

# The Fractal and Scaling Analysis of Chemical Reactions

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**Abstract:** It is shown that the geometrical factor controlling a thermooxidative degradation course is effective spectral dimension  $d'_s$  or factor  $\beta$ . In turn, parameters  $d'_s$  and  $\beta$  are a function of a polymer melt structure characterized by its fractal dimension  $\Delta_f$ . The applicability of this or that scaling relationship allows the evaluation of general features of chemical reactions in the thermooxidative degradation pro-

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**Key words:** polyether; thermooxidative degradation; scaling approach; fractal analysis; chemical reactions; macromolecular coil structure

## INTRODUCTION

The scaling approach to chemical reactions allows us to receive the relevant information on the course and conditions of these reactions. Such information is given by the decay laws of reactants concentration in reaction course. Djordjevic<sup>1</sup> has considered a reaction, in which particles  $P$  of chemical substance diffuse in medium containing random located statistical nonsaturated traps  $T$ . At contact of the particle  $P$  with the trap  $T$ , the particle disappears. Nonsaturation of the trap means that the reacting  $P + T \rightarrow T$  can repeat itself an infinite number of times. It is usually considered that if the concentration of particles and traps is large or the reaction occurs at intensive stirring, the process can be considered as the classical reaction of first order. In this case, it is possible to consider that the law of the concentration decay of particles in some time will look like<sup>1</sup>

$$c(t) \cong \exp(-At) \quad (1)$$

where  $A$  is a constant proportional to trap concentration, and  $t$  is reaction duration.

However, if the concentration of the random located traps is low, with necessity there exist areas of space practically free from traps. The particles getting into these areas can reach the traps only during a rather long time and, hence, the decay of their number in the course reaction will be slower. The formal analysis of this problem shows that the concentration of particles falls under the law.<sup>2</sup>

$$c(t) \cong \exp(-Bt^{d/(d+2)}) \quad (2)$$

being dependent on the dimension of space  $d$  ( $B$  is constant).

The simulation of reactions with mobile reactants, where all particles diffuse randomly with the same diffusivity, gives the following laws of concentration decay.<sup>3</sup>

$$c_A(t) \sim t^{-d/2}, \quad \text{for } d < d_c = 2 \quad (3)$$

and

$$c_A(t) \sim t^{-d/4}, \quad \text{for } d < d_c = 4 \quad (4)$$

In the case of reactions;



and



accordingly. Besides there are some more similar models,<sup>4–6</sup> which will be discussed below.

The purpose of the present article was to consider the general basis of dependences of reactant concentration decay within the framework of the fractal analysis and to clarify what information these dependences can give on the example of thermooxidative degradation reactions of heterochain polyether, polyarylatearylenesulfonoxide (PAASO).<sup>7</sup>

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## EXPERIMENTAL

PAASO, obtained by low-temperature (PAASO-1) and emulsive (PAASO-2) methods of polycondensation, was studied. These block copolymers are synthesized out of diene, a mixture (1 : 1) of dichloroanhydrides of tere- and isophthalic acids, oligoarylenesulfonoxide on the basis of diene, and 4,4'-dichlorodiphenylsulfone with molecular weight of 4600.

The average weight molecular weight ( $\bar{M}_w$ ) is determined by method of an approach to equilibrium (Archibald method) in ultracentrifuge 3170 corporations MOM (Hungary). The values  $\bar{M}_w$  for PAASO-1 and PAASO-2 are equal to  $76 \times 10^3$  and  $58 \times 10^3$ , respectively.<sup>7</sup>

The glass transition temperature ( $T_g$ ) of the studied copolymers is determined by the dielectric method. The studies are carried out on the quantummeter BM-560 Tesla at a frequency of 1 MHz in the temperature range 293–573 K. The  $T_g$  values for PAASO-1 and PAASO-2 are equal to 471 and 489 K, respectively.<sup>7</sup>

For the studies of the thermooxidative degradation processes in the air, the ampullary technique is used. The working volume of ampoules is equal to  $3 \times 10^{-5}$  L. The average initial contents of oxygen make up the value 2.5–3.0 mol O<sub>2</sub>/mol of polymer. The kinetic curves of the oxygen consumption  $\text{No}_2(t)$  are obtained at a temperature of 623 K.

