

Efficiency of the Stabilization Process of a Poly(arylate-arylenesulfoxide) Melt: The Fractal Approach

G. V. Kozlov, G. E. Zaikov

Institute of Biochemical Physics of Russian Academy of Sciences, Kosygin St. 4, Moscow 119991, Russian Federation

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ABSTRACT: The present study has shown that the parameter ε can be accepted as a characteristic of polymer (stabilized or nonstabilized) resistance to thermooxidative degradative action. This parameter can characterize the number of steps number required for a random walk (molecule or atom of oxidant) to achieve the reactive center of a polymer macromolecule. The main structural factor for de-

fining polymer resistance to thermooxidative degradation is effective spectral dimension. It also shows the physical sense of the term *structural stabilization*. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2614–2618, 2006

Key words: structure; stabilization; antioxidants; melt; polyethers

INTRODUCTION

Nowadays, a number of methods are used to estimate the efficiency of thermooxidative degradative stabilizers for polymeric materials.^{1,2} Thus, Emanuel¹ showed that the parameter for estimating this efficiency can be the rate constant of the oxidizability of a polymer. For the same purpose, Shlyapnikov² proposed that an induction period, that is, the time during which the datum concentration of an antioxidant inhibits a polymer oxidation process, be used. In addition, Kopelman and Argyrakis³ proposed a physical treatment within which stabilizer efficiency can be described as follows:

$$\varepsilon = \frac{n}{\theta}, \quad (1)$$

where n is the number of sites on the lattice-visited random walk and θ is dimensionless time or the number of steps in the walk on this lattice.

Within the considered problem, the parameter n can be treated as the number of macromolecular reactive centers and the parameter θ as dimensionless time, which a molecule (atom) of oxidant should expend for the achievement of this reactive center.

It is easy to see that all the suggested methods are not allowed for the polymer structure. It is necessary to note that the particular resistance that nonstabilized polymers have to thermooxidative degradative action is mainly defined by their structure.⁴

In the last few years the development of fractal analysis methods to describe polymers^{5,6} has provided hope that these methods could be successfully applied to the datum problem as well. The purpose of the present study was to determine the characteristics capable of describing polymer (stabilized or nonstabilized) resistance to thermooxidative degradative with allowance for its structure, using the block copolymer poly(arylate-arylenesulfoxide) (PAASO) as an example.⁷

EXPERIMENTAL

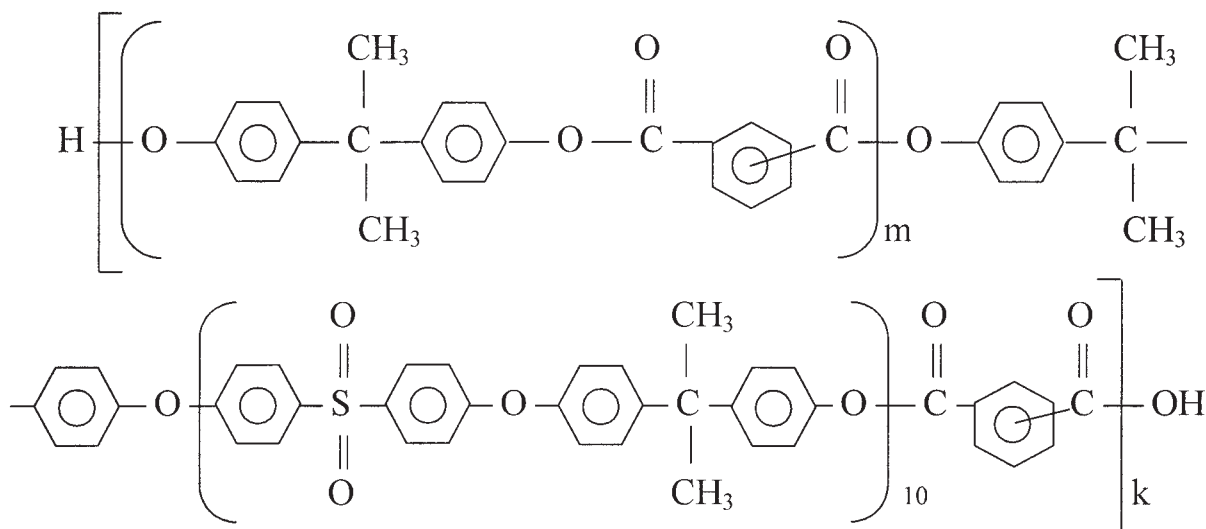
PAASO, obtained by low-temperature polycondensation, was studied. These block copolymers were synthesized from bisphenol A, a mixture of (1 : 1) dichloroanhydride of tere- and isophthalic acids, dihydroxyl-containing oligoarylenesulfonoxide on the basis of diene, and 4,4'-dichlorodiphenylsulfone with a molecular weight of 4600, whose chemical composition is shown in Scheme 1.

