# NONISOTHERMAL POLYMERIZATION IN A SPHERICAL REACTOR. TEMPERATURE DISTRIBUTION AND REACTION KINETICS

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The possibility of solving the converse thermal conductivity problem beginning with temperature measurements during the process of nonisothermal polymerization is demonstrated.

The reaction of polymer formation from monomers is usually accompanied by significant thermal effects. The heat produced is usually released to the surrounding medium. But because of the poor thermal conductivity of the polymer and the very high volume to surface ratios of the reaction vessels even in the case of laboratory reactors, even more so in industrial reactors, the amount of heat extracted is always insufficient for maintenance of isothermal conditions. Therefore the reaction occurs in a nonisothermal mode over time and reactor volume. The temperature rise then causes an increase in reaction rate and, generally speaking, a change in composition of the final product. Such a reaction mechanism makes it necessary to solve a thermal and a kinetic problem simultaneously when undertaking a theoretical study of the reaction. For a spherical reactor the two problems are formulated in the form of two equations:

$$\frac{\partial T}{\partial t} = a\left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial T}{\partial r}\right) + \frac{Q}{c}\cdot\frac{d\eta}{dt}, \tag{1}$$

$$\frac{d\eta}{dt} = Kf(\eta)\exp(-E/RT) \tag{2}$$

with the following boundary conditions: at $t = 0$, $T(r) = T_0$ and $\eta = 0$, at $r = r_0$, $(\partial T/\partial r) = -(B/r_0)(T - T_0)$, where $T_0 = \text{const}$ is the temperature of the surrounding medium.

The system (1), (2) may be used to solve either the direct or converse problems. The former of these consists of finding $T(r, t)$ and $\eta(r, t)$ given values of all constants and the function $f(\eta)$. The latter problem consists of determining the constants K, E, Q, B from values of the functions $T(t, r_k)$ measured at several points $r = r_k$. The direct problem is considered in [1], primarily in connection with a study of the conditions for "thermal explosion."

The present study is dedicated to analysis of the possibilities of numerical solution of the converse problem using the example of anion-activated polymerization of dodecalactam "en masse," occurring with 100% output and leading to the production of polyamide-12 articles [2].

The kinetics of this reaction were determined independently in the adiabatic regime and recalculated to isothermal conditions [3]. The final expression, which will be verified below, may be written in the form of Eq. (2), where $K = K_0A = 2.9 \cdot 10^5 A\ \text{min}^{-1}$; $f(\eta) = 1 - \eta$ (at least to $\eta = 0.7$), $Q = 43\ \text{J/cm}^3$; E is dependent on $\eta$, but for the initial stage of the process $E = 12$ kcal/mol.

We attempted to find K, E, Q, B in Eqs. (1), (2) for $f(\eta) = 1 - \eta$ using experimental data for $T(t, 0)$ and $T(t, r_0)$, corresponding to various regimes: values of $A = 0.35$; 0.50, 0.75, 1.0 mol. %, and $T_0 = 160$, 170, 180, 190°, beginning with the condition that the system (1), (2) with the constants so found should best describe the entire set of experimental data.

Such a problem belongs to the class of so-called converse problems. Its solution is based on the introduction of some function of the parameters — in the given case $\Phi(K, E, Q, B)$ — which characterizes the norm of the deviation of the theoretical curves: solutions of

