A Theoretical Description of the Oxidation Kinetics of Polymer Melt in Fractal Mediums

G. V. Kozlov,[1] I. V. Dolbin,[2] G. E. Zaikov[2]

[1]Kabardino-Balkarian State University, Nal'chik-360004, Russian Federation
[2]Institute of Biochemical Physics, Russian Academy of Sciences, Moscow 119991, Russia

ABSTRACT: It is shown that the fractal approach using fractional integration and derivation gives an adequate description of decelerated curves in relation to consumed oxygen—and time. A clear physical interpretation of the fractal exponent as a fractional part of the fractal dimension of a macromolecular coil is obtained. It also indicates that classical equation is a particularly limiting case of the fractal relationship applicable to Euclidean mediums. The initial oxygen amount is represented as a constant in basic fractal relationship, which is also a function of the macromolecular coil structure. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3761–3764, 2006

Key words: block copolymer; polyether; thermooxidative degradation; polymer melt; fractional derivation

INTRODUCTION

There are several basic types of consumed oxygen vs. time $N_{o_2}(t)$ curves in the thermooxidative degradation of polymers[1]. One of these types, namely, autodecelerated curves, will be considered in the present study. Within the framework of a classical chemical treatment, a deceleration of oxygen consumption with time is explained by a "burn-up" of reactive groups.[1]

However, another theoretical treatment of the aforementioned $N_{o_2}(t)$ curves, based on the fractal conception,[2] is possible. In this connection, two remarks may be made.
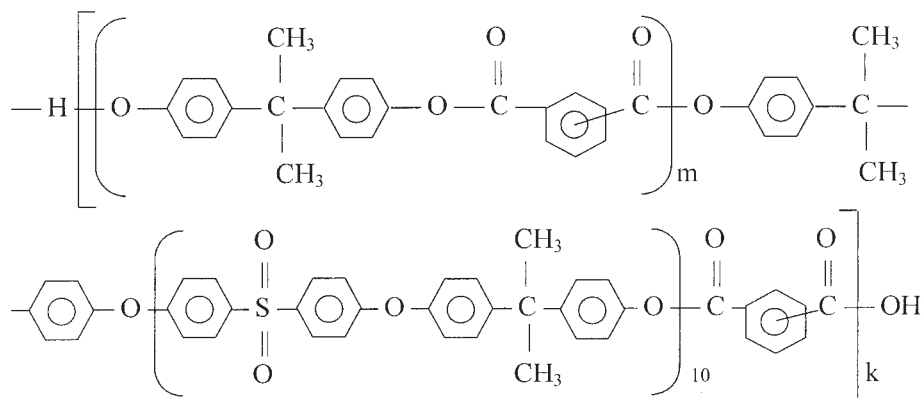
First, curves of the aforementioned type, where a process rate decreases with passing time, are observed in both physics and chemistry, and are not restricted to polymers. Typical examples would be curves of sorption,[3] positron annihilation,[4] kinetic curves of conversion (degree of reaction vs. time) at polymer synthesis,[5] stress–strain curves,[6] etc. Second, the dependence of a process rate on time by itself assumes the fractality of the medium in which the process occurs.[4,7] This allows one to suppose that the causes of oxygen consumption deceleration with time for $N_{o_2}(t)$ curves with autodeceleration have a much more general character than assumed earlier.[1,8] As mentioned earlier, this cause can be the fractality of a medium in which a thermooxidative degradation has occurred.

There can two possible fractal approaches to the description of $N_{o_2}(t)$ curves.[3] The first of them relates to using fractal (Hausdorff) dimension geometry. This approach has been successfully used for the description of autodecelerated $N_{o_2}(t)$ curves.[9] The second approach is by using fractional integration and derivation.[3,4,10–12] Within the framework of this formalism, one may call it a success if it allows sequentially complicated nonlinear phenomena such as memory affects and spatial correlations. Besides the earlier known solutions, which explain its nontrivial generalization, one more important feature is related to a self-similarity property of the fractal structures. In the fractal conception, when "wipe-out" of a microscopic level takes place, description on the basis of various average procedures is allowed (unlike those in the traditional methods of the system), for self-affined medium structures, and then within the framework of the fractal conception, the micro- and macroscopic levels of the system description are combined. Such a method is important for complicated systems, which are far away from the state of thermodynamic equilibrium.[3,12] However, an intensive application of this approach is restrained by the absence of clear physical interpretation of the fractional exponent in fractional integration and derivation.[10] The purpose of the present work is a description of autodecelerated $N_{o_2}(t)$ curves within the framework of the second, using the fractal approaches and having a physical sense of the fractional exponent in the thermooxidative degradation of melts of a heterochain polyether-*block*-copolymer polyarylatearylenesulfonoxide (PAASO).[13]

