

Description of the Model Transesterification Reaction Within the Framework of a Strange Diffusion Concept

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ABSTRACT: There is a principal difference between the descriptions of general reagent diffusion and diffusion defining the course of a chemical reaction. The latter process is described within the framework of a strange (anomalous) diffusion concept and is controlled by the active (fractal) reaction duration. The

exponent α , which defines the active duration in comparison with the real time, is dependent on the reagent structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2791–2794, 2008

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INTRODUCTION

One possible way of searching for effective inorganic filler/catalyst combinations for complex polyesters is the kinetic study of a transesterification model reaction performed in the presence of various inorganic compounds.¹ This method allows the obtained results to be used in the synthesis of filled complex polyesters.²

Synthesis processes commonly can be considered complex systems of self-organization, developing over time, that lead to the formation of time-dependent fractal structures.³ In such reactions, the important role is played by diffusive processes, which in the considered case have a very specific nature. This specificity is due to the fact that in chemical reactions, not all reagent contacts occur with proper orientation of the reacting molecules for the product formation. This aspect of the reaction is explained by the steric factor p ($p \leq 1$).⁴ The variation of p can lead to changes in the type of diffusion and the structure of the reaction product, and as a result, the rate of the chemical reaction can change. This can be explained by a simple example. As is known,⁵ the characteristic size of a region $[r(t)]$ that can be visited by the reagent molecule during time t can be described as follows:

$$r(t) \sim t^{1/(2+\theta)} \quad (1)$$

where θ is the connectivity index of the reactive medium.

For the case of classical Gaussian diffusion, $\theta = 0$, and if $r(t) = 2$ and $t = 4$ relative units, equality within the framework of relationship (1) can be obtained. Such equality assumes $p = 1$; that is, each contact of reagent molecules results in the formation of the reaction product. Let us assume that the value of p decreases up to 0.05; that is, only 1 of 20 contacts of reagent molecules forms a new chemical species. This means that t increases 20 times, and then at $r(t) = 2$ and $t = 80$ relative units, $\theta = 4.33$ will be obtained from relationship (1). θ is connected to the dimensions of the walk trajectory of the reagent molecules (d_w) by the following simple equation:⁵

$$d_w = 2 + \theta \quad (2)$$

Therefore, an increase in θ results in an increase in d_w ; that is, it slows down the chemical interaction process.

In turn, the value of d_w is connected to the Hurst exponent (H) by the following equation:⁵

$$d_w = \frac{1}{H} \quad (3)$$

A change in θ from 0 to 4.33 results in d_w increasing from 2 (Brownian motion) to 6.33 according to eq. (2), and it also results in a reduction of H from 0.5 to 0.158 according to eq. (3). As is known,⁵ subdiffusive (slow) transport processes correspond to $0 \leq H \leq 0.5$, and classical Gaussian diffusion corresponds to $H = 0.5$. Therefore, a decrease in p from 1.0 to 0.05 results in a qualitative change in the diffusion type too: it changes from classical Gaussian diffusion to anomalous (strange) diffusion. The aforementioned transition can occur without a change in the general diffusive processes in the

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reactive medium too because it is due to the rejection of all diffusive phenomena not resulting in a chemical reaction, that is, the formation of a new chemical substance. On this basis, the purpose of this article is to study the influence of diffusive processes within the framework of the offered treatment on the main characteristics of the transesterification model reaction.

EXPERIMENTAL

The kinetics of the transesterification model reaction of methyl benzoate with heptanole-1 in the presence of mica were studied at 443 K. The catalytic activity of mica was determined on the basis of the observed first-order rate constant (k_1) with a 20-fold excess of heptanole-1 and a mica concentration of 30 mass % with respect to methyl benzoate.²

The transesterification kinetics were studied on a Biokhrom gas chromatograph with diphenyl oxide as the internal standard according to a method described earlier.¹ The rate constant k_1 was calculated according to the equation of the irreversible reaction of the first order.

Flagopit mica with a polydispersity of 0.749 and average probable particle size of 0.23×10^{-6} m supplied by the firm General Electric, was used. The initial mica (NMM), mica chemically modified by sodium hydroxide (SMM), and mica chemically modified by sulfur acid (AMM) were applied.

RESULTS AND DISCUSSION

Elsewhere,⁶ it has been shown that for a reaction of the type



where A and B are reagents of a different kind. The following scaling relationship is true:

$$\rho_A \sim t^{D/4} \quad (5)$$

where ρ_A is the concentration of particles surviving in the reaction, t is the reaction duration, and D is the dimension controlling the course of the reaction.

