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G. V. Kozlov, G. E. Zaikov, E. Klodzinska,
Richert Jozef

THE FRACTAL KINETICS OF POLYMERIZATION CATALYZED BY NANOFILLERS (PART 2)

Keywords: polymerization, kinetics, catalyst, nanofiller, fractal analysis, strange diffusion.

The fractal analysis of polymerization kinetics in nanofiller presence was performed. The influence of catalyst structural features on chemical reaction course was shown. The notions of strange (anomalous) diffusion conception was applied for polymerization reactions description.

Ключевые слова: полимеризация, кинетика, катализатор, нанонаполнитель, фрактальный анализ, аномальная диффузия.

Был выполнен фрактальный анализ кинетики полимеризации в присутствии нанонаполнителя. Было показано влияние структурных особенностей катализатора на ход химической реакции. Понятие странной (аномальной) диффузии было использовано для описания реакций полимеризации.

Introduction

By Sergeev's definition the nanochemistry is a science field connected with obtaining and studying of physical-chemical properties of particles having sizes of nanometer scale. Let's note that according to this definition polymers synthesis is automatically a nanochemistry part as far as according to the Melikhov's classification polymeric macromolecules (more precisely macromolecular coils) belong to nanoparticles and polymeric sols and gels – to nanosystems. Catalysis on nanoparticles is one of the most important sections of nanochemistry.

The majority of catalytic systems are nanosystems. At heterogeneous catalysis the active substance is tried to deposit on carrier in nanoparticles form in order to increase their specific surface. At homogeneous catalysis active substance molecules have often in them selves nanometer sizes. The most favourable conditions for homogeneous catalysis are created when reagent molecules are adsorbed rapidly by nanoparticles and are desorbed slowly but have high surface mobility and, consequently, high reaction rate on the surface and at the reaction molecules of such structure are formed at which desorption rate is increased sharply. If these conditions are realized in nanosystem with larger probability than in macrosystem, then nanocatalyst has the raising activity that was observed for many systems. In the connection such questions arise as adsorption and desorption rate, surface mobility of molecules and characteristics frequency of reagents interaction acts depend on the size, molecular relief and composition of nanoparticles and the carrier.

The presence paper purpose it the application of fractal analysis for description of polymerization kinetics in nanofiller presence.

Results and Discussion

In previous part of the article the solid-state imidization reactions were represented [1]. Let's consider the interfacial interactions problem of PI forming macromolecular coil and Na^+-montmorillonite on nanofiller surface. As Pfeifer shows [2], a macromolecular coil on hard surface changes its configuration (structure), which can be characterized by its fractal dimension D_f. This change is described with the help of the following equation [2]:

$$\frac{d_{surf} D_f^{sol}}{D_f} = d_{surf}^0, \qquad (1)$$

where d_{surf} and d^0_{surf} are fractal dimensions of nanofiller surface in nanocomposite and in initial state, respectively, D_f^{sol} and D_f are fractal dimensions of PI macromolecular coil in solution (the blending of PAA and Na^+-montmorillonite was carried out in N,N-dimethylacetamide solution [3]) and in solid-phase state on nanofiller surface, respectively.

Let's consider the estimation of the parameters including in the equation (1). As it was shown in paper [4], a polymer chain, possessing by finite rigidity and consisting of statistical segments of finite length, was not capable to reproduce growing surface roughness at d^0_{surf} increase and at d^0_{surf} >2.5 the value d_{surf} is determined as follows [5]:

$$d_{surf} = 5 - d_{surf}^0. \qquad (2)$$

For Na^+-montmorillonite the value d^0_{surf} is determined experimentally and equal to 2.78 [6]. The value D_f^{sol} can be accepted in the first approximation equal to macromolecular coil dimension in a good solvent (D_f^{sol} =1.667 [7]). Then the estimation according to the equation (1) gives D_f=1.33. It is obvious, that this dimension of the macromolecular coil, stretched on Na^+-montmorillonite surface will be designated further as D_f^0.

