The Structural Treatment of a Number of Effective Centers of Polymeric Chains in the Process of the Thermooxidative Degradation

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ABSTRACT: It is shown that the effective number of the polymeric macromolecule reactive centers depends on the macromolecular coil structure. The quantitative characteristic of the latter one can be received within the framework of the fractal analysis. The increase in macromolecular coil fractal dimension, meaning the rise of a degree of its compactness, results in lowering the effective number of the reactive (accessible to the molecules of oxidant) sites of a polymeric macromolecule. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1764–1767, 2003

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INTRODUCTION

The number of the reactive centers of a polymeric macromolecule which is capable of reacting with the oxidant molecules is defined by the chemical constitution of polymer.[1] However, the polymeric macromolecule both in a solution and in a condensed state represents a macromolecular coil which is a fractal.[2] One feature of fractal structures is the different degree of accessibility of their units in different areas of a fractal: it is much larger on the surface of fractal than in its internal areas.[3] Therefore, it is necessary to assume that the effective number of the reactive sites of a polymeric macromolecule is defined not only by its chemical constitution, but also by the macromolecular coil structure. The purpose of the present study is to define the influence of the macromolecular coil structure on the effective number of the macromolecule reactive centers by an example of a melt of the block copolymers of poly(arylatearylene sulphonoxide) (PAASO), obtained by the different methods of polycondensation.[4] To achieve this purpose, representations of the fractal analysis[5,6] and the scaling approach[7] were used.

EXPERIMENTAL

PAASO (Kabardino-Balkarian University, Nalchik, Russia), obtained by the different methods of polycondensation, was studied. The methods and legends of block copolymers are listed in Table I. PAASO is synthesized from diane, a mixture (1 : 1) of dichloroanhydrides of tere- and isophalic acids, and 4,4′-dichlorodiphenylsulfone with a molecular weight of 4600, having the structure:

The average molecular weight ($\overline{M}_w$) is determined by method of approaching equilibrium (Archibald method) in an ultracentrifuge 3170 (corporation MOM, Hungary). The values $\overline{M}_w$ for PAASO are listed in Table I.

The glass transition temperature (T_g) of the studied copolymers is defined by the dielectric method. These studies are carried out by a quantometer BM-560 Tesla at a frequency of 1 MHz within the temperature range of 293–573 K.[4] The T_g values for PAASO are also listed in Table I.

For studies of the thermooxidative degradation processes in the air, the ampullary technique is used. The working volume of ampoules is equal to 3×10^{-5} L. The average initial contents of oxygen make up the value 2.5–3.0 mol O_2/mol of polymer. The kinetic curve of oxygen consumption $N_{O_2}(t)$ is obtained within temperature range 573–723 K.[4] Liquid gaseous products of thermooxidative degradation are analyzed on a chromatograph LHM-8MD. To determine the amounts of the product-calibrating graphs, which are built-up by the exponents, the dissolution method was used. Then, the amount of oxygen in the studied products is recalculated in the following units: moles O_2 per basic mole of polymer.

The plotting of logarithmic anamorphoses of kinetic curves (t) allows us to determine the constant of the reaction rate k_d for thermooxidative degradation (see Table I).
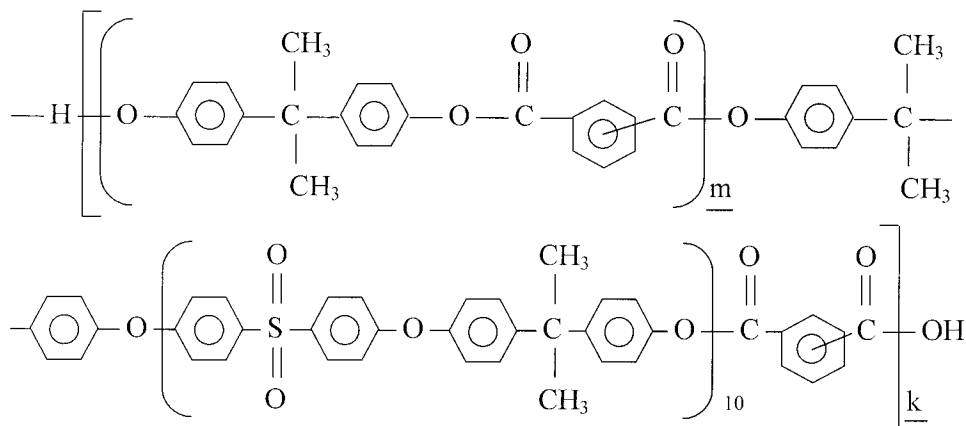
RESULTS AND DISCUSSION

