

# A Structural Model of an Accessibility of Polycarbonate Melt to Thermooxidative Degradation Processes

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**ABSTRACT:** It is shown that the "accessibility" of a polymer for oxidation is the only structural factor and quantitative estimate within the framework of the fractional derivation. The oxidation rate of the "accessible" part of a macromolecular coil is independent on its structure, which allows to assume its dependence only on the chemical constitution

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**Key words:** polycarbonate; thermooxidative degradation; polymer melt; macromolecular coil structure; fractal theory

## INTRODUCTION

The authors<sup>1</sup> have assumed that in solid polymers an anisotropy about structural characteristics always takes place. Therefore, they used the term of an accessibility of polymer bonds for various reactions realization. Besides, they have demonstrated that at accessibility allowance for the rate of amide bonds, hydrolysis and water solubility in polyamide-12 are independent of sample structure.

The application of the fractal analysis methods for the determination of structure and properties of polymers<sup>2,3</sup> allows to assume that the term "accessibility" of polymers structure for various processes realization is concerned with not only solid but also with any other state of polymers. This phenomenon has a fundamental cause, namely, the fractality of polymer structure. For this postulate confirmation, in the present study the theoretical structural definition of "accessibility" and its application for description of a thermooxidative degradation of polycarbonate melt will be given.

## EXPERIMENTAL

Polycarbonate (PC) on the basis of bisphenol A of commercial production, with average viscosity molecular weight  $M_{\eta} = 5 \times 10^4$ , is studied. PC film samples with a thickness of  $\sim 0.08$  mm are obtained from solutions of a polymer in three different solvents (chloroform, methylene chloride, and chlorobenzene).

These films were obtained by pouring their 5% solutions in indicated solvents on the horizontal glass substrate. The films were dried in vacuum under  $\sim 353$  K for 2 days for perfect dehumidification and desolvation. PC film samples are exposed to heat aging on air at 513 K for 12 h. After each 1.5 h of heat aging, the samples were taken out and their intrinsic viscosity  $[\eta]$  of PC in 0.5% solution of chloroform was determined. Using the value of  $[\eta]$ , an average viscosity molecular weight  $M_{\eta}$  according to the Mark-Kuhn-Sacurada equation<sup>4</sup> was estimated. Then, a ruptures number  $S$  for the initial macromolecule, according to equation<sup>5</sup> was calculated:

$$M_{\eta} = \frac{2M_{\eta}^0}{S^2(S-1+e^{-S})} \quad (1)$$

where  $M_{\eta}^0$  and  $M_{\eta}$  are average viscosity molecular weights of polymer before and after degradation, respectively.

The technique of the fractal dimension of a macromolecular coil in melt determination is described in Kolov et al.<sup>6</sup> and the thus obtained values  $\Delta_f$  are equal to 2.54, 2.45, and 2.43 for PC films produced from solutions in chloroform, methylene chloride, and chlorobenzene, respectively.

## RESULTS AND DISCUSSION

Let us consider parameters describing a polymer melt structure. As it was mentioned earlier, the studies of the process of PC thermooxidative degradation is carried out at 513 K and the glass transition temperature for PC  $T_g$  is equal to 423 K.<sup>4</sup> As it is known,<sup>7</sup> the

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temperature of the so-called transition "a liquid 1-liquid 2"  $T_{11}$  can be estimated as follows:

$$T_{11} \approx (1.20 \pm 0.05)T_g \quad (2)$$

From the eq. (2) and the above quoted data, the condition  $T > T_{11}$  ( $T$  is testing temperature) follows. At  $T_{11}$ , there occurs a transition of the polymer melt from "liquid with fixed structure" (where residual structural ordering is observed<sup>7</sup>) to true liquid state or "unstructured liquid."<sup>8</sup> Nevertheless, "structurelessness" of melt at  $T > T_{11}$  relates to the absence of a supermolecular structure, but the structure of a macromolecular coil in melt remains the important structural factor (in essence, unique at  $T > T_{11}$ ).

Thus, the main structural element in polymer melt remains a macromolecular coil, which represents a fractal object. This means that the degradation processes in a coil volume proceed not in Euclidean, but in fractal space with dimension  $\Delta_f$ . In the latter space, the degradation process can be presented by the way of "devil's staircase."<sup>8</sup> Its horizontal segments correspond to time intervals, where the reaction does not proceed. In this case, a degradation process is described with the use of fractal time, which belongs to the points of Cantor's set.<sup>8</sup> If the reaction is considered in an Euclidean space, the time belongs to the set of real numbers.

