CALCULATION OF THE GEL-POINT FOR NON-EQUILIBRIUM POLYCONDENSATION TAKING INTO ACCOUNT THE "SUBSTITUTION EFFECT"

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Critical conversion \( p^* \) at the gel point was calculated for the first time for irreversible polycondensation of monomer \( A'N' \), for which the activity of functional groups \( A \) varies on reacting with adjacent groups. Results of calculation of the gel point were compared for irreversible and equilibrium polycondensation and it was shown that the dependence of \( p^* \) on parameters determining the degree of mutual thermodynamic and kinetic effect of functional groups in the monomer is qualitatively different. For example, under conditions of the irreversible process the value of \( p^* \) may change suddenly on increasing relative activities of functional groups, when critical conversion passes through a maximum. This type of dependence of \( p^* \) within the framework of the model examined is, in principle, impossible for equilibrium polycondensation.

One of the main problems of the theory of branched polycondensation is to establish the quantitative dependence of the conversion of functional groups in the gel-point on stoichiometric and kinetic parameters of the reaction system. In the case of ideal polycondensation this problem was solved in a most general form [1] for a random monomer mixture containing any number of types of independently reacting functional groups. If activity changes markedly during the reaction of adjacent groups, formulating the general quantitative theory of polycondensation considering this "substitution effect" is a more complex problem, which has not yet so far been completely solved.

In equilibrium polycondensation it may be confirmed by an accurate thermodynamic study that all configuration statistical characteristics of the polymer, including the gel-point, may be calculated by standard methods using the theory of branching processes. It was shown [1, 2] that the probability configuration measure of products of equilibrium polycondensation is described by a branching process with a single type of propagating particle which corresponds to monomer units. Generating functions of this Galton-Watson process are determined by

\[
F^n(\omega) = \sum_{i=0}^{\infty} \omega^i F(\omega) = \frac{1}{1 - \omega F(\omega)},
\]

where \( \omega = \omega^* \), after substituting it in equation (3), gives the formula for the conversion of \( p^* \) in the gel-point. In the case of \( f = 3 \), in particular, equation

\[
p^* = \frac{2F'(2) + \sqrt{F'(3)}}{3F(2) + F'(3) + 4\sqrt{F'(3)}} = \frac{2\sqrt{\omega^*}}{\omega^* + 3} + \frac{1}{\omega^* + 3}
\]

is obtained.

In the case of non-equilibrium polycondensation the gel point is determined from equilibrium conditions and in the second, from kinetic equations. In addition to quasi-ideal systems, there may also
be non-ideal systems, statistics of which, as indicated [1, 4], are not described by the branching process. Based on a previous study [3], we give the calculation of the gel-point for a very simple non-ideal system, using irreversible polycrystallization of RA monomers, all notations of this study [3] remaining unchanged; when referring to formulae contained in it, in contrast with formulae of this paper, corresponding numbers will be marked by a.

By definition of the gel-point all statistical moments of MWD simultaneously become infinite, their order being higher than, or equal to, two [1]. Since molecules in the kinetic model examined differ in numbers $l_1, l_2, ..., l_n$ of units of different types $L_1, L_2, ..., L_n$ at the moment of gel-formation values of $\mu_2(l) = \sum l_i (l_i - 1) c(l_i, l_i),$ (0)

become infinite, where $\delta_{ij}$ is Kronecker's symbol and summation in equation (0) is extended over all possible values of vector $\mathbf{l}$. Since $\mu_2$ is equal to the second derivative according to arguments $l_1$ and $l_2$ of generating function $g(l_1, l_2)$ (3) at point $s-1$, after two-fold differentiation term-by-term of equation (4) and assuming that $s = 1$, the following equation system may be derived for $\mu_2$:

$$\frac{d\mu_2}{dt} = N \sum_{l_{-1}} \left( k_{l_{-1}} - 1 \right) \mu_2(l_{-1}) + N \sum_{l_{+1}} \left( k_{l_{+1}} - 1 \right) \mu_2(l_{+1})$$

$$+ \eta_{l_{-1}, l_{-1}} + \eta_{l_{+1}, l_{+1}} - \eta_{l_{-1}, l_{+1}} - \eta_{l_{+1}, l_{-1}} + N \eta_{l_{-1}, l_{+1}} - \eta_{l_{+1}, l_{-1}} - \mu_2(0) = 0$$ (7)

