Prediction of Kinetic Curves of Oxygen Consumption on a Thermooxidative Degradation Process for Polymer Melts

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ABSTRACT: The possibility of theoretical prediction of oxygen consumption kinetic curves in a thermooxidative degradation process for polymer melts under conditions that allow for both chemical constitution of polymer and physical structure of melt is shown, the last of which can be quantitatively identified within the framework of fractal analysis. Although obtained for the purposes of predicting kinetic curves, the equation does not contain empirical-fitting parameters. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3601–3604, 2004

Key words: polymer melt; degradation; kinetic curves; oxygen consumption; fractal analysis

INTRODUCTION

As previously established,[1] kinetic curves of the amount of consumed oxygen versus the time $N_{O_2}(t)$ of an autodecelerated type during the process of a polymer's thermooxidative degradation are described by the following equation:

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

where $N_{O_2}^{\infty}$ is a limiting amount of oxygen that is capable of being consumed at oxidation and k is the effective rate constant of oxidation, the value of which depends on temperature and polymer structure.

Although eq. (1) adequately describes experimental curves $N_{O_2}(t)$ of an autodecelerated type, it is not suitable for prediction of these curves, given that the characteristics of $N_{O_2}^{\infty}$ and k on their physical nature are empirical-fitting parameters.

In Emanuel and Buchachenko[2] the perspectivity of structural–physical methods, based on physical principles, for stabilization of solid polymeric materials was shown. However, no less-relevant geometrical factor remains in the case of polymer melts and the quantitative model of structure of this polymers state is necessary for definition of its degree of influence.

Therefore, for prediction of kinetic curves $N_{O_2}(t)$ it is necessary to define parameters that take into account the influence of the polymer chemical constitution and its structure on a thermooxidative degradation process. In Batyrova[3] it was shown that block copolymers polyarylatearylenesulfonoxides (PAASO), obtained

by different methods of polycondensation, have significantly different $N_{O_2}(t)$ curves. As with any method of polycondensation the chemical constitution of PAASO remains invariable, although the difference in $N_{O_2}(t)$ curves supposes different structures of the indicated block copolymers in a melt, which makes the indicated PAASO series a convenient object for study of the influence of a melt structure on the thermooxidative degradation process. The present study proposes a technique of theoretical prediction of $N_{O_2}(t)$ kinetic curves by using representations of fractal analysis.

EXPERIMENTAL

Series of PAASO, obtained by different methods of polycondensation, were investigated. The methods and notation of block copolymers are listed in Table 1. PAASO was synthesized out of diane, a mixture (1 : 1) of dichloroanhydrides of tere- and isophthalic acids, oligoarylenesulfonoxide on the basis of diane and 4,4'-dichlorodiphenylsulfone with molecular weight 4600 of the following constitution:

The average weight molecular weight $\bar{M}_w$ was determined by the method of approaching equilibrium
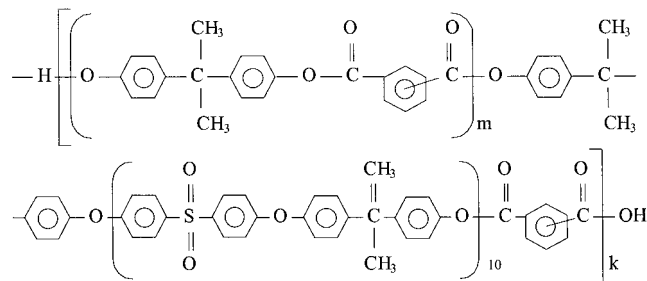
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Method of polycondensation	Notation	T_g (K)	$\bar{M}_w \times 10^{-3}$	$k \times 10^4$ (s)[a]
Low-temperature	PAASO-1	472	76	0.19
High-temperature	PAASO-2	474	64	0.24
Interphase	PAASO-3	491	66	0.07
Emulsive	PAASO-4	489	58	0.11

[a] At $T = 623$ K.

(Archibald method) in ultracentrifuge 3170 (MOM Corp., Hungary). The $\bar{M}_w$ values for PAASO are listed in Table I.

The glass-transition temperature T_g of the studied copolymers was determined by the dielectric method. The studies were carried out on the quantometer BM-560 "Tesla" at a frequency of 1 MHz in the temperature range 293–573 K.[3] The T_g values for PAASO are also listed in Table I.

For studies of thermooxidative degradation processes in air the ampullary technique was used. The working volume of ampoules is equal to 3×10^{-5} L. The average initial oxygen contents make up the value 2.5–3.0 mol O_2/mol of polymer. The kinetic curves of the oxygen consumption $N_{O_2}(t)$ are obtained in temperature range $T = 573$–723 K.[3]

Plotting the logarithmic anamorphoses of $N_{O_2}(t)$ kinetic curves allows us to determine the constant of the reaction rate k for the thermooxidative degradation (see Table I).

