

## **DETERMINATION OF DEGRADATION APPARENT ACTIVATION ENERGY VALUES OF POLYMERS Regression of kinetic parameters derived from TG data**

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### **Abstract**

The isothermal degradation of three aromatic polyetherketones was studied in an inert environment at various temperatures in the range 683–803 K. In the first degradation stage (mass loss  $D \leq 20\%$ ) a linear increase of  $D$  as a function of heating time ( $t$ ) was observed and the corresponding kinetic  $D = D_0 + \beta t$  equations at various temperatures were directly drawn by smoothing the experimental TG data. The  $\beta$  values, which represent the mass loss rates during degradation, increased as a function of temperature according to Arrhenius-type equations, from which degradation  $E_a$  values were determined, which appear in agreement with those from literature methods. Some differences observed were discussed and interpreted.

**Keywords:** kinetic parameters, polyetherketones, thermal degradation, thermogravimetric analysis

### **Introduction**

The determination of the kinetic parameters of degradation is important for evaluating the thermal stability of polymers. Thermogravimetric (TG) technique is widely used for this purpose and many TG methods in various experimental conditions are reported in some excellent reviews [1–7]. All these methods are based on equations obtained by making assumptions and restrictions not always satisfied, so that several workers have pointed out that great care should be exercised in giving physical significance to the activation energy ( $E_a$ ) and the reaction order ( $n$ ) determined by them [3, 8, 9]. Also recent methods reported in literature do not appear free from assumptions and/or complicated calculations [10–12].

In the last years our group has carried out a wide research work regarding the comparative study of the kinetics of degradation of thermoplastic aromatic polyethers containing carbonyl and sulfone groups. Such materials are of potential interest to be used as matrices for high performance composite materials [13–18]. Recently [19] we found that the first isothermal degradation stage of three polyetherketones in static

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air atmosphere proceeded through an exponential increase of the mass loss rate ( $V$ ) as a function of heating time ( $t$ ). The kinetic  $V = V_0 2^{\alpha t}$  equations at the various temperatures of isothermal experiments could be then directly derived by the experimental TG curves ( $V = dD/dt$  where  $D =$  degree of degradation) without any assumption or restriction. The  $\alpha$  values ( $\text{min}^{-1}$ ) obtained, which represent the fragmentation rates of polymer chains, increased with temperature according to Arrhenius-type equations for all investigated polymers. The  $E_a$  values from these equations in the considered degree of degradation were in very good agreement with those determined by the classical Kissinger [20] and MacCallum [21, 22] methods.

On continuing our work in this field we studied here the kinetics of isothermal degradation in inert environment of the same polymers



(where Ar=1,4-substituted phenylene) previously studied in an oxidative atmosphere [19].

The aims of this work were:

- to compare the results in an inert environment with those in a static air atmosphere;
- to draw, if possible, the  $D = f(t)$  and then the derived  $V = f(t)$  relationships (where the mass loss  $D = (W_0 - W)/W_0$ ,  $t =$  heating time and  $V = dD/dt$ ) at the various temperatures of the isothermal degradations directly from the experimental mass loss data;
- to verify the possibility of obtaining Arrhenius-type relationships, and then reliable apparent activation energy values ( $E_a$ ) of degradation, by the parameters of the reported equations, as found in the oxidative environment;
- to compare the  $E_a$  values so obtained with those from other methods.

## Experimental

### Materials

Polymers were synthesized according to the procedure previously reported [14] and were used in the powder form. Powders of samples were dried under vacuum at room temperature and kept in a desiccator under vacuum until use.

### Isothermal degradations

A Mettler TA 3000 thermogravimetric analyser, coupled with a Mettler TC 10A processor, was used for the isothermal degradations. The temperature calibration of thermobalance was made according to the procedure reported in the user's manual of equipment [23], based on the change of magnetic properties of three metal samples

(Isatherm, Nickel and Trafoperm) at their Curie points (142.5, 357.0 and 749.0°C, respectively). The temperature calibration was repeated every month.

Degradation experiments were carried out at  $T = 683, 703, 713, 723, 733, 743, 753, 763, 773, 783, 793$  and  $803$  K under a pure  $N_2$  flow ( $20 \text{ mL min}^{-1}$ ). The temperature range 683–803 K, quite more extended than that (743–803 K) previously employed by us for determining the  $E_a$  values of degradation of the same polymers in the molten state [14], was used for the isothermal degradations, in order to include, where possible, also temperatures lower than the melting temperatures of the various crystal forms of studied polymers [19]. Experiments at temperatures lower than 683 K were also attempted, but no reliable  $D = f(t)$  equations were obtained due to the very low mass loss rates of samples.