The average molecular weight, M_w , of the PAASO was 7.2×10^4 .

The stabilizer used was 4,4'-dimethyl-6,6'-ditertbutyl-2,2'-methylene-bisphenyl ether of phenylphosphoric acid (Stafor-2), whose chemical composition is shown in Scheme 2.

The preliminary thermogravimetric studies allowed determination of the optimal stabilizer concentration, which was 0.5 wt. %. Stafor-2 was incorporated into PAASO by careful blending, subsequently making a solution of the mixture in chloroform, and precipitating it by isopropyl alcohol. After precipitation the stabilized PAASO was dried in the absence of isopropanol. The basic block copolymer was conditionally

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



Scheme 1

designated as PAASO-1 and the stabilized block copolymer as PAASO-2.

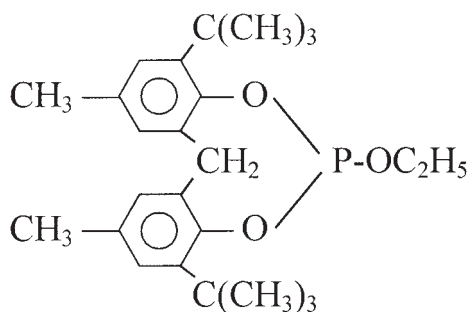
For investigation of the thermooxidative degradative processes in air, the ampullary technique was used. The working volume of ampules was 3×10^{-3} L, and the average initial oxygen content was 2.5–3.0 mol O_2 /basic mol PAASO.

RESULTS AND DISCUSSION

Within the framework of fractal analysis, the parameters of eq. (1) can be directly and strictly connected to a polymer structure. So, the average number of sites (S) visited by a random walk on a fractal object after N steps can be expressed as⁸:

$$\langle S \rangle \sim N^{d_s/2}, \quad (2)$$

where d_s is the spectral (fracton) dimension of a polymer structure characterizing its degree of connectivity.⁹



Scheme 2

Then, dividing both parts of eq. (2) by N and assuming $N \sim t$ (where t is time), it is easy to obtain a fractal analog of eq. (1)¹⁰:

$$\varepsilon \sim t^{d_s/2-1} \quad (3)$$

The physical sense of parameter ε is very simple: it demonstrates how many steps, N (or what amount of time), should be taken by a molecule (atom) of oxidant to achieve the reactive center of macromolecule. Apparently, the higher the N (or t), the higher is polymer resistance to thermooxidative degradative action and the smaller is the ε (as $d_s \leq 2$).¹⁰