For the description of evolutionary processes with fractal time, the mathematics of fractional derivation and integration will be used.<sup>8</sup> As shown in Bolotov,<sup>9</sup> in this case fractional exponent  $\nu$  coincides with fractal dimension of Cantor's set and indicates a fraction of system unchanged for all time of evolution  $t$ . Let us remind that the Cantor's set is considered in one-dimensional Euclidean space ( $d = 1$ ) and consequently its fractal dimension  $d_f < 1$  by the definition of fractal dimension.<sup>2</sup> For fractal objects in Euclidean spaces with higher dimensions ( $d > 1$ ) as  $\nu$ , it is necessary to accept a fractional part of  $d_f$  (in our case— $\Delta_f$ ) or

$$\nu = \Delta_f - (d - 1) \quad (3)$$

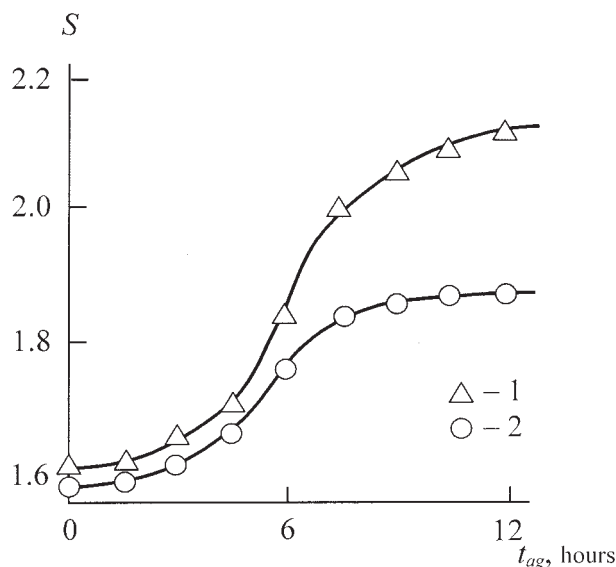
Then, the value of  $\nu$  characterizes a fraction of fractal (macromolecular coil), which is unchanged during a degradation process. Apparently, the fraction of a macromolecular coil  $\beta$  that is breaking up during  $d$  degradation is determined as follows:

$$\beta = 1 - \nu = 1 - (\Delta_f - (d - 1)) = d - \Delta_f \quad (4)$$

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

$$\beta = 3 - \Delta_f \quad (5)$$

In Figure 1, the dependences of a ruptures number  $S$  on the initial macromolecule on the duration of heat



**Figure 1** The dependences of ruptures number  $S$  on one macromolecule on heat aging duration  $t_{ag}$  at  $T = 513$  K for PC films obtained from solutions in chloroform (1) and methylene chloride (2).

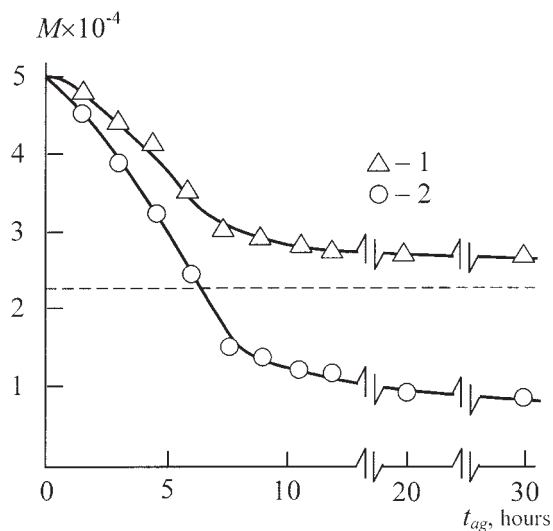
aging  $t_{ag}$  for PC films, obtained from solutions in chloroform and methylene chloride, are shown. The PC films, obtained from solutions in methylene chloride and chlorobenzene, have very similar curves  $S(t_{ag})$ , practically coinciding with each other, and that's why the data for the latter are not shown in Figure 1. As it is possible to see that these kinetic curves  $S(t_{ag})$  are concerned to mixed sigmoidal type of kinetic curves, where an initial part (up to  $t_{ag} \leq 6$  h) the autoacceleration regime is observed, crossing to autodeceleration regime and at  $t_{ag} \geq 9$  h the reaching of the curve  $S(t_{ag})$  on asymptotic branch happens.<sup>10</sup> The last part of the kinetic curve is explained by decreasing the thermooxidative degradation rate because of burnup of reactive groups.<sup>10</sup> The fact that the achievement of asymptotic branch of curves  $S(t_{ag})$  is realized at different values of  $t_{ag}$  for the same polymer (in our case—PC) has drawn attention. This means that different structure of PC films, obtained from different solvents, is preserved in polymer melt, and this circumstance is confirmed by different values of  $\Delta_f$ .

In Bazumovskii et al.,<sup>1</sup> the following equation for calculation of intrinsic viscosity  $[\eta]_{exp}$  was offered:

$$[\eta]_{exp} = [\eta]_1 f_1 + [\eta]_2 f_2 \quad (6)$$

where  $[\eta]_1$  and  $[\eta]_2$  are intrinsic viscosities and  $f_1$  and  $f_2$  are the fractions of total mass of accessible and nonaccessible for oxidation phases. It is assumed that  $[\eta]_2 \approx [\eta]_0$ , where  $[\eta]_0$  is intrinsic viscosity of initial polymer.