Degradation experiments were carried out as follows: samples were quickly heated ( $40 \text{ K min}^{-1}$ ) from r. t. to the selected temperature and then maintained at this temperature for 900 min. The mass of the sample at the start of isothermal heating was considered to be the initial one. Samples of  $4 \cdot 10^{-3} - 6 \cdot 10^{-3}$  g, held in alumina open crucibles, were used and their mass were measured as a function of heating time. At the end of each experiment the TG and DTG curves were recorded and the mass of the sample at the various times, taken in three min intervals, were transferred to a PC and there stored for next elaboration, for which also the TG data previously obtained by us in the 743–803 K temperature range, in the same experimental conditions [14], were used.

## Results and discussion

At all selected temperatures of the considered range (683–803 K) the isothermal degradations under  $N_2$  flow proceeded, for all investigated polymers, differently than in oxidative environment [19]. A first degradation stage was observed, showing appreciable mass loss rate, followed by a second one in which the mass of sample remained practically constant because of the formation of a stable residue. The comprehensive mass losses in 900 min found for the polymers 1, 2 and 3 at various temperatures are reported in Table 1.

A quantitative analysis of the experimental data of the first stage evidenced a linear increase of degree of degradation as a function of heating time, thus indicating constant mass loss rates. Single linear  $D = f(t)$  relationships were obtained at lower temperatures, where mass losses only within 15% could be detected in reasonable time. By contrast, for the isothermal experiments at higher temperatures, where higher mass losses were observed, two linear degradation steps ( $5 \leq D \leq 15\%$  and  $15 \leq D \leq 20\%$  about, respectively) were found.

This behaviour was different than that in a static air atmosphere, where an exponential increase of  $D$  as a function of  $t$  was found in the same range of degrees of conversion [19].

For the three investigated polymers the  $D$  values at various heating times, calculated by the experimental TG data, fitted very well into  $D = D_0 + \beta t$  linear relationships. The regression coefficients of the equations obtained at the various tempera-

tures of isothermal experiments ( $T_{\text{iso}}$ ) are reported in Tables 2 and 3 for the  $5 \leq D \leq 15\%$  and  $15 \leq D \leq 20\%$  degradation steps, respectively.

**Table 1** Mass loss (%) in 900 min of polymers 1, 2 and 3 at the various temperatures of isothermal degradations ( $T_{\text{iso}}$ )

$T_{\text{iso}}/\text{K}$	Polymer 1	Polymer 2	Polymer 3
	Mass loss/ %	Mass loss/ %	Mass loss/ %
683	15.10 (3387)*	15.18 (4090)*	15.28 (3231)*
703	15.41 (1335)*	15.26 (1515)*	15.12 (1421)*
713	16.80	15.02 (970)*	17.84
723	22.73	18.89	19.61
733	26.72	23.37	21.23
743	29.33	26.97	26.17
753	31.13	29.50	29.55
763	33.10	30.65	34.54
773	37.42	32.10	40.18
783	43.43	37.78	46.78
793	44.97	40.78	54.78
803	46.14	41.29	51.20

\* time (min) employed by sample to reach the reported mass loss

The  $\beta$  parameter ( $dD/dt$ ), which represents the mass loss rate during degradation, increased exponentially in both steps as a function of  $(-1/T_{\text{iso}})$ , as shown in Figs 1 and 2, then giving rise to Arrhenius-type equations. The obtained Arrhenius relationships were expressed in the form  $\ln\beta = \ln A - B/T_{\text{iso}}$ . The corresponding linear correlation coefficients for the three investigated polymers are reported in Table 4, where the apparent activation energy values for the two observed degradation steps, calculated by the slopes ( $B = E_a/R$ ) of the obtained straight lines, were also reported.

Relatively high standard deviations were found for the 15–20% degradation step, probably due to the more complex process which does not allow a very precise determination of the degradation rate.

