Estimation of the Oxygen-Limiting Amount Consumed by Polymeric Melt in the Thermooxidative Degradation Process

G. V. Kozlov,[1] G. B. Shustov,[2] G. E. Zaikov[2]

[1]*Kabardino-Balkarian State University, Chernishevskaya st. 173, 360004, Nalchik, Russia*
[2]*Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin st. 4, 117334, Moscow, Russia*

ABSTRACT: Fractal analysis representations were shown to elucidate quantitative relationships between the parameters of thermooxidative degradation and polymeric melt structure. The process of oxidative consumption during degradation was defined by both the polymer's chemical con-
stitution and the structure of the macromolecular coil. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2840–2844, 2004

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INTRODUCTION

The most common type of oxygen consumption kinetic curves, used to elucidate the thermooxidative degradation process of polymers, is the autodeceleration-type curve.[1] Such dependencies of the consumed oxygen amount N_{O_2} on time t are observed at temperatures above about 473 K and their main reaction of the chain continuation becomes the composition reaction of the peroxide radical.[1] The $N_{O_2}(t)$ autodeceleration-type curves are described by the following equation[1]:

$$N_{O_2} = N_{O_2}^{\infty}(1 - e^{-k_d t}) \qquad (1)$$

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

Note that the value k_d in a physical sense is a fitting coefficient defined from the relationship between the reaction rate W and concentration of reactants [A] and [B][2]:

$$W = k_d \, [A]^p \, [B]^q \qquad (2)$$

where p and q represent the reaction order on reagents [A] and [B], respectively.

Although it has been determined[1] that the value k_d depends on the polymer's structure, the concrete form of such dependency has not yet been established. One of the basic reasons for such dependency, however, is presently lacking, which is attributed to the absence of a quantitative structural model for the amorphous
state of polymers. During the past few years, progress has been made in fractal analysis methods to provide a solution to this problem,[3–5] yielding tools for obtaining more precise analytical representations of the thermooxidative degradation characteristics with respect to the polymer structure. In the present article these problems will be considered by using the example of heterochain polyethers–polyarylates (PAr) and polyarylatearylenesulfonoxides (PAASO) block-copolymers, obtained by different methods of polycondensation.[6]

EXPERIMENTAL

PAr and PAASO, obtained by different methods of polycondensation, were the focus of our investigation. PAASO was synthesized from diane, a mixture (1 : 1) of dichloroanhydrides of tere- and isophthalic acids and 4,4'-dichlorodiphenylsulfon (molecular weight 4600), and also PAr, synthesized on the basis of dichloroanhydride 1,1-dichloro-2,2-di(n-carboxiphenil) ethylene and diane.

The methods and designations of polymers are listed in Table I.

The weight-average molecular weight $\overline{M}_w$ was determined by the method of approaching to equilibrium (Archibald method) in an ultracentrifuge 3170 (MOM, Budapest, Hungary). Values of $\overline{M}_w$ for PAr and PAASO are listed in Table I.

The glass-transition temperature T_g of the studied polymers was determined by the dielectric method. Studies were carried out on a quantometer BM-560 "Tesla" at a frequency of 1 MHz within the temperature interval 293–573 K.[4] The T_g values for PAr and PAASO are listed in Table I.

Thermooxidative degradation processes in air were studied by use of an ampullary technique. The work-

ing volume of ampoules was equal to 3×10^{-5} L. The average initial contents of oxygen were equivalent to a value of 2.5–3.0 mol O_2/mol of polymer. The kinetic curves of oxygen consumption $N_{O_2}(t)$ were obtained within the temperature range 573–723 K.[4]

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

RESULTS AND DISCUSSION

PAr and PAASO, obtained by different methods of polycondensation, were convenient materials of study because, with identical chemical constitutions, they generated different kinetic $N_{O_2}(t)$ curves, which thus isolated the differences to their structures. Thus in Figure 1 the kinetic $N_{O_2}(t)$ curves for PAr are shown at the same testing temperature, 723 K. As may be observed, the oxygen consumption process depends on the method of polycondensation or, as mentioned above, on the polymer's structure. Therefore we shall consider the problem of the quantitative estimation of the polymeric melt structure. As it was mentioned above, the study of the thermooxidative degradation process of PAr and PAASO was carried out within the temperature range 573–723 K, and the temperature range of the glass-transition temperatures (T_g's) of these polymers was T_g = 272–491 K (Table I). It was previously established[7] that the temperature of the so-called transition of liquid 1 to liquid 2 (T_{ll}) can be estimated as follows:

