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An iterative model-free method to determine the activation energy of non-isothermal heterogeneous processes

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A new iterative model-free (isoconversional) method with integration over a given range of conversion for determination of the activation energy using non-isothermal data recorded at several heating rates has been suggested. The advantages of applying this method in comparison with often used linear and nonlinear isoconversional methods are put in evidence. The suggested method was applied to experimental non-isothermal data for degradation of polyvinyl chloride, decomposition of ammonium perchlorate and crystallization of poly(ethylene terephthalate) melt. The so obtained values of the activation energy were compared with those resulting from other methods of analysis.

1. Introduction

Under non-isothermal conditions at a linear heating rate, the kinetics of heterogeneous reactions is usually described by the rate equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} \equiv \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α is the degree of conversion, t is the time, T is the temperature, β is the linear heating rate, A is the pre-exponential factor, E is the activation energy, $f(\alpha)$ is the differential function of conversion and R is the gas constant.

Starting with this equation, various procedures for evaluating the kinetic triplet (A, E, $f(\alpha)$) were developed. As has results from some critical analyses [1–14], the correct determination of non-isothermal kinetic parameters involves the use of experimental data recorded at several heating rates. These data have allowed applying the isoconversional (model-free) methods in assessing the activation energy on the conversion degree that can be correlated with the investigated process mechanism. Isoconversional procedures are classified as either linear or nonlinear. In the linear procedures, from which we mention Friedman (FR) [15], Flynn–Wall–Ozawa (FWO) [16,17], Kissinger–Akahira–Sunose (KAS) [18], Li–Tang (LT) [19,20], the activation energy is evaluated from the slope of a straight line, while in integral [21–25] and differential [26] nonlinear procedures the activation energy is evaluated from a specific minimum condition. Both linear and nonlinear procedures may be either differential or integral according to the equation that underlies them, namely Eq. (1) or its integral form:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} \equiv g(\alpha) = \frac{A}{\beta}\int_0^{T_\alpha}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T \equiv \frac{A}{\beta}I(E_\alpha, T_\alpha) \tag{2}$$

where $g(\alpha)$ is the integral conversion function and $I(E_\alpha, T_\alpha)$ is the temperature integral that cannot be exactly resolved.

The linear methods use some simple approximations of the temperature integral, like those suggested by Doyle [27] and Coats and Redfern [28], which exhibit a relative low accuracy. On the other hand, the integral nonlinear procedures allow using more precise approximations of this integral, like the rational expressions given by Senum and Yang [29]. Therefore, the application of integral nonlinear procedures leads to accuracy values of E. However, in comparison with linear methods, the use of nonlinear methods need a longer computational time. An attempt to outrun this disadvantage was performed by Gao et al. [30] who suggested an iterative procedure in which is assumed the reaction order model.

The derivation of equations that underlie the integral linear or nonlinear procedures assumes the independence of the activation parameters (E and A) on the conversion degree. On the other hand, it was pointed out [3,31–34] that when E depends on α, some important differences exist between E values determined by differential and integral isoconversional methods. In such a case, the differential isoconversional methods, like FR [15] and nonlinear differential [26] methods, as well as the modified (advanced) nonlinear method suggested by Vyazovkin [24] are recommended as the results obtained by integral isoconversional methods are dependent on the history of the system in the range 0–α [4]. For

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some cases in which activation energy changes with conversion degree, the dependence of E_α on lower limit of integral was also put in evidence [35] by applying LT method.

Because differential methods employ instantaneous rate values, it is sensitive to inherent noise and tends to be numerically unstable [36]. The corresponding errors could be reduced by smoothing of the experimental data. In order to eliminate this systematic error, Vyazovkin [24] suggested a modification of the integral nonlinear method previously worked out by him [21], which consists in determining the integral $I(E_\alpha, T_\alpha)$ over a small $\Delta\alpha$ range (modified nonlinear method). Budrugeac [26] pointed out that for $\Delta\alpha \to 0$, the E_α values obtained by this method are practically equal to those obtained by FR method. Recently Cai and Chen [37] suggested a iterative linear integral isoconversional method for E_α evaluation that also uses the integration over a small $\Delta\alpha$ range and leads to correct values of the activation energy in much less time than Vyazovkin method.

In this paper, a new iterative integral isoconversional method with integration over a given range of conversion will be suggested. It will pointed out the following advantages of this method: the applicability for large and small $\Delta\alpha$ ranges; the possibility of using of precise approximations for temperature integral, even the values of this integral obtained by numerical integration performed by Mathematica software system; put in evidence the importance of lower limits of integration for E_α evaluation when E depends on α; the method can be applied even when the initial temperature corresponding to $\alpha = 0$ is randomly choice from the range 0 – minimum onset temperature; the application of this method in certain favorable cases could indicate the range of conversion degree in which the kinetics of the complex investigated process is determined by a certain step characterized by activation parameters that do not depend on α.

2. Theoretical part

The integration of Eq. (1) for the limits $\alpha_1(T_1)$ and $\alpha_2(T_2)$, and constant heating/cooling rate leads to:

$$g(\alpha_2) - g(\alpha_1) = \frac{A}{\beta}\int_{T_1}^{T_2}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T \tag{3}$$

In the integral linear isoconversional methods, as FWO [19,20] and KAS [21], as well as in nonlinear integral isoconversional method suggested by Vyazovkin [21], it is considered the case in which $\alpha_1 = 0$. In such condition, $\int_0^{T_1}[\exp(-E/RT)]\mathrm{d}T \approx 0$ [38] and Eq. (3) turn into Eq. (2).

The integral temperature from the right member of Eq. (3) can be expressed as [25]:

$$I(E, T_1, T_2) = \int_0^{T_2}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T - \int_0^{T_1}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T \equiv \frac{E}{R}[p(x_2) - p(x_1)] \tag{4}$$

where $x = E/RT$.

From the numerous approximations suggested for $p(x)$ in Section 3, we will use the four order approximation given by Senum and Yang [29], which exhibits a very high accuracy (the relative error lower than 0.6% for $x \geq 1$):

$$p(x) = \frac{e^{-x}}{x}\,\frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{5}$$

Eq. (3) can be written as:

$$g(\alpha_2) - g(\alpha_1) = \frac{AE}{R\beta}(T_2 - T_1)\left[\exp\left(-\frac{E}{RT_2}\right)\right]\frac{p(x_2) - p(x_1)}{(T_2 - T_1)\left[\exp\left(-\frac{E}{RT_2}\right)\right]} \tag{6}$$

from which it results:

$$\ln\frac{\beta}{T_2 - T_1} = \ln\frac{A}{g(\alpha_2) - g(\alpha_1)} + \ln R_I - \frac{E}{RT_2} \tag{7}$$

where $R_I = \frac{\int_{T_1}^{T_2}[\exp(-E/RT)]\mathrm{d}T}{(T_2 - T_1)[\exp(-E/RT_2)]} = \frac{E}{R}\frac{p(x_2) - p(x_1)}{(T_2 - T_1)[\exp(-E/RT_2)]}$. Considering that $\alpha_1 = 0$, $T_1 = T_0$ (onset temperature of the considered process) and $R_I = 1$, this relation turn into:

$$\ln\frac{\beta}{T - T_0} = \ln\frac{A}{g(\alpha)} - \frac{E}{RT} \tag{8}$$

Eq. (8) was derived by Kennedy and Clark [39] by integration of rate Eq. (1) assuming T=const. and introducing in the obtained relation $\beta = T - T_0/t$. As was recently noted by Ortega [40] the derivation of Eq. (8) is conceptually erroneous because, in non-isothermal condition, the change of variable t with T must be performed before the integration of Eq. (1) considering T = const.

