Role of Diffusion Processes in a Model Reaction of Reesterification

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ABSTRACT: A model of diffusion processes for chemical reactions is shown to describe well the main characteristics of a model reaction of reesterification. The structure of the reaction product (a heptylbenzoate molecule) and the formation of its parts are the main factors controlling the diffusion processes in this case. The processes are described within the framework of strange (anomalous) diffusion. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2837–2840, 2007

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INTRODUCTION

One potential way of searching for effective inorganic filler catalysis for complex polyethers is the investigation of the kinetics of a model reesterification reaction performed in the presence of various inorganic compounds.[1] This method allows us to use the obtained results for the synthesis of filled complex polyethers.[2]

In general, synthesis processes can be considered complex self-organization systems evolving over time. This results in the formation of time-dependent fractal structures.[3] Diffusion processes play a very important role in such reactions, which have a very specific nature in the considered case. This specificity is due to the fact that not all reagents in chemical reactions take place with orientation for the proper reaction product formation of the reacting molecules. This aspect of the reaction is taken into account by steric factor p ($\leq$1).[4] The variation of p can result in changes in the diffusion type, structure, and reaction product and, consequently, in changes in the rate of the chemical reaction. This question can be explained by a simple example. As is well known,[5] the characteristic size of the region [$r(t)$] that can be visited by the reagent molecule during time t can be determined as follows:

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

where θ is the connectivity index of the reaction medium.

For classical Gaussian diffusion, θ is 0, and if $r(t)$ is 2 and t is 4 for the relative units, the equality within the framework of eq. (1) will be obtained. Such an equality assumes $p = 1$; that is, each contact of reagent molecules results in reaction product formation. Let us assume that p decreases to 0.05; that is, only one of 20 contacts of reagent molecules forms a new chemical type. This means that with 20 increases in t, at $r(t) = 2$ and $t = 80$ relative units, from eq. (1), $\theta = 4.33$ will be obtained. θ is connected to the dimension of the walk trajectory of reagent molecules (d_w) by this simple equation:[5]

$$d_w = 2 + \theta \tag{2}$$

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

In turn, d_w is connected to the Herst exponent (H) as follows:[5]

$$d_w = \frac{1}{H} \tag{3}$$

The 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 in H decreasing from 0.5 to 0.158 according to eq. (3). Subdiffusion (slow) transport processes are known to correspond to $0 \leq H < 0.5$, and classical Gaussian diffusion corresponds to $H = 0.5$.[5] Therefore, p decreasing from 1.0 to 0.05 results in a qualitative change of the diffusion type too: it changes from Gaussian classical to anomalous (strange). The aforementioned transition can happen without changes in the general diffusion processes in the reactive medium because it is due to the rejection of all diffusion phenomena, not resulting in a chemical reaction, that is, in the formation of a new chemical substance. On this

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basis, the purpose of this article is to study the influence of diffusion processes within the framework of the offered treatment on the main characteristics of a model reesterification reaction.

EXPERIMENTAL

The kinetics of a model reesterification reaction of methylbenzoate with heptanole-1 in the presence of mica was studied at 443 K. The catalytic activity of mica was determined from the first-order rate constant (k_1) at the twentieth multiple of an excess of heptanole-1 and with a mica concentration of 30 mass % for the calculation on methylbenzoate.[2]

The reesterification kinetics were studied with a Biokhrom gas chromatograph (Experimental Works, Moscow, Russia) with diphenyl oxide as an internal standard according to a method described earlier.[1] k_1 was calculated according to the first-order equation of the irreversible reaction.

A mica flagopit with a polydispersity of 0.749 and an average probable particle size of 0.23×10^{-6} m was used. The initial mica (NMM) and mica chemically modified by sodium hydroxide (SMM) and sulfur acid (AMM) were applied.

RESULTS AND DISCUSSION

Previously,[6] it has been shown that for a reaction of the following type

$$A + B \rightarrow \text{Inert product} \qquad (4)$$

this scaling relationship is true:

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

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

If the reaction occurs in Euclidean spaces, D is equal to the dimension of this space (d), and for fractal spaces, D is equal to the spectral dimension (d_s).[6] Through the graphing of $\rho_A = (1 - Q)$ (where Q is the degree of conversion) as a function of t in double logarithmic coordinates, the value of D can be determined from the slopes of the graph. This graphs 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, d_s varies within the limits of 0.069–3.060. Because these reactions occur in Euclidean space, as indicated by the linearity of the Q–t kinetic curves, this means that the reesterification reaction occurs in a specific medium with Euclidean dimension d but with a connectivity degree, characterized by d_s, typical for fractal spaces.[5]