The experimental TG data were also treated according to the MacCallum equation

$$\ln t = a + b/T_{\text{iso}}$$

where  $t$  = time employed to reach a fixed degree of degradation  $D$ ,  $a = \ln[F(1-D)] - \ln A$ ,  $b = E_a/R$ ,  $T_{\text{iso}}$  = temperature of isothermal degradation and  $F(1-D)$  is a function of degree of degradation. Thus the apparent activation energy, at each degree of degradation, could be obtained by the slope of the  $\ln t$  vs.  $1/T_{\text{iso}}$  straight line.

In the whole investigated temperature range ( $683 \text{ K} \leq T \leq 803 \text{ K}$ ), linear  $\ln t = f(1/T_{\text{iso}})$  relationships at various degrees of degradation in the  $5 \leq D \leq 15\%$  interval were obtained

**Table 2** Regression coefficients of the  $D=D_0 + \beta t$  equations at the various temperatures of isothermal experiments for the ( $5 \leq D \leq 15\%$ ) degradation step

$T_{\text{iso}}/\text{K}$	Polymer 1			Polymer 2			Polymer 3		
	$D_0$	$\beta/\text{min}^{-1}$	$r^*$	$D_0$	$\beta/\text{min}^{-1}$	$r^*$	$D_0$	$\beta/\text{min}^{-1}$	$r^*$
683	0.0155	0.00004	0.9917	0.0291	0.00005	0.9975	0.0171	0.00005	0.9985
703	0.0205	0.0001	0.9907	0.0345	0.0001	0.9993	0.0091	0.0001	0.9987
713	0.0102	0.0002	0.9948	0.001	0.0002	0.9973	0.017	0.0002	0.9947
723	0.0017	0.0004	0.9968	-0.0085	0.0003	0.9991	0.0255	0.0003	0.9910
733	-0.015	0.0008	0.9997	-0.0182	0.0006	0.9994	-0.005	0.0006	0.9909
743	-0.0301	0.001	0.9966	-0.0155	0.0009	0.9988	-0.0195	0.0013	0.9984
753	-0.0375	0.0017	0.9959	-0.0446	0.0014	0.9983	-0.039	0.0021	0.9967
763	-0.0649	0.003	0.9978	-0.0468	0.0021	0.9982	-0.0435	0.0029	0.9951
773	-0.0917	0.0048	0.9987	-0.0656	0.0036	0.9990	-0.0686	0.0047	0.9966
783	-0.1275	0.008	0.9977	-0.1000	0.0060	0.9991	-0.1186	0.0083	0.9971
793	-0.1883	0.0126	0.9977	-0.1501	0.0096	0.9990	-0.1563	0.012	0.9950
803	-0.2801	0.0198	0.9979	-0.2218	0.0152	0.9996	-0.2364	0.0186	0.9956

\* product moment correlation coefficient

**Table 3** Regression coefficients of the  $D=D_0 + \beta t$  equations at the various temperatures of the isothermal experiments for the ( $15 \leq D \leq 20\%$ ) degradation step

$T_{\text{iso}}/\text{K}$	Polymer 1			Polymer 2			Polymer 3		
	$D_0$	$\beta/\text{min}^{-1}$	$r^*$	$D_0$	$\beta/\text{min}^{-1}$	$r^*$	$D_0$	$\beta/\text{min}^{-1}$	$r^*$
743	0.0613	0.0004	0.9903	0.0628	0.0004	0.9935	0.102	0.0003	0.9914
753	0.0917	0.0005	0.9963	0.0445	0.0008	0.9927	0.1008	0.0005	0.9936
763	0.0949	0.0008	0.9955	0.0454	0.0011	0.9956	0.0735	0.0010	0.9903
773	0.0080	0.0015	0.9941	0.0350	0.0019	0.9914	0.0716	0.0014	0.9893
783	0.0397	0.0032	0.9914	-0.0146	0.0040	0.9916	0.0756	0.0024	0.9944
793	0.0120	0.0054	0.9854	-0.0562	0.0066	0.9955	0.0601	0.0034	0.9912
803	-0.0109	0.0079	0.9943	-0.0966	0.0101	0.9930	0.0309	0.0056	0.9878

\* product moment correlation coefficient

**Table 4** Correlation coefficients of the  $\ln \beta = \ln A - B/T_{\text{iso}}$  equations for both  $5 \leq D \leq 15\%$  and  $15 \leq D \leq 20\%$  degradation steps (standard deviations in brackets)