The calculation of real values of macromolecular coil fractal dimension D_f for the first order reaction, which is solid-state imidization [3], can be fulfilled with the help of the equation:

$$t^{(D_f-1)/2} = \frac{c_1}{k_1(1-Q)} \qquad (3)$$

In other words the calculation according to this equation shows that for the studied imidization reactions the condition $D_f^0 < D_f$ is fulfilled. Such relation allows to assume that only part of PI macromolecular coils interacts with Na^+-montmorillonite surface. This is confirmed by the data of Fig. 1, where the difference $\Delta D_f = D_f - D_f^0$ is plotted on the graph as a function of nanofiller contents W_c for four imidization temperatures. As it follows from this Figure plots, the

ΔD_f value decreases at W_c growth or $D_f \to D_f^0$ and these plots extrapolation shows, that at $W_c \approx 17.5$ mass. % $D_f = D_f^0$ or $\Delta D_f = 0$. Let's note, that the indicated value W_c is true only for exfoliated (nonaggregated) nanofiller.

The ΔD_f decrease at W_c growth assumes the interacting phase fraction φ_{int} increase in the imidization process. The value φ_{int} can be determined according to the mixtures law from the equation [8]:

$$D_f = \varphi_{int} D_f^0 + (1 - \varphi_{int}) D_f', \tag{4}$$

where D_f' is the macromolecular coil fractal dimension in nanofiller absence.

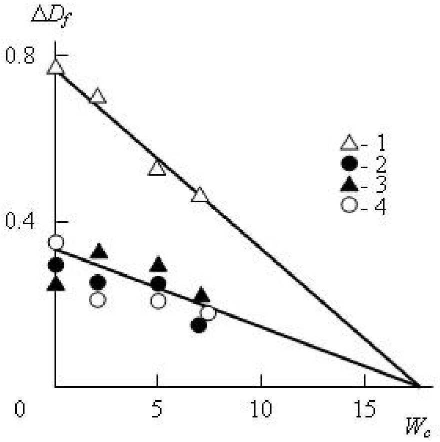

Fig. 1 - The dependences of the fractal dimension difference $\Delta D_f = D_f - D_f^0$ on nanofiller contents W_c for nanocomposites polyimide/Na$^+$-montmorillonite at imidization temperatures: 423 (1), 473 (2), 503 (3) and 523K (4) [8]

In Fig. 2 the dependence $\varphi_{int}(W_c)$ for T_i=423K is adduced. As one can see, this correlation is linear, passes through coordinates origin and is described analytically by the following empirical equation [8]:

$$\varphi_{int} = 0.0575 W_c, \tag{5}$$

where W_c is given in mass. %.

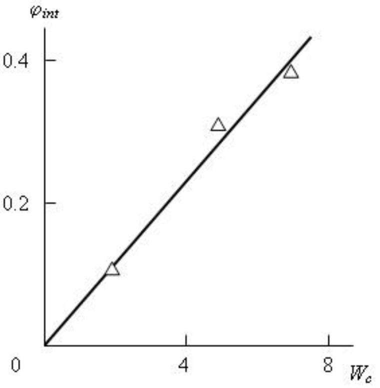

Fig. 2 - The dependence of interacting phase relative fraction φ_{int} on nanofiller contents W_c for nanocomposites polyimide/Na$^+$-montmorillonite at imidization temperature 423K [8]

It is obvious, that at W_c =17.5 mass.%, obtained by plots of Fig. 1 extrapolation, the value φ_{int} =1.0, i.e. in an imidization reaction the entire reactionary system PAA-Na$^+$-montmorillonite is influenced.

In Fig. 3 the dependence of reaction rate constant k_1 on interacting phase relative fraction φ_{int}, is adduced which turns out approximately linear and shows k_1 growth at φ_{int} increase. This allows to assume the direct dependence of solid-phase imidization rate on interfacial interactions level in the reactionary system [8].

