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Publisher *Taylor & Francis*

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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Medvedevskikh, Ju. G. , Zahladko, E. A. , Turovski, A. A. and Zaikov, G. E.(1997) 'Kinetics of the Three-Dimensional Thermopolymerization', International Journal of Polymeric Materials, 38: 3, 329 – 337

To link to this Article: DOI: 10.1080/00914039708041028

URL: <http://dx.doi.org/10.1080/00914039708041028>

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Kinetics of the Three-Dimensional Thermopolymerization

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(Received 22 April 1997)

A kinetic model of the three-dimensional radical polymerization of oligomers bulk is proposed. The presented analysis shows that the proposed equation agrees with the known experimental kinetic data of the three-dimensional polymerization. The construction of the equation is based on the concept of the microheterogeneous model and the postulate that the rate of the three-dimensional polymerization is the sum of the rates of the homophase processes, which run in various phases and interphases, and that the initiator is distributed uniformly between the phases and interphase layer. The clusters of the solid polymer in liquid oligomer phase and clusters of the liquid oligomer in solid polymer matrix are assumed to have the fractal structure.

Keywords: Thermopolymerization; radicals; three dimensional; kinetic model; oligomers; clusters; fractal structure

THEORY AND DISCUSSION

Kinetic curves of the thermopolymerization of the polyfunctional oligomers have the clear S-like dependence of conversion Γ on time t . This is characteristic for the autocatalytic reactions. The point of inflection of the kinetic curve corresponds to the maximum rate of polymerization, and this maximum is observed also with normalized process rate.

These and the other features of three-dimensional polymerization find the quantitative explanation in the microheterogeneous model [1].

However, their quantitative interpretation is prevented by the absence of a general kinetic equations of the process. Particular kinetic equations of the steps of the autoacceleration and of the auto deceleration [1] describe unsatisfactory the experimental data and donot correlate in the area of the maximum rate of the process.

We propose the following kinetic equation, which allows us to describe quantitatively the three-dimensional polymerization of the polyfunctional oligomers in bulk in the entire interval of transformation level

$$dP/dt = k_1(1 - P)V_i^{1/2} + k_2P(1 - P)V_i \quad (1)$$

Here $P = \Gamma/\Gamma_0$ – relative extent of polymerization determined by the relation of current conversion Γ to limit Γ_0 , V_i – rate of the initiation, k_1 and k_2 – kinetic constants.

Kinetic equation (1) shows the S-like dependence of P from t , with ordinate P_1 being the point of inflection, which is determined from the condition $d^2P/d^2t = 0$

$$k_2V_i - k_1V_i^{1/2} - 2k_2PV_i + [k_1(1 - P)V_i^{1/2}/2 + k_2P(1 - P)V_i]dV_i/V_idP = 0 \quad (2)$$

The estimates [1] of the maximum rate of the process $W_1 = (dP/dt)_{\max}$, corresponding to ordinate P_1 – point of inflection of the kinetic curve $P = P(t)$, show that the principal contribution into the kinetics of the process belongs to the second term in (1). Therefore without a significant error, the expression in the square brackets in (2) may be considered equal to dP/dt . From the expression $V_i = -dc/dt = k_i c$, in which c – concentration of the initiator, k_i – rate constant of its decomposition, follows $dV_i/V_idt = -k_i$. Thus, the solution (2) may be described as

$$P_1 = (a - b)/2a, \quad (3)$$

where $a = k_2V_i^{1/2}/k_1$, $b = 1 + k_i/k_1V_i^{1/2}$.

According to (3) in the area of position P , the ordinate P_1 representing the point of inflection of the kinetic curve $P = P(t)$, may have a value in the interval $0 \leq P \leq 1/2$. This agrees with the experimental data [1].

For the maximum rate W_1 of the process we have the expression

$$W_1 = k_1 V_i^{1/2} (a + b) \cdot (a - b + 2)$$

from which it follows that at $a \gg b$ and $P \simeq 1/2$ $W \simeq k_2 V_i / 4$. This allows us to estimate immediately $k_2 V_i$ on W_1 . In accepted terms of a normalized rate of the process we have $-d \ln(1 - P)/dt$. Its maximum corresponds to the point of inflection of the kinetic curve of the form $\ln(1 - P) = f(t)$ with the ordinate P_2 and rate W_2 of the process, connected according to the analysis (1), by the relation

$$P_2 = W_2 / k_i - 1/2a \quad (4)$$

Solution (4) does not limit the values of P_2 in the area of positive $P \geq 0$, that also agrees with the experimental data [1].

