

Fractal Analysis of Thermooxidative Degradation Process of Polymeric Melts

G. V. Kozlov,¹ G. B. Shustov,¹ G. E. Zaikov²

¹Kabardino-Balkarian State University, Chernishevsky st., 173, KBR, Nalchik—360004, Russia

²Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin st., 4, Moscow—119991, Russia

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ABSTRACT: The fractal dimension of a macromolecular coil is used for the characterization of a polymeric melt structure. It is shown that the kinetics of oxygen consumption is defined by both the chemical constitution of a polymer and its structure. The quantitative analysis of the kineti-

cal curves of the oxygen consumption in the thermooxidative degradation process was carried out in the framework of the fractal approach. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2378–2381, 2003

INTRODUCTION

As is well known,^{1,2} the analysis of the experimental data on oxygen consumption at the thermooxidative degradation of different polymers both in open and in closed systems has shown that there are three main types (under other data, four types³) of kinetic curves of the “amount of consumed oxygen – time” ($N_{O_2} - t$). In the present article, one of the indicated types of curves, $N_{O_2}(t)$, was considered: curves that exponentially decrease with time (autodecelerated), which are described by the following equation¹:

$$N_{O_2} = N_{O_2}^{\infty}(1 - e^{-kt}) \quad (1)$$

where $N_{O_2}^{\infty}$ is the limiting amount of oxygen that is capable of being consumed at oxidation and k is an effective constant of the oxidation rate.

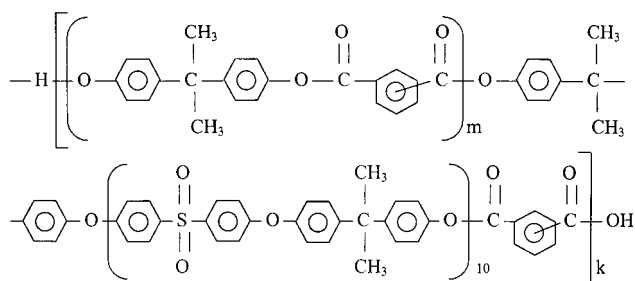
The dependence (1) is usually explained by the heterogeneity of a polymer, which defines the noticeable differences in the oxidation rates of its separate sites. As more reactive sites are oxidized, first, after their practically complete transformation, the rate of the summary process is strongly reduced. Besides it was exhibited that the value $N_{O_2}^{\infty}$, determined using eq. (1), can be many times lower than is the concentration of the monomer units in the individual polymer: During the experiment, some part of these units behaves as an inert substance.²

The value k depends on the temperature and the polymer structure. From the above-mentioned, it follows that, in essence, both N_{O_2} and k are simply fitting

parameters, as their quantitative relation with the polymer structure is not clarified. Until recently, the situation became complicated by the absence of a quantitative structural model of polymers, especially when the consideration is about the structure of their melts. However, in the last years, development of the methods of fractal analysis for the description of the polymer structure and properties^{4,5} allows one to hope for its successful application in this case. The purpose of the present work was to clarify the structural sense of the parameters $N_{O_2}^{\infty}$ and k for a polymeric melt on an example of two block copolymers, polyarylatearylenesulfonoxide (PASSO), obtained by different methods of polycondensation at three testing temperatures.⁶

EXPERIMENTAL

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



Correspondence to: G. E. Zaikov.

The average molecular weight \overline{M}_w is determined by the method of approaching equilibrium (Archibald method) in an ultracentrifuge 3170 of the MOM Corp. (Hungary). The values \overline{M}_w are equal to 76×10^3 for PAASO-1 and 69×10^3 for PAASO-2.⁵ The glass transition temperature T_g of the studied copolymers was defined by the dielectric method. The studies were carried out by a BM-560 "Tesla" quantumeter at a frequency of 1 MHz in the temperature range 293–573 K.⁶ The value of T_g is equal to 471 K for PAASO-1 and 491 K for PAASO-2.

For the studies of the thermooxidative degradation processes in air, the ampullary technique was used. The working volume of the ampules was equal to 3×10^{-5} L. The average initial contents of the oxygen have the value of 2.5–3.0 mol O₂ mol⁻¹ of the polymer. The kinetic curves of the oxygen consumption $N_{O_2}(t)$ were obtained at the temperatures of 623 and 723 K.⁶ The plotting of the logarithmic anamorphoses of the kinetic curves $N_{O_2}(t)$ allows one to determine the constant of the reaction rate k_d for the thermooxidative degradation.