The spectral (fracton) dimension, d_s , characterizes the topology and internal connectivity of a polymer structure as follows. If on this structure, having the fractal dimension, d_f , get a random walk (oxidant molecule or atom), then the trajectory of its displacement is described by dimension d_w , which is different from the dimension of structure, d_f . Then d_s is determined by⁹

$$d_s = \frac{2d_f}{d_w}. \quad (4)$$

In its turn, the number of steps, N , on a polymer structure covered by oxidant molecules (atoms) during time t is expressed as⁸

$$N \sim t^{1/d_w}. \quad (5)$$

From a comparison of eqs. (4) and (5), it follows that in a condition where d_f is constant, a decrease in d_s would mean an increase in d_w and therefore a reduction in N during the same time t . In its turn, from eq. (2), it

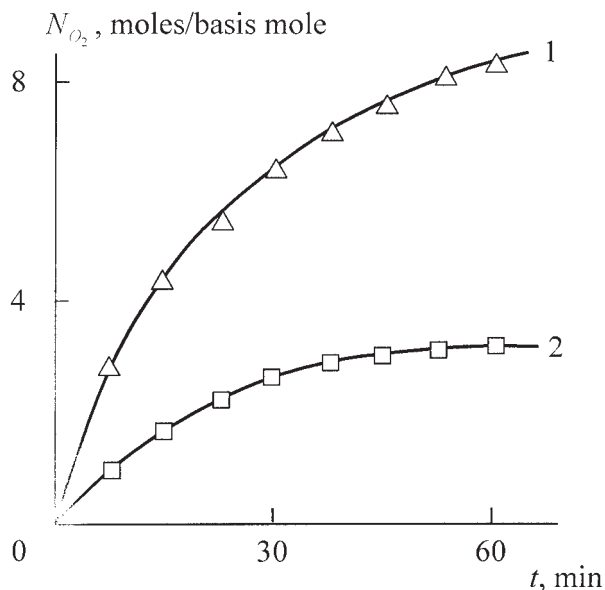


Figure 1 Dependence of amount of oxygen consumed, N_{O_2} , on time t for (a) PAASO-1 and (b) PAASO-2.

follows that a simultaneous decrease in N and d_s would sharply reduce (S) and, therefore, would sharply inhibit the thermooxidative degradative process.

Kopelman¹¹ showed that in chemical reactions, d_s should be replaced by the effective spectral dimension, d'_s , which is connected to d_s as follows (the theorem on subordination)¹¹:

$$d'_s = \beta d_s, \quad (6)$$

where β is the parameter characterizing an energetic (temporal) disorder of a system.

The general property of reactions proceeding in fractal spaces is the dependence of its rate, k , on time t , expressed by^{10,11}:

$$k \sim t^{-h}, \quad (7)$$

where h is the heterogeneity exponent ($0 \leq h \leq 1$).

The condition $h = 0$ is achieved only for homogeneous samples, and the reaction kinetics then becomes classical (Euclidean): k is constant. The parameters d'_s and h are connected by the following simple equation¹¹:

$$d'_s = 2(1 - h). \quad (8)$$

From eq. (7) it is easy to see that the sure property of reactions, proceeding in fractal spaces, is their deceleration in due time. The dependence of the amount of oxygen consumed, N_{O_2} , on time t for nonstabilized and stabilized PAASO samples, shown in Figure 1, demonstrated that the oxygen consumption rate es-

entially decreased with time. This means that the thermooxidative degradative of these samples proceeded in fractal space [in a case of Euclidean space, the dependence, $N_{O_2}(t)$, would be linear and pass through the origin]. Note that linear dependence, $N_{O_2}(t)$, also occurs in practice.¹² In the present study, $h = 0$; $d'_s = d = 2$ [from eq. (8)]; and, from eq. (2), the maximal value of ε was 1 (without allowance for the proportionality coefficient), corresponding to minimal resistance of the polymer to oxidation.

It is possible to determine the values of h for PAASO by plotting the dependence $k(t)$ in double log-log coordinates, where k is determined by¹³

$$k = \frac{N_{O_2}^i}{t_i}, \quad (9)$$

where $N_{O_2}^i$ is the amount of oxygen consumed during time t_i .