If the time dependence of the rate of the initiation is considerably slower than the rate of the polymerization, then for the initial stage of the process we may assume that $a = \text{const}$, $b = 1$. Thus, the equation gets the integral form

$$\ln[(1 + ap)/(1 - p)] = k_1 V_i^{1/2} (1 + a)t$$

which is convenient for estimating the kinetic constants from the experimental data.

According to the principal concept of microheterogeneous model [1] the rate of the three-dimensional polymerization in volume of the system V_0 may be represented by the sum of the rates of the homophase process, run in the volume V_f of liquid oligomer and heterophase, which runs in the interlayer volume V_m on the boundary of solid polymer - liquid oligomer in the regime of gel effect

$$V_0 W = V_f W_f + V_m W_m \quad (5)$$

where $W = d[M]/dt$, $W_f = d[M_f]/dt$ and $W_m = d[M_m]/dt$ - specific rates of the total, homo and heterophase processes, which are determined correspondingly through the average on the volume of the system concentration of the monomer (M) and its concentration in liquid phase $[M_f]$ and the interphase layer $[M_m]$. In this case W_f and

W_m are described as the rates of the chain evolution

$$W_f = k_{pf}[M_f][R_f], \quad W_m = k_{pm}[M_m][R_m] \quad (6)$$

The homogeneous nucleation in the three-dimensional polymerization begins and finishes at low conversions $P < 0.01$ [1]. In the remaining interval of $P > 0.01$ the liquid solution of the oligomer is saturated with the new polymer phase, but the concentration of the saturation is small. Therefore $[M_f]$ in the liquid phase is constant in time and practically equal to the initial one $[M]$: $[M_f] \approx [M]_0$. Correspondingly, the volume V_f of the oligomer phase changes with time according to the law $V_f = V_0(1 - P)$, which is based on the assumptions: the extent of polymerization in solid phase is close to its limit [1, 2]; the difference of the densities of the solid and liquid phase may be neglected, volume V_m of the interphase layer is much less than the volume V_0 of whole system. Consequently, $V_0 = V_f + V_i$, where $V_i = V_0 P$ – volume of the solid phase.

At further analysis of the kinetic model the question arises about the distribution of the initiator between the solid and liquid phases between them and the interphase layer. Two cases are probable. The first case is based on the assumption, that the dissolution of the initiator in the polymer is small, therefore during the polymerization it is pressed out from the solid into the liquid phase, where its concentration increases. In this case, the relationship between the specific rate of the initiation V_i , which is determined in the volume V_0 of the whole system, and the specific rate V_{if} in the volume of liquid phase is given by $V_i V_0 = V_{if} V_f$ or $V_{if} = V_i / (1 - P)$. The analysis shows, that with this relationship it is impossible to obtain from (5) – (6) the final equation satisfying the initial one (1). Therefore we choose the second variant, which assumes the uniform distribution of the initiator between the phases and interphase layer and leads to equality $V_i = V_{if}$. At the abrupt chain termination cut off in the liquid oligomer phase we have $[R_f] = (V_i / k_{if})^{1/2}$, where k_{if} – rate constant of recombination of the radicals.

Uniting the obtained relations in (6) and taking into account the current volume V_f of the liquid phase, we find

$$V_f W_f = V_0 (k_{pf} / k_{if}^{1/2}) [M]_0 (1 - P) V_i^{1/2} \quad (7)$$

For the functional determination of the volume V_m of the interphase layer we compare two approaches – the geometric and the fractal one. According to geometric approach, in the initial stage of the process ($0 \sim P \ll 1$), the solid phase is represented by grains of the sphere shape, so that $V_t = V_0 P = 4h\pi r^3/3$, where n – number of the grains, r – their radius. With the thickness of the interphase h we have $V_m(0) = 4h\pi r^2$ and $V_m(0) = 3(h/r)V_0 P$.