According to relation (7):

$$E = -R\frac{\mathrm{d}\ln\left(\beta/(T_2 - T_1)\right)}{\mathrm{d}\left(1/T_2\right)} - R\frac{\mathrm{d}\ln R_I}{\mathrm{d}\left(1/T_2\right)} \equiv E_{KC} - R\frac{\mathrm{d}\ln R_I}{\mathrm{d}\left(1/T_2\right)} \tag{9}$$

where $E_{KC} = -R(\mathrm{d}\ln(\beta/T_2 - T_1))/d(1/T_2))$ is the activation energy corresponding to a procedure based on the relation:

$$\ln\frac{\beta}{T_2 - T_1} = \ln\frac{A}{g(\alpha_2) - g(\alpha_1)} - \frac{E}{RT_2} \tag{10}$$

This is similar with that derived by Kennedy and Clark [39].

In order to evaluate the activation energy using Eq. (9), the following iterative procedure is proposed:

I. For R_I = const., by plotting $\ln(\beta/(T_2 - T_1))$ vs. $1/T_2$ activation energy $E^{(1)} \equiv E_{KC}$ is obtained from the slope of this straight line.
II. $E^{(1)}$ being introduced in the expression of R_I, the value of $E^{(2)}$ is evaluated from the slope of the straight line ($\ln(\beta/(T_2 - T_1)) - \ln R_I$) vs. $1/T_2$.
III. Let $E^{(2)}$ replace $E^{(1)}$ and repeat the step II until $|(E^{(i+1)} - E^{(i)})| \leq 0.1$ kJ mol^{-1}.

In comparison with integral isoconversional methods, like FWO and KAS methods, the above suggested iterative procedure exhibits the advantage of the possibility of using for temperature integral one of the more precise approximations or the values of this integral exactly numerically evaluated by Mathematica software system. Another advantage is that this procedure can be applied for all ranges of $\Delta\alpha$, even small $\Delta\alpha$ ranges.

Obviously, $E = E_{KC}$ for R_I = const. = C. In order to put in evidence the cases in which this condition is respected, we will consider that for relative small range of T_2 (in the experimental cases which will be analyzed in Section 3: $\Delta T_2 \leq 50$ K), the exact value of $I(E, T_2, T_1)$ is proportional with the following gross approximate expression of the temperature integral suggested by Mianowscki and Radko [41]:

$$I(E, T_2, T_1) \approx C^* I_{MR}(E, T_2, T_1) = C^*\left\{T_2\left[\exp\left(-\frac{E}{RT_2}\right)\right] - T_1\left[\exp\left(-\frac{E}{RT_1}\right)\right]\right\} \tag{11}$$

As we will show in Section 3, C^* value exhibits a relative standard deviation around the average value lower than 4%.

Substituting the expression (11) in the relation of R_I, the condition $R_I = C$ becomes:

$$T_2(C^* - C)\left[\exp\left(-\frac{E}{RT_2}\right)\right] + T_1\left\{C\left[\exp\left(-\frac{E}{RT_2}\right)\right] - C^*\left[\exp\left(-\frac{E}{RT_1}\right)\right]\right\} = 0 \tag{12}$$

Table 1
The values of the activation energy obtained by isoconversional methods for thermal degradation of PVC.

α	E_{FR} (kJ mol^{-1})	E_{FWO} (kJ mol^{-1})	E_{KAS} (kJ mol^{-1})	$E_{NL\text{-}INT}$ (kJ mol^{-1})	E_{IT} (T_1 = 0 K) (kJ mol^{-1})	E_{IT} (T_1 = 400 K) (kJ mol^{-1})	E_{IT} ($\Delta\alpha$ = 0.05) (kJ mol^{-1})
0.10	104.2 ± 2.0	105.1 ± 4.2	102.0 ± 4.4	102.0	102.2 ± 4.6	102.1 ± 4.6	107.5 ± 7.2
0.20	101.5 ± 2.2	104.9 ± 2.8	101.7 ± 3.0	101.7	102.7 ± 2.8	102.6 ± 2.8	103.2 ± 2.7
0.30	101.9 ± 3.2	105.6 ± 1.9	102.3 ± 2.0	102.3	102.5 ± 2.0	102.4 ± 2.0	107.9 ± 5.0
0.40	101.0 ± 3.9	104.9 ± 1.8	101.5 ± 1.9	101.5	102.4 ± 1.9	102.4 ± 1.9	101.6 ± 4.8
0.50	101.8 ± 4.5	105.3 ± 2.1	102.8 ± 2.3	102.8	102.2 ± 2.6	102.2 ± 2.6	103.9 ± 9.4
0.60	103.2 ± 5.7	105.4 ± 2.5	101.8 ± 2.6	101.8	102.3 ± 3.2	102.3 ± 3.2	101.1 ± 5.8
0.70	105.2 ± 6.4	105.8 ± 3.2	102.2 ± 3.2	102.2	102.4 ± 4.1	102.4 ± 4.1	105.2 ± 9.8

The indexes FR, FWO, KAS, NL-INT and IT refer to the isoconversional methods FR, FWO, KAS, nonlinear integral method (Senum–Yang approximation for the temperature integral) and the suggested iterative method, respectively.

It follows that $E = E_{KC}$ for:

$$C = C^* \quad \text{and} \quad T_1 = 0 \tag{13}$$

Consequently, the relation:

$$\ln \frac{\beta}{T_\alpha} = \ln \frac{A}{g(\alpha)} - \frac{E}{RT_\alpha} \tag{14}$$

could be used for evaluation of E from the slope of the straight line $\ln(\beta/T_\alpha)$ vs. $(1/T_\alpha)$ only if the conditions (13) are carried out. The possibility of using this isoconversional method was previously discussed by Popescu and Segal [42].

As was above mentioned, the suggested iterative method can be applied for all ranges of $\Delta\alpha = \alpha_2 - \alpha_1$.

If E does not depend on α, it is expected that the activation energy evaluated by this method is independent on $\Delta\alpha$ and is closed to that obtained by all differential and integral isoconversional methods. It is also expected that, for $\alpha_1 = 0$, the iterative method leads to correct value of E for constant or random choice of T_1 values in the range $0 \le T_1 \le T_{\text{onset}}^{(\text{min})}$, where $T_{\text{onset}}^{(\text{min})}$ is the onset temperature corresponding to the minimum used heating rate.

When E depends on α, it is expected that for a very small value of $\Delta\alpha$ and a given α, E evaluated by iterative method to be close to that obtained by differential isoconversional methods. On the other hand, in this case, for $0 \le T_1 \ll T_{\text{onset}}^{(\text{min})}$, the value of E for a given α, must be closed to that obtained by the integral isoconversional methods, like FWO, KAS and nonlinear integral methods.

Finally, we will discuss the applicability of the suggested iterative method for the evaluation of the apparent activation energy corresponding to non-isothermal crystallization from melts. Vyazovkin and Sbirrazzuoli [43,44] pointed out that the more popular representatives multiple heating rate methods FWO [16,17] and Kissinger [45] cannot be directly applied for such processes because these methods require taking the logarithm of β that exhibits a negative value. Therefore, for the processes occurring on cooling, reliable values of E are obtained by differential isoconversional method of Friedman [15] and/or the modified nonlinear method of Vyazovkin [24] in which the integration of rate equation id performed for small $\Delta\alpha$ range.