$$T_{ll} \cong (1.20 \pm 0.05) \, T_g \qquad (3)$$

From eq. (3) and the data of Table I the condition $T > T_{ll}$ follows. At T_{ll} there is a transition of a polymeric melt from "liquids to the fixed structure" (where the residual structural ordering is observed[7]) to the true liquid state or "unstructured liquid."[8] However, the unstructured nature of a melt at $T > T_{ll}$ concerns the absence of a supermolecular structure, although the
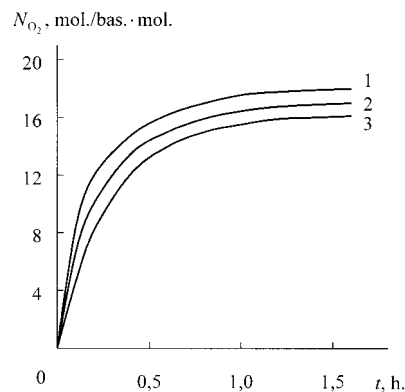
Figure 1 Kinetic curves of oxygen consumption $N_{O_2}(t)$ at T = 723 K for PAr-1 (1), PAr-2 (2), and PAr-3 (3).

structure of a macromolecular coil in a melt remains an important structural factor (essentially, unique at $T > T_{ll}$). The usage of temperature T_{ll} is attributed to that fact that, below this temperature, the short-lived dynamic local order is preserved. At $T > T_{ll}$ this order is destroyed and the fractal dimension of a macromolecular coil remains the only structural parameter. The condition $T > T_{ll}$ confirms the correctness of the last choice.

It is possible to describe the structure of a macromolecular coil, which is the fractal object,[9] more exactly with the help of its fractal (Hausdorff) dimension Δ_f, describing the distribution of coil units in space.[4] Estimation of the value of Δ_f can be made as follows.[10] The formal kinetics of the chemical reactions can be described by the following equation:

$$\frac{dQ}{dt} = k_d \, (1 - Q) \qquad (4)$$

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

The general fractal relationship, also used for the description of the chemical reaction kinetics, may be expressed as[5]

TABLE I
Methods of Polycondensation, Designations, and Basic Characteristics of Studied Polymers

Polymer	Methods of polycondensation	Designation	T_g (K)	$\bar{M}_w$ ($\times 10^{-3}$)	$k_a \times 10^4$,[a] (s^{-1})
PAr	Low-temperature	PAr-1	471	76	0.34
	High-temperature	PAr-2	476	72	0.26
	Interfacial	PAr-3	462	69	0.17
PAASO	Low-temperature	PAASO-1	472	76	0.19
	High-temperature	PAASO-2	474	64	0.24
	Interphasic	PAASO-3	491	66	0.07
	Emulsive	PAASO-4	489	58	0.11

[a] At T = 623 K.

$$Q \sim t^{(3-\Delta_f)/2} \tag{5}$$

By differentiating eq. (5) by relative time t and equating the derivative dQ/dt to the similar derivative in eq. (4), we obtain[10]

$$t^{(\Delta_f-1)/2} = \frac{C_1}{k_d(1-Q)} \tag{6}$$

where C_1 is a constant, which can be estimated from the boundary conditions[10]; and the value Q is defined as the ratio $N_{O_2}/N_{O_2}^{lim}$, where $N_{O_2}^{lim}$ is the limiting amount of oxygen that is capable of being consumed during polymer oxidation.

Estimations of $N_{O_2}^{\infty}$ according to eq. (1) showed considerable (up to triple) variation of this parameter for polymers obtained by different methods of polycondensation, even at one testing temperature. This conclusion may be drawn from the data of Figure 2, where the results for various values of T in the interval $T = 573–723$ K (see Experimental section) are shown. Thus for PAASO-1 the N_{O_2} values were different in five measurements, which means that the limiting amount of consumed oxygen in eq. (1) is essentially a fitting parameter. At the same time the estimations showed[11] that the oxidation of all methylic and aliphatic groups of PAASO requires $N_{O_2}^{lim} = 24.1$ mol O_2/bas mol polymer. Besides, from the data of Figure 1 it follows that, at some value N_{O_2}, kinetic $N_{O_2}(t)$ curves reach the asymptotic value $N_{O_2}^{as}$ (i.e., reach the plateau). The value of N_{O_2} depends on the testing temperature and the method of polycondensation (i.e., the structure melt), characterized by the dimension Δ_f. As studies of all $N_{O_2}(t)$ dependencies at all T have shown, the most evident plateau was observed at $T = 723$ K (this follows, for example, from the comparison of Fig. 1 and Fig. 3). However, the plateau was observed for all $N_{O_2}(t)$ curves of the autodecelerated
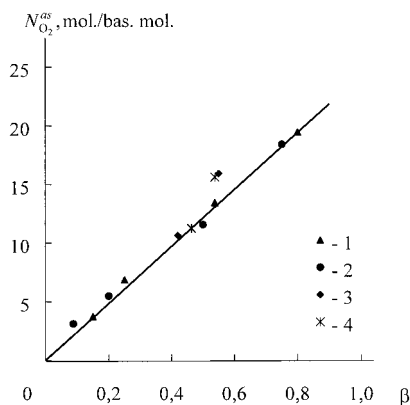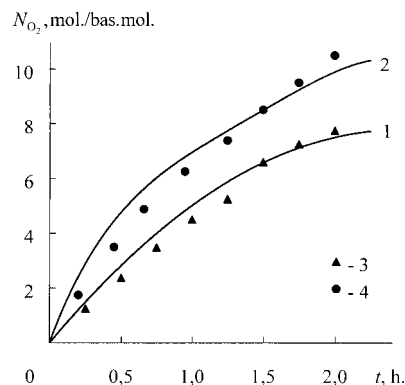

