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Quantitative Theory of Living Chain Copolymerization Covering Anionic and Free-Radical Mechanisms

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Summary: Main results of our original general theory of a chain copolymerization are presented which enable the calculation of any statistical characteristic of a copolymer prepared. Outlined theoretical approach also permits one to find thermodynamic and scattering properties of solutions and melts of these copolymers.

Chain polymerization is one of the most extensively employed methods of the synthesis of high-molecular compounds. A wealth of advanced materials are being manufactured by radical and ionic polymerization. Recent trends are toward increased use of ''living'' free-radical polymerization (LRP) [1,2] which has a number of indisputable advantages over traditional free-radical polymerization (TRP). Combining the merits of a TRP and ''living'' anionic polymerization (LAP) LRP is nearly free of their shortcomings.

The method of copolymerization is known to offer ample potentialities in governing properties of polymer materials at the stage of their synthesis. The macromolecules formed during such processes differ not only in number l of monomeric units but also in chemical composition. The distinctive feature of products of TRP is the pronounced inhomogeneity of their macromolecules in size l and composition. This can induce the phase separation in the course of the synthesis, responsible for the turbidity of a reaction system and for the considerable deterioration of the physico-chemical properties of the copolymers formed. Largely free from this serious drawback is the ''living'' controlled copolymerization. The products of such a process proceeding either by ionic or free-radical mechanism normally show very low intermolecular inhomogeneity which is characterized by the narrowness of the distribution $f(\zeta)$ of macromolecules in their

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composition ζ (Fig.1a). However, the macromolecules formed in the course of "living" controlled copolymerization propagating throughout the process of the synthesis exhibit the intramolecular inhomogeneity. This shows up in the appearance of a noticeable gradient of the profile P_α^i of monomeric units along a chain (Fig.1b). This means that the probability P_α^i to find a monomeric unit of the type α in a macromolecule changes markedly with the distance i from its edge.

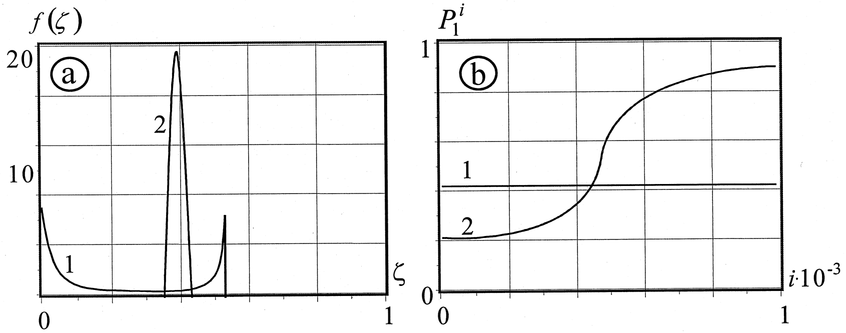

Figure 1. Differences in intermolecular (a) and intramolecular (b) chemical inhomogeneities of the products of TRP (1) and "living" controlled (2) copolymerizations

Essentially, the qualitative distinction in the character of the chemical inhomogeneity of the products of TRP and "living" controlled copolymerization leads to the respective qualitative difference in the character of the phase separation that a reaction system may undergo during the synthesis. While in the first case the system separates into two homogeneous macroscopic phases, in the second one the formation of a mesophase is observed which has spatially-periodic structure.

Table 1. Peculiarities in the character of chemical inhomogeneity inherent in different types of a chain copolymerization

Copolymerization	chemical inhomogeneity	
	*inter*molecular	*intra*molecular
traditional	large	small
"living" controlled	small	large