Eq. (7) that grounds the suggested iterative method permits substitution of negative value of β because during cooling $T_2 < T_1$ and consequently $\beta/(T_2 - T_1)$ and R_I have positive values. In order to apply this method, the numerically calculated values of the temperature integral could be used. For $E < 0$ and $|E/R|$ in the range 6×10^3–37×10^3 K, a very good agreement between the numerically calculated values of $\int_{T_1}^{T_2} \left[\exp(-E/RT)\right] \mathrm{d}T$ and those evaluated using Senum–Yang approximation was obtained. Consequently, the Senum–Yang approximation of temperature integral can be also used in such cases. For a given T_2, $p(x_2)/p(x_1)$ increases with T_1, and for high values of T_1 at which $\alpha_1 = 0$: $p(x_2) - p(x_1) \approx p(x_2)$. Consequently, for such values of T_1:

$$g(\alpha_2) \equiv g(\alpha) \approx \frac{A}{\beta}\frac{E}{R} p\left(\frac{E}{RT_2}\right) \tag{15}$$

Considering the simple approximations of the temperature integral suggested by Doyle [27] and Coats and Redfern [28]:

$$\ln p\left(\frac{E}{RT_2}\right) = -5.331 - 1.052\frac{E}{RT_2} \tag{16}$$

and

$$p\left(\frac{E}{RT_2}\right) = \frac{R^2 T_2^2}{E^2} \quad \exp\left(-\frac{E}{RT_2}\right) \tag{17}$$

respectively, the following relations result:

$$\ln(-\beta) = \ln\left[-\frac{AE}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E}{RT_2} \tag{18}$$

$$\ln\left(-\frac{\beta}{T_2^2}\right) = \ln\left[-\frac{AR}{Eg(\alpha)}\right] - \frac{E}{RT_2} \tag{19}$$

Consequently, FWO and KAS integral isoconversional methods, based on Eqs. (18) and (19), respectively, can be used for evaluation of activation energy corresponding to the crystallization from melt. Obviously, if E depends on conversion degree, as was observed for majority crystallization from melt (see for example Refs. [43,44,46]), for a given α, the value of activation energy determined by these integral methods differs than that evaluated by a differential isoconversional method.

3. Applications

The applicability of the suggested iterative isoconversional procedure for some ranges of $\Delta\alpha$, $\alpha_1 = 0$ and some choices of T_1 was checked for the following cases: (a) the non-isothermal degradation of polyvinyl chloride (PVC) that exhibits a large range of α in which E = *constant*; (b) the non-isothermal decomposition of ammonium perchlorate (AP) characterized by a strong dependence of E on α; (c) crystallization of poly(ethylene terephthalate) (PET) melt.

(a) *Non-isothermal degradation of PVC*

The TG curves recorded in air static atmosphere at 2, 3, 4, 5 and 10 K min^{-1}, and corresponding to thermal degradation of a sort of pure PVC with average molecular weight of 172,000 were reported in a previous paper [47]. In a next work [3], we applied the isoconversional methods (FR, FWO, KAS, integral nonlinear method) and obtained that for $0 < \alpha \le 0.70$ the activation energy does not depend on the conversion degree. In Table 1 there are given the values of E obtained by these methods as well as those resulted using the suggested iterative method for $\Delta\alpha = 0.05$; $T_1 = 0$ K and $T_1 = 400$ K (at all considered heating rates, and $\alpha = 0$ for $T_1 < 460$ K). One notes that, for a given α_2, only two iterations are necessary. The inspection of this table shows that, in the limits of inherent experimental errors, a good agreement among the E values determined by all considered isoconversional methods was obtained. However, the relative higher values of E obtained by FWO method could be explained by worst approximation for temperature integral on which this method is based.

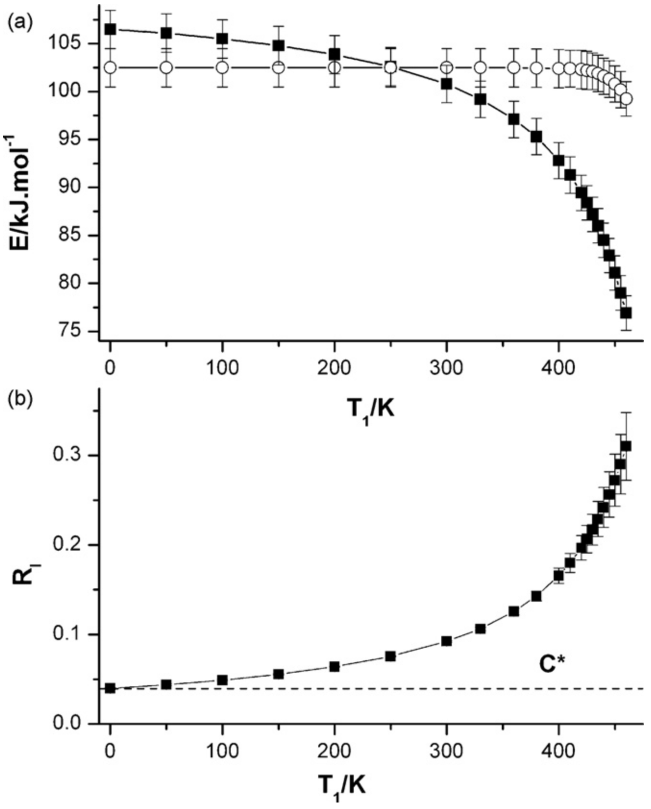

Fig. 1. The dependencies of E_{KC}, E and R_I on T_1, for non-isothermal degradation of PVC and $\alpha_2 = 0.3$.
(a) (■) E_{KC} vs. T_1; **O** E vs. T_1; (b) (■)R_I vs. T_1.

Table 2
The values of activation energy obtained by random choice of T_1 for non-isothermal degradation of PVC.

α	T_I for β = 2; 3; 4; 5 and 10 K min^{-1} K	Iteration	E (kJ mol^{-1})
0.1	50; 400; 155; 95; 320	0	121.7 ± 67.9
		1	102.2 ± 4.6
		2	102.2 ± 4.6
0.2	376; 33; 139; 286; 87	0	26.8 ± 62.8
		1	88.6 ± 7.1
		2	101.8 ± 2.3
		3	102.1 ± 2.5
		4	102.1 ± 2.5
0.3	450; 10; 200; 350; 80	0	18.0 ± 73.3
		1	72.4 ± 19.2
		2	98.4 ± 1.7
		3	100.7 ± 1.2
		4	100.8 ± 1.3
		5	100.8 ± 1.3
0.4	376; 33; 139; 286; 87	0	56.2 ± 44.9
		1	102.4 ± 1.8
		2	102.4 ± 1.9
0.5	391; 27; 169; 258; 92	0	49.7 ± 45.3
		1	101.8 ± 2.7
		2	102.3 ± 2.6
		3	102.3 ± 2.6
0.6	23; 420; 123; 64; 317	0	119.8 ± 69.5
		1	102.2 ± 3.2
		2	102.3 ± 3.3
		3	102.3 ± 3.3
0.7	341; 49; 154; 246; 46	0	61.0 ± 32.7
		1	102.6 ± 4.1
		2	102.4 ± 4.1
		3	102.4 ± 4.1

Iteration 0 corresponds to $R_I = 1$.

