

KINETICS OF THE THERMAL DEGRADATION OF POLYETHYLENE TEREPHTHALATE

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ABSTRACT

A study of the kinetics of the thermal degradation of polyethylene terephthalate (PET) employing differential kinetic models and rapid computer analysis of thermogravimetric weight-loss data is presented. The influence of heating rate in non-isothermal degradation kinetics is investigated. The kinetic parameters for the pyrolysis of PET in inert atmosphere are presented. It is shown that the rate of degradation, activation energy, and pre-exponential factor depend strongly on heating rate whereas the order of reaction, found to be one, remains unchanged. Estimates of low temperature ($< 300^{\circ}\text{C}$) isothermal kinetics, and hence isothermal stability of PET films, from non-isothermal kinetics are shown to be similarly dependent on the heating rates employed in dynamic thermogravimetry. The observed variation of kinetic parameters with heating rate is attributed to the coupling of physical transport processes with chemical processes.

INTRODUCTION

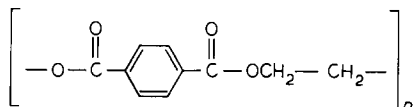
The aromatic linear polyester polyethylene terephthalate (PET), as with most synthetic polymers, undergoes complex physicochemical transformations after its initial formation by polymerization. Such degradative processes may be induced by thermal, chemical, or radiative agents encountered during processing or when in normal use. Consequently, various aspects of the mechanisms and kinetics of degradation of PET have long been of interest [1–3]. In early work, semi-quantitative and quantitative methods were used to investigate the products of thermal decomposition and the kinetics were studied by melt-viscosity techniques [1–3]. It is now believed that the thermal decomposition process of PET in inert atmosphere can be

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represented by the reaction scheme



where A_1 is the solid or liquid polymer with the structure



The primary degradation process is attributed to a random scission of ester links in the main chain yielding A_2 which has been shown to be a mixture of monomeric terephthalic acid and vinyl ester oligomers [1,3-5]. Subsequently there follows rapid production of low molecular weight volatile fragments with consequent weight loss. The volatiles (A_3) have been shown to be mostly COOH, acetaldehyde, CO, CO₂, C₂H₄, H₂O and CH₄ [3-5].

Since few detailed studies of the kinetics of PET pyrolysis by thermogravimetric (TG) analysis have been reported in the literature, we present results of such an investigation employing differential kinetic models and rapid computer analysis of TG weight-loss data. The influence of heating rate on non-isothermal degradation kinetics is also reported.

KINETIC MODEL AND METHODS OF ANALYSIS

Non-isothermal kinetics

In the non-isothermal mode of the thermogravimetric analyzer (TGA) a known weight of the solid or liquid polymer is heated at a constant rate and the weight-loss curve $\alpha[T(t)]$ is recorded, where α is the fraction of weight decomposed at temperature T and time t . In order to determine the reaction rate and kinetic parameters, i.e., activation energy, order of reaction, and frequency factor, from $\alpha [T(t)]$, various methods of analysis have been tried with varying degrees of success [6]. Here we employ a differential method of kinetic analysis. A rate expression of the form

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = k(T)(1 - \alpha)^n \quad (2)$$

where n , the order of reaction, can be assumed. The specific rate constant $k(T)$ is given by the Arrhenius relation

$$k(T) = A \exp(-E/RT) \quad (3)$$

where A is the frequency factor, E is the activation energy of the overall reaction of eqn. (1), R is the gas constant, and T is the absolute temperature. Since the temperature of the sample is increased at a constant rate β ,

$T = T_0 + \beta t$, the reaction rate can be obtained from $\alpha[T(t)]$ by

$$\frac{d\alpha}{dt} = \beta \frac{\partial\alpha}{\partial T} \quad (4)$$

and consequently

$$\ln \left[\frac{\beta (\partial\alpha/\partial T)}{(1-\alpha)^n} \right] = \ln k(T) = \ln A - \frac{E}{R} \frac{1}{T} \quad (5)$$

Equation (5) provides a basis for extracting kinetic parameters E , A , and n from TG data obtained at any fixed β . However, since n , E and A are not known a priori eqn. (5) alone cannot furnish the set (n, E, A) by the standard least-squares fit techniques. If the order of reaction is known then eqn. (5) yields both E and A immediately by least-squares analysis. We adopt a method which trial-fit values of $n = 0, 1/3, 1/2, 2/3, 1$, etc., anticipated for polymer decomposition reactions [6,7]. Reaction rates [eqn. (4)] are obtained from a TG curve $\alpha[T(t)]$ by a numerical differentiation technique using a second-order Lagrangian interpolation polynomial [8]. The numerical differentiation scheme, least-squares analysis routine for calculating E and A , and a plotting routine were incorporated in a Fortran program implemented on an interactive terminal using a Honeywell level 6 (or Multics) computer.