RESULTS AND DISCUSSION

Let us consider parameters describing the structure of a polymer melt. As mentioned earlier, the study of a thermooxidative degradation process of PAASO was carried out within the temperature range 573–723 K, and the temperature range of the glass-transition temperature of these copolymers was $T_g = 472$–491 K (Table I). As previously established,[4] the temperature of the so-called transition "liquid 1–liquid 2" T_{ll} can be estimated as follows:

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

From eq. (2) and data of Table I the condition follows: $T > T_{ll}$. At T_{ll} there is a transition of a polymeric melt from "liquid with the fixed structure" (where the residual structural ordering is observed[4]) to the true liquid state or "structureless liquid."[5] Nevertheless, the "absence of melt structure" at $T > T_{ll}$ concerns the absence of supermolecular structure, but the macromolecular coil structure in a melt remains the important structural factor (in essence, only the structural factor at $T > T_{ll}$).

Most precisely the structure of a macromolecular coil, which is a fractal object,[6] can be characterized with the help of its fractal (Hausdorff) dimension Δ_f, describing distribution of coil elements in space.[7] The estimation of the Δ_f value can be made as follows.[8] The formal kinetics of chemical reactions can be described by the following equation:

$$\frac{dQ}{dt} = k(1 - Q) \qquad (3)$$

where Q is a reaction degree of completeness, t is its duration, and k is a reaction rate constant.

The general fractal relationship, also used for the description of the kinetics of chemical reactions, has the following form[9]:

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

Differentiating eq. (4) by time t and equating the derivative dQ/dtx to a similar derivative in eq. (3), we obtain[8]

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

where C_1 is a constant, which can be estimated from the boundary conditions[8]; the values k are accepted according to the data of Batyrova[3]; and the value Q is determined as the ratio $N_{O_2}/N_{O_2}^\infty$, where $N_{O_2}^\infty$ for PAASO in the case of full oxidation of methyl and aliphatic groups is equal to 24.1 mol O_2/mol polymer.[10]

Thus it follows that the structure of a polymer melt in conditions of the present experiment can be treated as a set of a large number of separate clusters (macromolecular coils), and the trajectory of an oxygen molecule on such structure is a modeled random walk.[11] In this case a relevant structural parameter, which describes a macromolecular coil connectivity and determining reaction rate, is the effective spectral dimension d_s'.[12] For an estimation of d_s' in the case of a large number of separate clusters the equation obtained in Argyrakis[13] is applicable:

$$d_s' = d_s\left(2 - \frac{d}{d - \beta/\nu}\right) \qquad (6)$$

where d_s is the spectral (fraction) dimension[14]; d is the dimension of a Euclidean space, in which fractal is considered; and β and ν are static percolation indices.

As previously established,[15] the fractal dimension Δ_f can be expressed as

$$\Delta_f = d - \frac{\beta}{\nu} \qquad (7)$$

Furthermore, Vilgis[7] has shown that for polymer melts the value Δ_f is determined as follows:

$$\Delta_f = \frac{d_s(d + 2)}{2} \qquad (8)$$

By combining eqs. (6)–(8), one obtains the final formula by which d'_s may be calculated from known values of Δ_f:

$$d'_s = \frac{2(2\Delta_f - d)}{d + 2} \qquad (9)$$

From the preceding analysis it follows that the thermooxidative degradation process for copolymers under consideration proceeds not in Euclidean, but in fractal space with dimension Δ_f. In such a space the process of degradation can be presented by way of the so-called devil's staircase.[16] Its horizontal segments correspond to time intervals during which the reaction does not proceed. In this case a degradation process is described with the use of fractal time, which belongs to points of Cantor's set.[17] If the reaction is considered in a Euclidian space, the time belongs to the set of real numbers.

For the description of evolutional processes with fractal time the mathematics of fractional integration and derivation will be used.[17] As shown in Nigmatullin,[18] in this case the fractional exponent ν coincides with the fractal dimension of Cantor's set and indicates a fraction of the system unchanged for the entire time of evolution. One should note that the Cantor's set is considered in a one-dimensional Euclidian space ($d = 1$) and consequently its fractal dimension $d_f < 1$ by definition of fractal dimension.[16] For fractal objects in Euclidian spaces with higher dimensions ($d > 1$) for ν it is necessary to accept a fractional part of d_s (in our case, Δ_f), or

$$\nu = \Delta_f - (d - 1) \qquad (10)$$

Then the value of ν characterizes a fraction of the fractal (macromolecular coil), unchanged during the degradation process.