The intrinsic viscosity represents complex characteristic, which depends on the structure of a macro-



**Figure 2** The dependences of an experimental molecular weight  $M_{\text{exp}}$  (1) and molecular weight  $M_1$  of accessible for oxidation part of structure (2) on heat aging duration  $t_{\text{ag}}$  for PC film obtained from solution in methylene chloride.

molecular coil in solution and molecular weight  $M$  by enough complicated matter.<sup>11</sup> As eq. (6) represents in essence a well-known mixture rule,<sup>11</sup> we change in it values of  $[\eta]$  on corresponding molecular weights of polymer  $M_{\text{exp}} = M_{\eta}$ ,  $M_1$  and  $M_2 = M_0$ . Besides, from the aforesaid discussion, we change the parameters  $f_1$  and  $f_2$  on relevant structural characteristics ( $3 - \Delta_f$ ) and  $(\Delta_f - 2)$ . Then, the eq. (6) accepts the following form:

$$M_{\text{exp}} = (3 - \Delta_f)M_1 + (\Delta_f - 2)M_0 \quad (7)$$

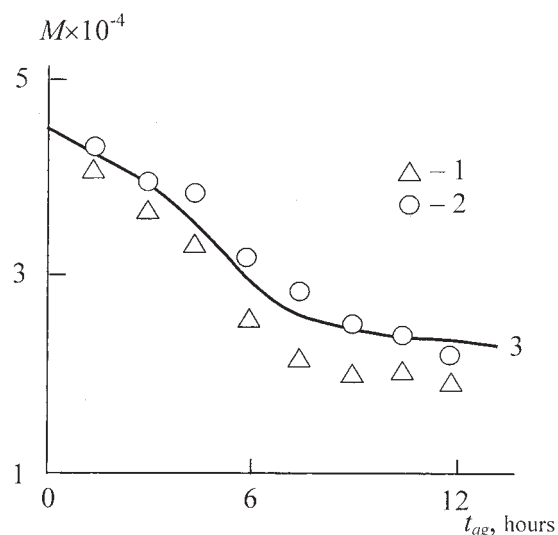
In Figure 2, the dependences of  $M_{\text{exp}}$  and  $M_1$  on heat aging duration  $t_{\text{ag}}$  are shown, and a dashed horizontal line the limiting value of molecular weight, which can be achieved by polymer in degradation processes, equal to  $(\Delta_f - 2)M_0$ , is also shown. As follows from the data of this Figure, at  $t_{\text{ag}} \geq 9$  h,  $M_{\text{exp}}$  is approaching asymptotically to the limiting value of  $M$  (at  $t_{\text{ag}} = 12$  h the difference is equal to  $\sim 22\%$ ), and value of  $M_1$  also asymptotically is approaching to zero. The extrapolation of  $M_1$  to zero demonstrates that this value should be achieved at  $t_{\text{ag}} \approx 80$  h. For verification of this assumption heat aging of PC films, obtained from solution in methylene chloride, at the aforementioned regimes for  $t_{\text{ag}} = 20$  and 30 h, were made. These tests have shown that at  $t_{\text{ag}} = 20$  h the value of  $M_1$  really decreases to  $\sim 14\%$  in comparison with  $M_1 \sim 7\%$  at  $t_{\text{ag}} = 12$  h and at  $t_{\text{ag}} = 30$  h, i.e., slow asymptotic approaching  $M_1$  to zero is observed.

If we assume that PC is inaccessible for oxidation part of structure undergoes thermooxidative degradation independent of its structural state, i.e., the value  $\Delta_f$ , then value  $M_1$  should be identical for all studied PC

films. To check this assumption, we calculated the values of  $M_1$  for PC films, obtained from solution in methylene chloride, according to eq. (7), and then according to the same equation we estimated values of  $M_T$  for PC films, obtained from solutions in chloroform and chlorobenzene, by using these  $M_1$  values. The comparison of the dependences  $M_{\text{exp}}(t_{\text{ag}})$  and  $M_T(t_{\text{ag}})$  for two last films is shown in Figure 3 (in this figure only one dependence  $M_T(t_{\text{ag}})$  is shown as for the mentioned films of PC the calculation of  $M_T$  according to eq. (7) gives close values). As it is possible to see that good enough correspondence of theory and experiment is obtained (the average disagreement 13.9% for films obtained from solution in chloroform and 5.8% from solution in chlorobenzene). The disagreement was calculated as a relative difference of experimental and theoretical data. The higher disagreement for the former from the mentioned films is probably due to the error of the  $\Delta_f$  estimation. However, the data of Figure 3 assume the correctness of a constant rate supposition at a thermooxidative degradation of accessible for this process part of polymer, independent of the melt structure.

## CONCLUSIONS

Thus, the results of the present article have shown that the "accessibility" of a polymer for oxidation is the only structural factor and quantitative estimate within the framework of the fractional derivation. The oxidation rate of "accessible" part of a macromolecular coil is independent on its structure, which allows to as-



**Figure 3** The comparison of an experimental (1, 2) calculated according to the eq. (7) and dependences of a molecular weight  $M$  on heat aging duration  $t_{\text{ag}}$  for PC films obtained from solutions in chloroform (1, 3) and chlorobenzene (2, 3).

sume its dependence only on chemical constitution of polymer.

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