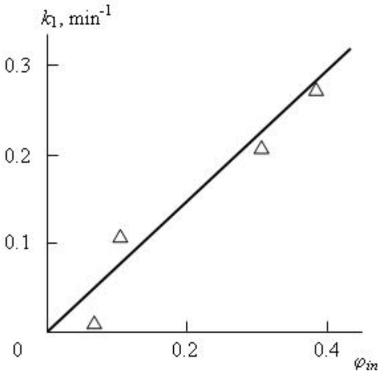

Fig. 3 - The dependence of the first order reaction rate constant k_1 on relative fraction of interacting phase φ_{int} for nanocomposites polyimide/Na$^+$-montmorillonite at imidization temperature 423K [8]

In paper [3] the reduction of imidization process activation energy E_{act} at W_c increase was found out – from 66 up to 51 kj/mole within the range W_c =0-7 mass.%. Earlier the authors [9] offered the following dependence of E_{act} on D_f in case of polyarylate thermooxidative degradation:

$$E_{act} = 16.6 D_f^2 - 2.8 D_f. \tag{6}$$

In table 1 the comparison of experimental E_{act} and calculated according to the equation (6) E_{act}^{th} activation energy values of solid-state imidization is adduced. As one can see, a good correspondence between the indicated values of activation energy is obtained (the average discrepancy of E_{act} and E_{act}^{th} makes less than 5%). This means, that association energy (imidization reaction) and dissociation one (thermooxidative degradation) are approximately equal, that was to expected.

Table 1 - The comparison of experimental E_{act} and calculated according to the equation (6) E_{act}^{th} values of solid-state imidization process activation energy [8]

W_c, mass. %	E_{act}, kj/mole	E_{act}^{th}, kj/mole
0	66.0	68.6
2	57.5	63.4
5	54.0	52.8
7	51.5	49.3

Hence, the results obtained above have demonstrated again that the cause of imidization process acceleration at nanofiller contents growth is macromolecular coil structure change owing to its interfacial interactions with Na$^+$-montmorillonite surface. The interacting phase relative fraction increases at nanofiller contents raising and at its content about 17.5 mass.% this phase ocuppies the entire reactionary system. The imidization process activation energy reduction at nanofiller contents increase is also due to structural factors, namely, to a macromolecular coil fractal dimension decrease.

The authors [3] have found out that the kinetic curves $Q(t)$ have typical shape for polymerization reactions with autodeceleration showing imidization rate reduction as time is passing [1]. As it is known [10], such curves $Q(t)$ are specific for the reaction course in heterogeneous medium and are described by a simple relationship [10]:

$$\frac{dQ}{dt} \sim t^{-h}, \qquad (7)$$

where h is heterogeneity exponent ($0<h<1$), turning into zero for homogeneous (Euclidean) mediums; incidentally the behavious is classical: dQ/dt = const.

The mentioned relationship supposes strong effect of this heterogeneity degree characterized by exponent h on reaction rate. Therefore the authors [9, 11] undertake an attempt of clarification of the reactionary medium heterogeneity physical significance in case of PAA solid-phase imidization and the factors defining the medium heterogeneity exponent value.

The solid-phase imidization reactions were shown earlier [1]. The obtained dependences are linear and according to their slope the value of spectral dimension d_s characterized reactionary medium connectivity can be obtained. T_i increase within the range 423-523K results to substantial growth of d_s: from 0.42 up to 1.68. Let's note that such d_s increase occurs without reactionary mixture composition change. This means, that the energetic restrictions result to the appearance of fractal space, in which instead of the value d_s an effective spectral dimension d_s' must be used, reflecting the existence of the restrictions mentioned above and connected with d_s by the equation [10]:

$$d_s' = \beta_j d_s, \qquad (8)$$

where β_j is the parameter, characterizing distribution of reagents "jumps" (displacements) times.

From the dependence $h(T_i)$ [1] one can see that fast decrease h or reduction of reactionary medium heterogeneity at T_i raising follows. At $T_i \approx 540$K exponent $h=0$, i.e. reactive medium becomes homogeneous. Since for PI $T_g \approx 533$K, then, as it was expected [12], that the reactionary medium in case of solid-phase imidization became homogeneous (Euclidean) at glass transition. The shape of the curve $h(T_i)$ [1], i.e. h goes to zero at temperature raising, assumes, that the fractal-like effects, namely, d_s' variation, are connected with energetic disorder [10]. In such case the energetic state of polymer structure can be characterized by an excess energy localization regions dimension D_f^e [13]. The value D_f^e can be estimated according to the following equation [14]:

$$D_f^e = \frac{4\pi T_i}{\ln(1/f_g)T_g}, \qquad (9)$$

where f_g is a relative fluctuational free volume.

