The Scaling Analysis of Thermooxidative Degradation of Poly(Arylatearylene Sulfonoxide)

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ABSTRACT: It is shown that scaling relationships adequately describe the process of oxygen consumption in the course of thermooxidative degradation of poly(arylatearylene sulfonoxide). The correspondence of the experimental curve amount of the consumed oxygen time to one or another scaling relationship allows the definition of the mechanism of thermooxidative degradation. So, for poly-(arylatearylene sulfonoxide), the mode of autodeceleration corresponds to the attack by oxygen molecules of the polymeric macromolecules reactive centers, and the mode of autoacceleration corresponds to the reaction of low molecular radicals. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1760–1763, 2003

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INTRODUCTION

Scaling concepts are widely applied in physics of polymers[1] and it was shown[2] that they can be used for the description of chemical reactions. The scaling laws always define some asymptotics, the applicability of which, taking into account the specificities of the system, needs to be analyzed for each concrete case.[3]

As an example, we considered the reaction in which particles P of a chemical substance diffuse in the environment containing randomly disposed static nonsaturated traps T. At the contact of particle P with trap T, the particle disappears. 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 occurs at the intensive stirring, the process can be considered a classical reaction of the first order. In this case, it is possible to consider that the law of decay of the particle concentration with time $c(t)$ will be[2]:

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

where a is a constant, proportional to the concentration of traps.

However, if the concentration of randomly disposed traps is small, with necessity there exist areas of space which are practically free from traps. The particles in these areas can reach traps only for a large amount of time, and, therefore, the decay of their number will be slower. The formal analysis of this problem shows that the concentration of particles decays under the law[2]:

$$c(t) \approx \exp(-Bt^{d/(d+2)}) \tag{2}$$

that depends on the dimension of space (B is a constant).

Note that the singular dependence on time in eq. (2) occurs simultaneously with the large-scale fluctuations of trap density. If the traps can move, their motion averages the effect of space fluctuations, so that the suppositions resulting in eq. (1) will be fulfilled better. It was shown that in this case the concentration of particles decays under the combined law[2]:

$$c(t) \sim \exp(-At)\exp(-Bt^{d/(d+2)}) \tag{3}$$

where a is proportional to the traps' diffusivity.

The purpose of the present study was to describe the kinetics of oxygen consumption in the process of a poly(arylatearylene sulfonoxide) (PAASO) thermooxidative degradation framework of the scaling approach. PAASO, obtained by different methods of polycondensation, is the convenient object of study, as at the identical chemical constitution they have detected the different curves' amounts of consumed oxygen-time $N_{O_2}(t)$ not only in quantitative, but also in qualitative, relation; for example, they have the different types of curves $N_{O_2}(t)$—with autoacceleration and autodeceleration.[4]
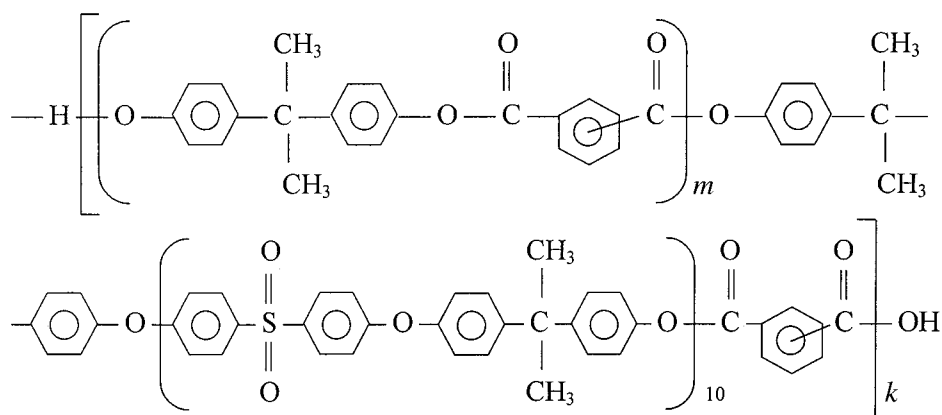
EXPERIMENTAL