In Figure 1, two typical kinetic curves of oxygen consumption $N_{O_2}(t)$ for PAASO-1 at two temperatures of testing $T = 623$ and 723 K are shown. As it follows from the data of Figure 1, these curves have two main differences: the different rates of oxygen consumption and the different values of N_{O_2}, corresponding to the outlet of a kinetic curve on a plateau of asymptotic values. Consider the analysis of these differences in frameworks of the scaling approach.[8] As an example, we shall consider the reaction in which particles P of the chemical substance diffuse in the environment containing randomly disposed static nonsaturated traps T. At the contact of a particle P with the trap T, the particle disappears. The nonsaturation of the trap means that the reaction $P + T \rightarrow T$ can be repeated an infinite number of times. It is usually considered that, if the concentration of particles and traps is great or the reaction happens at intensive stirring, the process can be considered as the classical reaction of the first order. In this case, it is possible to consider that the law of decay of particle concentration with time $c(t)$ will look similar to[8]:

$$c(t) \approx \exp(-At) \tag{1}$$

where a is a constant proportional to the concentration of traps (reactive centers of polymeric macromolecules).

In Figure 2, the dependences $c(t)$ according to eq. (1) for curves $N_{O_2}(t)$, plotted in Figure 1, where the value

c is defined as $(N_{O_2}^{\infty} - N_{O_2})$ ($N_{O_2}^{\infty}$ is the limiting quantity of oxygen which is capable of being consumed at oxidation), are shown. The values $N_{O_2}^{\infty}$ are accepted to be equal to 12 mol/basic mol for $T = 623$ K and 24 mol/basic mol for $T = 723$ K.[9] As it follows from the data of Figure 2, dependences $c(t)$ plotted according to eq. (1) are linear (i.e., this equation correctly describes the process of thermooxidative degradation PAASO-1), which means that in the considered case, the high concentration of particles (molecules of oxygen) and traps (reactive centers of macromolecules) takes place and the latter, as it should have been expected, is immobile. The dependences $c(t) \approx \exp(-At)$, which are similarly shown in Figure 2, allow the determining values of A for PAASO.

Further, we consider the parameters describing the structure of a polymeric melt. As it was mentioned above, the study of the process of thermooxidative degradation of PAASO is carried out in temperatures ranging from 573 to 723 K, and the temperature range of T_g of these copolymers is $T_g = 472$–491 K (Table I). As reported,[10] the temperature of the so-called transition liquid 1 − liquid 2 in T_{ll} can be estimated as:

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

From eq. (2) and the data of Table I, the condition $T \geq T_{ll}$ follows. At T_{ll}, there is a transition of a polymeric melt from liquid with a fixed structure (where the residual structural ordering[10] is observed) to the true

TABLE I
Methods of Polycondensation, Legends, and Basic Characteristics of Studied PAASO

Method of polycondensation	A legend	T_g (K)	$\overline{M_w} \times 10^{-3}$	$k_d \times 10^{-4\,a}$ (s^{-1})
Low-temperature	PAASO-1	472	76	0.19
High-temperature	PAASO-2	474	64	0.24
Interfacial	PAASO-3	491	66	0.07
Emulsive	PAASO-4	489	58	0.11

[a] At $T = 623$ K.
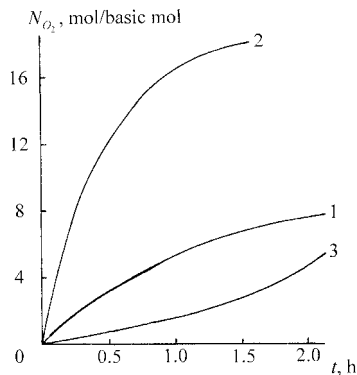
Figure 1 Kinetic curves of oxygen consumption N_{O_2} as the function of time t for PAASO-1 at $T = 623$ (1) and 723 K (2).

liquid state or a structureless liquid.[11] However, the term structureless at $T \geq T_{ll}$ concerns the absence of the supermolecular structure, but the structure of a macromolecular coil in a melt remains the important structural factor (essentially, unique at $T \geq T_{ll}$).

It is possible to describe the structure of a macromolecular coil, which is the fractal object,[2] more exactly with the help by its fractal (Hausdorff) dimension Δ_f, describing the distribution of coil units in space.[12] The estimation of the value Δ_f can be made as follows.[13] The formal kinetics of chemical reactions can be described by the equation:

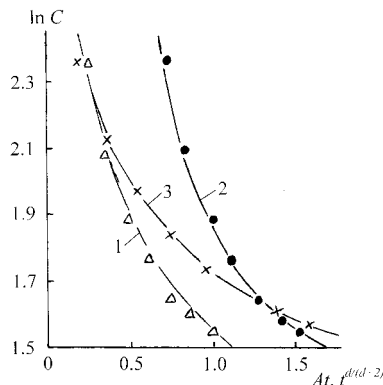$$\frac{dQ}{dt} = k_d(1 - Q) \qquad (3)$$

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

The general fractal relationship also used for the description of kinetics of chemical reactions is[6]

$$Q \sim t^{(3-\Delta_f)/2} \qquad (4)$$
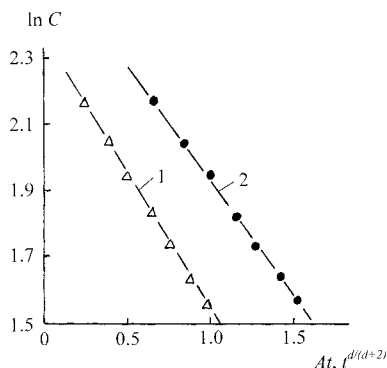
Figure 2 Dependences of particle concentration c decay with time t in log–log coordinates according to eq. (1) for PAASO-1 at $T = 623$ (1) and 723 K (2).