Correspondence to: G. E. Zaikov (chembio@sky.chph. rasru).

EXPERIMENTAL

PAASO, obtained by low-temperature (PAASO-1) and high-temperature (PAASO-2) polycondensation, were studied.[14,15] These block-copolymers were synthesized using diane, a 1:1 mixture of dichloroanhydrides of tere- and isophthalic acids, and dihydroxil-containing olygoarylenesulfonoxides at different proportions of diane and 4,4'-dichlorodiphenylsulfone having a molecular weight of 4600 and having the following chemical constitution:

The average molecular weight $\overline{M_w}$ was determined by the approach to equilibrium (Archibald) method, using ultracentrifuge 3170 of MOM Corp. (Hungary). The $\overline{M_w}$ values are equal to 76×10^3 for PAASO-1 and 72×10^3 for PAASO-2.[13] The glass transition temperature T_g of the studied copolymers were determined by the dielectric method. The studies were carried out in quantometer BM-560 "Tesla" at frequency 1 MHz within the temperature range 293–573 K.[13] The T_g value was 471 K for PAASO-1 and 476 K –for PAASO-2.

For studies of thermooxidative degradation processes in air, the ampullary technique was used. The working volume of ampoules is 3×10^{-5} L. The average initial oxygen contents were of the order of 2.5–3.0 mol O_2/mol of polymer. The kinetic curves $N_{o_2}(t)$ of oxygen consumption were obtained within a temperature range of 623–723 K.

The plotting of logarithmic anamorphoses of kinetic curves $N_{o_2}(t)$ allows one to determine the reaction rate constant k_d for the thermooxidative degradation.[13]

RESULTS AND DISCUSSION

Let's consider the parameters characterizing a polymer melt structure. As mentionedearlier, studies on the thermooxydative degradation process of PAASO were carried out within a temperature range of 623–723 K, and the glass transition temperature range of these copolymers was 471–476 K. It is known[16] that the temperature of the so-called transition "a liquid 1–liquid 2" T_{ll} can be estimated as follows:

$$T_\pi \approx (1.20 \pm 0.05)T_g \qquad (1)$$

From eq. (1) and the data mentioned earlier, the condition that $T > T_{ll}$ follows. At T_{ll} there occurs a transition of polymer melt from "liquid with fixed structure" (where the residual structural ordering is observed[16]) to a true liquid state or "structureless liquid."[17] Nevertheless, the "structurelessness" of melt at $T > T_{ll}$ is related to the absence of supermolecular structure, but the structure of a macromolecular coil in melt remains an important structural factor (infact, unique at $T > T_{ll}$).

The structure of a macromolecular coil, which is a fractal object,[18] can be exactly described with the help of its fractal (Hausdorff) dimension Δ_f, describing the distribution of coil units in space.[5] Δ_f can be estimated as described here.[19] The formal kinetics of chemical reactions can be described by the following equation[19]:

$$\frac{dQ}{dt} = k_d(1 - Q) \qquad (2)$$

where Q is the reaction degree of conversion, t its duration, and k_d is the reaction rate constant.