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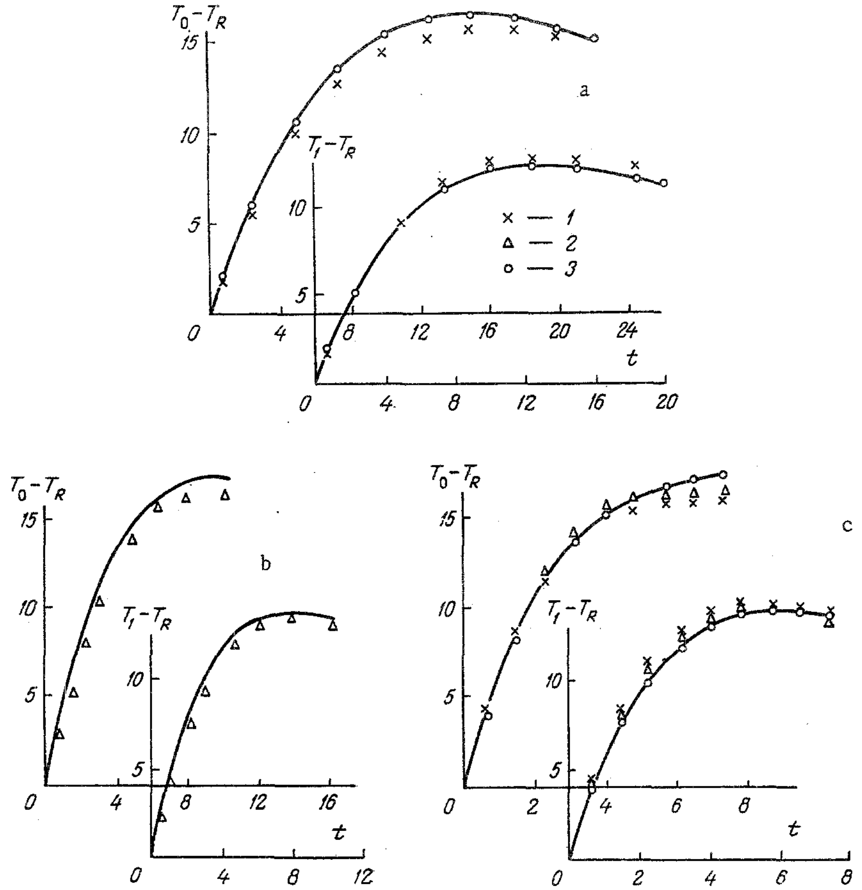

Fig. 1. Comparison of calculated functions $T_0(t)$ and $T_1(t)$ with original data used for machine experiment at $T_0 = 160$ (a), 180 (b), 190 (c) °C; 1) $\Phi = 0.11$, 2) 0.06, 3) 0.01; t, min.

Eqs. (1), (2) versus corresponding experimental data. We take as the solution those values of the constants for which the norm of the deviation is smaller than some given value (as a rule, this value is the experimental error involved). For the most part, the problem has an ambiguous solution. If the set of solutions lies in some sufficiently small region ($K_0 \pm \Delta K$, $E_0 \pm \Delta E$, $Q_0 \pm \Delta Q$, $B_0 \pm \Delta B$), the problem is considered solved.

Success in solution of the converse problem depends most of all on correct choice of a mathematical model, and then on the character and quantity of experimental data available, i.e., on the informativeness of the data.

Thus in solving a concrete converse problem it is necessary to distinguish these two factors and to study the question of the information content of the available experimental data either qualitatively or by numerical experiment on the mathematical model.

For such a numerical experiment one can consider the set of functions $T(t, 0)$ and $T(t, r_0)$ found from Eqs. (1), (2) at certain fixed values of the constants K, E, Q, B for various $T_0$ as experimental data for the converse problem. The solution is then sought as a minimization of the function $\Phi$.

In such an experiment errors of the model are eliminated and there remains the pure problem of finding the constants in the given model. Since the solution is known, the result of the numerical experiment should give an answer to the question of the accuracy of determining the constants ($\Delta K$, $\Delta E$, $\Delta Q$, $\Delta B$) as a function of the value of the norm $\Phi$. These estimates should serve as a criterion of the accuracy of the solution of the converse problem for a real experiment with the mathematical model considered, and also serve as a basis for relating the uncertainty in the solution, which exceeds the estimate thus made, to inaccuracy in description of the real experiment by the model considered.

Generally speaking, the norm of the deviation may be chosen in various manners. We chose the following norm:

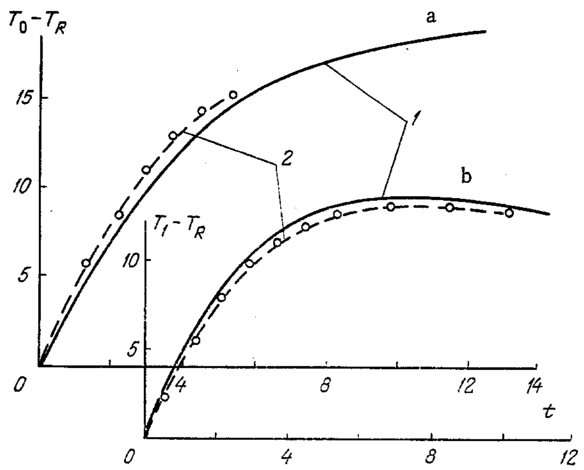

Fig. 2. Comparison of experimental (1) and calculated (2) data on temperature change of reaction mass in center and at wall of reaction volume upon polymerization of dodecalactam under conditions of heat exchange with constant temperature sink. Experimental conditions: A = 0.5 mol. %; $T_r$, 180°C (a) and 190°C (b); 1) experimental; 2) calculated curve.