Values of statistical moments of first order $l_i$ and functions $\eta_{l_i}$ in the right-hand sides of equation (7) are determined from equations (5). Since $\mu_2 = 0$ for all $0 < l < s$ and $\mu_2 = \mu_2$, system (7) consists of $f(f+1)/2$ independent equations, which are integrated together with $f-1$ equations (5). In order to determine critical conversion $P^*$ at the gel-point, it is convenient to change in these equations from time to conversion using the equation

$$f \frac{dP}{dt} = \sum_{l_i} \lambda_i \eta_{l_i}$$

In the right-hand sides of the system $(f^2 + 3f - 2)/2$ only contain as coefficients values of $(f - 1)/(f + 2)/2$ of relative activities $k_{l_i} = k_{l_i}/K_{l_i}$ for groups incorporated in different types of unit. In the case of a simplified kinetic model of the "neighbour effect" used by authors of a previous study [5] constants $k_{l_i} = k_{l_i} K_{l_i}$ and $k_{l_i} = k_{l_i} K_{l_i}$ form factors and the number of independent kinetic parameters $k_{l_i} = k_{l_i} K_{l_i}$ which determine conversion $P^*$ in the gel-point, decreases to $f-1$.

In equilibrium polycrystallization of the monomer RA the number of thermodynamic parameters $k_{l_i} = K_{l_i}/K_0$ in the same $f-1$, and they have a similar meaning. Results of calculation of the gel-point within the framework of a simplified model of the "neighbour effect" of irreversible polycrystallization allow a simple comparison to be made with similar results for equilibrium conditions in the same chemical system. Results of such a comparison for polycrystallization of

![Fig. 1. Theoretical dependence of critical conversion at the gel-point on parameter $s$ with $s$ values of 0-01 (1); 0-05 (2); 0-1 (3); 0-2 (4); 0-3 (5); 1-0 (6); 2-0 (7); 2-5 (8); 5 (9); 10 (10). Broken curves were calculated using formulae (3) for equilibrium polycrystallization of RA monomer and continuous curves—using equations (7) for a simplified model of the "neighbour effect" of irreversible polycrystallization. Points were obtained by calculating $P^*$ within the framework of this model by integration of equations (10).](image1)

![Fig. 2. Theoretical dependence of critical conversion in the gel-point on parameter $s$ with $s$ values of 0-01 (1); 0-1 (2); 0-3 (3); 0-5 (4); 1-0 (5); 5 (6); 10 (7); 100 (8). Broken and continuous lines show equilibrium and irreversible polycrystallization, respectively.](image2)
a three-functional monomer (Figs. 1–3) show quite a different dependence of critical conversion on parameters \( k_1 \) and \( k_2 \), determining the extent of mutual effect of functional groups of the same monomer unit. The surface of gel-formation, which, over the surface of parameters \( k_1 \) and \( k_2 \), is given by the function \( p^*(k_1, k_2) \) is of different form qualitatively for equilibrium and irreversible conditions of polycrystallization. For the former (Fig. 1) on intersecting this surface by planes \( k_1 = \text{const} \), monotone curves are obtained while for the latter curves with a maximum are obtained. With an increase in \( k_1 \), the position of this maximum is displaced to the left and the curves themselves are lower.

![Graph](image)

**Fig. 3. Lines of the level of gel-formation surface \( p^*(k_1, k_2) \) calculated for the simplified model of the "neighbour effect" of irreversible polycrystallization of RA^1 monomer. Numbers at the curves correspond to constant \( p^* \) along this line.**

In addition to direct integration of system (7), another method of calculating the gel-point may be indicated, which is based on the fact that at this point the simple dependence of \( \zeta (n, t) \) is disrupted when \( n = 1 \), which is derived from the solution of equations of characteristics (6) and (7). The mathematical condition of this [6] is the determinant \( \Delta \) of the matrix with elements \( x_{ij} \) becoming zero

\[
\Delta = \frac{\partial S_1(l,t)}{\partial \zeta_1} \quad y_{ij} = \frac{\partial S_1(l,t)}{\partial \zeta_j},
\]

for which equations together with \( y_{ij} \) may be derived from equations (6) and (7) and considering equations (9).