In Fig. 4 the dependence $h(D_f^e)$ is adduced, from which the expected result: follows polymer structure energetic excitation degree raising, due to thermal energy "pumping" at T_i increase, results to h reduction. At $D_f^e \approx 6.3$ the reactionary medium becomes homogeneous ($h=0$).

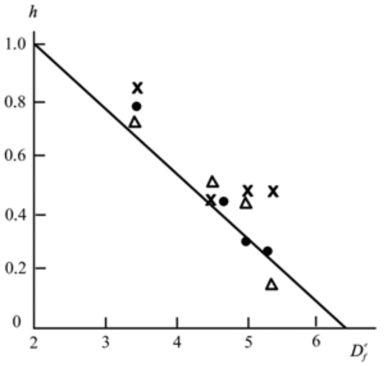

Fig. 4 - The dependence of heterogeneity exponent h of reactionary medium on excess energy localization regions dimension D_f^e for PAA solid-phase imidization at Na$^+$-montmorillonite contents W_c: 0 (1), 2 (2) and 5 (3) mass.% [11]

Therefore, the data of Fig. 4 and the curve $h(T_i)$ [1] give the answer to the question, at what conditions $h=0$, i.e. when the reactionary medium becomes homogeneous. Nevertheless, the physics of this process remains vague. The glass transition gives singularities neither in f_g behavior nor in D_f^e behavior. Therefore for the explanation of heterogeneous↔homogeneous medium transition let's use representations of the conception of fractal (local) free volume f_g^{fr}. According to this conception free volume microvoid is necessary to simulate not by three-dimensional sphere, as it was accepted in classical polymer physics [15], but by D_f^e-dimensional sphere with the volume ν_h^{fr}. The value ν_h can be estimated as follows [14]:

$$\nu_h^{1/3} = \left(\frac{T_m - T_i}{T_m}\right)^{-\nu}, \qquad (10)$$

where percolation index ν was accepted equal to 0.85 [16].

Further from geometrical considerations in the assumption of three-dimensional microvoid of free volume its radius r_h can be estimated and then ν_h^{fr} can be calculated according to the equation [11]:

$$\nu_h^{fr} = \frac{\pi^{D_f^e/2} r_n^{D_f^e}}{\left(D_f^e/2\right)!}, \qquad (11)$$

where r_n is radius of free volume microvoid.

In Fig. 5 the dependence $h(f_g^{fr})$ is adduced where value f_g^{fr} was calculated according to the equations (9), (10) and

$$f_g^{fr} = f_g \frac{\nu_h^{fr}}{\nu_h}, \qquad (12)$$

where relative fraction of fluctuational free volume f_g can be accepted equal to 0.060 for solid-phase polymers [12].

As it follows from the data of this Figure, value $h=0$ or reactionary medium homogeneity at $f_g^{fr} = 0.34$ is achieved. Let's remind that the mentioned value f_g^{fr} corresponds to percolation threshold for overlapping spheres [17]. In other words, at f_g^{fr} =0.34 fluctuational free volume microvoids, simulated by D_f – dimensional sphere, form continuous percolation network or continuous diffusion channels [18]. Therefore, between heterogeneous and homogeneous reactionary medium, at any rate, in case of solid-phase imidization, qualitative difference exists. For heterogeneous reactionary medium dehydration product (water molecule), which is in a free volume microvoid, is forced to expect the opening of overlapping it neighbouring microvoid, after that it makes “jump” from the first to the second and further the process repeates. For homogeneous reactionary medium such process of “expectation” is not required by virtue of the existence of through percolation channels of free volume. Let’s note, that the mentioned processes of “jumps” are realized on local level. The indicated effect is the cause of diffusive processes intensification in solid-phase imidization course, which was mentioned above.