## RESULTS AND DISCUSSION

Consider the physical sense of an exponent in the right part of eq. (2). As is known,<sup>8</sup> the dimension of phantom (not taking into account effects of excluded volume) of fractal  $D$  can be determined as

$$D = 2d_s / (2 - d_s) \quad (7)$$

where  $d_s$  is the spectral (fracton) dimension characterizing connectivity of fractal.<sup>9</sup>

From eq. (7), it follows

$$d_s/2 = D / (D + 2) \quad (8)$$

The right part of eq. (8) coincides with an exponent of eq. (2) at replacement  $d$  by  $D$ . As the dimension  $d$  in eq. (7) does not appear, it means the equivalence of  $D$  and  $d$ . In other words, the replacement of  $d$  by  $D$  is valid. Then, by using  $d$ , the reaction occurs in an Euclidean space with dimension  $d$ , and using  $D$ , in fractal space, having the corresponding dimension. Phantomity of the fractal, the dimension of which is determined according to the formula (7), means participation in the reaction of only low molecular weight substances, of which trajectories of motion (walk) can multiply, intercepting one another.

For reactions on fractal lattices, the authors<sup>3</sup> received the following relationship:

$$c_A(t) \sim t^{-d_s/2} \quad (9)$$

and

$$c_A(t) \sim t^{-d_s/4} \quad (10)$$

for reactions (5) and (6), respectively.

With allowance for eq. (8), relationship (2) can be written as

$$c(t) \cong \exp(-Bt^{d_s/2}) \quad (11)$$

At last, as for Euclidean spaces  $d_s = d$ , eq. (3) and (4) resulted in (9) and (10), respectively. In other words, the passage of reaction in any case is determined by the connectivity of the space in which it occurs. However, if such space has a definite degree of temporary (energetic) disorder, the dimension  $d_s$  should be replaced with effective spectral dimension  $d'_s$ , connected with  $d_s$  like.<sup>10</sup>

$$d'_s = \beta d_s \quad (12)$$

where  $0 \leq \beta \leq 1$  is the factor describing degree of temporary (energetic) disorder of a system.

The calculation of value  $d'_s$  for polymeric melts can be made according to<sup>11</sup> eq.

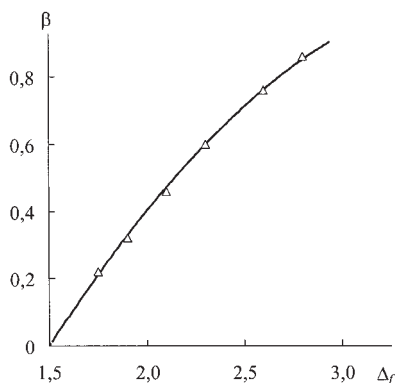
$$d'_s = 2(2\Delta_f - d) / (d + 2) \quad (13)$$

where  $\Delta_f$  is the fractal dimension of a macromolecular coil in a melt, which value is possible to estimate according to.<sup>12</sup>

The comparison of values  $d'_s$ , determined according to eq. (13), and  $d_s$ , calculated on eq. (8) at  $D = \Delta_f$  has shown that, as it appeared,  $d'_s \leq d_s$ . It means that the values  $d'_s$  and  $d_s$  for polymer melts obey the subordination theorem, to eq. (12). Further, from the combination of the eqs. (8), (12), and (13), it is possible to estimate parameter  $\beta$ . As it has appeared, value  $\beta$  is a function  $\Delta_f$  being increased with the increase in  $\Delta_f$  (Fig. 1). From the data of Figure 1, it is possible to receive analytical dependence  $\beta(\Delta_f)$

$$\beta \cong 0.72(\Delta_f - 1.5)^{0.8} \quad (14)$$

As follows from eq. (14), the lower limiting value  $\beta = 0$  is reached at  $\Delta_f = 1.5$  (i.e., for transparent coil<sup>13</sup>, in a case when both low-molecular and high-molecular substance can freely move through such coil. In this case, connectivity of a macromolecular coil does not matter. The maximal value  $\beta = 1$  is reached at  $\Delta_f = 3 = d$  [i.e., for Euclidean objects and, according to eq. (12), in this case,  $d'_s = d_s$ ]. In other words, temporary



**Figure 1** The dependence of a factor  $\beta$  in eq. (12) on fractal dimension  $\Delta_f$  of a macromolecular coil in a melt.

(energetic) disorder is the property of only fractal objects. According to eqs. (8) and (14), the value  $d'_s$  for phantom fractals can be determined as

$$d'_s \cong 1.44(\Delta_f - 1.5)^{0.8}(\Delta_f / (\Delta_f + 2)) \quad (15)$$

Thus, from eq. (15), it follows  $d'_s = 0$  for  $\Delta_f = 1.5$  and  $d'_s = 1.2$  for  $\Delta_f = 3 = d$ .