	$5 \leq D \leq 15\%$				$15 \leq D \leq 20\%$			
	$\ln A$	$B \cdot 10^{-3}$	$r^*$	$E_a/\text{kJ mol}^{-1}$	$\ln A$	$B \cdot 10^{-3}$	$r^*$	$E_a/\text{kJ mol}^{-1}$
Polymer 1	33.0 ( $\pm 0.6$ )	29.6 ( $\pm 0.5$ )	0.9988	246 ( $\pm 4$ )	34 ( $\pm 3$ )	32 ( $\pm 3$ )	0.9819	263 ( $\pm 23$ )
Polymer 2	31.7 ( $\pm 0.7$ )	28.8 ( $\pm 0.5$ )	0.9985	239 ( $\pm 4$ )	35 ( $\pm 3$ )	32 ( $\pm 2$ )	0.9896	265 ( $\pm 17$ )
Polymer 3	33.2 ( $\pm 1.1$ )	29.7 ( $\pm 0.8$ )	0.9961	247 ( $\pm 7$ )	30.4 ( $\pm 1.6$ )	28.5 ( $\pm 1.3$ )	0.9950	237 ( $\pm 11$ )

\* product moment correlation coefficient

**Table 5** Regression coefficients and apparent activation energies by MacCallum equation for the isothermal ( $683 \leq T \leq 803$  K) degradations of polymers 1, 2 and 3 (under  $N_2$  flow) at various degrees of conversion ( $D\%$ ) in the  $5 \leq D \leq 15\%$  range (standard deviations in brackets)

$D\%$	Polymer 1				Polymer 2				Polymer 3			
	$a$	$b \cdot 10^{-3}/$ K	$r^*$	$E_a/$ kJ mol $^{-1}$	$a$	$b \cdot 10^{-3}$ K	$r^*$	$E_a/$ kJ mol $^{-1}$	$a$	$b \cdot 10^{-3}/$ K	$r^*$	$E_a/$ kJ mol $^{-1}$
5	-27.5 ( $\pm 1.1$ )	23.4 ( $\pm 0.8$ )	0.9945	194 ( $\pm 1$ )	-27.5 ( $\pm 0.9$ )	23.6 ( $\pm 0.6$ )	0.9962	196 ( $\pm 5$ )	-29.3 ( $\pm 0.9$ )	24.6 ( $\pm 0.7$ )	0.9963	205 ( $\pm 6$ )
7.5	-29.0 ( $\pm 0.8$ )	24.8 ( $\pm 0.6$ )	0.9972	206 ( $\pm 5$ )	-28.9 ( $\pm 0.6$ )	24.9 ( $\pm 0.5$ )	0.9982	207 ( $\pm 4$ )	-30.4 ( $\pm 0.7$ )	25.7 ( $\pm 0.5$ )	0.9979	214 ( $\pm 4$ )
10	-30.3 ( $\pm 0.7$ )	25.9 ( $\pm 0.5$ )	0.9983	215 ( $\pm 4$ )	-29.8 ( $\pm 0.5$ )	25.8 ( $\pm 0.4$ )	0.9989	214 ( $\pm 3$ )	-31.1 ( $\pm 0.6$ )	26.5 ( $\pm 0.4$ )	0.9986	220 ( $\pm 4$ )
12.5	-31.1 ( $\pm 0.6$ )	26.7 ( $\pm 0.4$ )	0.9988	222 ( $\pm 4$ )	-30.3 ( $\pm 0.5$ )	26.3 ( $\pm 0.4$ )	0.9991	219 ( $\pm 3$ )	-31.4 ( $\pm 0.8$ )	26.9 ( $\pm 0.6$ )	0.9975	224 ( $\pm 5$ )
15	-32.2 ( $\pm 0.9$ )	27.7 ( $\pm 0.7$ )	0.9976	230 ( $\pm 6$ )	-30.7 ( $\pm 0.6$ )	26.7 ( $\pm 0.4$ )	0.9988	222 ( $\pm 3$ )	-31.0 ( $\pm 1.4$ )	26.8 ( $\pm 1$ )	0.9934	223 ( $\pm 8$ )

\* product moment correlation coefficient

**Table 6** Degradation  $E_a$  values for polymers 1, 2 and 3 by our method and MacCallum (average values) and Kissinger equations (standard deviations in brackets)

