively).

For heteropolymer globules, heavily swollen in multicomponent solvent in the vicinity of the Θ-point, explicit analytical expressions describing the sorption equilibrium have been found out.[41] It has been demonstrated[45] that for the equilibrium degree of swelling of such globules $\Phi = \Phi_{\mathrm{G}}$, one can use the following formula

$$\Phi_{\mathrm{G}} = -\frac{B}{2C} \ll 1 \tag{18}$$

derived earlier[34] in the theory of homopolymer globules, by replacing in eq 18 the second, B, and the third, C, virial coefficients by their effective values $\hat{B}$ and $\hat{C}$:

$$\hat{B} = \frac{1}{2} - \hat{\chi} \qquad \hat{\chi} = \hat{\chi}^{(1)} + \hat{\chi}^{(2)}$$

$$\hat{\chi}^{(1)} = \sigma^{\mathrm{LP}} - \frac{1}{2}(\sigma^{\mathrm{LL}} + \sigma^{\mathrm{PP}}) \qquad \hat{\chi}^{(2)} = \frac{1}{2} \sum_{\alpha\beta}^{r} \theta_{\alpha\beta} z_\alpha z_\beta \tag{19}$$

$$\hat{C} = \frac{1}{6}[1 + \sum_{\alpha\beta}^{r} \{3\theta - \theta \chi^{\mathrm{LL}} \theta\}_{\alpha\beta} z_\alpha z_\beta] \qquad z_\alpha = \sigma_\alpha^{\mathrm{LP}} - \sigma_\alpha^{\mathrm{LL}} \tag{20}$$

Here the matrix $\boldsymbol{\theta}$, characterizing thermodynamic properties of r low molecular weight components in the absence of a polymer, has the elements

$$\theta_{\alpha\beta} = g^{\mathrm{L}}_{\alpha\beta} - \frac{H_\alpha H_\beta}{H}, \quad H_\alpha = \sum_{\beta}^{r} g^{\mathrm{L}}_{\alpha\beta}, \quad H = \sum_{\alpha}^{r} H_\alpha = \sum_{\alpha\beta}^{r} g^{\mathrm{L}}_{\alpha\beta} \tag{21}$$

which are related in a trivial fashion to the elements $g^{\mathrm{L}}_{\alpha\beta}$ of the matrix $\mathbf{g}^{\mathrm{L}}$, inverse to the matrix $\mathbf{M}^{\mathrm{L}}$, with elements

$$M^{\mathrm{L}}_{\alpha\beta} = (y^0_\beta)^{-1}\delta_{\alpha\beta} + \chi^{\mathrm{LL}}_{\alpha\beta} \tag{22}$$

The effective Flory-Huggins parameter $\hat{\chi}$, describing the pair interactions inside a globule is, according to (19), the sum of two terms. The first of them characterizes the change of the system enthalpy caused by the mixing of components and quasi-components in the absence of preferential sorption, whereas its effect on the partitioning of monomers and solvents inside the globule is allowed for by the second term. Unlike the first term, the second one is always positive,[45] being greater in value the closer the mixture of monomers and solvents to the spinodal point is, the latter defined by the condition $H = 0$. As this spinodal point is approached, the coefficients of preferential sorption (17) also increase and for heavily swollen globules $\Phi_{\mathrm{G}} \ll 1$ can be calculated by the simple formula[45]

$$\kappa_\alpha \equiv \lim_{\Phi \to 0} \kappa_\alpha(\Phi) = -\sum_{\beta=1}^{r} \theta_{\alpha\beta} z_\beta \tag{23}$$

Such phenomenon of preferential sorption magnification by homopolymers in a mixture of binary solvents, when worsening the compatibility of these latter, has already been established experimentally for a number of specific systems.[46−49]