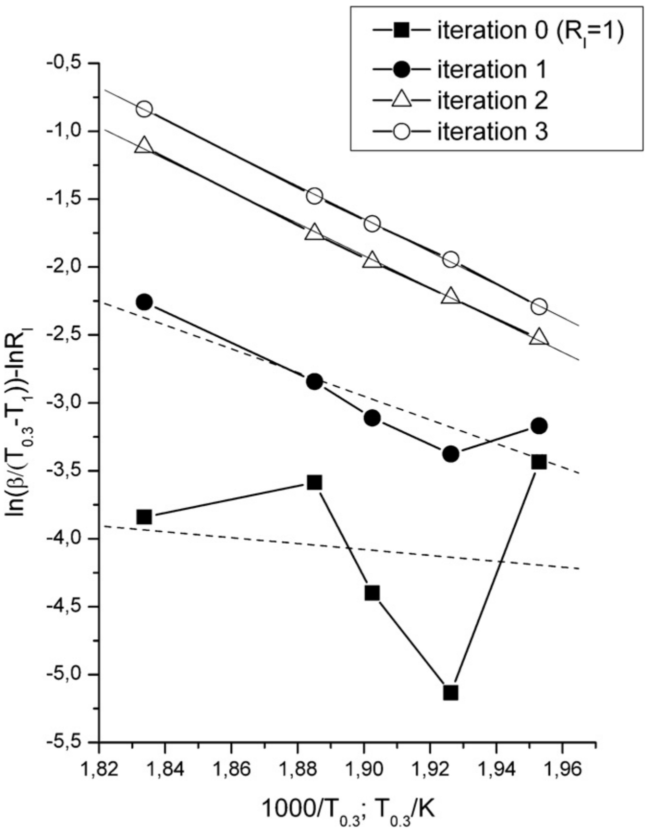

Fig. 2. The dependencies $\ln(\beta/(T_2 - T_1)) - \ln R_I$ vs. $(1/T_2)$ for non-isothermal degradation of PVC and $\alpha_2 = 0.3$ (T_1 = 450; 10; 200; 350 and 80 K for 2; 3; 4; 5 and 10 K min^{-1}, respectively).

In the range $0 \le T_1 \le T_{\text{onset}}^{(\text{min})}$ and a given α_2, C^* does not depend on T_1 (for $\alpha_2 = 0.1$: $\overline{C^*} = 0.03702 \pm 0.00080$; for $\alpha_2 = 0.3$: $\overline{C^*} = 0.03966 \pm 0.00088$; for $\alpha_2 = 0.6$: $\overline{C^*} = 0.04012 \pm 0.00091$), but C^* increases with α_2.

Fig. 1 shows the dependencies of E_{KC}, E and R_I on T_1 for $\alpha_2 = 0.3$; similar dependencies were obtained for each conversion degree from the range $0.05 \le \alpha_2 \le 0.70$. The considered T_1 values are lower than $T_{\text{onset}}^{(\text{min})}$. The inspection of this figure shows that:

(1) E_{KC} decreases with T_1, while E is practically independent on this temperature.
(2) The dependencies E_{KC} vs. T_1 and R_I vs. T_1 are correlated, namely the increase of R_I corresponds to the decrease of E_{KC}.
(3) $R_I = C = C^*$ for $T_1 = 0$ K.

The statements (1) and (2) put in evidence the importance of the term $R(\mathrm{d}\ \ln R_I/\mathrm{d}(1/T_2))$ from Eq. (9), which grounds the suggested iterative method.

As it was noted above, it is expected that the iterative method is also applicable for random choice of T_1 from the range $0 \le T_1 \le T_{\text{onset}}^{(\text{min})}$. Table 2 lists the results obtained for some conversion degrees and random choice of T_1. As an example, in Fig. 2 is presented the corresponding curves $[\ln(\beta/(T_{0.3} - T_1)) - \ln R_I]$ vs. $(1/T_{0.3})$ for $\alpha_2 = 0.3$. For each $\alpha(=\alpha_2)$, $\ln \beta/(T_2 - T_1)$ vs. $(1/T_2)$ is not a straight line, but after two iterations the linearization of $\left[\ln(\beta/(T_2 - T_1)) - \ln R_I\right]$ vs. $(1/T_2)$ was obtained. The last necessary iteration leads to E values close to those listed in Table 1.

(b) *Non-isothermal decomposition of AP*

In this section, the suggested iterative procedure will be applied to the experimental data distributed to the participants in the ICTAC Kinetic Project [48] for the decomposition of AP at the heating rates of 2.52, 5.16, 7.58, 10.49, 12.79, and 15.45 K min^{-1}. The values of

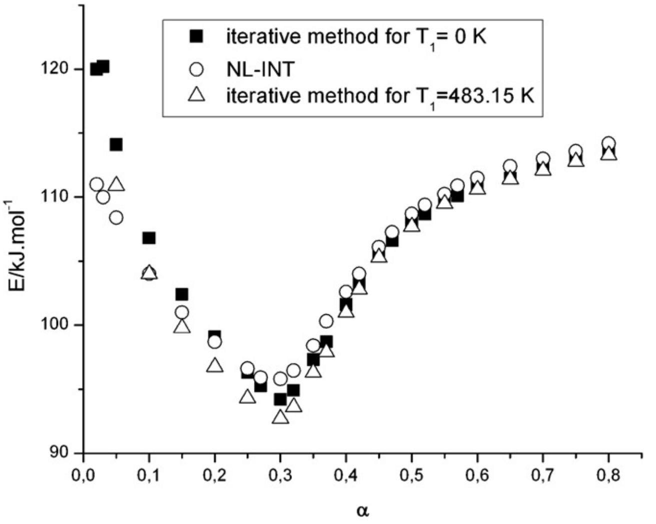

Fig. 3. Dependence on conversion degree of the apparent activation energy of AP decomposition evaluated by means of iterative method for T_1 = 0 K and T_1 = 483.15 K, and NL-INT method.

the activation energy determined by linear and nonlinear isoconversional methods were reported by the participants at this Project in the Refs.[2,49]. Subsequently [25], the kinetic analysis of these non-isothermal data put in evidence the high differences between E values determined by differential and integral isoconversional methods. It was obtained [25] that the activation energy changes strongly with the conversion degree, and the shape of E_{dif} (E evaluated by a differential method) vs. α curve is different than E_{int} (E evaluated by an integral method) vs. α curve.

The results obtained by iterative, FR and FWO methods are comparatively presented in Figs. 3 and 4.

According to the results presented in Fig. 3, the E values determined by iterative method for T_1 in the range $0 \le T_1 \le T_{\text{onset}}^{(\text{min})}$ are closed to those obtained by nonlinear integral isoconversional method (NL-INT with Senum–Yang approximation for temperature integral). This can be explained by the fact that, for a given α, E evaluated by both methods reflects the history of the system in the range 0–α. Unlike the integral isoconversional methods, the differential isoconversional methods and the methods which use small ranges of $\Delta\alpha$ leads to “punctual” values of activation energy, which are in good agreement (see Fig. 4). Therefore, when E depends on α, for a given α, E_{dif} and E_{int} exhibit different values, as was obtained for decomposition of AP (Figs. 3 and 4). On the other hand, it is expected that in such cases, E evaluated by iterative method for a given $\alpha(=\alpha_2)$ to be dependent on α_1. Such a dependence for $\alpha_2 = 0.4$ is illustrated in Fig. 5.