Calculated results in Figs. 1 and 3 confirm that the dependence of conversion at the gel-point on parameters \( k_1 \) and \( k_2 \) varies from a qualitative point of view for equilibrium and non-equilibrium conditions of polycrystallization. For the former the direction of shift of conversion \( p^* \) in relation to the value of \( p^* = 0.5 \) in an ideal system is determined only by the value of \( k_1 \) so that \( p^* > 0.5 \) when \( k_1 < 1 \) and \( p^* < 0.5 \) when \( k_1 > 1 \), independent of \( k_2 \). For the latter case there is a certain maximum value of \( k_2^* \), which is close to two so that when \( k_2 > k_2^* \), it is certain that \( p^* < 0.5 \) for all \( k_1 \) values and when \( k_2 < k_2^* \), the difference of \( p^* = 0.5 \) will be negative with fairly low, or high \( k_2 \) values, and positive, in the intermediate range. For example, when \( k_1 = 1 \) such a range is \( 0.1 - 0.5 \), where \( p^* > 0.5 \).

An important fact should be noted: in polycrystallization systems, where is a "substitution effect", unlike ideal systems, the position of the gel-point does not simply determine the topology of the polymer network formed. This applies to the same extent in equilibrium and non-equilibrium polycrystallization. During displacement along any lines of the surface level of gel-formation (Fig. 2), the value of \( p^* \) remaining unchanged, \( x_{ij} \) values at the gel-point will vary considerably, being the simplest characteristics of the configuration structure of the polymer system. Changes of this structure on transition from some points of the level line to others correspond to the fact that the topological structure of the network formed varies for different systems, parameters \( k_1 \) and \( k_2 \) being on a given line. A manifestation of this is the variation of kinetics of formation of the gel-fraction in systems with the same critical conversion value \( p^* \) previously observed for equilibrium polycrystallization of RA^1 monomer.

It is interesting to compare results of the accurate calculation of the gel-point given in this study for irreversible polycrystallization of RA^1 monomer within the framework of the model of "neighbour effect" with those obtained
when using the empirical algorithm proposed by Gordon and Scantlebury [8] for calculating $p^*$ on the basis of the theory of branching processes. According to this algorithm, the value of $p^*$ was found from equation (4) or the equivalent relationship

$$f \sum_{i=1}^{N} i(i-2) \lambda_i = 0, \quad (11)$$

in which the dependence of $\lambda_i$ on conversion is determined from the solution of kinetic equations (9) of a previous study [3]. In a simplified form of the model of "neighbour effect", when $k_i = k_i^{\beta}$ and $\phi_i = \phi_i^{\alpha}$, this dependence may be found in analytical form

$$\lambda_i = (-1)^{i-1} \left[ \lambda_{i-1} (k_j - k_i) (k_{j+1} - k_i) \ldots (k_{N-1} - k_i) \right]^{\alpha - \beta}. \quad (12)$$

via parameter $\theta$, which is simply linked with the $p$ value of the last formula (6) of the study mentioned [3]. Substituting equation (12) into (11) results in an algebraic equation in relation to $p^*$, the solution of which determines the conversion $p^*$ at the gel-point. Numerical results of this calculation are given [8] when $f = 3.4, 6$ using only a single-parameter model of "linear substitution effect", which corresponds to the particular case of $k_i = k_i^{\beta}(j = 1, \ldots, f)$. Comparison of these results with $f = 3$ with those which are given by the theory of gel-formation shows a remarkable agreement within the range of 1-2% for a small range of $k_i$, where calculations were carried out previously [8].

Using the Monte-Carlo method for calculating $p^*$ within the framework of the simplified model of "neighbour effect" of condensation of a RA polymer, Mitschik and Dusek [9] came to the general conclusion that for most systems the theory of branching processes is a very satisfactory approximation to the description of configuration statistics of the polymer, with formation kinetics corresponding to the model indicated. Authors of this study [9] note that it is only with non-monotone variation in the activity series of group A $k_1$, $k_2$, and $k_3$ in units $L_a$, $L_b$, and $L_c$ that consumption may exceed 0.01 values of $p^*$ and $p^*$ calculated theoretically and using Gordon's empirical algorithm [8].

These claims are inaccurate in our opinion for several reasons.

Firstly, authors of the earlier study [5] did not, apparently, carry out calculations for all necessary ranges of parameters $k_1$, $k_2$, since there are kinetic constants which show monotoneous variation in the series $k_1$, $k_2$, and $k_3$ for which the difference between $p^*$ and $p^*$ exceeds 0.01. As an example we may cite the system $k_1 = k_2 = k_3 = 1$, for which asymptotic values $p = 6/9 = 0.666$ and $p^* = 1/\sqrt{3} = 0.577$ may be obtained; the lower value of $k_3$ the higher the accuracy of these values.

The error in this case on using the Gordon algorithm $\delta = (p^* - p^*)/p^*$ is 3-8% and increases with an increase in monomer functionality (RA). A study of

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REFERENCES