4. Quantitative Description of Copolymerization in Anomalous Systems

As pointed out in the Introduction, there are two specific peculiarities qualitatively distinguishing these systems from the classical ones: (i) intramolecular chemical inhomogeneity of polymer chains, which in turn is responsible for (ii) the dependence $\mathbf{X}$ of the composition of macromolecules on their length l. Experimental data for several nonclassical systems indicate that, at fixed monomer mixture compositions and temperature, such dependence of $\mathbf{X}$ on l is of universal character for any concentration of initiator and chain transfer agent.[23,32,36] This function $\mathbf{X}(l)$, within the context of the theory proposed here, is obtainable from the solution of the kinetic eq 1, supplemented by the thermodynamic eq 9 used for determining the dependence $\mathbf{x} = \mathbf{F}(\mathbf{X})$ of the monomer mixture composition $\mathbf{x}$ inside the globule on the composition $\mathbf{X}$ of the associated heteropolymer chain. For heavily swollen globules, when $\Phi_{\mathrm{G}} \ll 1$, the components of the vector-function $\mathbf{F}(\mathbf{X})$ can be presented in explicit analytical form:

$$x_\alpha = F_\alpha(\mathbf{X}) = x^0_\alpha + \kappa_\alpha \Phi_{\mathrm{G}} \qquad (\alpha = 1, ..., m) \tag{24}$$

where the dependence of the values Φ_{G} and κ_α, characterizing the total and the preferential sorption of monomers in the microreactor, respectively, on $\mathbf{X}$ is given by expressions 18−23.

In nonclassical systems a growing polymer chain, on attaining the length $l = l^*$, turns into globule, whose associated monomer mixture composition $\mathbf{x}' = \mathbf{F}(\mathbf{x}^0)$ (where $\mathbf{X}^0 = \boldsymbol{\pi}(\mathbf{x}^0)$) differs, generally speaking, from that, $\mathbf{x}^0$, observed in bulk. This leads to the evolution of the growing macroradical composition, described by the set of equations in (1) and, consequently, to the drift of the monomer mixture composition in the microreactor in accordance with the dependence $\mathbf{x} = \mathbf{F}(\mathbf{X})$. Here the obvious question arises to which limiting values $\mathbf{X}^\infty$ and $\mathbf{x}^\infty$ the above compositions will tend at $l \to \infty$. A general answer to this question for copolymerization of an arbitrary number m of monomers is more readily attained by considering this process in terms of the theory of dynamical systems just like it has been done earlier[50,51] when dealing with classical multicomponent copolymerization within the region of high conversions.

For the case of interest copolymerization dynamics is described by a set of nonlinear equations in (1), where the variable ζ plays the role of time, supplemented by the thermodynamic relationship $\mathbf{x} = \mathbf{F}(\mathbf{X})$. The instantaneous state of the system, characterized by vector $\mathbf{X}$, may be represented by a point in the $(m - 1)$-dimensional phase space, which is an m-simplex, $X_1 + ... X_m = 1$. When $m = 2$, 3, and 4, such a simplex will be denoted by a straight-line segment with unit length, by the Gibbs-Roozeboom triangle and by the inner part of a regular tetrahedron, respectively. In correspondence to the evolution of the composition $\mathbf{X}$ in the course of the polymer chain growth there will be the displacement of the point, which characterizes the system state, inside the m-simplex along a specific trajectory, the position on which is determined by the value of the variable ζ. Knowing such a trajectory is of prime importance since it controls the main statistical characteristics of the copolymer formed. Thus, its average composition can be found by the formula

$$\langle X_\alpha \rangle = \int_1^\infty f_{\mathrm{W}}(l) X_\alpha(l)\, \mathrm{d}l \tag{25}$$

where angular brackets denote that the value inside is averaged over the weight distribution of macromolecules $f_{\mathrm{w}}(l)$ for a number l of their units. In order to find the weight composition distribution $f^{\mathrm{c}}_{\mathrm{w}}(\zeta)$ the Dirac delta function should be analogously averaged

$$f^{\mathrm{c}}_{\mathrm{W}}(\zeta) = \langle \delta[\zeta - \mathbf{X}(l)] \rangle \tag{26}$$

because in this case the compositional dispersion ζ of macromolecules of the same degree of polymerization l is neglected. In parallel with the first-order statistical moments (25), the second-order moments of composition distribution

$$\int ... \int \zeta_\alpha \zeta_\beta f^{\mathrm{c}}_{\mathrm{W}}(\zeta)\, \mathrm{d}\zeta_1, ..., \mathrm{d}\zeta_m = \langle X_\alpha X_\beta \rangle \tag{27}$$

characterizing its width are of utmost significance.