Highly efficient for the prediction of the properties of the chain copolymerization products is the mathematical modeling method based on the quantitative theory of these processes. Such a theory thoroughly developed for TRP [3,4] served as the basis for the user-friendly software modeling tool [5]. This software enables one not only to calculate the statistical characteristics of the chemical structure of a copolymer but to predict also some of its service properties. As for other types of a chain copolymerization, their rigorous quantitative theory has been elaborated just recently. In the framework of the commonly accepted kinetic models theoretical approaches have been developed for the description of LAP [6] and LRP [7]. These approaches provide the possibility along with the composition and the structure of the copolymers formed to calculate the thermodynamic and scattering properties of their solutions and melts. In the present paper the results are reported of the general theory of chain copolymerization covering all three its above mentioned types. They differ in the way of a polymer chain growth. For TRP case, being initiated at the instant τ the chain grows for a time (substantially less than the characteristic time of copolymerization) to become "dead" afterwards. Conversely, under LAP all polymer chains initiated almost simultaneously grow continuously throughout the process of the synthesis. The manner of a polymer chain formation in the case of an LRP is intermediate between those of TRP and LAP. Indeed, once initiated the polymer chain having added a number of monomers becomes dormant. Then, after a lapse of time the macromolecule "wakes up" to propagate right up to the moment of falling asleep again and so on. Thus, a Polymer Chain (PC) propagation proceeds in a step-wise fashion, by the successive addition of Elementary Chains (EC). For the model under examination an EC growth is supposed to be instantaneous because its duration is much shorter than that of the process. Evidently, from the viewpoint of the way of a PC propagation TRP and LAP can be considered as two opposite limiting LRP cases. In the first of them a PC consists of a sole EC whereas in the second case every EC contains just one monomeric unit. Consequently it seems to be pertinent to expound the key points of our general theoretical approach in terms of LRP.

Each PC built up in the course of LRP comprises, generally speaking, a number of ECs formed at different instants $\tau_1, \tau_2, \ldots$. These ECs vary in composition and structure due to the distinction in the monomer feed composition at the moments of their formation.

The statistical characteristics of any EC formed at the instant τ are known from the theory of TRP [3] since the pattern of the arrangement of monomeric units in it is described by the Markov chain. Each its regular state S_α corresponds to the α-type monomeric unit. The recourse to the Superposition Principle [7,8] makes possible the calculation of any statistical characteristics of the chemical structure of LRP products. In the framework of our approach it is convenient for this purpose to resort to the "labeling trick". Its essence is in marking each monomeric unit by time τ of its formation. Then a stochastic process of conventional movement along a PC is considered. Its regular states $S_\alpha(\tau)$ correspond to α-th type monomeric units formed at the moment τ. Inasmuch as this process is markovian [7] it proves possible to find any statistical characteristics of a PC with labeled units. Subsequent "erasing" of labels, implying the integration over times of the monomeric units' formation, enables one to determine the analogous characteristics of the macromolecules of real copolymers.

Extending the "labeling trick" to all types of a chain copolymerization it becomes possible to provide an exhaustive description of the chemical structure of its products which are present in the reaction system by the moment t provided the characteristics are known of a stochastic markovian process whose states correspond to labeled units. The complete set of such characteristics is:

1. transition intensities $K_{\alpha\beta}(\eta,\tau)$ of transition from regular state $S_\alpha(\eta)$ to regular state $S_\beta(\tau)$;
2. probabilities $T_{\alpha 0}(\tau;t)$ of transition from regular state $S_\alpha(\eta)$ into absorbing one S_0 corresponding to abandoning the limits of a macromolecule;
3. vector-function $w_\alpha(\tau;t)$ having the sense of the density of probability for the first unit of a Polymer Chain to be formed at instant τ and to be of α-th type.

For these characteristics we managed to obtain the following expressions:

$$K_{\alpha\beta}(\eta,\tau) = \nu_{\alpha\beta}(\tau)\delta(\eta-\tau) + \nu_{\alpha 0}(\eta)\upsilon_{\alpha\beta}(\eta,\tau) \qquad (1)$$

$$T_{\alpha 0}(\tau;t) = \nu_{\alpha 0}(\tau)\exp\left[-\int_\tau^t d\xi \sum_\gamma u_{\alpha\gamma}(\xi)\right] \qquad (2)$$

$$w_\alpha(\tau;t) = \upsilon_\alpha(\tau)\rho(\tau;t) \qquad (3)$$

where $\upsilon_{\alpha\beta}(\eta,\tau) = \exp\left[-\int_\eta^\tau d\xi \sum_\gamma u_{\alpha\gamma}(\xi)\right] u_{\alpha\beta}(\tau)$ (4)