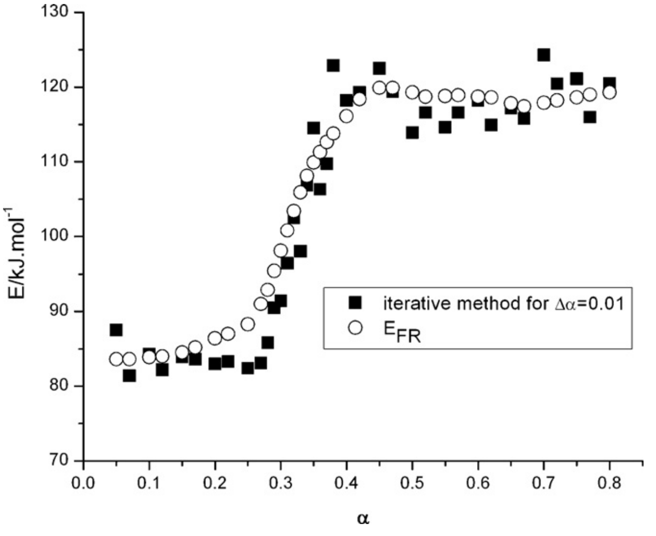

Fig. 4. Dependence on conversion degree of the apparent activation energy of AP decomposition evaluated by means of iterative method for $\Delta\alpha = 0.01$, and FR method.

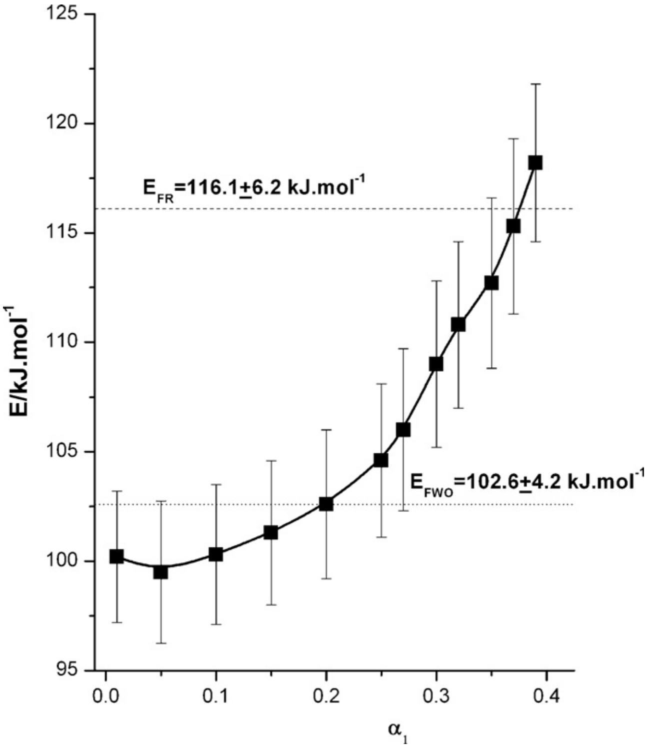

Fig. 5. Dependence on E – evaluated by iterative method vs. α_1 for $\alpha_2 = 0.4$ (AP decomposition).

We also note that E (evaluated by iterative method for $\Delta\alpha = 0.01$) vs. α curve is not so smooth like E_{FR} vs. α curve (see Fig. 4). This could be do to the accuracy of T evaluation for such small range of the conversion degree.

The application of the iterative method for $\alpha_1 = 0.05$ and $\alpha_2 = 0.25$, and for $\alpha_1 = 0.40$ and $\alpha_2 = 0.80$ leads to $E = 84.2 \pm 3.2\ \text{kJ mol}^{-1}$ and $E = 117.5 \pm 5.3\ \text{kJ mol}^{-1}$, respectively. These values are in good agreement with those shown in Fig. 4. Therefore, the use of the suggested iterative method could indicate the range in which the kinetic of a complex process is determined by certain step characterized by activation parameters independent on α.

Fig. 6 shows the dependencies of E_{KC}, E and R_I on T_1 from the range $0 \le T_1 \le T_{\text{onset}}^{(\text{min})}$ for $\alpha_2 = 0.2$; similar dependencies were obtained for each conversion degree. In the mentioned range of T_1, C^* does not depend on T_1, but depends on α_2 (for $\alpha_2 = 0.2$: $\overline{C^*} = 0.04424 \pm 0.00118$; for $\alpha_2 = 0.5$: $\overline{C^*} = 0.03988 \pm 0.00106$; for $\alpha_2 = 0.75$: $\overline{C^*} = 0.04129 \pm 0.00108$). As it was expected, E determined by iterative method is in good agreement with that obtained by NL-INT method. The remarks (1–3) performed for PVC degradation are also valid for kinetic analysis of AP decomposition.

Table 3 lists the results obtained for some conversion degrees and random choice of T_1. As an example, in Fig. 7 is presented the corresponding curves $[\ln(\beta/(T_{0.2} - T_1)) - \ln R_I]$ vs. $(1/T_{0.2})$ for $\alpha_2 = 0.2$. It was obtained once again that, for each $\alpha(=\alpha_2)$, $\ln \beta/(T_2 - T_1)$ vs. $(1/T_2)$ is not a straight line, but after the first iteration the linearization of $[\ln(\beta/(T_2 - T_1)) - \ln R_I]$ vs. $(1/T_2)$ was achieved.

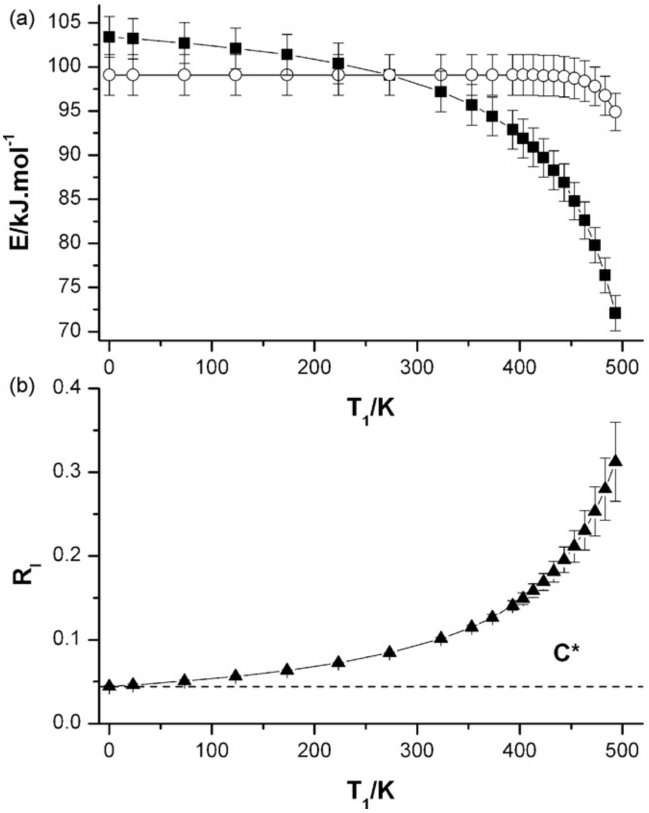

Fig. 6. The dependencies of E_{KC}, E and R_I on T_1, for AP decomposition and $\alpha_2 = 0.2$. (a) (■) E_{KC}; **O** E; (b) (▲)R_I.