We studied PAASO, obtained by the low-temperature acceptor-catalytic (PAASO-1) and interphase (PAASO-2) polycondensation. This block copolymer is synthe-

sized from diane, a mixture of (1:1) dichloroanhydride of tere- and isophalic acids and 4,4'-dichlorodi-

phenylsulfone with a molecular weight of 4600, being of the following structure:

The average molecular weight ($\bar{M}_w$) is determined by a method of approaching to equilibrium (Archibald method) in ultracentrifuge 3170 of Corporation MOM (Hungary). The values $\bar{M}_w$ are equal to 76×10^3 for PAASO-1 and 69×10^3 for PAASO-2.[5] The glass transition temperature (T_g) of studied copolymers is defined by the dielectric method. The studies are carried out by a quantometer BM-560 Tesla at a frequency of 1 MHz in a temperature range of 293–573 K.[5] The T_g value is equal to 471 K for PAASO-1 and 491 K for PAASO-2.

For the 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 contents of oxygen make up the values 2.5–3.0 mol O_2/mol of polymer. Liquid gaseous products of thermooxidative degradation were analyzed on a chromatograph LHM-8MD. To determine the amounts of the product, calibrating graphs, which were built up by exponential dissolution method, were used. Then, the oxygen amounts in the studied

products were recalculated in a summary amount of consumed oxygen according to known equations. The kinetic curves of the oxygen consumption $N_{O2}(t)$ were obtained at temperatures of 623 and 723 K.

RESULTS AND DISCUSSION

In Figure 1, three kinetic curves $N_{O_2}(t)$ for PAASO are shown. As can be seen, at $T = 623$ K, the curves $N_{O2}(t)$ for these copolymers differ by type: for PAASO-1, the curve $N_{O_2}(t)$ has the autodecelerated character, and for PAASO-2, curve $N_{O_2}(t)$ has the autodecelerated autoaccelerated character. The curve $N_{O_2}(t)$ for PAASO-1 at $T = 723$ K also has the autodecelerated character, but with a much bigger gradient of change N_{O_2} in accordance with the increase of time t. Consider the scaling treatment shown in Figure 1; $N_{O_2}(t)$ curves with the use of eqs. (1)–(3).[2] In Figure 2, the dependences $c(t)$ according to eqs. (1) and (2) for PAASO-1 are shown at $T = 623$ K (mode of autodeceleration), where the value c is defined as $(N_{O_2}^\infty - N_{O_2})$ ($N_{O_2}^\infty$ is a limited quantity of oxygen which is capable of being consumed at oxidation). The values $N_{O_2}^\infty$ are accepted to be over 12 mol/
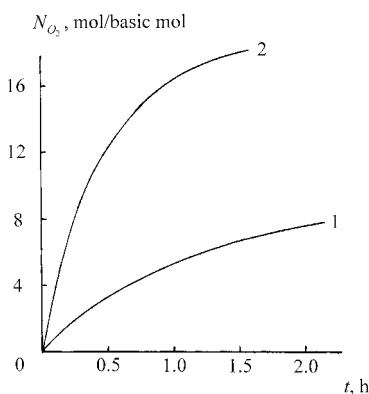

Figure 1 Kinetic curves of oxygen consumed amount N_{O_2} as the function of time t for PAASO-1 at $T = 623$ (1) and 723 K (2) and PAASO-2 at $T = 623$ K (3).
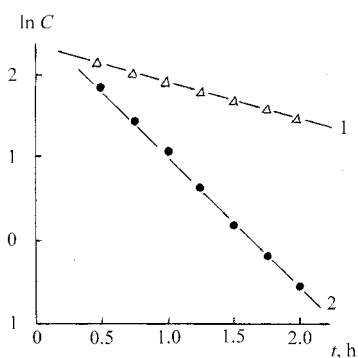