The solution to the problem of sequence distribution as well as that of composition inhomogeneity (26) reduces to the calculation of simple integrals along the trajectory within the phase space. For this purpose to describe copolymerization dynamics it appears convenient to switch from $\mathbf{X}$ to the vector $\mathbf{x}$ using the relationship $\mathbf{x} = \mathbf{F}(\mathbf{X})$ and to examine within m-simplex the trajectories $\mathbf{x}(l)$. Hence the probability $P\{U\}$ of an arbitrary sequence $U = \{\bar{M}_\alpha \bar{M}_\beta ... \bar{M}_\psi \bar{M}_\omega\}$ of units of the *m*-component copolymer can be calculated by the following formula:

$$P\{U\} = \left\langle \frac{1}{l}\int_1^l \pi_\alpha[\mathbf{x}(l')]\nu_{\alpha\beta}[\mathbf{x}(l')]...\nu_{\psi\omega}[\mathbf{x}(l')]\,\mathrm{d}l' \right\rangle \tag{28}$$

where the dependence of the components π_α of the stationary vector $\boldsymbol{\pi}$ and elements $\nu_{\alpha\beta}$ of the matrix of transition probabilities on monomer mixture composition is given by formulas 2 and 3.

For the calculation of statistical characteristics of a copolymer using expressions 25−28 it is necessary to substitute into them the distribution function $f_\mathrm{w}(l)$ for the number of units in macromolecules, being formed under initial conversions. For such function one may choose the Flory distribution[50]

$$f_\mathrm{W}(l) = \left[\frac{1-\gamma}{2}\frac{l}{l_\mathrm{av}} + \gamma\right]\frac{l}{l_\mathrm{av}^2}\exp\left\{-\frac{l}{l_\mathrm{av}}\right\} \tag{29}$$

involving two parameters: (i) the fraction γ of radicals terminating by disproportionation and (ii) the average length of kinetic chain, l_av, expressed in a simple manner as $l_\mathrm{av} = (1+\gamma)P_\mathrm{N}/2 = P_\mathrm{w}/(3-\gamma)$ through number-average P_N or weight-average P_w degree of polymerization. The expression 29 has been derived for a polymerization in the absence of a chain transfer agent, which, if present, does not affect the form of the function $f_\mathrm{w}(l)$ being only responsible for the redefinition of its parameters.[50] These latter, along with reactivity ratios $\{r_{\alpha\beta}\}$, monomer feed composition $\mathbf{x}^0$ and the Flory-Huggins parameters $\{\chi_{\alpha\beta}\}$ constitute a complete set of control parameters, which in terms of the proposed theory are required to calculate statistical characteristics of copolymers in nonclassical systems.

The alteration of propagating copolymer chain composition is defined by the limiting value $\mathbf{X}^\infty$ which tends to $\mathbf{X}(l)$ when $l \to \infty$. To this value in *m*-simplex, a stable stationary point (SP) corresponds, where all trajectories, starting within the basin of attraction of the given SP, terminate. If a dynamic system (1) has several stable SPs, the *m*-simplex is partitioned into the basins of attraction of each of them. The coordinates of any SP in this system can be found as solutions of algebraic equations

$$X_\alpha = \pi_\alpha(\mathbf{x}) \qquad x_\alpha = F_\alpha(\mathbf{X}) \qquad (\alpha = 1, ..., m) \tag{30}$$

obtainable from the differential equations in (1), provided their right-hand parts are equated to zero. It is readily noticed that for any value of the parameters the equations in (30) have the trivial solution $x_\alpha = x_\alpha^0$, $X_\alpha = X_\alpha^0$, corresponding to the coil state of the polymer chain with $\Phi = 0$.