	$5 \leq D \leq 15\%$ (743–803 K)		$5 \leq D \leq 15\%$ (683–803 K)		$15 \leq D \leq 20\%$ (743–803 K)		
	MacCallum*	our method	MacCallum	our method	Kissinger*	MacCallum*	our method
Polymer 1	239 ( $\pm 3$ )	245 ( $\pm 8$ )	213 ( $\pm 4$ )	246 ( $\pm 4$ )	237 ( $\pm 4$ )	264 ( $\pm 8$ )	263 ( $\pm 23$ )
Polymer 2	234 ( $\pm 3$ )	234 ( $\pm 13$ )	212 ( $\pm 4$ )	239 ( $\pm 4$ )	233 ( $\pm 3$ )	255 ( $\pm 6$ )	265 ( $\pm 17$ )
Polymer 3	220 ( $\pm 8$ )	219 ( $\pm 13$ )	217 ( $\pm 6$ )	247 ( $\pm 7$ )	216 ( $\pm 5$ )	234 ( $\pm 7$ )	237 ( $\pm 11$ )

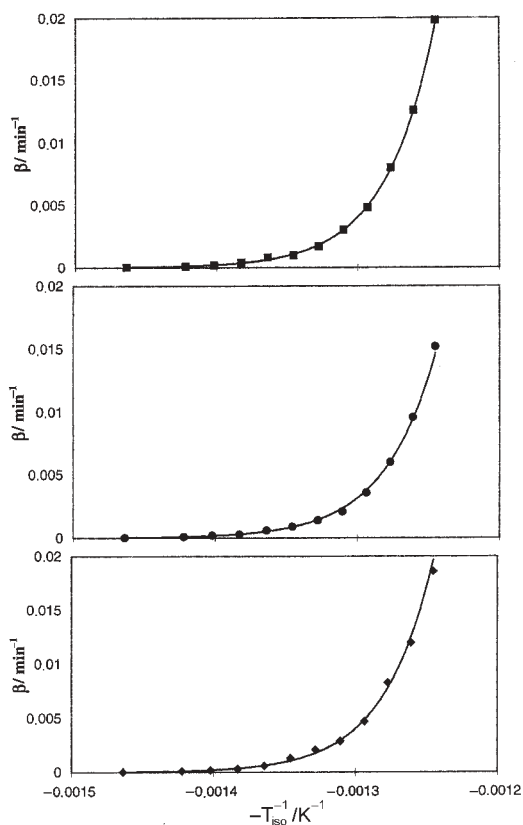
\* From Ref. [14]

for the three polymers. The relative regression coefficients are reported in Table 5 together with the corresponding  $E_a$  values.

Higher degrees of conversion ( $15 \leq D \leq 20\%$  about) were observed only at temperatures higher than 733 K. The corresponding MacCallum equations and apparent activation energy values were reported by us in a previous paper [14].

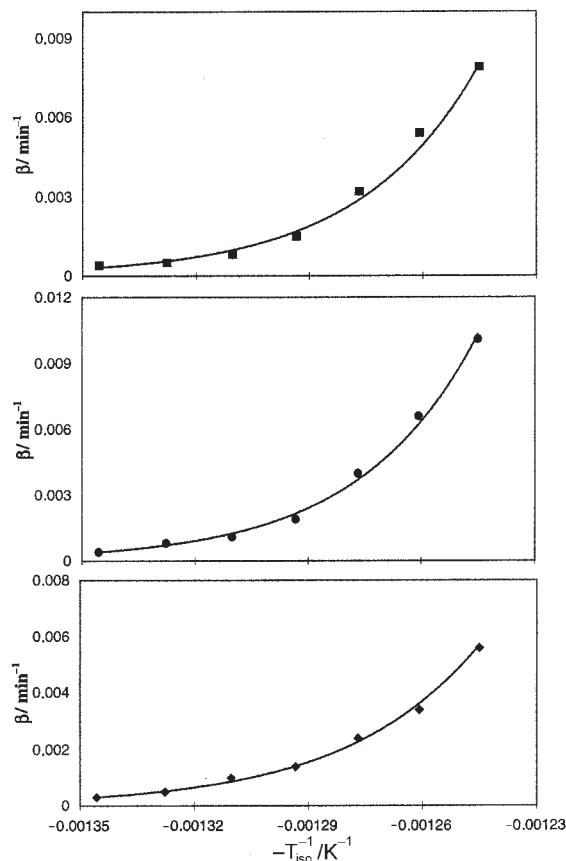
In order to confirm that the found  $\ln \beta = \ln A - B/T_{iso}$  relationships can be considered Arrhenius equations for the degradation processes of our polymers, the obtained  $E_a$  values ( $B = E_a/R$ ) were compared with the average apparent activation energies here determined by the MacCallum method in the same temperature range and those previously obtained by us in both isothermal ( $T \geq 733$  K) and dynamic heating conditions by the MacCallum and Kissinger method, respectively [14].