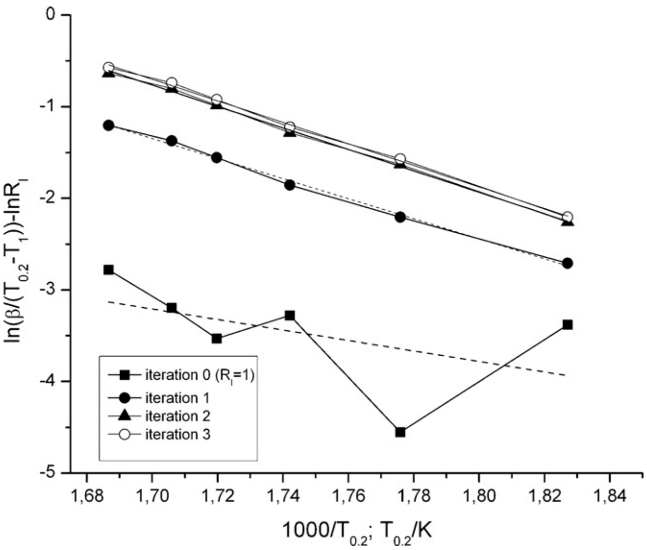

Fig. 7. The dependencies $\ln \beta/(T_2 - T_1) - \ln R_I$ vs. $(1/T_2)$ for AP decomposition and $\alpha_2 = 0.2$ ($T_1 = 473.15$; 73.15; 373.15; 223.15; 273.15 and 203.15 K for 2.52; 5.16; 7.58; 10.49; 12.79 and 15.45 K min^{-1}, respectively).

(c) *Crystallization of PET melt*

The investigated PET with 0.7% TiO_2 was produced by Hoechst-Germany. The main characteristics of this material are density 1.418 g cm^{-3}; melting point 255 °C; α relaxation temperature evaluated by DSC measurement performed at of 10 K min^{-1}: 85.1 °C (for PET this is essentially the glass transition temperature); crystallinity evaluated by DSC measurements: 32.8 ± 1.7%.

DSC 204 F1 Phoenix apparatus, produced by Netzsch-Germany, was used to study the PET non-isothermal crystallization. Each DSC

Table 3
The values of activation energy obtained by random choice of T_1 for non-isothermal decomposition of AP.

α	T_1 for β = 2.52; 5.16; 7.58; 10.49; 12.79 and 15.45 K min^{-1} K	Iteration	E (kJ mol^{-1})	E_{KAS} (kJ mol^{-1})	$E_{NL\text{-}INT}$[a] (kJ mol^{-})^{1}
0.1	450.00; 50.00; 225.00; 345.00; 110.00; 87.00	0	34.4 ± 40.0	106.5 ± 2.8	106.9
		1	98.0 ± 2.2		
		2	106.4 ± 2.6		
		3	106.5 ± 2.7		
		4	106.5 ± 2.7		
0.2	473.15; 73.15; 373.15; 223.15; 273.15; 203.15	0	47.6 ± 41.7	98.7 ± 2.3	99.1
		1	91.0 ± 2.7		
		2	97.4 ± 2.0		
		3	97.7 ± 2.1		
		4	97.1 ± 2.1		
0.3	95.35; 150.50; 320.64; 70.00; 225.84; 482.00	0	148.6 ± 32.3	93.8 ± 2.4	94.3
		1	94.1 ± 2.4		
		2	94.4 ± 2.4		
		3	94.4 ± 2.4		
0.4	252.00; 11.00; 125.70; 400.85; 60.15; 300.00	0	127.2 ± 36.3	101.0 ± 3.0	101.6
		1	101.6 ± 2.9		
		2	101.6 ± 2.9		
0.5	10.20; 415.25; 223.38; 333.10; 120.73; 93.55	0	110.7 ± 38.3	106.9 ± 3.9	108.0
		1	108.0 ± 3.7		
		2	108.0 ± 3.7		
0.6	60.61; 395.20; 275.00; 133.52; 254.77; 400.00	0	143.1 ± 28.6	110.4 ± 4.1	110.8
		1	110.7 ± 4.1		
		2	110.8 ± 4.1		
		3	110.8 ± 4.1		
0.7	440.00; 25.07; 320.00; 215.63; 88.47; 155.00	0	58.8 ± 30.2	111.8 ± 4.3	112.2
		1	112.1 ± 4.3		
		2	112.2 ± 4.3		
		3	112.2 ± 4.3		
0.8	260.00; 377.75; 115.42; 301.15; 55.00; 450.00	0	123.1 ± 35.8	103.0 ± 4.5	113.5
		1	113.4 ± 4.5		
		2	113.4 ± 4.5		

Iteration 0 corresponds to $R_I = 1$.

[a] $E_{NL\text{-}INT}$ was evaluated using Senum–Yang approximation for the temperature integral.

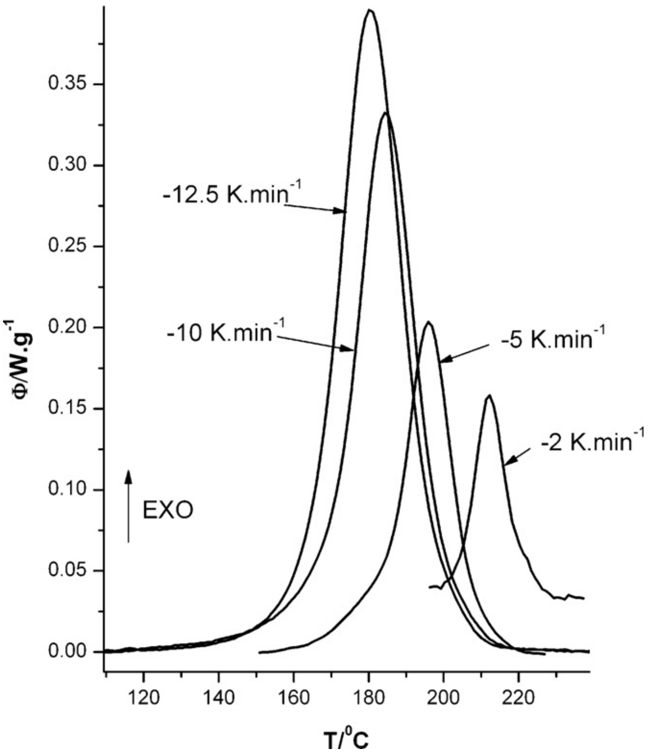

Fig. 8. Non-isothermal melt crystallization exotherms of PET.