Figure 2 Dependences of decay of concentration of particles c on time t in logarithmic coordinates according to eqs. (1), (1) and (2), (2) for PAASO-1 at $T = 623$ K.
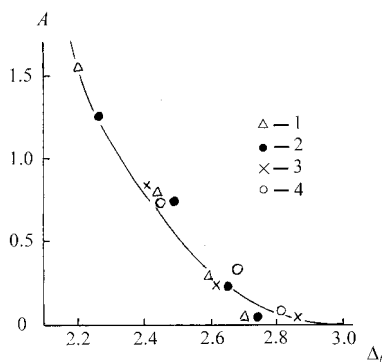
Figure 3 Dependences of decay of concentration of particles c on time t in logarithmic coordinates according to eqs. (1), (1); (2), (2); and (3), (3) for PAASO-1 at $T = 723$ K.

basic mol for $T = 623$ K and 24 mol/basic mol for 723 K.[6] It follows from the data in Figure 2 that the dependences $c(t)$, drawn according to both mentioned equations, are linear (i.e., these equations correctly describe the thermooxidative degradation process of PAASO-1). It means that in the considered case the intermediate concentration of particles (molecules of oxygen) and traps (reactive centers of polymeric macromolecules) takes place, and the latter, as well as it was necessary to expect, are immobile. In Figure 3, the dependences $c(t)$, drawn according to eqs. (1)–(3) for PAASO-1, are shown at $T = 723$ K. Unlike the graphs of Figure 2 for the same copolymer but at lower temperature, none of the indicated equations describe the experimental data. As it is shown in Kozlov et al.[7] in an example of crosslinking reaction of epoxy polymers, the reaction takes place not in an Euclidean, but in a fractal space, with dimension d_f. Hence, it is necessary to consider the physical sense of this fractal dimension. As it was mentioned above, the study of the thermooxidative degradation process of PAASO is made within the temperature range of 623–723 K and the temperature range of glass transition of these copolymers is equal to 471–491 K. The temperature of so-called transition,[8] a liquid 1 − liquid 2, T_{ll} can be estimated as:

$$T_{ll} \approx (1.20 \pm 0.05)T_g \qquad (4)$$

From eq. (4) and the data quoted above, the condition $T > T_{ll}$ follows. At T_{ll}, there occurs a transition of polymeric melt from liquid with fixed structure (where the residual structural ordering is observed[8]) to true liquid state or structureless liquid.[9] Nevertheless, absence of melt structure at $T > T_{ll}$ relates to the absence of supermolecular structure, but the structure of a macromolecular coil in melt remains the important structural factor (in essence, unique at $T > T_{ll}$).

The structure of a macromolecular coil, which is a fractal object,[10] may be precisely described with the help of its fractal (Hausdorff) dimension Δ_f, describing the distribution of units of a coil in space.[3] Therefore, in the considered case, the fractal space of reaction is formed by the fractal structure of a macromolecular coil and consequently $d_f = \Delta_f$. Further, in an exponent of the right part of eq. (2), it is necessary to replace the Euclidean dimension d with the fractal dimension Δ_f. In Figure 4, the dependence $c(t)$ for PAASO-1 is shown at $T = 723$ K, corresponding to eq. (2) with the above-mentioned replacement. As can be seen in this case, the linear relationship, ln c as the function t, is obtained (i.e., the process of oxidation is realized at a small concentration of oxygen molecules in the fractal space). At first, the temperature rise from 623 K up to 723 K causes the change of the reactionary environment character from the Euclidean to the fractal. However, more in-depth study has shown that the problem consists of the value Δ_f or, more precisely, of the closeness of dimension Δ_f to d, that determines the closeness of numerical values of an exponent in eq. (2) at usage Δ_f and d. So, for PAASO-1 at $T = 623$ K, $\Delta_f \approx$ 2.6 and at $T = 723$ K, $\Delta_f \approx 2.2$.[11] Correspondingly, in the first case, the difference of the values of $t^{d/(d+2)}$ and $t^{\Delta_f/(\Delta_f+2)}$ does not exceed 2.5%, and in the second case, this difference is more than 5%. Therefore, the plotting of dependence ln $c(t^{\Delta_f/(\Delta_f+2)})$ for PAASO-1 at $T = 623$ K has shown that these dependences for Euclidean ($d = 3$) and fractal ($d = 2.6$) spaces are practically described by one linear correlation. For PAASO-1 at $T = 723$ K, the difference for cases $d = 3$ and $\Delta_f = 2.2$ is already apparent, which follows from comparing the graphs of Figures 3 and 4, drawn according to eq. (2). Finally, in Figure 5, the dependences $c(t)$ drawn according to eqs. (1)–(3) of PAASO-2 are shown at $T = 623$ K, (i.e., for the mode of autoacceleration). From the pointed graphs, it follows that eqs. (1) and (2) do not describe the behavior of PAASO-2 in the mode of autoacceleration, whereas the linearity of dependence $c(t)$, drawn according to eq. (3), shows the correctness
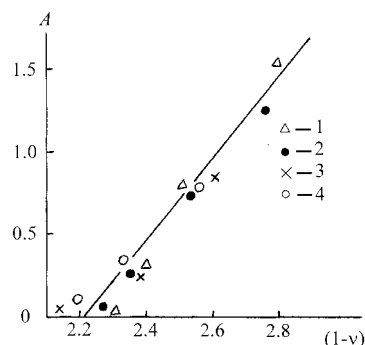