The general fractal relationship, which is also used for the description of the chemical reaction kinetics, looks like[2]:

$$Q \sim t^{(3-\Delta_f)/2} \qquad (3)$$

Differentiating the relationship (3) by time t and equating the derivative dQ/dt to a similar derivative in eq. (2), we receive[19]:

$$t^{(1-\Delta_f)/2} = \frac{k_d(1 - Q)C_1}{C_1} \qquad (4)$$
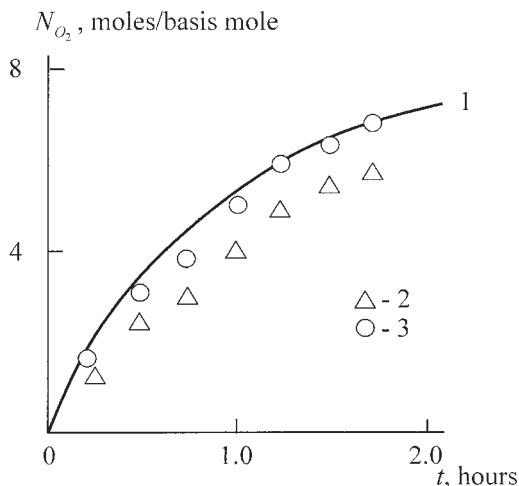
N_{O_2}, moles/basis mole

Figure 1 The dependences of a consumed oxygen amount N_{o_2} on time t for PAASO-1 at $T = 623$ K. (1) experimental data; (2), (3) calculation according to the eq. (5) at $N_{o_2}^0 = 1.0$ (2) and 1.25 mol/basic mol (3).

where C_1 is constant (which can be estimated from the boundary conditions[19]), and the values k_d are accepted according to the data of.[13] The value Q was determined as $N_{o_2}/N_{o_2}^\infty$, where $N_{o_2}^\infty$ is the maximum oxygen amountthat can be consumed at oxidation. For PAASO $N_{o_2}^\infty \approx 24$ mol O_2/mol of polymer.[20]

For theoretical description of the $N_{o_2}(t)$ curves in the present work, the following equation was used[4]:

$$N_{o_2}(t) = N_{o_2}^0 E_v(1 - t^v) \qquad (5)$$

where $N_{o_2}^0$ is initial oxygen content, $E_v(1-t^v)$ is function Mittag-Leflere, which looks like[21]:

$$E_v(1 - t^v) = \sum_{k=0}^{\infty} \frac{(1 - t^v)^k}{\Gamma(vk + t)} \quad v > 0, \quad t > 0 \qquad (6)$$

In eq. (6) v is fractional exponent, Γ is the γ-function of Euler, and $k = 1, 2, 3$ (which is enough for obtaining of the necessary exactness in practical application[21]). γ-function of Euler is determined for variable x as follows[22]:

$$\Gamma(x) = \left(\frac{\pi}{2}\right)^{1/2} x^x e^{-x} \qquad (7)$$

As shown in ref. 10, the fractional exponent v coincides with the fractal dimension of Cantor's set and indicates that a fraction of the system is unchanged during the time of evolution. We also note that Cantor's set is considered in one-dimensional Euclidean space ($d = 1$) and that its fractal dimension d_f is less than 1 by virtue of fractal definition.[22] For the fractal objects in Euclidean spaces with higher dimensions, d

is greater than 1 as v it is necessary to accept the fractional part d_f (in our case Δ_f) or:

$$v = \Delta_f - (d - 1) \qquad (8)$$

In this case the value v characterizes the fraction of a fractal (macromolecular coil), unchanged during evolution (thermooxidative degradation). When $v = 1$, the equation for the $N_{o_2}(t)$ curves description is written as follows[3]:

$$N_{o_2}(t) = N(1 - \exp(-t)) \qquad (9)$$

where N is some constant.

Within the framework of the classical approach, the equation describing autodecelerated $N_{o_2}(t)$ curves, looks like[1]:

$$N_{o_2}(t) = N_{o_2}^\infty(1 - e^{-kt}) \qquad (10)$$

where k is effective oxidation rate constant.

From eq. (8) it follows that $v = 1$ corresponds to $\Delta_f = d$, i.e., the oxidation reaction proceeds in Euclidean (but not fractal) medium, and a comparison of the eqs. (9) and (10) indicates that the classical eq. (10) is a particularly limiting case of description of oxidation reaction in a Euclidean medium. For this it is typical to use in this equation an exponential function, which is generally used in traditional physics and indicates process taking place in Euclidean mediums.[3] The Mittag-Leflere function plays analogous role for fractal mediums.