Zelenyi and Milovanov[5] formulated a fractional equation of transport processes:

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

where $\psi = \psi(t,r)$ is the distribution function of the particles, $\partial^{2\beta}/\partial r^{2\beta}$ is a Laplacian operator in d-dimensional Euclidean space, and B is the relation of the transport generalized coefficient and d. The introduction of fractional derivatives $\partial^\alpha/\partial t^\alpha$ and $\partial^{2\beta}/\partial r^{2\beta}$ allows us to account for the effects of memory (α) and nonlocality (β) in the context of a common mathematical formalism.[5]

The introduction of $\partial^\alpha/\partial t^\alpha$ into the kinetic equation [eq. (6)] allows us to take into account random walks in fractal time (RWFT), the time component of strange dynamic processes in turbulent media.[5] The absence of any noticeable jumps in the particle behavior serves as a distinctive feature of RWFT; in this case, the root-mean-square displacement [$\langle r^2(t) \rangle$] increases with t as t^α. The parameter α has the 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, exponent 2β in eq. (6) takes into account instantaneous jumps of particles (Levy flights) from one region to another. Therefore, the exponent relation α/β relates the RWFT contact frequencies and Levy flights. β in the first approximation can be adopted as
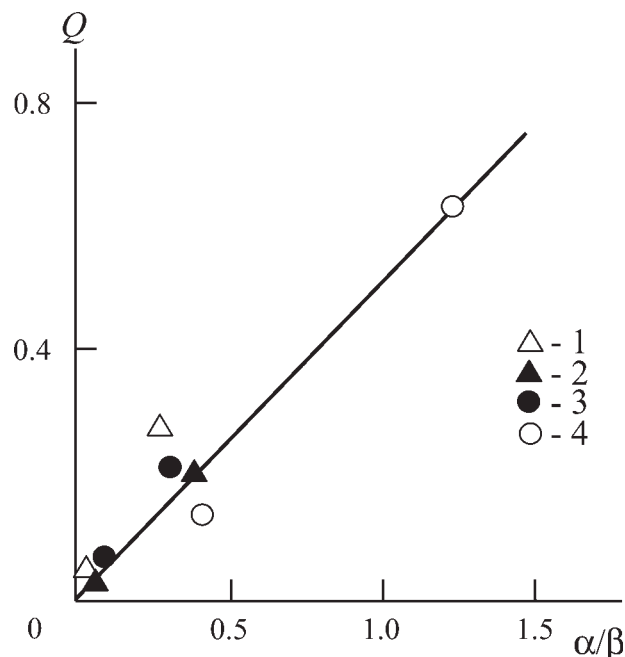
Figure 1 Dependence of Q at $t = 60$ min and $t = 300$ min on the relationship of exponents α and β of eq. (6) for reesterification reactions (1) without mica, (2) with NMM, (3) with SMM, and (4) with AMM.
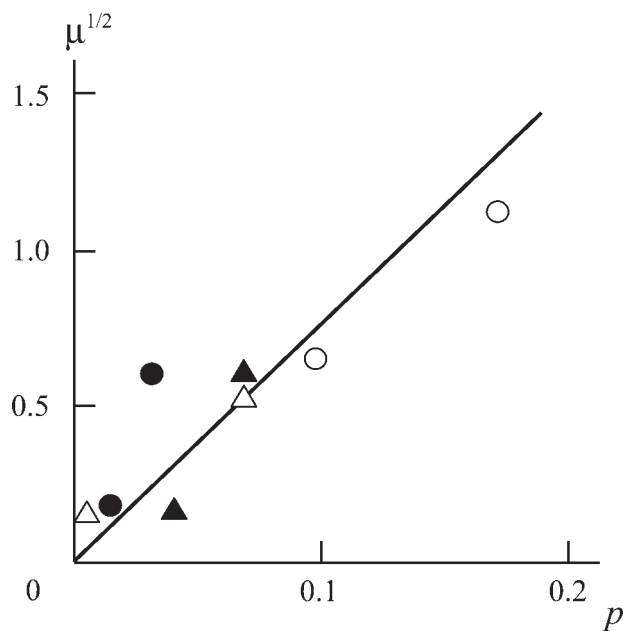
Figure 2 Dependence of μ on p for reesterification reactions (see Fig. 1 for the notation).

a constant, and then relation α/β will be inversely proportional to the waiting time of the chemical reaction realization. α/β is equal to[5]

$$\frac{\alpha}{\beta} = \frac{d_s}{d} \tag{7}$$

In Figure 1, the dependence of Q on α/β for the boundary times of the previously mentioned parts of dependence $\ln(1 - Q) - \ln t$ ($t = 60$ or 300 min) is shown. A linear correlation of $Q(\alpha/\beta)$ passing through the origin coordinates, with increasing Q as α increases, is obtained. Therefore, the larger active time t^{α} is, the more intensively the reaction elapses; this in general has been expected.

