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Abstract

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MOLECULAR-WEIGHT DISTRIBUTION OF POLYMERS DURING CHAIN TRANSFER WITH SCISSION

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The study of the kinetics and mechanism of ionic polymerization of monomers leading to the formation of macromolecules with heteroatoms in the chain has shown [^1] that, alongside the four known types of elementary acts (initiation, propagation, termination, and chain transfer), there also occurs a fifth elementary act—chain transfer with scission—which is a special type of chain transfer to a polymer. The essence of chain transfer with scission is as follows. A growing active macromolecule (a free ion or ion pair) can react with a polymer chain according to the "law of chance," with the formation of a new macromolecule and a new active center. Schematically, this elementary act may be represented as:

$$\sim R_1{-}R_2 \sim +^{*}R_3 \sim \longrightarrow \sim R_1{-}R_3 \sim +^{*}R_2 \sim$$

where I and III are "dead" macromolecules, and II and IV are growing active macromolecules.

It is obvious that the presence of the elementary act of chain transfer with scission, without changing the number-average molecular weight, leads to a change in the molecular-weight distribution.

We have considered the problem of the molecular-weight distribution resulting from chain transfer with scission. Suppose that at the initial moment there is a polymer with a certain molecular distribution, characterized by the average degree of polymerization $\bar{P}$ and by the total number of polymer molecules R. Let all ends of the molecules be active and let the process

$$R_i + R_j \to R_{i+l} + R_{j-l}, \qquad (1)$$

take place, where R_j is the concentration of molecules containing j monomer units. The rate of change of the concentration of molecules of length j will be described by the system of equations

$$\frac{dR_j}{dt} = -2k_jR_jR - 2kR_j\sum_{i=1}^{N} iR_i + 2k\sum_{i=j}^{N}\sum_{l=j}^{N} R_{iR}l +$$

$$+ 2k\sum_{i=1}^{j}\sum_{l=j-i}^{j} R_{iR}l + 4k\sum_{i=j}^{N}\sum_{l=1}^{j} R_{iR}l, \tag{2}$$

where k is the rate constant of chain transfer with scission; it is evident that k does not depend on i, j, and l. The first and second terms on the right-hand side of (2) account for the loss of R_j, the third for the formation of R_j through collisions of molecules with $i, l > j$, the fourth with $i, l < j$ $(i + l > j)$, and the last with $i > j,\ l < j$. Transforming equation (2) and taking into account that the number of monomer units $\sum_{i=1}^{N} iR_i$

does not change in the course of the process and is equal to $\bar{P}R$, we obtain

$$\frac{dR_j}{dt} = -2kR_{jR}(\bar{P} + j) + 2kR^2 - 2k\sum_{l=1}^{j} R_l \sum_{i=1}^{j-l} R_i. \tag{3}$$

Replacing the sum on the right-hand side of equation (3) by a double integral, we obtain

$$\frac{dR_j}{dt} = -2kR_{jR}(\bar{P} + j) + 2kR^2 - 2k\int_0^j R_l \int_0^{j-l} R_i\, di\, dl. \tag{3a}$$

In the stationary state

$$R_j(\bar{P} + j) - R + \frac{1}{R}\int_0^j R_l \int_0^{j-l} R_i\, di\, dl = 0. \tag{4}$$

The solution of (4) is the function

$$R_j = \frac{R}{\bar{P}} e^{-j/\bar{P}}. \tag{5}$$

The same solution is obtained for the stationary system of equations when only part of the molecular ends are active.

The distribution function (5) has the same form as the distribution function obtained, for example, in polycondensation or in polymerization with transfer to monomer. For the distribution (5), the ratio of the weight-average and number-average degrees of polymerization is $\bar{P}_w/\bar{P} = 2$. Thus, if the polymerization mechanism, without taking into account chain transfer with rupture, gives a distribution narrower than (5), then the superposition of process (1) will lead to its broadening. The form of function (5) is analogous to the Maxwell-Boltzmann distribution; this is explained by the fact that redistribution of the chain lengths of colliding macromolecules is analogous to redistribution of the energies of particles in random collisions.

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Note: Figure translations are in progress. See original paper for figures.