$$\Phi = \frac{1}{n}\sum_{i=1}^{n}\sqrt{\sum_{k=1}^{m}\frac{\lambda_k}{4\,(t_{k+1}-t_k)}\int_{t_k}^{t_{k+1}}\left[\left(1-\frac{T_0^m(t)}{T_0^e(t)}\right)^2+\left(1-\frac{T_1^m(t)}{T_1^e(t)}\right)^2+\left(1-\frac{T_0^e(t)}{T_0^m(t)}\right)^2+\left(1-\frac{T_1^e(t)}{T_1^m(t)}\right)^2\right]dt.} \tag{3}$$

The functions $T_0^m(t)$ and $T_1^m(t)$ are solutions of Eqs. (1), (2) T(t, r) for r = 0 and r = $r_0$ obtained by numerical methods.

Numerical integration of Eqs. (1), (2) was performed by an implicit difference scheme with linearization of the nonlinearity $e^{-E/RT}(1-\eta)$ in each layer and solution of the corresponding linear system by the drive method.

Preliminary analysis revealed that for a successful determination of the constants considered it was necessary to have the curves T(t, 0) and T(t, $r_0$) for two $T_0$ values differing as much as possible, since data for close-lying values of $T_0$ determine basically the complex $K_0\exp(-E/RT_0)$, as will be demonstrated below with the example of two numerical experiments.

For the initial "experimental" data we chose T(t, 0) and T(t, $r_0$) calculated for B = 0.9 from Eqs. (1), (2) using values of the constants K, Q, E obtained in an adiabatic experiment. Their dimensionless values were: $\hat{K} = 0.15$; $\hat{E} = 0.032$. In the first numerical experiment temperatures $T_0$ = 160 and 190° were considered; the second experiment considered two close-lying temperatures: $T_0$ = 180 and 190°. For the initial point in the calculations values quite far removed from the true ones were chosen: $\hat{K} = 0.01$; $\hat{E} = 0.1$; B = 0.04; Q = 2 J/cm³, which corresponds to Φ = 73.5.

By solving the converse problem in the first numerical experiment we obtained: $\hat{K}$ = 0.15; $\hat{E}$ = 0.0331; Q = 42.7 J/cm³; B = 0.878, and Φ = 0.01. A comparison of theoretical and original "experimental" data obtained for this case is shown in Fig. 1.

The following data characterize the accuracy of constant determination as a function of the value of the deviation norm Φ, obtained in the minimization process at $\hat{K}$ = 0.15:

| | | | |
|---|---|---|---|
| $\hat{E} = 0{,}04$ | $B = 0{,}575$ | $Q = 35{,}7$ | $\Phi = 0{,}11$ |
| 0,0385 | 0,5775 | 39,27 | 0,06 |
| 0,0339 | 0,706 | 41,17 | 0,02 |

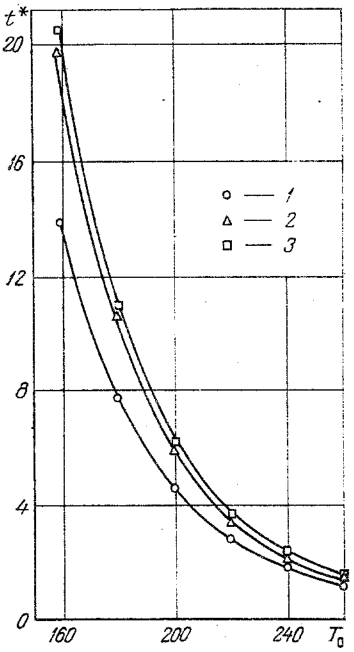

Fig. 3. Calculation of required process duration for various initial temperatures, °C; heat transfer conditions; and spherical part sizes: 1) B = 0; 2) 0.5; 3) 1-3.

From this it follows that if the original experimental data are obtained with an error greater than 6% the error in calculation of, for example, E will then be as follows: E = 14.2 kcal/mol (calculation), E = 12 kcal/mol (true value).