Thus, we obtain a full set of dimensions describing the structure of fractal object (a macromolecular coil)[19]: the dimension of Euclidian space d, in which an oxidation process proceeds; the fractal (Hausdorff) dimension of a macromolecular coil Δ_f, describing its structure; and the effective spectral dimension d'_s describing connectivity of a coil set, and also the degree of temporary (energetic) disorder.[20] The chemical constitution of PAASO is allowed for by the parameter $N_{O_2}^\infty$, which is calculated analytically and does not depend on the method of polycondensation.[10]
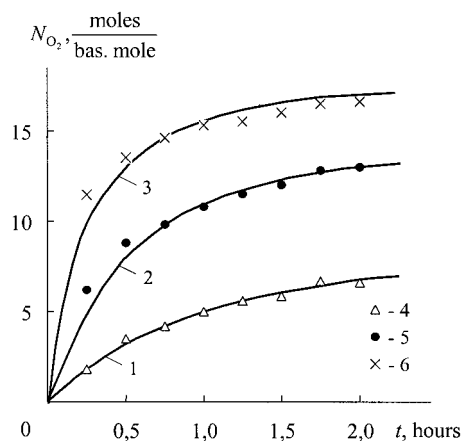
Figure 1 Comparison of kinetic curves $N_{O_2}(t)$ [experimental (1–3) and those calculated using eq. (13) (4–6)] for PAASO-1 at the following temperatues (T in K): 623 (1, 4); 673 (2, 5); and 723 (3, 6).

The oxidation process describing a pseudomonomolecular reaction (reaction of oxidant with reactive centers of macromolecules) is typical for $N_{O_2}(t)$ curves of an autodecelerated type. Such a reaction in a general form is described by the following equation[12]:

$$N_{O_2}(t) = N_{O_2}^\infty[1 - \exp(-C_2 t^{d'_s/2})] \qquad (11)$$

where C_2 is a constant.

Equation (11) allows us to make the following supposition: the constant C_2 determines a macromolecular coil fraction, subjected to a thermooxidative degradation (then the greater the value of C_2, the greater the value of $N_{O_2}(t)$ and the faster the degradation process), which gives

$$C_2 = 1 - \nu \qquad (12)$$

Then it is possible finally to write eq. (11) in a form that does not have empirical-fitting parameters, and is therefore suitable for prediction of $N_{O_2}(t)$ kinetic curves:

$$N_{O_2}(t) = N_{O_2}^\infty[1 - \exp(-(1 - \nu)t^{d'_s/2})] \qquad (13)$$

Figure 1 provides an example of the comparison of $N_{O_2}(t)$ curves, obtained experimentally[3] and calculated according to eq. (13), for PAASO-1 at three testing temperatures T: 623, 673, and 723 K ($\Delta_f = 2.78$, 2.40, and 2.0, respectively) is shown. As may be seen, eq. (13) allows us to predict $N_{O_2}(t)$ curves with sufficient accuracy.

In Figure 2 the comparison of values at $t = 0.5$ h for all PAASO studies in the range $T = 573$–723 K, obtained experimentally[3] and calculated from eq. (13), is shown. The good correspondence of the theory and
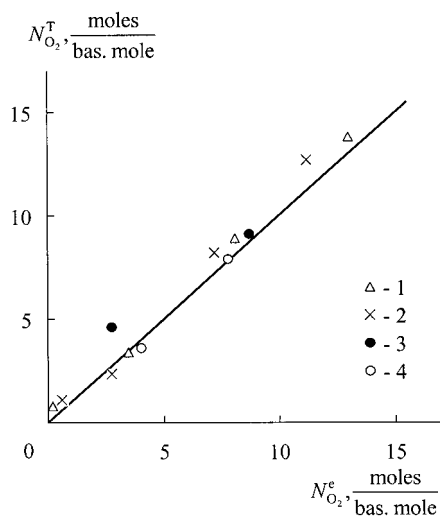
Figure 2 Comparison of experimental $N_{O_2}^e$ and $N_{O_2}^T$, calculated using eq. (13), of values of consumed oxygen amount during $t = 0.5$ h for (1) PAASO-1, (2) PAASO-2, (3) PAASO-3, and (4) PAASO-4 in the temperature range $T = 573–723$ K.

experiment is obtained again. Note that an estimation of the value of $N_{O_2}^\infty$ according to eq. (1) for PAASO-1 and PAASO-2 at $T = 623$ K is 103.3 and 67.1 mol O_2/mol of polymer, respectively, thus confirming the empirical-fitting nature of this parameter in treatment of eq. (1).

CONCLUSIONS

Thus, the results of the present study demonstrated the possibility of a theoretical prediction of oxygen consumption kinetic curves in a thermooxidative deg-

radation process for polymer melts under conditions that allow for both chemical constitution of polymer and physical structure of melts, the last of which can be quantitatively identified within the framework of fractal analysis. Although obtained for the purposes of predicting kinetic curves, the equation does not contain empirical-fitting parameters.

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