Using further the assumption, that the thickness of the interphase layer is proportional to the radius of the grain, that is $h = mr$, where $m = \text{const}$, we finally obtain $V_m(0) = 3mV_0 P$. Analogical considerations for the final stage of the process ($P \simeq 1$), that is after the inversion of phases, lead to the expression $V_m(1) = 3mV_0(1 - P)$ [1].

According to fractal approach [3–5] we suppose, that the growing grains or the clusters of the polymer phase have the fractal structure, the dimension of which in the general case does not coincide with the measurement of the Euclid space. For example, the volume V of the cluster and its average radius r are connected by the relation $V \sim r^{d_v}$, in which $d_v \leq 3$. For the surface S of the cluster we have $S \sim r^{d_s}$, where $2 \leq d_s \leq 3$ [4, 5].

Using the fractal dimensions, the volumes of the solid polymer phase and of the interphase layer on the initial stage of the process is expressed by the relation $V_t = nF'_v r^{d_v} = V_0 P$, $V_m(0) = nhF'_s r^{d_s}$, where h – thickness of the interphase layer and F'_v and F'_s – fractal characteristics of the volume and of the surface of the polymer clusters, which do not depend of r . From numerous available estimates [3–6] of d_v and d_s it follows that the cluster, which grows by diffusion limited mechanism has the properties of the mass fractal, for which $d_v = d_s$ [4]. Accepting this equality for the initial stage of the process we obtain $V_m(0) = h(F'_s/F'_v)V_0 P$. For the final stage of the process, that is after the inversion of the phases, similar arguments lead to the expression $V_m(1) = h(F''_s/F''_v)V_0(1 - P)$, in which F''_s and F''_v are the fractal characteristics of the volume and the surface of the liquid oligomer clusters in polymer matrix.

Thus, geometric and fractal approaches lead to similar functional dependences of the volume of the interphase layer from the depth of polymerization. The difference between them is only in the interpretation of thickness of the interphase layer. However, in the geometric approach the linear relation $h = mr$ is not founded, and the thickness of the interphase layer loses its physical meaning.

Evidently the stage of the monolytization and the following inversion of phases can not be considered as the phase transition, which takes place at well defined extent of polymerization, for example $P_k \simeq 0.6$, which corresponds to the close pack of the grains of the same size [1]. Aggregation of the grains begins from the moment of their formation. These aggregates of grains, include in their structure the liquid phase with local areas, where the conversion of the phase has already taken place.

Thus the grows of grains and their aggregation run simultaneously and continuously; in correspondence with the previous analysis the first one increases the volume of the interphase layer according to the law $V_m(0) \sim P$, the second one decreases according to the law $V_m(1) \sim (1 - P)$.

As far as the total form of the dependence V_m from P is unknown, we approximate it with the function

$$V_m = h(F_s/F_v)P(1 - P), \quad (8)$$

in which $F/F_v = F_s F_s''/F_v' F_v''$, and which satisfies the condition of the continuous change of V_m from P has the maximum value at $P = 1/2$ and as the particular cases contain the obtained above expressions for $V_m(0)$ and $V_m(1)$.

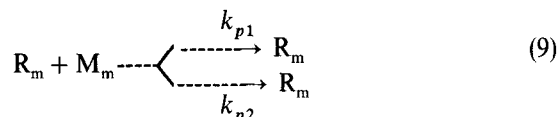
“Catalytical” role of the interphase layer in three-dimensional polymerization, is connected with the decrease of the rate of the chain termination.

In addition, the kinetic order of the reaction on radical concentration changes from the second to the first order. It is possible to indicate several reasons of the observed effect. For example, according to [7, 8], the chain termination is the diffusion – controlled reaction and its rate depends on the mobility of the macroradical. If it decreases so, that the condition $t_d/t_p \gg 1$ is fulfilled, where t_d and t_p are the respective characteristic times of removing of, a) the active center of the macroradical through translation or segmental movement, and b) the reaction of chain growth, the control on the chain cut off rate will go to its growth rate. In this limit the effective constant of rate of chain termination becomes proportional to $k_p[M]$ [8]. Acceleration of the radical polymerization in presence of porous fillers [9] indicates that, the structural pores, formed on aggregation of the dispersed

particles of fillers, represent the micropores that are in accessible to macroradicals. Therefore, the rate of the macroradical decay in these isolated microreactors is determined mainly by the rate of their growth. The same role is assigned to isolated macroreactors in the photopolymerization matrix [10, 11].