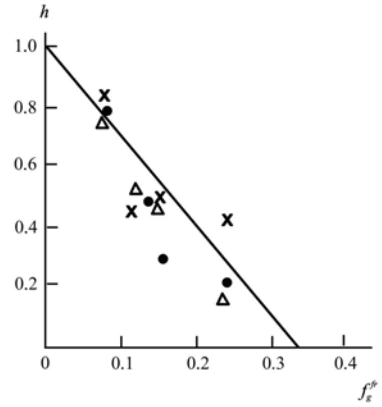

Fig. 5 - The dependence of heterogeneity exponent *h* of reactionary medium on relative fractal free volume f_g^{fr} for PAA solid-phase imidization. The notation is the same, that in Fig. 4 [11]

And lastly, in Fig. 6 the dependence of coefficient β_j in the equation (2) on f_g^{fr} is adduced. Again the value β_j reaches its limiting magnitude β_j =1 (i.e. $d_s'=d_s$) at f_g^{fr} =0.34. The relationship between β_j and f_g^{fr} is given by the simple empirical equation [11]:

$$\beta_j = 2.94 f_g^{fr}. \qquad (13)$$

The plot of Fig. 6 demonstrates that the energetic restriction, defining transition from d_s to d_s', is the necessity of “jumps” of reaction product or reagents between free volume microvoids. It is clear, that T_i raising decreases “jump” expectation time and the formation of through percolation channels of free volume microvoids cancels these restrictions.

Hence, the results considered above demonstrated that the notion of reactionary medium heterogeneity in case of solid-phase imidization was connected with free volume representations that were expected for diffusion-limited solid-phase reactions. If free volume microvoids are not connected with one another, then medium is heterogeneous, and in case of formation of overlapping percolation network of such microvoids it’s homogeneous. To obtain such definition is possible only within the framework of the fractal free volume conception.

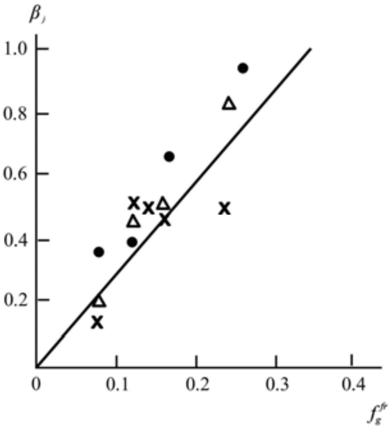

Fig. 6 - The dependence of the coefficient β_j in the equation (8) on relative fractal free volume f_g^{fr} for PAA solid-phase imidization. The notation is the same that in Fig. 4 [11]

As it was shown in paper [3], the temperature imidization T_i raising within the range 423-523K and the nanofiller contents W_c increase within the range 0-7 mass.% results to essential imidization kinetics change expressed by two aspects: by an essential increase of reaction rate (reaction rate constant of the first order k_1 increases almost on two orders) and by raising of conversion (imidization) limiting degree $Q_{\lim}$ almost: from 0.25 for imidization reaction without nanofiller at T_i =423K up to 1.0 at Na^+-montmorillonite content 7 mass. % and T_i =523K. Let’s also remind, that all kinetic curves $Q(t)$ for the indicated imidization reactions have typical shape of curves with autodeceleration [1], characteristic for fractal reactions, i.e. either fractal objects reactions, or reactions in fractal spaces [19]. In other words, the indicated imidization reaction aspects in sufficient degree have general character. If for the first effect (k_1 increase) the authors [3] offered probable chemical treatment considering nanofiller as a catalyst, then the second effect ($Q_{\lim}$ raising) did not obtain any explanation, although its theoretical and practical significance is obvious. Therefore the authors [20] offered structural treatment of limiting conversion degree in solid-phase imidization process based on the general principles of fractal analysis [19].

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© **G. V. Kozlov** – ст. науч. сотр. каф. высокомолекулярных соединений, Кабардино-Балкарский госуд. ун-тет **G. E. Zaikov** – д.х.н., проф., Институт биохимической физики им. Н.М. Эмануэля РАН, проф. каф.ТПМ КНИТУ, ov_stoyanov@mail.ru; **E. Klodzinska** – проф., Institute for Engineering of Polymer Materials and Dyes, Torun, Poland; **Richert Jozef** – проф. Institute for Engineering of Polymer Materials and Dyes, Torun, Poland.