Further, we shall consider application scaling of relationships for a type definition of chemical reactions in thermooxidative degradation process of PAASO melts. In Figure 2, the experimental kinetic curves of oxygen consumption  $\text{No}_2(t)$  are shown at  $T = 623 \text{ K}$  for two samples of PAASO, obtained by low temperature and emulsive polycondensation. These curves differ not only quantitatively, is obtained, but also qualitatively, if for PAASO-1, the curve  $\text{No}_2(t)$  of an autodecelerated type is obtained; than for PAASO-2 the curve  $\text{No}_2(t)$  of an autoaccelerated type is obtained. From the above-mentioned scaling of relationships, and also the relationships given in refs.<sup>4-6</sup>, it follows that these relationships can be of two kinds: either power type or exponential functions. The plotting on the dependences  $\text{No}_2(t)$  in double log-log coordinates has shown that the curves of an autodecelerated type in the indicated coordinates can be linearized, whereas curves of an autoaccelerated type cannot. It means that description of curves of the first type need an power-type function and for curves of the second type, an exponential type function is needed.

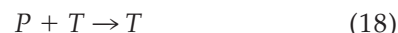
For graphing of the dependences corresponding to scaling relationships, it is necessary to determine the value  $c(t)$ , a fraction of the particles (in our case, molecules of oxygen), which have survived during a degradation. As shown in<sup>14</sup>, limiting value  $\text{No}_2(\text{No}_2^\infty)$  for PAASO required for full oxidation of aliphatic and aromatic groups is equal to  $\sim 24.1 \text{ mol O}_2$  per mole of polymer. Then, the fraction of the nonreacted particles will make  $\text{No}_2(t)/\text{No}_2^\infty$ , and value  $c(t)$

$$c(t) = 1 - \text{No}_2(t)/\text{No}_2^\infty \quad (16)$$

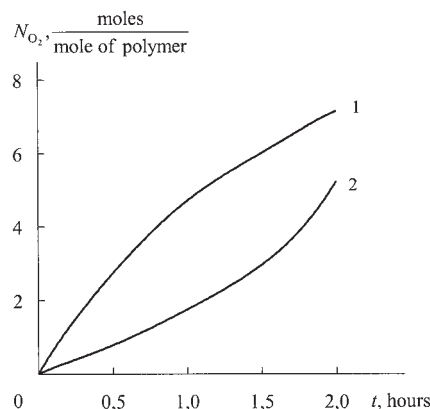
It is possible to analyze curves  $\text{No}_2(t)$  with the help of scaling relationships. The linearization of a curve  $\text{No}_2(t)$  of an autodecelerated type for PAASO-1 gives such a relationship

$$1 - \text{No}_2(t)/\text{No}_2^\infty \sim t^{-\gamma} \quad (17)$$

where exponent  $\gamma \approx 0.70$ . Such a value  $\gamma$  eliminates the application of relationships (3) and (4) for  $d = 3$  in the case of a degradation passage in an Euclidean space. According to eq. (15), value  $d'_s$  for PAASO is equal to  $\approx 0.76$  at  $\Delta_f = 2.45$ .<sup>12</sup> Formally such value  $d'_s$  enables the application of a relationship (9) for the description of the degradation PAASO in an autodecelerated mode, but it is necessary to remember that this relationship describes a reaction such as (5) (i.e., reaction of identical molecules). For the considered case, the reaction of an oxygen radical with a radical of a macromolecule is supposed. Therefore, the most probable variant of a scaling relationship for the description of curves  $\text{No}_2(t)$  of an autodecelerated type is the relationship for reaction trap-particle, where the trap is unmobile, and the particle diffuses.<sup>6</sup> Equation (17), under the condition of  $\gamma = \beta$ , is correct in this case. The calculation eq. (14) gives  $\beta = 0.69$ , that is, close to the above-mentioned value  $\gamma$ . As shown in Figure 3, the dependence  $(1 - \text{No}_2(t)/\text{No}_2^\infty)$  on  $t^{-\beta}$  is linear, that enables finally the determining type of reaction as follows. It is a reaction of particle ( $P$ )-trap ( $T$ ) (notation of<sup>1</sup>), which looks like



The mobile particles  $P$  are identified as a molecules  $\text{O}_2$  (or microradicals<sup>15</sup>), immobile traps  $T$ —as macromolecular coils (or macroradicals<sup>15</sup>). The reaction occurs in the fractal space (value  $\beta$  is determined by



**Figure 2** Kinetic curves of oxygen consumption  $\text{No}_2(t)$  for PAASO-1 (1) and PAASO-2 (2) at  $T = 623 \text{ K}$ .

value  $\Delta_f$  and less than a unit). In this case, fractal space is considered as a phantom trajectory of particles  $P$  motion.