Fig. 2

Figure 2 Dependencies of the consumed oxygen amount $N_{O_2}^{as}$ on a plateau of curves $N_{O_2}(t)$ on parameter β for PAASO-1 (1), PAASO-2 (2), PAASO-3 (3), and PAASO-4 (4).

Figure 3 Simulation of kinetic curves $N_{O_2}(t)$ within the framework of eq. (10) for PAASO-1 at $T = 623$ K (1.3) and $T = 673$ K (2.4). (1) and (2): experimental data; (3) and (4): theoretical calculation.

type. In particular, the $N_{O_2}(t)$ curves that reached the plateau were clearly observed at high temperatures, where the thermooxidative degradation processes occur rather quickly (see Fig. 1). Within the framework of the classical approach, for kinetic $N_{O_2}(t)$ curves to reach the plateau is explained by "burnup" of the reactive groups. Besides, eq. (1) assumes that the condition $N_{O_2} = N_{O_2}^{\infty}$ is reached only at $t \to \infty$.

The fractal structure of macromolecular coils shown above assumes that the thermooxidative degradation process of PAr and PAASO occur not in a Euclidean, but in a fractal space with the dimension Δ_f. In such space the degradation process can be presented by the segments that correspond to the time intervals, where the reaction does not occur. In this case the degradation process is described with the usage of fractal time, which is described by the parameters of Cantor's set.[13] If the reaction is considered in a Euclidean space, the time is described by the set of real numbers.

For the description of the evolutional processes with fractal time the mathematical model of fractional differentiation and integration will be used.[13] As described in the literature,[14] in this case, a fractional exponent ν coincides with the fractal dimension of Cantor's set and indicates a fraction of the system that remains unchanged over all evolution times. We emphasize that Cantor's set is considered in one-dimensional Euclidean space ($d = 1$) and, consequently, its fractal dimension $\Delta_f < 1$ according to fractal definition.[5] For fractal objects in a Euclidean space with higher dimensions ($d > 1$) for ν it is necessary to accept the fractional part d_f (in our case Δ_f) or

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

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

lecular coil β, which breaks up during the degradation, is determined, and thus

$$\beta = 1 - \nu = 1 - [\Delta_f - (d - 1)] = d - \Delta_f \quad (8)$$

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

$$\beta = 3 - \Delta_f \quad (9)$$

Now it is possible to construct the dependency of $N_{O_2}^{as}$ on the value β (i.e., the fraction of a macromolecular coil subjected to degradation). Such dependency is shown in Figure 2 and from it the linear correlation between $N_{O_2}^{as}$ and β follows, from whose slope it is possible to determine the coefficient of the proportionality, equal to about 24.4 mol O_2/bas mol polymer. This value agrees substantially with the estimation of the limiting amount of consumed oxygen $N_{O_2}^{lim}$, calculated from the chemical constitution of PAASO.[11] Therefore, the kinetic $N_{O_2}(t)$ curves reaching a plateau means that the degradation of the fraction of a macromolecular coil, characterized by the parameter β, is accessible by this process. Further this process is sharply decelerated and can be finished by complete disintegration of the macromolecular coil only at $t \to \infty$ [eq. (1)[rsqb].

The above-noted reasons assume that the increase in β should generate an increase in the thermooxidative degradation rate and, consequently, an increase in k_d. By analogy with eq. (1), for kinetic autodeceleration-type $N_{O_2}(t)$ curves it is possible to obtain:

$$N_{O_2} = N_{O_2^{lim}} (1 - e^{-c\beta t}) \quad (10)$$

where c is a constant.