For the course of the reaction in Euclidean space, D is equal to the dimension of this space (d), and for fractal spaces, D is accepted to be equal to the spectral dimension (d_s).⁶ By plotting $\rho_A = (1 - Q)$ (where Q is the degree of conversion) as a function of t in log-log coordinates, we can determine the value of D from the slopes of these plots. These plots can be divided into two linear parts: at $t < 100$ min, the slope is small, and at $t > 100$ min, the slope essentially increases. In this case, the value of d_s varies within the limits of 0.069–3.06. Because these reactions proceed in Euclidean space, which is indicated by the linearity of

the kinetic curves of Q versus t , the reesterification reaction proceeds in a specific medium with Euclidean dimension d but with a connectivity degree, characterized by d_s , typical for fractal spaces.⁵

Zelenyi and Milovanov⁵ formulated a fractional equation for transport processes:

$$\frac{\partial^\alpha \psi}{\partial t^\alpha} = \frac{\partial^{2\beta}}{\partial r^{2\beta}} (B\psi) \quad (6)$$

where $\psi = \psi(t, r)$ is the distribution function of particles, $\partial^{2\beta}/\partial r^{2\beta}$ is a Laplacian operator in d -dimensional Euclidean space, B is the relation of the transport generalized coefficient and d , and t^α is the active time. The introduction of a fractional derivative ($\partial^\alpha/\partial t^\alpha$) allows us to account for the effects of memory (α) and nonlocality (β) in the context of common mathematical formalism.⁵ The introduction of $\partial^\alpha/\partial t^\alpha$ into the kinetic equation [eq. (6)] allows us to account for random walks in fractal time (RWFTs), that is, the temporal component of the strange dynamic processes in turbulent media.⁵ The absence of any noticeable jumps in the particle behavior serves as the distinctive feature of RWFTs; in this case, the root-mean-square displacement [$\langle r^2(t) \rangle$] increases with t as t^α . The parameter α has a sense of the fractal dimension of active time, in which real walks of particles look like random processes; the interval of active time is proportional to t^α .⁵

In turn, the exponent 2β in eq. (6) accounts for instantaneous jumps of particles (Levy flights) from one region of turbulence to another. The existence of turbulence zones in a transesterification reaction follows from the necessity of intense mixing of reactive medium both owing to the inert gas passing and to the mechanical stirring. Therefore, the exponent relation α/β gives the relation of RWFT contact frequencies and Levy flights. The value of β in the first approximation can be adopted as a constant, and then the relation α/β will be inversely proportional to the waiting time of the chemical reaction.

According to the concrete value of α , persistent (superdiffusive, $1 < \alpha \leq 2$) and antipersistent (subdiffusive, $0 \leq \alpha < 1$) processes can be distinguished. In the case of antipersistent processes, the active time represents itself as Cantor's set ($0 \leq \alpha < 1$), consisting of breaks at any point of the t ray. Breaks correspond to those time moments at which particles stick for just another time in a turbulent field. On the contrary, persistent processes assume a faster course ($1 < \alpha \leq 2$) of active time in comparison with real time t .⁵ The value of α/β can be determined according to the following relationship:⁵

$$\frac{\alpha}{\beta} = \frac{d_s}{d} \quad (7)$$

We assume that the dependence of Q on t^α should be linear, and according to these considerations, we

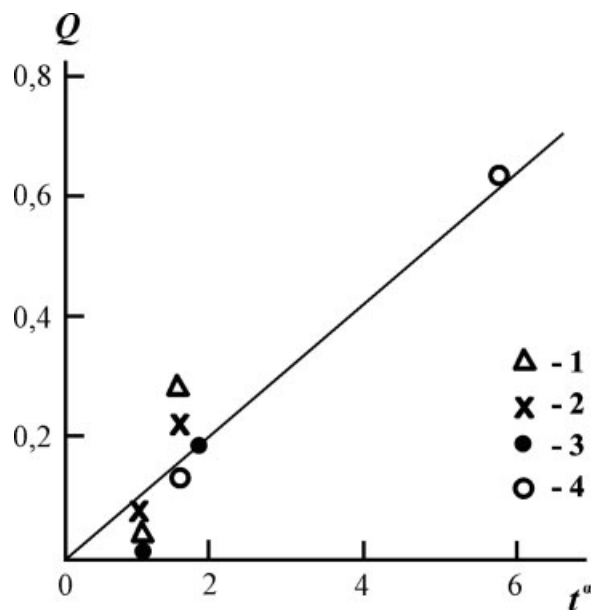


Figure 1 Dependence of Q at $t = 60$ min and $t = 300$ min on t^α for the transesterification reaction (1) without mica and (2–4) in the presence of NMM, SMM, and AMM, respectively.