Figure 3 Dependence of the parameter A on the fractal dimension of a macromolecular coil Δ_f for PAASO-1 (1), PAASO-2, PAASO-3 (3), and PAASO-4 (4).

Differentiating the relationship[4] by time t and equating the derivative dQ/dt to a similar derivative in eq. (3), we obtain[13]

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

where C_1 is a constant which can be estimated from the boundary conditions,[13] and the value Q is defined as a ratio $N_{O_2}/N_{O_2}^{\infty}$.

Vilgis[12] offered a simple mean-field Flory-de-Gennes-type estimation of swollen fractal dimension, which accounts for excluded volume interactions. The first part of the Flory free-energy for macromolecular coil is given by the entropic elastic contribution. The second part is the two-body repulsion. Both these parts depend on the gyration radius R_g of the coil. The value R_g in turn depends on interactions of macromolecular coil elements, which are varied with coil structure and testing temperature. Thus, the value Δ_f can depend on the temperature and method of polycondensation.

In Figure 3, the dependence $A(\Delta_f)$ for PAASO is shown. As expected, the increase in Δ_f or the rise of a degree of a macromolecular coil compactness[12] results in lowering A or a decrease of the effective number of reactive centers of a macromolecular coil and at $\Delta_f \approx 2.8$ the access of oxidant in these domains is screened by its surface (i.e., in this case, only those reactive centers of a macromolecule can be exposed to the oxidation, which is likely on a coil surface).

Thus, the process of a melt PAASO oxidation is passed in a fractal space with dimension Δ_f. In such a space, the process of degradation can be presented by the way of devil's staircase.[14] Its horizontal segments correspond to time intervals where the reaction does not pass. In this case, the degradation process is described with the usage of fractal time t, which belongs to a point of Cantor's set.[15] If the reaction is considered
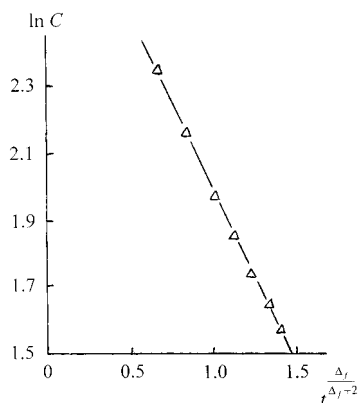
Figure 4 Dependence of the parameter A on fraction $(1 - \nu)$ of macromolecular coil subjecting degradation for PAASO-1 (1), PAASO-2 aand PAASO-3 (3), and PAASO-4 (4).

in an Euclidean space, the time belongs to the set of real numbers.

For the description of evolutional processes with fractal time, the mathematics of fractional differentiation and integration will be used.[15] As shown in ref. [16], in this case the fractional exponent ν coincides with the fractal dimension of the Cantor set and indicates an unchanged fraction of the system for all time of evolution t. We are reminded that the Cantor set is considered a one-dimensional Euclidean space $(d = 1)$ and consequently its fractal dimension $d_f < 1$ by virtue of fractal definition.[14] For 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:

$$\nu = \Delta_f - (d - 1) \qquad (6)$$

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

It is possible to assume that the value A or effective number of the reactive centers is in proportion to the part of a macromolecular coil exposed to the degradation, or $(1 - \nu)$. In Figure 4, the dependence A on $(1 - \nu)$ for PAASO is shown; it appeared linear and value A at $(1 - \nu) \approx 0.21$ or $\Delta_f \approx 2.79$ reaches approximately the constant value that is small according to the absolute magnitude: $A \approx 0.04$. This value A corresponds to the oxidant reaction only on the surface of a macromolecular coil. For $\Delta_f < 2.80$, it is possible to write the analytical relationship between A and ν as:

$$A = 0.5(4 - 5\nu) \qquad (7)$$

Then, with the allowance for eq. (1), we obtain

$$Q \approx 1 - \exp[-0.5(4 - 5\nu)t] \qquad (8)$$

From eq. (8), it follows that at $\nu > 0.8$ the mechanism of the thermooxidative degradation changes, as an exponent in this equation becomes positive.

CONCLUSION

The results of the present study have shown that the effective number of the polymeric macromolecule reactive centers depends on the macromolecular coil structure. The quantitative characteristic of the latter one can be obtained within the framework of the fractal analysis. The increase of macromolecular coil fractal dimension, meaning the rise of a degree of its compactness, results in lowering the effective number of the reactive (accessible to the molecules of oxidant) sites of a polymeric macromolecule.

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