Equation (10) rather successfully (at $c = 0.5 \times 10^{-4}$) describes the experimental $N_{O_2}(t)$ curves, which is confirmed by the data of Figure 3. Nevertheless, there are no grounds to recommend it for this purpose for at least two reasons. First, in this equation there is once again an empirical fitting coefficient c. Second, as follows from the data of Figure 3, some qualitative discrepancy with respect to the form of the experimental and theoretical $N_{O_2}(t)$ curves may be observed. The reason for this discrepancy is obvious: for the description of processes in fractal spaces it is necessary to use a Mittag–Lefleur function, instead of an exponential function, which is strictly correct only for Euclidean spaces.[15] Nevertheless, eq. (10) is useful from that perspective, such that the comparison of exponents of the exponential function of this equation and eq. (1) allows us to obtain the following approximation:

$$k_d = 0.5 \times 10^{-4}\beta \quad (11)$$
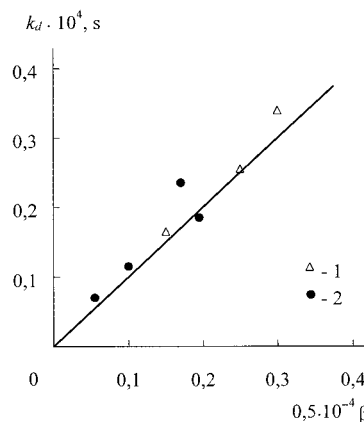
Figure 4 Relation between a constant of the thermooxidative degradation rate k_d and parameter $0.5 \times 10^{-4} \beta$ for PAr (1) and PAASO (2).

The relationship between k_d and $0.5 \times 10^{-4}\beta$ is shown in Figure 4, which is well approximated by the linear correlation with a unit slope. This circumstance confirms that the value k_d is controlled by a macromolecular coil structure. At $\beta = 0$ [or $\Delta_f = 3$; see eq. (9)] the thermooxidative degradation is stopped ($k_d = 0$). This statement confirms that, well known in practice, thermooxidative degradation does not occur in crystalline areas of semicrystalline polymers,[2] given that the indicated areas constitute a three-dimensionally ordered Euclidean object.[16]

CONCLUSIONS

The $N_{O_2}(t)$ dependencies can be described by exponential curves including the parameters that are defined by the chemical constitution of the polymer ($N_{O_2}^{lim}$) and by the physical structure of the macromolecular coil in the melt (β or Δ_f). It is supposed that the more precise description can be obtained by using the Mittag–Lefleur function—the analogue of the exponential function for fractal spaces. The new postulate is that in the process of thermooxidative degradation not all of the macromolecular coil but only its fraction β, which is defined by the fractal dimension of a coil, is destroyed. The greater the value β, the higher the rate of thermooxidative degradation. Thus, for the increase of the polymer melt resistance the destructive processes require a decrease in the value of N_{o2}^{lim} and an increase in the value of Δ_f.

References

1. Emanuel, N. M. Vysokomol Soedin A 1985, 27, 1347.
2. Shlyapnikov, Yu. A.; Kiryushkin, S. G.; Mar'in, A. P. The Oxidative Stabilization of Polymers; Khimiya: Moscow, 1986 (in Russian).
3. Kozlov, G. V.; Novikov, V. U. Synergetics and Fractal Analysis of Crosslinked Polymers; Klassika: Moscow, 1998 (in Russian).
4. Novikov, V. U.; Kozlov, G. V. Russ Adv Chem 2000, 69, 378.

5. Novikov, V. U.; Kozlov, G. V. Russ Adv Chem 2000, 69, 572.

6. Batyrova, H. M. The Influence of Synthesis Method on Structure and Properties of Polyarylates and Poly(arylate-arylenesulfoxide) Block-Copolymers (Dis Kand Khim Nauk); MKhTI: Moscow, 1985.

7. Bershtein, V. A.; Egorov, V. M. Differential Scanning Calorimetry in Physico-chemistry of Polymers; Khimiya: Leningrad, 1990.

8. Lobanov, A. M.; Frenkel, S. Ya. Vysokomol Soedin A 1980, 22, 1045.

9. Baranov, V. G.; Frenkel, S. Ya.; Brestkin, Yu. V. Dokl Akad Nauk SSSR 1986, 290, 369.

10. Ligidov, M. H.; Kozlov, G. V.; Bejev, A. A. Izvest VUZov Khim 2001, 44, 27.

11. Shabaev, A. S. A Thermic and Thermooxidative Degradation of Poly(arylate-arylenesulfoxide) Block-Copolymers (Dis Kand Khim Nauk); MKhTI: Moscow, 1985.

12. Halsey, T. C.; Jensen, M. N.; Kadanoff, L. P.; Procaccia, I.; Shraiman, B. I. Phys Rev A 1986, 33, 1141.

13. Bolotov, V. N. Pis'ma Zh Tekh Fiz 1995, 21, 82.

14. Nigmatullin, R. R. Teor Matemat Fiz 1992, 90, 354.

15. Meilanov, R. P.; Sveshnikova, D. A.; Shabanov, O. M. Izvest VUZov Severo-Kavkaz Reg Estestv Nauki 2001, 1, 63.

16. Kozlov, G. V.; Beloshenko, V. A.; Varyukhin, V. N.; Novikov, V. U. Zh Fiz Issledov 1997, 1, 204.