Figure 2 shows such dependence values for both PAASO samples at temperatures of 623 and 723 K. As can be seen, in all cases dependence $k(t)$ values in double log-log coordinates were straight lines, which enabled determining h from the slope. It is interesting to note that the slope increased for samples of stabilized PAASO after approximately 30 min of testing. From the data in Table I, which lists the values for h , d'_s , and ε , for PAASO-2 samples, the heterogeneity exponent in the range of $t = 0-30$ min was essentially smaller than that for PAASO-1; after that, in the range of $t = 30-60$ min, it increased substantially (from 0.28

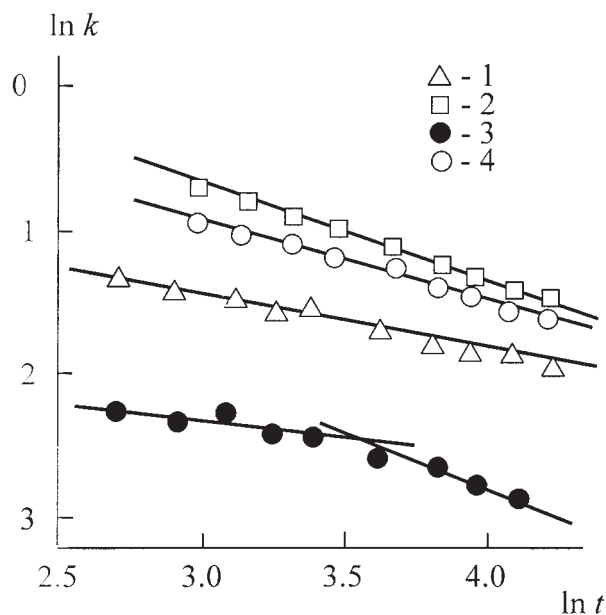


Figure 2 Dependence of rate of oxygen consumption, k , on time t in double log-log coordinates for: (a) PAASO-1 at $T = 623$, (b) PAASO-1 at $T = 723$ K; (c) PAASO-2 $T = 623$, (d) PAASO-2 at $T = 723$ K.

TABLE 1
The parameters, characterizing a thermooxidative degradative process PAASO

Polymer	T , K	t , min	h	d'_s	ε	$\varepsilon_{30}/\varepsilon_{120}$
PAASO-1	623	0-60	0,44	1,12	0,223	1,83
	723	0-60	0,74	0,52	0,081	2,79
PAASO-2	623	0-30	0,28	1,44	0,385	1,47
	623	30-60	0,64	0,72	0,113	2,40
	723	0-60	0,52	0,96	0,170	2,05

up to 0.64). This observation assumes the influence of a stabilizer on the polymer structure (increasing d'_s from 1.12 for PAASO-1 to 1.44 for PAASO-2). This effect is easily observed in the $N_{O_2}(t)$ curves shown in Figure 1: in the beginning the dependences of PAASO-1 and PAASO-2 were approximately similar, and after $t = 30$ min, the N_{O_2} of PAASO-2 increased much more slowly than did that of PAASO-1. There is an interesting aspect of the comparison of the d'_s values obtained at the testing temperatures of 623 and 723 K. At the former temperature, d'_s was greater than 1, and at the latter temperature, it was less than 1. As is known,⁹ a decrease in d'_s of less than 1 means connectivity failure (topology failure) of a macromolecular coil. Intensive thermal degradation of PAASO begins within the temperature range of 665–693 K.⁷ Therefore, at $T = 623$ K, samples would be influenced only by thermooxidative degradative, and at $T = 723$ K, the samples would be influenced by both thermooxidative and thermal degradation. Note that the thermal degradation process, leading to the breaking of the polymer chain bonds and to a decrease in connectivity, that is, to a decrease in d'_s , increased polymer structure efficiency as stabilizer of thermooxidative degradative (Table I). From this, it can be assumed that the sharp reduction in d'_s at $t = 30$ min for PAASO-2 occurred because of the increased thermooxidative degradative of this polymer within the range of $t = 0-30$ min, that is, because of structure loosening when the stabilizer was incorporated.