The degradation  $E_a$  values determined by the MacCallum equation and those obtained by our method, based on the derivation of Arrhenius relationships directly from TG data, are listed in Table 6, where the values determined through the Kissinger equation are also reported.



**Fig. 1** Dependence of mass loss rate ( $\beta$ ) as a function of ( $-T_{iso}^{-1}$ ), for polymers 1 (■) – 2 (●) – and 3 (◆) – in the  $5\% \leq D \leq 15\%$  degradation step





**Fig. 2** Dependence of mass loss rate ( $\beta$ ) as a function of  $(-T_{\text{iso}}^{-1})$ , for polymers 1 (■) – 2 (●) – and 3 (◆) – in the  $15\% \leq D \leq 20\%$  degradation step

For the  $5\% \leq D \leq 15\%$  degradation step a very good agreement among the results from the three different methods was found in the temperature range 743–803 K, where all studied polymers are completely in the molten state.

On the contrary, in the same  $5\% \leq D \leq 15\%$  degradation step, some differences were observed if the isothermal data in the whole temperature range investigated (683–803 K) are considered. The  $E_a$  values from the Arrhenius relationships were still in very good agreement with those from Kissinger equation for the polymers 1 and 2, for which all isothermal degradations in the considered temperature range were substantially carried out in the molten state as well as those in the scanning mode, while for the polymer 3 a higher  $E_a$  value was found by our method. This discrepancy could be explained on considering that temperatures lower than the melting temperature of polymer 3 are included in the 683–803 K temperature interval, and then data from degradations in the solid state were also considered for the evaluation of the apparent

activation energy by our method, while the degradations in the scanning mode occurred substantially in the molten phase.

Moreover, the treatment according to the MacCallum equation of the same isothermal experimental data in the 683–803 K range gave rise to lower  $E_a$  values for polymers 1 and 2, while for polymer 3 the same value of Kissinger method was found (Table 6). These results do not appear consistent with the lower mass loss rates experimentally observed during isothermal degradations at lower temperatures (Table 2).

For the  $15 \leq D \leq 20\%$  degradation range, which could be observed only at higher temperatures, the  $E_a$  values from the MacCallum and our methods were in very good agreement with each other (Table 6), thus confirming the validity of our procedure. The apparent activation energies from the Kissinger equation did not agree with our and MacCallum values, probably because of the impossibility of this method to appreciate, at least in this case, the difference of the mass loss rate between the two steps. In addition, in dynamic heating conditions, the mass losses at the temperature of maximum mass loss rate, which is the parameter used by the Kissinger equation to calculate  $E_a$  values, were for all polymers within 16–17% only.

The results here reported, together with those found for the same polymers in an oxidative environment [19], suggest some conclusions:

- for the studied polymers the thermal behaviour under  $N_2$  flow is different than that in static air atmosphere;
- also in an inert environment it was possible to draw kinetic  $D = f(t)$  equations directly from the mass loss data, but, differently than in oxidative environment, these equations are linear equations, thus indicating a constant mass loss rate in both steps of the  $5 \leq D \leq 20\%$  degradation range;
- the coefficient of time ( $\beta$ ) of the obtained linear kinetic equations, which is, from a dimensional viewpoint, a velocity and represents the mass loss rate of polymer during degradation, increases exponentially as a function of  $(-1/T_{iso})$  as well as the e-folding time  $\alpha$  in oxidative atmosphere [19];
- the results obtained suggest that it is possible to determine reliable apparent  $E_a$  values for the degradation of polymers by using kinetic equations directly derived from TG isothermal experimental data, without any assumption concerning the reaction order or the mechanism of degradation. The coefficients of time in the  $D = f(t)$  equations at various temperatures represent the mass loss rates of sample in the considered range of mass loss. These values increase, at least for the polymers here studied, as a function of the temperature of isothermal experiments according to Arrhenius-type equations, independently on the nature (exponential or linear) of the  $D = f(t)$  relationships, thus allowing the determination of the  $E_a$  values associated with the degradation process in the considered mass loss interval. This finding will be tested by us in the next future by using other polymers in various experimental conditions.

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