choose the β value of 0.25. Constructed by the indicated method, the dependence at $t = 60$ min and $t = 300$ min is deduced in Figure 1. It is approximately linear and passes through the origin of the coordinates. Attention is attracted by the fact that t^α is much smaller (50–150 times) than real time t . Although this difference is due to the chosen value of β and consequently α , it is close to reality. Therefore, for transesterification in the presence of NMM and SMM, $Q \approx 0.20$ is achieved in 300 min, whereas in other polycondensation reactions under analogous conditions, synthesis is practically complete within 20 min;⁷ that is, it proceeds approximately 60 times faster. Analytically, the relationship $Q(t^\alpha)$ for transesterification reactions can be expressed as follows:

$$Q = 0.108t^\alpha \quad (8)$$

Let us further consider the question of which parameters define the values of α and hence t^α . As is known,⁵ α/β is connected to exponent μ at t in the generalized transport equation as follows:

$$\frac{\alpha}{\beta} = \mu \quad (9)$$

In turn, μ and H are connected to each other as follows:⁵

$$\mu = 2H \quad (10)$$

Under definite conditions, the value of H is defined only by dimension D_f (Euclidean or

fractal) of the reaction product (heptyl benzoate molecule):⁸

$$H = 2 - D_f \quad (11)$$

The combination of eqs. (9)–(11) allows us to obtain a simple theoretical relationship between α and D_f (at $\beta = 0.25$):

$$\alpha = 0.5(2 - D_f) \quad (12)$$

The value of dimension D_f can be determined with the aid of the following equation:⁹

$$t^{(D_f-1)/2} = \frac{c_1}{k_1(1-Q)} \quad (13)$$

where c_1 is a constant estimated from boundary conditions and is accepted here to be equal to $8 \times 10^{-4} \text{ c}^{-1}$.

The value of D_f characterizes reagents (methyl benzoate and heptanole-1) and the final product of the transesterification reaction (heptyl benzoate) structure. The variation of D_f is 1.48–1.96. In Figure 2, the values of α calculated according to eqs. (9) and (12) are compared as the function of D_f is deduced. As expected, an increase in α with a reduction of D_f can be observed, along with a good correspondence of the calculations according to the two equations. This means that the values of α and hence t^α are defined by the reagent structure in the transesterification reaction process.

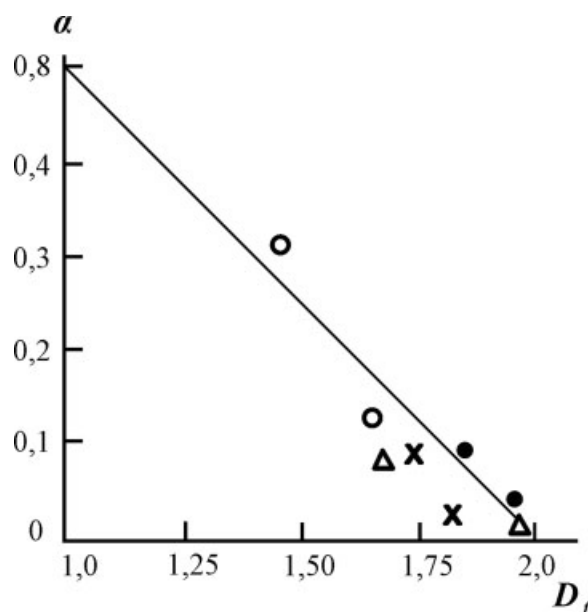


Figure 2 Dependence of exponent α , calculated according to eqs. (9) (symbols) and (12) (solid line), on the reagent molecule dimension (D_f) for the transesterification reaction (see Fig. 1 for the definitions of the symbols).

The data of Figure 2 demonstrate that with $\beta = 0.25$, in the course of the transesterification reaction, only antipersistent (subdiffusive) transport processes are possible ($\alpha = 1$ is achieved for low-molecular-weight substances with $D_f = 0$ only); that is, the active time is always less than the real time. This indicates the important role of Levy flights in the definition of strange diffusion.

CONCLUSIONS

The results of this article show that there is a principal difference between the description of general reagent diffusion and the diffusion defining the course of a chemical reaction. The last process is described within the framework of a strange (anomalous) diffusion concept and is controlled by the active (fractal) reaction duration. The exponent α , defining

the value of the active duration in comparison with the real time, is dependent on the reagent structure.

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