RESULTS AND DISCUSSION

Let us consider the parameters characterizing a polymeric melt structure. The studies of the thermooxidative degradation process of PAASO were carried out within the temperature range of 623–723 K and the temperature range of the glass transition of these copolymers was equal to 472–474 K. As is known,⁷ the temperature of the so-called transition a liquid 1 – liquid 2, T_{ll} can be estimated as follows:

$$T_{ll} \approx (1.20 \pm 0.05)T_g \tag{2}$$

From eq. (2) and the above-quoted data, the condition $T > T_{ll}$ follows: At T_{ll} , there a transition occurs of the polymeric melt from a "liquid with a fixed structure" (where the residual structural ordering is observed⁷) to a true liquid state or "unstructured liquid."⁸ Nevertheless, the "unstructurality" of melt at $T > T_{ll}$ relates to the absence of the supermolecular structure, but the structure of a macromolecular coil in the melt remains the important structural factor (in essence, unique at $T > T_{ll}$).

The structure of a macromolecular coil, which is a fractal object,⁹ may be precisely described with the help of its fractal (Hausdorff) dimension Δ_f describing the distribution of units of a coil in a space.¹⁰ The estimation of the value Δ_f can be made as follows¹¹: The formal kinetics of chemical reactions can be described by the following equation:

$$\frac{dQ}{dt} = k_d(1 - Q) \tag{3}$$

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

The general fractal relationship also used for the description of the kinetics of chemical reactions looks like⁵

$$Q \sim t^{(3-\Delta_f)/2} \tag{4}$$

By differentiating relationship (4) by time t and equating the derivative dQ/dt to a similar derivative in eq. (3), we shall obtain¹¹

$$t^{(\Delta_f-1)/2} = \frac{C_1}{k_d(1 - Q)} \tag{5}$$

where C_1 is a constant, which can be estimated from the boundary conditions,¹¹ and the values k_d are accepted under the data of ref. 6.

From the above-mentioned description, it follows that the thermooxidative degradation process for the considered copolymers proceeds not in a Euclidean, but in a fractal space with dimension Δ_f . In the latter space, the process of degradation can be presented by the way of the "devil's staircase."¹² Its horizontal segments correspond to the time intervals, where the reaction does not occur. In this case, the degradation process is described with the usage of the fractal time t , which belongs to the points of Cantor's set.¹³ If the reaction is considered in an Euclidean space, the time belongs to the set of real numbers.

For the description of the evolutionary processes with the fractal time, the mathematics of fractional differentiation and integration will be used.¹³ As is shown in ref. 14, in this case, the fractional exponent ν coincides with the fractal dimension of Cantor's set and indicates a fraction of the system not changed at all during the time of evolution t . We remind the reader that the Cantor set is considered in one-dimensional Euclidean space ($d = 1$) and, consequently, its fractal dimension $d_f < 1$ by virtue of the fractal definition.¹² For the fractal objects in Euclidean spaces with higher dimensions ($d > 1$) as ν , it is necessary to accept the fractional part d_f (in our case, Δ_f) or

$$\nu = \Delta_f - (d - 1) \tag{6}$$

Then, the value ν characterizes the fraction of a fractal (macromolecular coil), unchanged during the process of degradation. Apparently, the fraction of a macromolecular coil β , which is breaking up during the destruction, is determined by

$$\beta = 1 - \nu = 1 - [\Delta_f - (d - 1)] = d - \Delta_f \tag{7}$$

or, as in the considered case $d = 3$, by

$$\beta = 3 - \Delta_f \tag{8}$$

Further, it is natural to assume that oxygen is consumed in a part of a macromolecular coil which is breaking up during the destruction. Then, having calculated the value $N_{O_2}^T$, which is necessary for the oxidation of all aliphatic and aromatic groups of PASSO (which is equal to 24.1 mol O₂ mol⁻¹ of polymer), it is possible to determine the parameter $N_{O_2}^\infty$ as follows:

$$N_{O_2}^\infty = \beta N_{O_2}^T \tag{9}$$

The change Δ_f means the variation of the compactness of a macromolecular coil.⁴ We should expect that the lowering of Δ_f , defining the decrease of the coil compactness, will result in an increase in N_{O_2} and, therefore, in k_d , which allows one to replace k_d by the structural parameter. It is possible to characterize the compactness degree of a macromolecular coil with the help of its density ρ . As is known,¹² the value ρ of a fractal is determined as follows:

$$\rho \sim R_g^{\Delta_f - d} \tag{10}$$

where R_g is a gyration radius of a macromolecular coil. For further simplicity, it was accepted that R_g is equal to 100 relative units (the values \bar{M}_w for PASSO-1 and PASSO-2 are close) and the density ρ was determined from the following equation for both polymers and all testing temperatures:

$$\rho = 8.2 R_g^{\Delta_f - d} \tag{11}$$

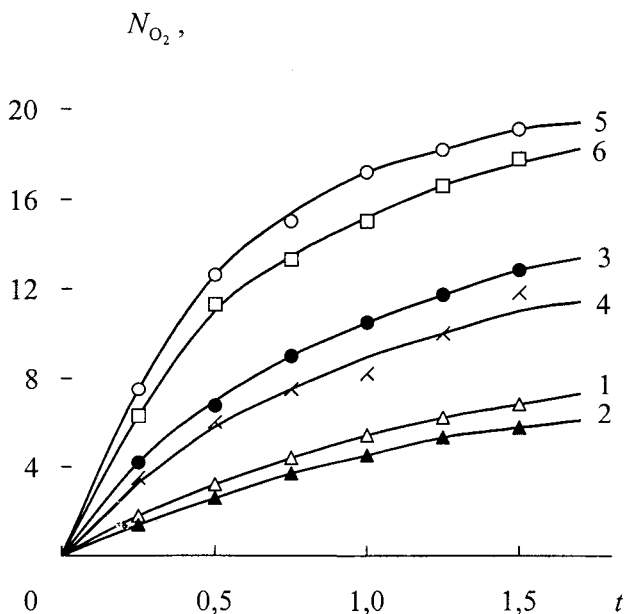


Figure 1 Dependencies of the consumed oxygen amount N_{O_2} on time t for (1,3,5) PASSO-1 and (2,4,6) PASSO-2 at the temperatures of (1,2) 623, (3,4) 673, and (5,6) 723 K.

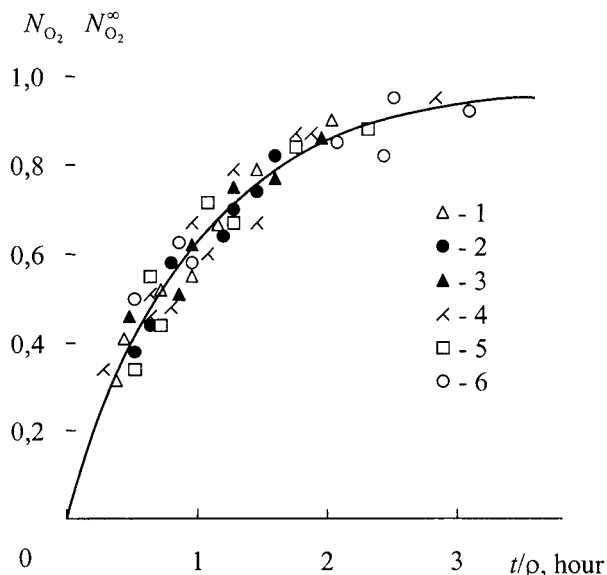


Figure 2 Generalized kinetic curve of the oxygen consumption corresponding to eq. (12), for (1–3) PASSO-1 and (4–6) PASSO-2 at temperatures of (1,4) 623, (2,5) 673, and (3,6) 723 K.

where coefficient 8.2 is defined empirically. Now, eq. (1) with the allowance of the considered geometrical factors can be written as

$$N_{O_2} = (3 - \Delta_f) N_{O_2}^T (1 - e^{-t/\rho}) \tag{12}$$

The index of an exponential curve $-(t/\rho)$ is written in such a form because the action of ρ is opposite to the action of t : The increase of ρ reduces the oxygen consumption and to the contrary. In Figure 1, the experimental dependencies $N_{O_2}(t)$ for both studied polymers are given at three temperatures of tests. As is possible to see, all kinetic curves $N_{O_2}(t)$ belong to the considered type: The value N_{O_2} exponentially decreases during the degradation. Such behavior of dN_{O_2}/dt uniquely indicates the proceeding of the thermooxidative degradation process in a fractal space.¹⁵

In Figure 2, the generalized kinetic curve of the oxygen consumption for PASSO-1 and PASSO-2 at three temperatures of the tests is given. As is possible to see, the experimental results are well described by eq. (12), not containing the empirical coefficients.

CONCLUSIONS

The results of the present work have shown the necessity of the application of the methods of the fractal analysis for the description of the thermooxidative degradation process of polymeric melts. The kinetics of the oxygen consumption is defined by the chemical constitution of the polymer ($N_{O_2}^T$) and its structure (Δ_f and ρ).

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