Therefore, the results show that the main structural factor, raising the resistance of a polymer to thermooxidative degradative, is a decrease in the degree of connectivity, characterized by d'_s , and in this case it did not matter by what method this reduction was achieved. The role of stabilizer in this process was apparent: it made possible the trapping of an oxidant molecule (atom) moving on a polymer structure that was similar to the breakup of the chain because of the impossibility of further oxidant transport. Figure 3 shows the dependence, $\varepsilon(d'_s)$, demonstrating the uniqueness of the dependence of ε on d'_s . At $d'_s = 0$ and $t \rightarrow \infty$, $\varepsilon = 0$. In our case the minimal value of ε was estimated in conditions where $d'_s = 0$ and $t = 60$ min. From this point the value of ε was about 0.033.

As follows from eq. (3), the value of ε is a function of time, decreasing with an increase in t , as $d'_s/2 \leq 1$.

In Table I the relation $\varepsilon_{30}/\varepsilon_{120}$ is shown to characterize the relation of polymer resistance to thermooxidative degradative at $t = 30$ and 120 min. As would be expected, an increase in this relation was observed with an increase in t ; however, the magnitude of this was different in different cases, shown in Table I. Figure 4 shows the dependence $\varepsilon_{30}/\varepsilon_{120}(d'_s)$, from which it follows that an increase in $\varepsilon_{30}/\varepsilon_{120}$ would occur with a decrease in d'_s . Figures 3 and 4 show that the general dependence levels obtained for stabilized and nonstabilized PAASO, providing evidence that the term *structural stabilization* correctly describes polymer degradation.

CONCLUSIONS

The results of the present study showed that the parameter ε , as a characteristic of polymer (stabilized or nonstabilized) resistance to thermooxidative degradative action, can acceptably characterize the required number of steps for a random walk (molecule or atom

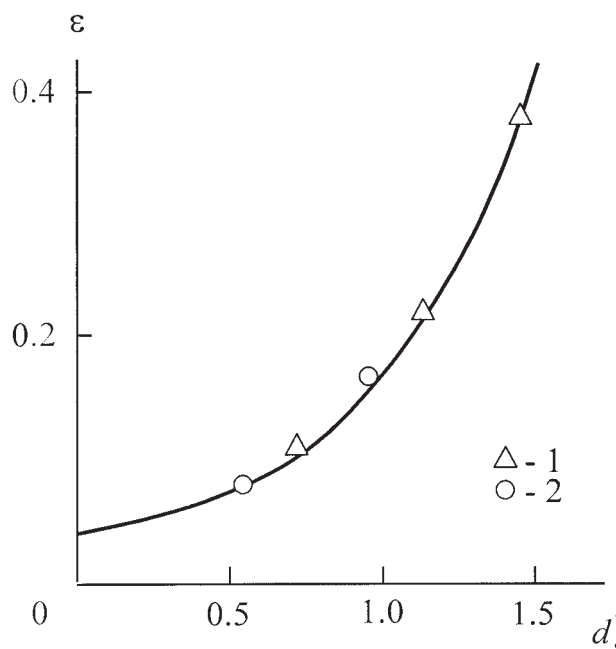


Figure 3 Dependence of the stabilization efficiency parameter, ε , on the effective spectral dimension, d'_s , for PAASO at (a) $T = 623$ and (b) 723 K.

