KINETICS OF REACTIONS IN MACROMOLECULES.

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Abstract

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KINETICS OF REACTIONS IN MACROMOLECULES.

THE INFLUENCE OF NEIGHBORING UNITS

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In chemical transformations of polymers, the rate constants for units having 0, 1, and 2 reacted neighboring units may, in the general case, have different values*. Depending on the relation between the rate constants, the chemical structure of the macromolecule, which determines the totality of its properties, including the instantaneous rate of reaction for the macromolecule as a whole, will change in different ways with the degree of conversion. Thus, for a quantitative interpretation of observed kinetic regularities and for characterization of the products of incomplete chemical transformation of macromolecules, it is necessary to find the dependence of the chain structure on conversion. Recently several works have been published ($^{1-5}$) devoted to a theoretical consideration of this dependence; however, the equations describing the chain structure were derived by the authors in a rather complicated way and are very cumbersome. Meanwhile, the problem can be solved extremely simply if one uses the recently proposed method for describing the chain structure of copolymers (^{6}).

For an AB copolymer the authors of (^{6}) introduce the concept of the number of sequences of identical units per 100 chain units, R. For example, for the segment of a chain of 20 units shown below, the number of such sequences (in the scheme they are underlined) is equal to 12 and, consequently, $R = 60$. The fractions of A units located at the center of the triads

–A–B–A–A–B–A–B–A–A–A–B–B–A–B–B–B–B–A–A–B–

A—A—A, A—A—B (and B—A—A) and B—A—B are, respectively,
$f_{\mathrm{AAA}} = (\%A - R/2)^2/\%A^2$;
$f_{\mathrm{AAB+BAA}} = R(\%A - R/2)/\%A^2$ and
$f_{\mathrm{BAB}} = R^2/4\%A^2$, where $\%A$ is the mole percent of A units in the copolymer. Thus, knowing R and the composition of the copolymer, one can calculate the distribution of A and B units in macromolecules, i.e., the chain structure.

Let an irreversible monomolecular reaction proceed in each unit of the macromolecule under homogeneous conditions (if a low-molecular-weight agent participates in the reaction, the latter is taken in large excess, so that the change in its concentration may be neglected). Let N_0, N_1, and N_2 be the mole percentages of unreacted units having, respectively, 0, 1, and 2 neighboring reacted units; $Y = N_0 + N_1 + N_2$ is the mole percent of all unreacted units at time t, and k_0, k_1, and k_2 are the corresponding rate constants. We neglect the influence of end groups on the kinetics of the process, assuming the chains to be sufficiently long.

In accordance with the results of work (6),

$$N_0 = (Y - R/2)^2/Y, \tag{1}$$

$$N_1 = R(Y - R/2)/Y, \tag{2}$$

$$N_2 = R^2/4Y. \tag{3}$$

* The influence of the microtacticity of the chain, conformational effects, and supramolecular structures on the reaction kinetics is not considered here.

Obviously, the rates of change of R and Y are described by the equations

$$dR/dt = 2k_0N_0 - 2k_2N_2, \tag{4}$$

$$-dY/dt = k_0N_0 + k_1N_1 + k_2N_2. \tag{5}$$

Dividing (4) by (5), using (1), (2), (3), and denoting $k = k_1/k_0$, $k' = k_2/k_0$, after simple transformations we obtain:

$$-\frac{dR}{dY} = 2\left(\frac{Y}{R} - 1 + \frac{1-k'}{4}\frac{R}{Y}\right) \Big/ \left[\frac{Y}{R} - (1-k) + \frac{1-2k+k'}{4}\frac{R}{Y}\right]. \tag{6}$$

Introducing the new variable $x = R/Y$ and, for convenience, denoting $a = 4/(1 - 2k + k')$, $b = a(1 - k)$, we transform (6):

$$-\frac{dY}{Y} = \frac{(x^2 - bx + a)\,dx}{x^3 - 2x^2 - ax + 2a}. \tag{7}$$

Integrating (7) over the limits from Y_0 to Y and from x_0 to x, we obtain for $a > 0$

$$-\ln\frac{Y}{Y_0} = C\ln\frac{x-2}{x_0-2}+$$

$$+D\ln\frac{x+\sqrt{a}}{x_0+\sqrt{a}} + E\ln\frac{x-\sqrt{a}}{x_0-\sqrt{a}}, \tag{8}$$

where $C = (4+a-2b)/(4-a)$, $D = (b/2+\sqrt{a})/(2+\sqrt{a})$, $E = (b/2-\sqrt{a})/(2+\sqrt{a})$, and for $a < 0$

$$-\ln\frac{Y}{Y_0} = C'\ln\frac{x-2}{x_0-2} + \frac{D'}{2}\ln\frac{x^2-a}{x_0^2-a}+$$

$$+\frac{E'}{\sqrt{-a}}\left(\operatorname{arctg}\frac{x}{\sqrt{-a}} - \operatorname{arctg}\frac{x_0}{\sqrt{-a}}\right), \tag{8a}$$

where

$$C' = (4+a-2b)/(4-a), \qquad D' = 2(b-a)/(4-a),$$

$$E' = a(b-4)/(4-a).$$

Fig. 1. Dependence of the quantities N_i and R on conversion $(100 - Y)$: $k = k' = 1$, $Y^0 = 100$, $R_0 = 1$; calculation according to (10), (1), (2), and (3).

Replacing x in (8) by R/Y, we find R as a function of Y, and using (1), (2), and (3), one can then calculate the dependence of the chain structure (i.e., the quantities N_0, N_1, N_2) on conversion.

In the particular case $k = k' = 1$, the solution of (6) leads to the equation

$$\frac{Y}{Y_0} = \frac{x-2}{x_0-2}. \tag{9}$$

If a homopolymer is taken as the initial product, then $Y_0 = 100$, $R_0 = 1$, $x_0 = 0.01$, and from (9) it follows that:

$$R = 2Y - 1.99\cdot 10^{-2}Y^2. \tag{10}$$

In accordance with (10), (1), (2), and (3), the figure presents the dependence of R and N_i on conversion $(100 - Y)$.

It should be noted that with the aid of (1)–(6) one can also describe the dependence of Y, R, N_0, N_1, and N_2 on time.

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REFERENCES

1. J. B. Keller, J. Chem. Phys., **37**, No. 11, 2584 (1962).
2. T. Alfrey jr, W. G. Lloyd, J. Chem. Phys., **38**, No. 2, 318 (1963).
3. C. B. Arends, J. Chem. Phys., **38**, No. 2, 322 (1963).
4. J. B. Keller, J. Chem. Phys., **38**, No. 2, 325 (1963).
5. L. Lazare, J. Chem. Phys., **39**, No. 3, 727 (1963).
6. H. J. Harwood, W. M. Ritchey, J. Polymer Sci., B2, No. 6, 601 (1964).

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

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