Figure 4 Dependences of decay of concentration of particles c on time t according to eq. (3), in a fractal space with dimension Δ_f for PAASO-1 at $T = 723$ K.
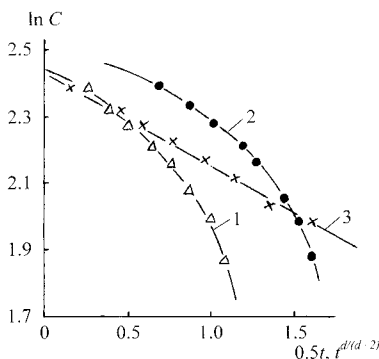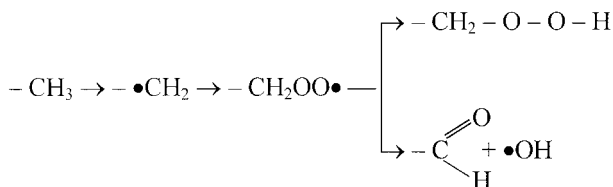
Figure 5 Dependences of decay of concentration of particles c on time t according to eqs. (1), (1); (2), (2); and (3), (3) for PAASO-2 at $T = 623$ K in logarithmic coordinates.

in this case. It means that the traps can move, similar to the particles. Therefore, as in the mode of autoacceleration, the thermooxidative degradation realizes at the expense of radical reaction,[12] their high mobility supposes that in the case of PAASO the low molecular radicals react. The probable chemical mechanism of formation of such radicals in the case of high-temperature oxidation is discussed in ref. [12]. It is supposed that the product, responsible for autoacceleration, is the aldehydic group, formed from the methyl groups according to the scheme[12]:

$$-CH_3 \rightarrow -\bullet CH_2 \rightarrow -CH_2OO\bullet \begin{cases} \rightarrow -CH_2-O-O-H \\ \\ \rightarrow -C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagdown}} + \bullet OH \end{cases}$$

The oxidation of the aldehydic groups is realized according to the scheme[12]:

$$R-C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup}} + O_2 \rightarrow R-CO\bullet + HO_2\bullet$$
$$\downarrow$$
$$R\bullet + CO$$
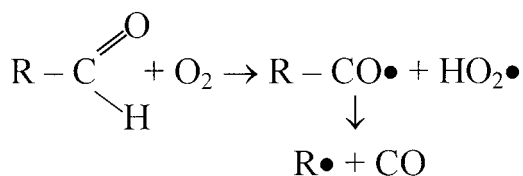
which results in the formation of active free radicals R· and low molecular radicals HO$_2$·.[12]

CONCLUSION

Thus, the results obtained in the present study have shown that scaling relationships adequately describe the process of oxygen consumption in the course of thermooxidative degradation of poly(arylatearylene sulfonoxide). The correspondence of the experimental curve amount of the consumed oxygen time to one or another scaling relationship allows the definition of the mechanism of thermooxidative degradation. So, for PAASO, the mode of autodeceleration corresponds to the attack by oxygen molecules of the polymeric macromolecules reactive centers, and the mode of autoacceleration corresponds to the reaction of low molecular radicals.

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