To analyze the stability of any SP of the dynamic system in (1), it should be established where the roots of its characteristic polynomial are positioned:[52]

$$\lambda^{m-1} + a_1\lambda^{m-2} + ... + a_{m-1} = 0 \qquad a_k = (-1)^k S_k^{(m)} \tag{31}$$

where coefficient a_k represents the sum $S_k^{(m)}$ of all principle minors of the *k*th order[52] of the matrix $\mathbf{T}$ with elements

$$T_{\alpha\beta} = \sum_{\gamma=1}^{m}\pi_{\alpha\gamma}F_{\gamma\beta} + \frac{1}{m} - \delta_{\alpha\beta} \qquad (\alpha, \beta = 1, ..., m) \tag{32}$$

Here the following designations are used

$$\pi_{\alpha\gamma} \equiv \frac{\partial\pi_\alpha}{\partial x_\gamma} \qquad F_{\gamma\beta} \equiv \frac{\partial F_\gamma}{\partial X_\beta} \tag{33}$$

for the derivatives of the components of vector-functions π and $\mathbf{F}$ taken at the SP under examination, e.g., at the corresponding solution of eq 30. To ensure that this SP is stable, it is necessary and sufficient for all the roots of its characteristic polynomial (31) to have negative real parts. The Routh-Hurwitz method[52] enables one to avoid calculating these roots and to point out simple relationships between the coefficients α_k, the fulfillment of which provides the stability of the SP chosen. For example, in the case of a terpolymer a criterion for such stability will be the positiveness of coefficients a_1 and a_2, whilst for a tetrapolymer along with the above condition the fulfillment of the inequality $a_3 < a_1a_2$ is also required. At an arbitrary number of components *m*, a necessary (but not sufficient!) condition of the SP stability is the positiveness of all coefficients a_k of its characteristic polynomial (31).

For the SP corresponding to the trivial solution the matrix elements in (33) will be read as

$$F_{\gamma\beta} = F_{\gamma\beta}^0 = \kappa_\gamma^0\, d_\beta^0 \qquad \text{where } d_\beta = \frac{1}{2\hat{C}}\frac{\partial\hat{\chi}}{\partial X_\beta} \tag{34}$$

with the superscript indicating that the corresponding function is taken at $\mathbf{x} = \mathbf{x}^0$ and $\mathbf{X} = \mathbf{X}^0$. The quantities κ_γ and $\hat{C}$ have been determined by the formulas 23 and 20, whereas the derivative of the effective Flory-Huggins parameter 19 with respect to the copolymer composition on trivial solution of the eq 30 may be presented with regard to (24) in the following form:

$$\frac{\partial\hat{\chi}}{\partial X_\beta} = \sigma_\beta^\mathrm{PL} - \sigma_\beta^\mathrm{PP} - \sum_{\gamma=1}^{m}\chi_{\beta\gamma}^\mathrm{PL}\kappa_\gamma^0 = \sum_{\gamma=1}^{m}\{\boldsymbol{\chi}^\mathrm{PL}\boldsymbol{\theta}\boldsymbol{\chi}^\mathrm{LP} - \boldsymbol{\chi}^\mathrm{PP}\}_{\beta\gamma}\,X_\gamma^0 - \sum_{\gamma=1}^{m}\{\boldsymbol{\chi}^\mathrm{PL}\boldsymbol{\theta}\boldsymbol{\chi}^\mathrm{LL} - \boldsymbol{\chi}^\mathrm{PL}\}_{\beta\gamma}x_\gamma^0 \tag{35}$$

in which

$$\sigma_\beta^\mathrm{PL} = \frac{\partial\sigma^\mathrm{PL}}{\partial X_\beta} = \sum_{\gamma=1}^{m}\chi_{\beta\gamma}^\mathrm{PL}x_\gamma^0 \neq \sigma_\beta^\mathrm{LP} \qquad \sigma_\beta^\mathrm{PP} = \sum_{\gamma=1}^{m}\chi_{\beta\gamma}^\mathrm{PP}X_\gamma^0 \tag{36}$$

Substituting the expression for $F_{\gamma\beta}$ (34) into (32) it is possible to find in an explicit form the expressions for the coefficients of the polynomial 31. For the case under consideration this polynomial in parallel with the root $\lambda = -1$, multiple of $(m-2)$, turned out to have one more root:

$$\lambda = \sum_{\alpha\beta} d_\alpha^0\pi_{\alpha\beta}^0\kappa_\beta^0 - 1 \tag{37}$$

whose sign defines the kinetic stability of the Θ-point lying on the hypersurface $\hat{B} = 0$ within the space of control parameters of the dynamic system. In the vicinity of this hypersurface, separating the domains of coil and globular states of polymer chain, the SP coordinates in *m*-simplexes