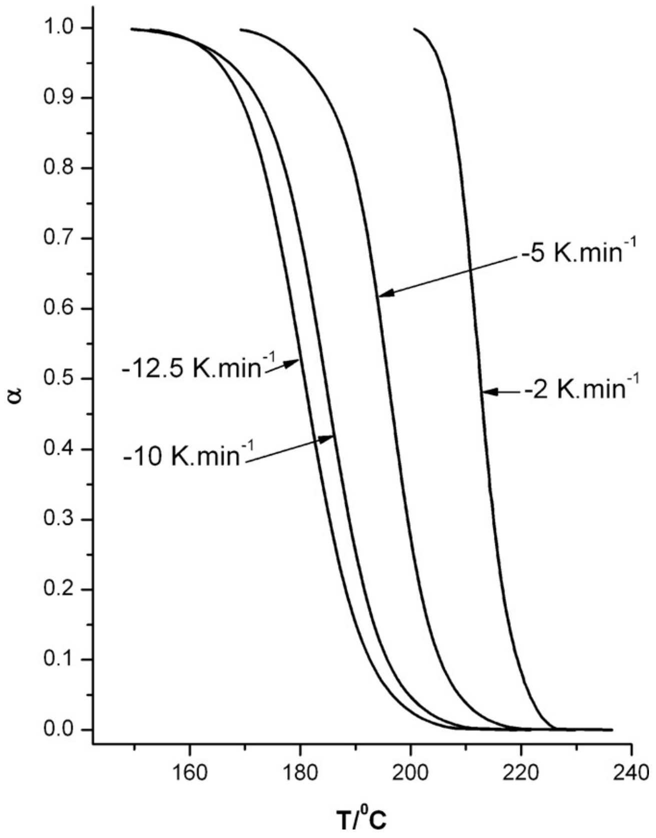

Fig. 9. α as a function of temperature for crystallization of PET.

analysis was performed in Ar flow (purity 99.999%; 20 mL min^{-1}), in an aluminum pan. The experiment started with heating the sample having ≈11 mg, from room temperature to 280 °C, where it was held for 10 min to eliminate small residual crystals. Then, the melt was cooled to crystallize at constant cooling rate (the experiments were performed at the following cooling rates: −2.0, −5.0, −10.0 and −12.5 K min^{-1}). It is noteworthy that each sample was used only once.

The crystallization exotherms of PET at the used four different cooling rates are shown in Fig. 8. Clearly, the exothermic curve becomes wider and shifts to the lower temperature regime as the absolute value of cooling rate increases. These data were used for evaluation of the relative degree of crystallization as a function of temperature by applying the formula:

$$\alpha(T)=\frac{\int_{T_{\text{onset}}}^{T}(\mathrm{d}H_c/\mathrm{d}T)\mathrm{d}T}{\int_{T_{\text{onset}}}^{T_\infty}(\mathrm{d}H_c/\mathrm{d}T)\mathrm{d}T} \qquad (20)$$

where T_{onset} and $T_{\propto}$ are the crystallization onset and end temperature, H_c is the enthalpy of crystallization.

Fig. 9 shows $\alpha=\alpha(T)$ curves, evaluated considering the sigmoidal baseline of curves from Fig. 8, which keeps into account the change of heat capacity as a result of crystallization. These data were used for evaluation of E vs. α curve by the following isoconversional methods: FR, iterative method for small values of $\Delta\alpha$ ($0.01 \le \Delta\alpha \le 0.05$), iterative method for $T_1 > T_{\text{onset}}^{(\text{min})}$, iterative method based on Eq. (18) and iterative method based on Eq. (19). The obtained results are shown in Fig. 10. Similar shape of E vs. α curve was previously reported by Vyazovkin and Sbirrazzuoli [46]. The differences between our results and that obtained by these authors could be due to different sorts of PET.

Our results are restricted to $\alpha \le 0.5$ because for higher values of conversion degree, E values evaluated by all mentioned methods exhibit relative standard deviation higher than 10%, which could be due to the complexity of the investigated process.

The inspection of this figure shows that:

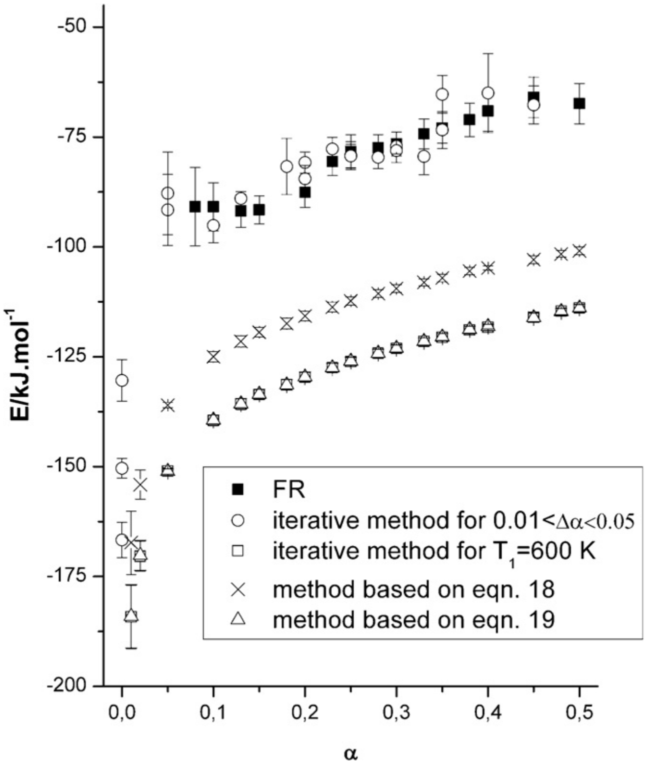

Fig. 10. Dependence on conversion degree of the apparent activation energy of PET crystallization evaluated by means of FR, iterative method and methods based on Eqs. (18) and (19).

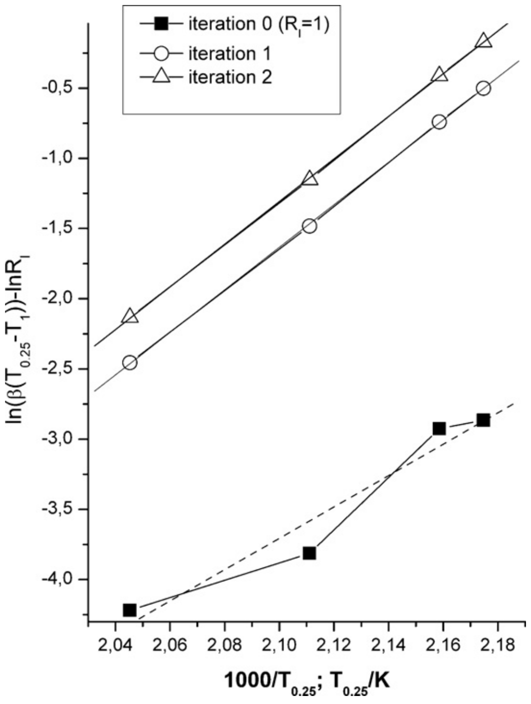

Fig. 11. The dependencies $\ln(\beta/(T_{0.25}-T_1))-\ln R_I$ vs. $(1/T_{0.25})$ for crystallization of PET and $\alpha_2 = 0.25$ (T_I = 626; 700; 650 and 680 K for 2; 5; 10 and 12.5 K min^{-1}, respectively).

(1) The apparent activation energy evaluated by all methods increases with the conversion degree.
(2) The values of E obtained by FR method and iterative method for small values of $\Delta\alpha$ are in a very good agreement.
(3) For a given α, $E_{FR} \approx E_{it}$ (small > $\Delta\alpha$) > E_{it} (Eq. (18)) > E_{it} (Eq. (19)) = E_{it} (T_1 = 600 K).

These results confirm the previously ones [3,31,32,34,50] according to which when E depends on α, some important differences exist between E values determined by differential and integral isoconversional methods. As it was above mentioned, in such cases, the application of differential isoconversional methods as well as the modified (advanced) nonlinear method suggested by Vyazovkin [24] is recommended. The statement (2) shows that this recommendation can be extended to iterative method for small $\Delta\alpha$. The differences between E values obtained by iterative methods based on Eqs. (18) and (19) could be explained by the different approximations of the temperature integral.