In Figures 1 and 2, experimental (curves 1) and calculated curves (curves 2, calculated according to the eq. (5) at $N_{o_2}^0 = 1$) of the $N_{o_2}(t)$ dependences for
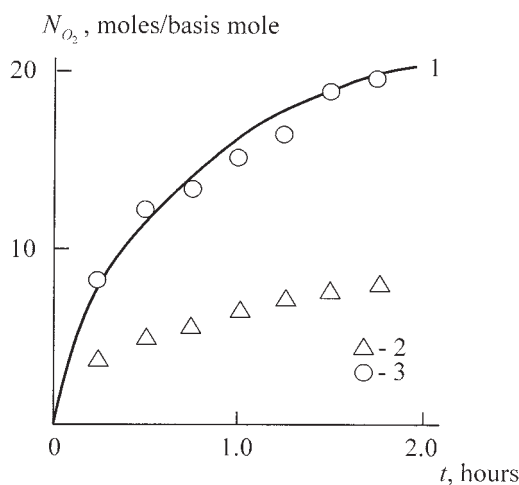
N_{O_2}, moles/basis mole

Figure 2 The dependences of a consumed oxygen amount N_{o_2} on time t for PAASO-1 at $T = 723$ K. (1) experimental data; (2), (3) calculation according to the eq. (5) at $N_{o_2}^0 = 1.0$ (2) and 2.55 mol/basic mol (3).
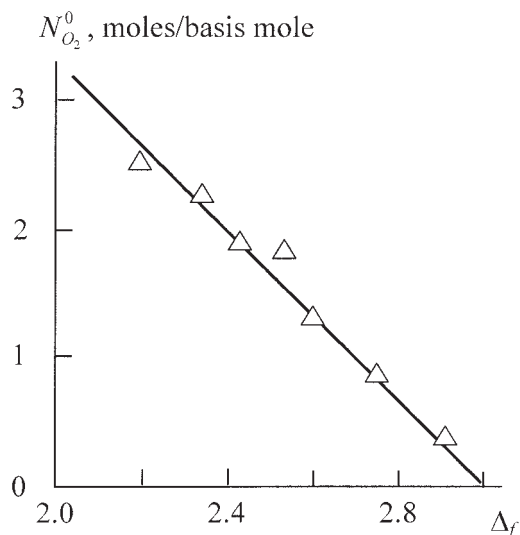
Figure 3 The dependence of an initial amount of consumed oxygen $N_{o_2}^0$ on fractal dimension Δ_f of a macromolecular coil for PAASO.

PAASO-1 at temperatures 623 and 723 K are shown, respectively. As may be seen, there is a great similarity between the theoretical and experimental $N_{o_2}(t)$ curves; it is also possible to obtain a quantitative correspondence by a determination of $N_{o_2}^0$ constant in eq. (5) by of the best fit method. So, for the $N_{o_2}(t)$ curve in Figure 1, $N_{o_2}^0 = 1.25$ mol/basic mol, and for the $N_{o_2}(t)$ curve in Figure 2, $N_{o_2}^0 = 2.55$ mol/basic mol. As the $N_{o_2}^0$ value represents an initial oxygen content in a macromolecular coil of melts, a correlation of the following nature between this parameter and a macromolecular coil structure may be expected: a decrease in macromolecular coil density or a reduction in Δ_f should give an increased $N_{o_2}^0$. The dependence $N_{o_2}^0(\Delta_f)$ shown in Figure 3 confirms this assumption. As expected, at $\Delta_f = d = 3$ (dense object) the $N_{o_2}^0$ value is extrapolated to a zero value.

CONCLUSIONS

The results of the present work have shown that the fractal approach using fractional integration and derivation gives an adequate description of decelerated curves in relation to amount of consumed oxygen and time. A clear physical interpretation of fractional exponent as a fractional part of the fractal dimension of a macromolecular coil is obtained. It also indicates that the classical equation is a particularly limiting case of the fractal relationship applicable to Euclidean mediums. The constant in a basic fractal relationship is represented as the initial oxygen amount, which is also function of the macromolecular coil structure.

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