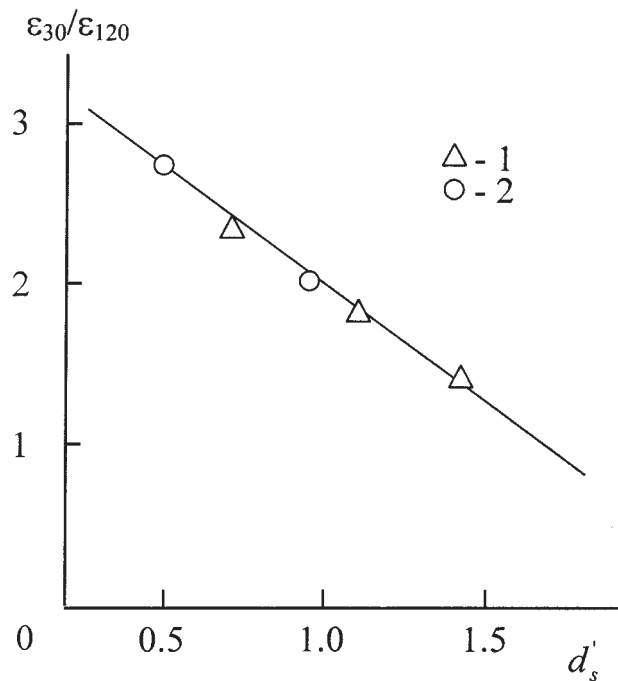


Figure 4 Dependence of the relation $\epsilon_{30}/\epsilon_{120}$ on the effective spectral dimension, d'_s , for PAASO at (a) $T = 623$ and (b) 723 K.

of oxidant) to achieve the reactive center of a polymer macromolecule. The main structural factor, defined polymer resistance to a thermooxidative degradative, has an effective degree of connectivity of a macromo-

lecular coil, characterized by d'_s . A decrease in d'_s leads to increased polymer resistance, in which case it does not matter by which method the decreased d'_s is achieved. A polymer structure is such a stabilizer of thermooxidative degradative, like any chain or non-chain inhibitor incorporated in a polymer for this purpose. Therefore, the term *structural stabilization* has been given a clear physical sense.

References

1. Emanuel, N. M. *Vysokomolekul Soed A* 1985, 27, 1347.
2. Shlyapnikov, Y. A.; Kiryushkin, S. G.; Mar'in, A. P. *The Anti-oxidative Stabilization of Polymers*; Khimiya: Moscow, 1986; p 256.
3. Kopelman, R.; Argyrakis, P. *J Chem Phys* 1980, 72, 3053.
4. Afaunov, V. V.; Kozlov, G. V.; Mashukov, N. I.; Zaikov, G. E. *Zhurnal Prikladn Khimii* 2000, 73, 136.
5. Novikov, V. U.; Kozlov, G. V. *Uspekhi Khimii* 2000, 69, 378.
6. Novikov, V. U.; Kozlov, G. V. *Uspekhi Khimii* 2000, 69, 572.
7. Kozlov, G. V.; Shustov, G. B.; Zaikov, G. E. In: *Aging of Polymers, Polymer Blends and Polymer Composites*; Zaiko, G.; Buchachenko, A.; Ivanov, V., Eds.; Nova Science Publishers: New York, 2002; Vol. 2, pp 151–160.
8. Rammal R.; Toulouse, G. *J Phys Lett (Paris)* 1983, 44, L13.
9. Alexander, S.; Orbach, R. *J Phys Lett (Paris)* 1982, 42, L625.
10. Klymko, P. W., Kopelman R. *J Phys Chem* 1983, 87, 4565.
11. Kopelman, R. In: *Fractals in Physics*; Pietronero, L.; Tosatti, E., Eds.; Elsevier: Amsterdam, The Netherlands, 1986; pp 524–527.
12. Kovarskaya, B. M.; Blumenfeld, A. B.; Levantovskaya, I. I. *Thermal Stability of Heterochain Polymers*; Khimiya: Moscow, 1986; p 256.
13. Kozlov, G. V.; Shogenov, V. N.; Afaunov, V. V.; Zaikov, G. E. *Oxidation Commun* 2003, 1, 121.