For crystallization from melt, it is also expected that the iterative method is applicable for random choice of T_1 with condition $T_1 > T_{\text{onset}}^{(\min)}$. A check of this is shown in Fig. 11. The corresponding values of E for iterations 0; 1 and 2 are -92.8 ± 16.4 kJ mol^{-1}; -125.8 ± 1.1 kJ mol^{-1}and -126.2 ± 0.9 kJ mol^{-1}, respectively. The last value of E is equal with that obtained by iterative method for T_1 = 600 K and iterative method based on Eq. (19) (see Fig. 10).

4. Conclusions

1. Using the integration of the general reaction rate for a given range of the conversion degree and constant heating/cooling rates, a new iterative isoconversional procedure to evaluate the activation energy from non-isothermal data recorded at several heating/cooling rates was worked out.
2. In comparison with often used linear integral isoconversional methods (FWO, KAS), the suggested iterative method remove the errors in activation energy evaluation due to the use of very simple approximate expressions of the temperature integral, which permit the determination of activation energy from the slope of a straight line.
3. The suggested iterative method is wide applicable no matter how little or how great the considered conversion range is, and is capable of providing valid values of the activation energy even if the latter strongly varies with the conversion degree.
4. In comparison with nonlinear isoconversional methods, which also allow using high accurate expressions of the temperature integral, the suggested iterative method is lower time-consuming.
5. The suggested method was checked for non-isothermal degradation of PVC, which exhibits a constant value of activation energy for a large range of conversion degree, for decomposition of AP, which exhibits a strong dependence of activation energy on the conversion degree, and crystallization of PET melt.
6. It was pointed out that the suggested iterative procedure could be useful for finding the conversion degree range for a rate-determining step.

References

[1] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340–341 (1999) 53–68.
[2] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A.K. Burnham, J. Opfermann, R. Srey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuhasni, Thermochim. Acta 355 (2000) 125–143.
[3] P. Budrugeac, E. Segal, Int. J. Chem. Kinet. 33 (2001) 564–573.
[4] P. Budrugeac, D. Homentcovschi, E. Segal, J. Therm. Anal. Calorim. 63 (2000) 457–463.
[5] R.R. Keuleers, F.J. Janssens, H.O. Desseyn, Thermochim. Acta 385 (2002) 127–142.
[6] A.K. Galwey, Thermochim. Acta 407 (2003) 93–103.
[7] A. Khawan, D.R. Flanagan, Thermochim. Acta 436 (2005) 101–112.
[8] L.A. Pérez-Maqueda, P.E. Sánchez-Jiménez, J.M. Criado, Int. J. Chem. Kinet. 37 (2005) 658–669.
[9] M.E. Brown, J. Therm. Anal. Calorim. 82 (2005) 665.
[10] P. Budrugeac, Polym. Degrad. Stab. 89 (2005) 265–273.
[11] H. Tanaka, M.E. Brown, J. Therm. Anal. Calorim. 80 (2005) 795–797.
[12] S. Vyazovkin, J. Therm. Anal. Calorim. 83 (2006) 45–51.
[13] A.K. Burnham, L.D. Dinh, J. Therm. Anal. Calorim. 89. (2007) 479–490.
[14] A. Pratap, T.L.S. Rao, K.N. Lad, H.D. Dhurandhar, J. Therm. Anal. Calorim. 89 (2007) 399–405.
[15] H.L. Friedman, J. Polym. Sci. C6 (1965) 183–195.
[16] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881–1886.
[17] J.H. Flynn, L.A. Wall, Res. J. Natl. Bur. Stand. A: Phys. Chem. 70A (1966) 487–523.
[18] T. Akahira, T. Sunose, Trans. Joint Convention of Four Electrical Institutes, Paper No. 246, 1969 Research Report/ Chiba Institute of Technology Sci. Technol. 16 (1971) 16–22.
[19] C.R. Li, T.B. Tang, J. Therm. Anal. 49 (1997) 1243–1248.
[20] C.R. Li, T.B. Tang, Thermochim. Acta 325 (1999) 43–46.
[21] S. Vyazovkin, D. Dollimore, J. Chem. Inf. Comput. Sci. 36 (1996) 42–45.
[22] S. Vyazovkin, J. Comput. Chem. 18 (1997) 393–402.
[23] S. Vyazovkin, J. Therm. Anal. 49 (1997) 1493–1499.
[24] S. Vyazovkin, J. Comput. Chem. 22 (2001) 178–183.
[25] P. Budrugeac, E. Segal, Int. J. Chem. Kinet. 36 (2004) 87–93.
[26] P. Budrugeac, J. Therm. Anal. Calorim. 68 (2002) 131–139.
[27] C. Doyle, J. Appl. Polym. Sci. 6 (1962) 639–642.
[28] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[29] G.I. Senum, R.T. Yang, J. Therm. Anal. 11 (1977) 445–447.
[30] Z. Gao, H. Wang, M. Nakada, Polymer 47 (2006) 1590–1596.
[31] P. Budrugeac, Polym. Degrad. Stab. 74 (2001) 125–132.
[32] P. Budrugeac, D. Homentcovschi, E. Segal, J. Therm. Anal. Calorim. 66 (2001) 557–565.
[33] N. Sbirrazzuoli, Macromol. Chem. Phys. 208 (2007) 1592–1597.
[34] N. Sbirrazzuoli, I. Vincent, A. Mija, N. Guido, Chemom. Intell. Lab. Syst. 96 (2009) 219–226.
[35] P. Budrugeac, E. Segal, J. Mater. Sci. 36 (2001) 2707–2710.
[36] J. Opfermann, J. Therm. Anal. Calorim. 60 (2000) 641–658.
[37] J. Cai, S. Chen, J. Comput. Chem. 30 (2009) 1986–1991.
[38] See for example A.K. Galwey, M.E. Brown, Kinetic background to thermal analysis and calorimetry, in: M.E. Brown (Ed.), Handbook of Thermal Analysis and Calorimetry, vol. 1, Elsevier, 1998 (Chapter 3).
[39] J.A. Kennedy, S.M. Clark, Thermochim. Acta 307 (1997) 27–35.
[40] A. Ortega, Thermochim. Acta 491 (2009) 116–117.
[41] A. Mianowski, T. Radko, Thermochim. Acta 204 (1992) 281–293.
[42] C. Popescu, E. Segal, Int. J. Chem. Kinet. 30 (1998) 313–327.
[43] S. Vyazovkin, Macromol. Rapid Commun. 23 (2002) 771–775.
[44] S. Vyazovkin, N. Sbirrazzuoli, J. Therm. Anal. Calorim. 72 (2003) 681–686.

[45] H.E. Kissinger, Anal. Chem. 29 (1957) 1702–1706.
[46] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 23 (2002) 766–770.
[47] A.L. Petre, P. Budrugeac, E. Segal, Rev. Roum. Chim. 42 (1997) 753–758.
[48] M.E. Brown, M. Maciejewski, S. Vyazovkin, Thermochim. Acta 307 (1997) 201–203.
[49] S. Vyazovkin, Thermochim. Acta 355 (2000) 155–163, 2000.
[50] N. Sbirrazzuoli, Y. Girault, L. Élégant, Thermochim. Acta 293 (1997) 25–37.