Next, we consider the influence on the diffusion processes in the course of the chemical reaction of p, the value of which can be estimated according to the following equation (at $t = 10600$ s):[7]

$$p = \frac{1.6}{10,600^{(D_f - 1)/2}} \tag{8}$$

where D_f is dimension of reesterification product (molecule of heptylbenzoate), determined with the aid of the equation:[8]

$$t^{(D_f - 1)/2} = \frac{C_1}{k_1(1 - Q)} \tag{9}$$

where C_1 is constant, determined according to the boundary conditions and adopted in this article equal to 8×10^{-4} s^{-1}.

In Figure 2, the dependence of $\mu^{1/2} = (\alpha/\beta)^{1/2}$ on p (such form of correlation was chosen with the purpose of its linearization) is shown. It is obvious that the correlation $(\alpha/\beta)^{1/2}(p)$ is actually linear and passes through the origin of coordinates. As it has been assumed above this points out that the diffusion processes in the course of reesterification reaction are controlled by the probability of new chemical substance formation, that is, molecule of heptylbenzoate.

Because μ is equal to $2H$,[5] then according to eq. (3) the value d_w or, more strictly, effective value d_w can be calculated. In Figure 3, the dependence $d_w(p)$ is shown, which has a very nonlinear form that can be relatively divided into three parts. For small values of $p < 0.025$, large values of $d_w \approx 10$–60 can be obtained, and, correspondingly, large values of $D_f \approx 2.13$ can be obtained. This value of D_f corresponds to a chemically limited mechanism of cluster–cluster aggregation ($D_f = 2.11$), which is characterized by a small probability of clusters sticking together or, in other words, by small values of p.[9] At $p = 0.025$–0.10, the d_w range is 2–10, and D_f decreases on average up to 1.71, which corresponds to a diffusion-limited mechanism of cluster–cluster aggregation ($D_f = 1.75$).[9] At last, a decrease in d_w to less than 2, that is, the approach of the particle trajectories to linearity with $d_w = 1$, results in the formation of a heptylbenzoate molecule with $D_f < 1.5$. This value of D_f corresponds to a transparent macromolecular coil dimension;[10] that is, the molecules of the reagents can freely pass through one another at such dimen-
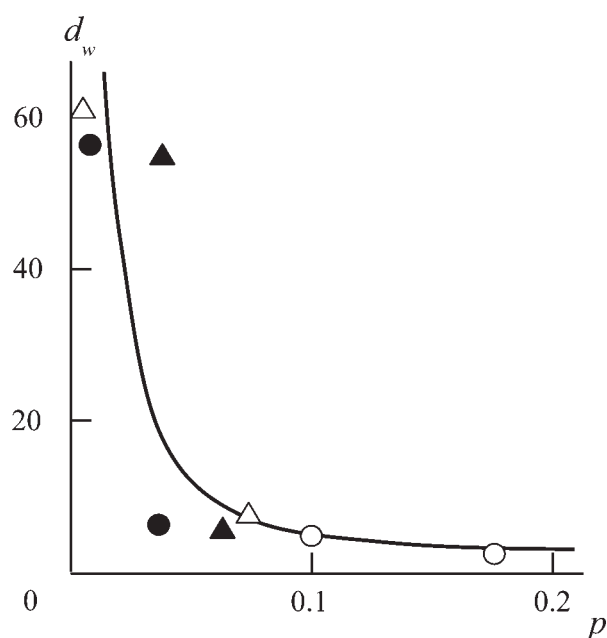
Figure 3 Dependence of d_w on p for reesterification reactions (see Fig. 1 for the notation).

sions, and this noticeably facilitates the occurrence of the reesterification reaction.

CONCLUSIONS

The results of this work have shown that the offered model of diffusion processes for chemical reactions describes the main characteristics of a model reaction of reesterification well. The structure of the reaction product (a heptylbenzoate molecule) and the parts forming it are the main factors controlling the diffusion processes in this case. The previously mentioned processes are described within the framework of strange (anomalous) diffusion.

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