The functions occurring in the right-hand parts of these expressions admit the following probabilistic interpretation:

1. $\upsilon_{\alpha\beta}(\eta,\tau)$ is the conditional density of probability to find among ECs, added to an EC with an α-th type terminal unit formed at instant η, an EC with a β-th type initial unit formed at instant τ;
2. $\nu_{\alpha\beta}(\tau)$ denotes the probability of transition from a regular state S_α to regular state S_β of a Markov chain describing chemical structure of an EC formed at instant τ;
3. $\nu_{\alpha 0}(\tau)$ has the same meaning but for transition from regular state S_α into absorbing one S_0;
4. $u_{\alpha\beta}(\tau)d\tau$ stands for the conditional probability of the event consisting in addition to an α-th type terminal unit of an EC during interval $(\tau;\tau+d\tau)$ of an EC starting with β-th type unit;
5. $\upsilon_\alpha(\tau)$ denotes the conditional probability for the first unit of a PC initiated at the moment τ to be of type α;
6. $\rho(\tau;t)d\tau$ represents the infinitesimal probability to find in a reaction system at the moment t a PC initiated during an interval $(\tau;\tau+d\tau)$.

Among the above six stochastic parameters due to relationship (4) only five are independent. Two of them, 5 and 6, are determined only by reaction of the initiation. The rest of the parameters, 2, 3 and 4, are controlled by the constants of the elementary reactions of an EC propagation as well as a PC reinitiation and termination. Expressions for these parameters of general mathematical model of a chain copolymerization can be found in Table 2.

Table 2. Stochastic parameters 2, 3 and 4 expressed through the kinetic characteristics of a reaction system for three different types of a chain copolymerization

Stochastic parameters	Traditional Free-Radical	"Living" Anionic	"Living" Free-Radical
$\nu_{\alpha\beta}(\tau)$	$\frac{a_{\alpha\beta}x_\beta(\tau)}{\sigma_\alpha(\tau)}$	0	$\frac{a_{\alpha\beta}x_\beta(\tau)}{\sigma_\alpha(\tau)}$
$\nu_{\alpha 0}(\tau)$	$\frac{T_\alpha(\tau)}{\sigma_\alpha(\tau)}$	1	$\frac{T_\alpha(\tau)}{\sigma_\alpha(\tau)}$
$u_{\alpha\beta}(\tau)$	0	$k_{\alpha\beta}M_\beta(\tau)$	$k_{d\alpha}\frac{a_{\alpha\beta}x_\beta(\tau)}{\sigma_\alpha(\tau)}$

The kinetic characteristics presented in Table 2 are:

1. fraction $x_\alpha(\tau)$ of an α-th type monomer;
2. dimensionless rate $T_\alpha(\tau)$ of termination of an α-th type macroradical;
3. constant $k_{d\alpha}$ of an α-th type labile bond decomposition;

4. constant $k_{\alpha\beta}$ of addition of a β-th type monomer to an α-th type macroion;
5. concentration $M_\alpha(\tau)$ of an α-th type monomer;
6. $\sigma_\alpha(\tau) \equiv \sum_\beta a_{\alpha\beta} x_\beta(\tau)$, where $a_{\alpha\beta} \equiv r_{\alpha\beta}^{-1}$ - reciprocal values of the reactivity ratios.

Expressions for the functions $T_\alpha(\tau)$ in Table 2 depend on the peculiarities of the chain termination reactions in the course of a free-radical copolymerization. Explicit relationships for $T_\alpha(\tau)$ expressing them through the constants of these reactions can be easily obtained for any particular kinetic scheme of a copolymerization.

The theory put forward permits one not only to calculate any statistical characteristics of the chemical structure of a chain copolymerization products but also to construct the phase diagram and to find the angular dependence of the amplitude of scattering of their solutions and melts.

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