The curves  $No_2(t)$  of an autoaccelerated type for PAASO-2 are described as exponential scaling relationships—eqs. (1), (2), and (11) or by the following relationship obtained in ref. <sup>5</sup> for reactions of a recombination

$$c(t) \sim \exp(-t^\alpha) \quad (19)$$

where the exponent  $\alpha$  depends on  $d$  as<sup>5</sup>

$$\alpha = d/4 \quad (20)$$

for unbiased diffusion of reacting particles and

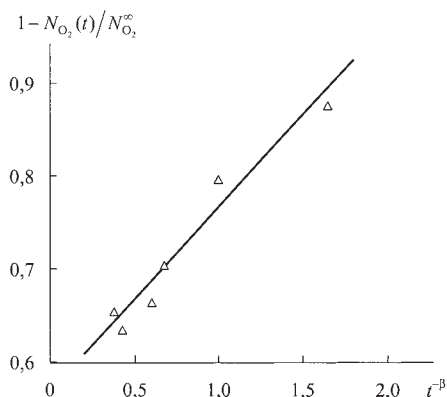
$$\alpha = (d + 1)/4 \quad (21)$$

for biased diffusion of these particles.

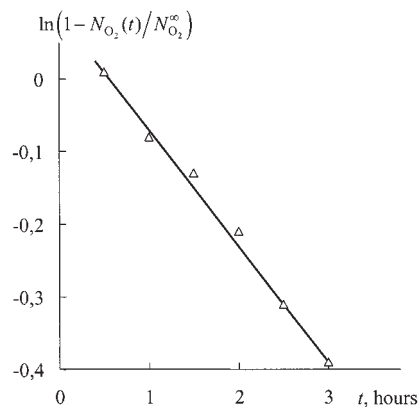
Usage of eqs. (1), (2), and (11) has not allowed us to linearize dependence  $[1 - No_2(t)/No_2^\infty]$  on  $t$ , but such a possibility gives a relationship (19) at  $\alpha = 1$  (see Fig. 4). It means that the curves  $No_2(t)$  of an autoaccelerated type describe reactions as a recombination of low molecular radicals  $A\bullet + B\bullet$ .<sup>4</sup>



As  $\alpha = 1$  means usage of eq. (21) in a case  $d = 3$ , it means that the mechanism of reaction is the biased diffusion in a three-dimensional Euclidean space. Apparently the obstacles of low molecular radical diffusion are created by a surface of a macromolecular coils. The recombination of different low molecular radicals  $A\bullet + B\bullet$  is supposed. A similar mechanism was reviewed in ref. <sup>16</sup> It is supposed that the product, responsible for the autoaccelerated nature of a thermooxidative degrada-

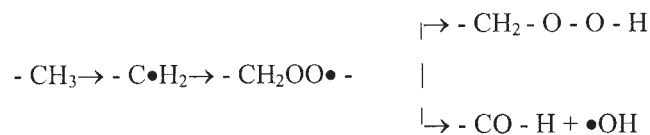


**Figure 3** The dependence  $[1 - No_2(t)/No_2^\infty]$  on the parameter  $t^{-\beta}$  for PAASO-1.

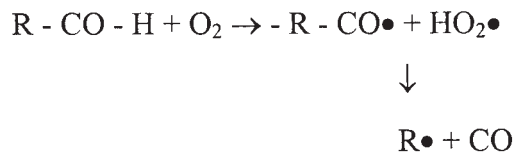


**Figure 4** The dependence  $[\ln(1 - No_2(t)/No_2^\infty)]$  on time  $t$  in log coordinates for PAASO-2.

tion, is the aldehydic group which is formed from methyl groups on the scheme:



Oxidation of aldehydic groups which is occurring on the scheme



results in formation of active free radicals  $R\bullet$  and low molecular radicals  $HO_2\bullet$ .<sup>16</sup>

## CONCLUSION

Thus, the results of the present article have shown that the geometrical factor controlling a thermooxidative degradation course is the effective spectral dimension  $d'_s$  or factor  $\beta$ . In turn, the parameters  $d'_s$  and  $\beta$  are a function of a polymer melt structure characterized by its fractal dimension  $\Delta_f$ . The applicability of this or that scaling relationship allows us to evaluate the general features of chemical reactions in a thermooxidative degradation process.

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