Finally note, that the observed first order of the rate of polymerization from the rate of initiation on the surface of the filler of the polymer initiator also finds the explanation in the important contribution of the chain termination by diffusion, that is of the migration of the reaction centers of the macroradicals towards each other on account of their growth [12].

The above factors acting in the interphase layer simultaneously control the growth rate of the chain as well as the rate of its termination. In this case the acts of the chain growth and its termination are the results of the interaction of the radical with the functional group of the oligomer, which may be "alive" or "frozen" radicals



The "alive" radical R_m is able for further growth of the chain, and the "forzen" radical R_z -only for recombination decay.

Thus, according to the scheme (9) the act of the chain growth with the probability $k_{p1}/(k_{p1} + k_{p2})$ forms the "alive" radical, and with the probability $k_{p2}/(k_{p1} + k_{p2})$ - the "frozen" one. With regard to the chain termination represented in (9), the chain growth defined in (6) requires $k_{pm} = k_{p1} + k_{p2}$.

The opposite points of view exist on the gel effect in connection with the rate of the chain growth and the rate of decomposition of the initiator [7, 8, 10, 13].

For the chain growth to be the second order reaction, it appears that the gel effect must take place. The recognition of this fact in this case means only, that due to gel effect in the interphase layer $k_{p1} \neq k_{pf}$. For the initiator decomposition as the second order reaction the gel effect appears most likely through cage effect.

That is through the coefficient of initiation, but not the constant of the rate of decomposition k_d . In this assumption the rate of initiation in the interphase layer and liquid oligomer phase are described by the

expressions: $V_{im} = 2k_d f_m c$ and $V_{if} = 2k_d f_f c$, from which follows the correction: $V_{im} = (f_m/f_f)V_i$, because the $V_{if} = V_i$ is accepted.

The condition of stationarity on the "live" radicals in correspondence with (9) may now be expressed in the form $(f_m/f_f)V_i = k_{p2}[M_m][R_m]$. Using this relation in (6), we obtain $W_m = (f_m/f_f)[(k_{p1} + k_{p2})/k_{p2}]V_i$.

The contribution of the heterophase polymerization with the specific rate W_m the total we write. By taking into account the approximation function (8) for the volume of the interphase interlayer we obtain for the heterophase polymerization with the specific rate W_m

$$V_m W_m = V_0 (f_m/f_f) ((k_{p1} + k_{p2}) k_{p2} h(F_s/F_v) P(1-P) V_i \quad (10)$$

From determinations $P = \Gamma/\Gamma_0$, $\Gamma = ([M]_0 - [M])/[M]_0$, $\Gamma_0 = ([M]_0 - [M]_s)/[M]_0$, where $[M]_s$ – remaining concentration of the unreacted functional groups, it follows that $W = -d[M]/dt = ([M]_0 - [M]_s)dP/dt$. Using this relation in the unifying equation (5) and taking into account its constituents (7) and (10), we obtain the initial kinetic equation (1), in which the physical aspect of the kinetic constants k_1 and k_2 is given by the expressions

$$k_1 = [k_{pf}\Gamma_0/k_{tf}]^{1/2},$$

$$k_2 = h(F_s/F_v)(f_m/f_f)(k_{p1} + k_{p2})/k_{p2}\Gamma_0[M]_0.$$

Thus, taking into account the factor Γ_0 of incomplete run of the three-dimensional polymerization k_1 is the ordinary rate constant of the homophase process of the polymerization in the area of the long chains with a rapid termination.

Conversely, k_2 is not a "true" the rate constant of the polymerization, its value depends on the fractal characteristics of the solid polymer cluster in liquid oligomer phase, and the liquid oligomer clusters in solid polymer matrix. Therefore k_2 is fluctuation – dependent parameter of the process, that determines the poor reproducibility of kinetic measurements [14] and erratic nature [15] of the three – dimensional polymerization.

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