$$x_\alpha^\mathrm{s} = x_\alpha^0 + \Phi_\mathrm{G}^0\kappa_\alpha^0 \qquad X_\alpha^s = X_\alpha^0 + \Phi_\mathrm{G}^0\sum_\beta\pi_{\alpha\beta}^0\kappa_\beta^0 \tag{38}$$

give limiting values $\mathbf{x}^\infty = \mathbf{x}^s$ and $\mathbf{X}^\infty = \mathbf{X}^s$, to which the composition of both the monomer mixture and the copolymer tends in a globule if the SP of interest is stable. At sufficiently small values of Φ_G^0 this SP will be stable when the quantity λ (37) is negative. In this case the growing macroradical composition starting with the instant of the transition into the globular state at a certain critical length $l = l^*$ will drift from $\mathbf{X}^0$ toward $\mathbf{X}^s$ until the kinetic chain terminates. Such a drift, as our theory postulates, must be accompanied by a simultaneous change of monomer feed composition in a globule from the value $\mathbf{x}'^0 = \mathbf{F}(\mathbf{X}^0)$ up to the values, close to $\mathbf{x}^0$. This has been experimentally verified for the bulk copolymerization of styrene with methacrylic acid and with acrylonitrile.[36]

In order to solve the problem of finding the critical length l^* of the propagating copolymer chain it is supposed to abandon the limits of the approximation used in the present paper, because in this case it is necessary to take into account the spatial inhomogeneity of the profile of monomer unit concentration in the vicinity of the globule surface. Such an account provides the possibility of finding the contribution σS to the free energy of a globule due to the gradient of unit concentrations in its surface layer, a contribution equal to the product of its area S by the surface tension σ at this layer boundary. Rigorous derivation of such a formula, connecting this quantity with thermodynamic parameters of a system, is intended to be performed elsewhere. Here, in order to evaluate the surface contribution to free energy, let us limit ourselves to the application of the expression $\sigma \approx TB^2C^{-3/2}$[37] for the surface tension of the homopolymer globule in the vicinity of the Θ-point by the replacement of virial coefficients B and C by their effective values $\hat{B}$ (19) and $\hat{C}$ (20). At the point of the coil-to-globule transition, by definition, the free-energy ΔG vanishes through mutual compensation of the negative volume contribution $-T\hat{B}^2\hat{C}^{-1}l$ and positive surface one $T\hat{B}^{2/3}\hat{C}^{-5/6}l^{2/3}$. From this condition $\Delta G = 0$ the simple estimate follows $l^* = 18\pi\hat{C}^{1/2}\hat{B}^{-2}$ for a critical degree of polymerization of a macroradical, under which this latter goes into the globular state. The values l^* are naturally the greater, the closer the system is to the Θ-point, where, by its definition, $l^* = \infty$.

5. Conclusions

The key feature of the theory of free-radical copolymerization presented here consists of its capability of taking into quantitative account the influence of thermodynamic factors that are responsible for the differences in monomer mixture composition inside and outside the domain of the polymer radical.[53] This distinction depends on the composition of the growing polymer chain, which in turn is controlled by the ratio of monomer concentrations in the vicinity of the propagating macroradical. This interplay between physical and chemical factors results in a situation in which statistical characteristics of a copolymer such as its composition, sequence distribution, and compositional inhomogeneity, in parallel with reactivity ratios, turn out to be governed also by thermodynamic parameters, characterizing physical interactions between the components of the reaction system. In the present paper, by proceeding from commonly accepted polymer models, general expressions for the above statistical characteristics of forming copolymers have been derived. In a subsequent paper we are going to demonstrate how the results of the calculations based on these expressions might be applied to interpret experimental data, obtained in free-radical copolymerizations of a variety of commercial monomers, which are indicative of the aforementioned compositional irregularities, impossible to explain in terms of traditional concepts.

Acknowledgment. Authors express their gratitude to J. Harwood, K. O'Driscoll, and A. Jenkins for fruitful discussions on "Bootstrap Effect" during the Symposium "SML-96". We are also very indebted to Dr. A. Mariani for his valuable assistance in preparing the manuscript for publication.

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MA961473M