As for the parameter B, it may be said that for its determination a very accurate experiment is required (error up to ∿1%). The combination of the parameters $K_0$ and E (i.e., $\hat{K}$) at $\Phi = 0.06$ is defined quite well (original value 0.15, value obtained 0.15), while Q is determined to 10%. The error in E determination produces an error in $K_0$, which is calculated as $\Delta K_0/K \approx \Delta\hat{K}/\hat{K} + \Delta\hat{E}T_*$. The basic contribution to error in $K_0$ calculation is produced by the term $\Delta\hat{E}T_*$. In our case $0.006 \cdot 433 \sim 2.6$, and, consequently, only the order of magnitude of the constant $K_0$ may be determined.

However, in the theoretical model the constants $\hat{K}$ and $\hat{E}$ appear (and not $K_0$ and E), which are found with a much higher relative accuracy and determine certain important characteristics, for example, the duration of the process.

The solution of the converse problem in the second numerical experiment produced the values $\hat{K} = 0.09645$; $\hat{E} = 0.05145$; Q = 40.2; B = 0.76 at $\Phi = 0.06$. Due to the closeness of the temperatures $T_0$ (180 and 190°), as was expected the constants $\hat{K}$ and $\hat{E}$ were determined individually with unsatisfactory accuracy, but the complex $K_0\exp(-E/RT_0)$ at $T_0 = 190°$ was equal to 0.411, which is close to the value of 0.405 found from the constants $\hat{K}$ and $\hat{E}$ of the first numerical experiment.

We will now process the experimental data obtained in a real experiment. For solution of the converse problem with $f(\eta) = 1 - \eta$ and E = const two experiments performed at $T_0$ = 180° and 190° were taken (A = 0.5 mol. %). Constants were determined by minimization of $\Phi(K, E, Q, B)$ beginning with two different initial points. In the one case at $\Phi = 0.06$, $\hat{K} = 0.13$; $\hat{E} = 0.029$; B = 0.568; Q = 44.98. In the other case at $\Phi = 0.08$, $\hat{K} = 0.169$; $\hat{E} = 0.021$; B = 0.92; Q = 45.7.

Curves of T(t) calculated from both sets of parameters agreed satisfactorily with the experimental data (Fig. 2). The complex $K_0\exp(-E/RT_0)$ for $T_0 = 190°$ for these parameter values was equal to 0.301 and 0.304, respectively.

The method used here makes it possible to use the constants found for the model of Eqs. (1), (2) to calculate the temperature changes, the degree of completion of the process of producing spherical parts by polymerization of the monomer "en masse," and the duration of the process $\hat{t}$ for various $T_0$ and various conditions of heat transfer to the surrounding medium.

For example, let $\hat{t}$ be defined as the time at which $\eta = 0.95$ is attained under worst case conditions $r = r_0$. The results of the calculations are shown in the form of the dependence of $t^* = at/r_0^2$ on $T_0$ for various B in Fig. 3. The calculations were performed with the model of Eqs. (1), (2) for the constant values presented above, found from "adiabatic" experiment. The calculations were also repeated for constant values obtained from nonisothermal experiment with the method described above. Divergence between the results does not exceed 10%.

Thus the study performed shows that solution of the converse problem of constant determination from the thermokinetic model given sufficient information in the form of experimental data with sufficient accuracy (including the accuracy of the model) makes it possible to determine these constants with a satisfactory degree of accuracy, which in turn makes possible solution of various engineering physics problems connected with nonisothermal polymerization of various monomers "en masse."

## NOTATION

T, temperature; t, time, min; $T_0$, temperature in reactor center; $T_1$, temperature on reactor surface; $T_R$, temperature of surrounding medium; r, current radius, cm; $r_0$, reactor radius, cm; $a$, thermal diffusivity coefficient, $cm^2/sec$; c, specific heat, $J/cm^3 \cdot deg$; Q, thermal effect of reaction, $J/cm^3$; E, activation energy, kcal/mol; $\eta$, degree of transformation; R, universal gas constant, kcal/mol•deg; B, Biot criterion; K, kinetic constant, $min^{-1}$; $\hat{K} = K_0Ae^{-E/RT_*}$; $\hat{E} = E/RT_*^2$; $\hat{t} = at/r_0^2$; $T_* = 160°C$; $f(\eta)$, kinetic function; m, number of segments into which integration interval is divided; n, number of series of measurements from which parameters are determined; $t_k$, segment ends; $\lambda_k$, weight of each segment; $t_{max}$, integration limit; A, concentration of catalytic system, mol. %; superscript m indicates theoretically calculated, superscript e, experimentally determined function T(t); t*, critical value of $\hat{t}$.

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