Another commonly used method of analysis for estimating kinetic parameters from non-isothermal TG data at different constant heating rates is the equation

$$\log \beta = \log \left(\frac{AE}{Rg(\alpha)} \right) - a - \frac{bE}{R} \frac{1}{T} \quad (\alpha = \text{constant}) \quad (6)$$

It can be shown that for $28 < E/RT < 50$, $b = 0.457$ [9,10] and hence

$$\Delta \log \beta = -0.457 \frac{E}{R} \Delta \left(\frac{1}{T} \right) \quad (7)$$

Isothermal kinetics and lifetime prediction

In isothermal thermogravimetric analysis the measured weight-loss curve is essentially $\alpha(t)$, the fraction of reactant decomposed with time at a constant temperature. Again starting with the rate expression of eqn. (2) the isothermal analog of eqn. (5) becomes

$$\ln \left[\frac{d\alpha/dt}{(1-\alpha)^n} \right] = \ln k(T) = \ln A - \frac{E}{R} \frac{1}{T} \quad (8)$$

where n , E and A are independent of heating rate β . However, for most materials it is impractical to obtain the weight-loss curve $\alpha(t)$ at other than high temperatures ($> 260^\circ\text{C}$ for PET). Thus one use of the kinetic parameters derived from non-isothermal kinetics is the estimation of isothermal

kinetics, e.g., estimation of durability or "lifetime" of the material at a constant temperature. Such a lifetime can be defined from an integrated form of eqn. (2)

$$t_{\alpha} = \frac{1}{k(T)} \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{g(\alpha; n)}{k(T)} \quad (9)$$

where for the chosen $f(\alpha)$ in eqn. (2)

$$g(\alpha; 1) = \ln \frac{1}{1 - \alpha} \quad (10)$$

$$g(\alpha; n \neq 1) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n} \quad (11)$$

EXPERIMENTAL

Apparatus

A Perkin-Elmer thermogravimetric analyzer (TGA) model TDS-2 was used along with a Du Pont 990 thermal analyzer equipped with a DSC cell and a 951 TGA. The primary data reported here were acquired on the Perkin-Elmer TGA and only checked with the Du Pont instrument.

Materials

The PET samples were obtained from Du Pont Co. as films (type D Mylar). All data reported here are for 3 mil (about 76 μ thick) films. The PET films were characterized for structure, phase transitions, and molecular weight. The IR spectra were similar to published ones. The phase transitions revealed in a DSC scan from room temperature to 300°C are shown in Fig. 1

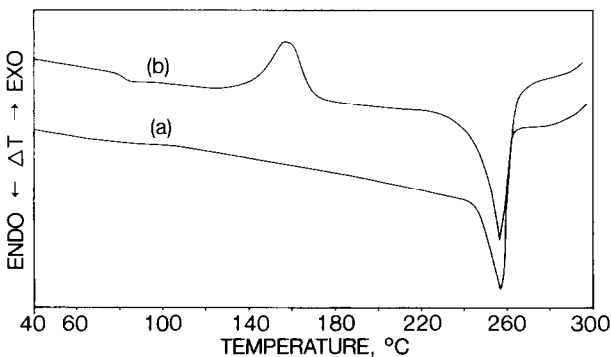


Fig. 1. DSC thermogram of PET: (a) as-received; (b) annealed.

where (a) shows the as-received sample which is semi-crystalline with about 45–50% crystallinity, and (b) shows an amorphous sample quenched from the melt. A T_g value of about 70°C, a recrystallization onset temperature of 120°C, and a crystalline melting point of about 245°C were obtained. A relative number average molecular weight determined by high temperature gel permeation chromatography (Waters Associate, model 150C GPC) was approximately 26 000. The true number average molecular weight of PET has been reported as 14–15 000 [11].

Procedure

PET samples for TG analysis were heated in aluminum pans in flowing nitrogen atmosphere at five different heating rates ranging from 0.31°C min⁻¹ (5.17×10^{-3} °C sec⁻¹) to 10°C min⁻¹ (0.167°C sec⁻¹). The pyrolysis was carried out in the temperature range 25–600°C. DSC scans were made at one fixed heating rate (10°C min⁻¹). TG weight-loss curves were digitized and stored in computer memory until full kinetic analysis was performed.

RESULTS AND DISCUSSION

Influence of heating rate on TG curves

Figure 2 shows scaled TG weight-loss curves of PET obtained at five different heating rates in nitrogen: 0.31°C min⁻¹ (5.17×10^{-3} °C sec⁻¹); 1.25°C min⁻¹ (2.08×10^{-2} °C sec⁻¹); 2.5°C min⁻¹ (4.17×10^{-2} °C sec⁻¹); 5°C min⁻¹ (8.33×10^{-2} °C sec⁻¹); 10°C min⁻¹ (1.67×10^{-1} °C sec⁻¹). The results indicate that a non-volatile residue, about 10% of the sample, remains after pyrolysis in inert atmosphere. That the overall degradation process is a one-step decomposition reaction can also be inferred from the family of curves. It is noteworthy that individual curves in the family are identical in shape except the displacement of one curve from the other along the temperature axis. The suggestion from this is that the same order of reaction prevails over the whole heating rate range. These results also underscore the inadequacy of such qualitative criteria of polymer stability as inception and final temperatures from the TG curve; depending on the heating rate and the person interpreting the weight-loss curves different inception and final temperatures will result.

The rate of decomposition of the polymer, using fraction reacted (per sec) as the reaction coordinate, normalized to the maximum rate, is plotted as a function of temperature in Fig. 3. A striking family of identical curves, displaced from one another on the temperature axis, similar to those in Fig. 2 is seen. From similarity of the normalized reaction rate at different heating rates, an identical decomposition reaction mechanism is suggested.

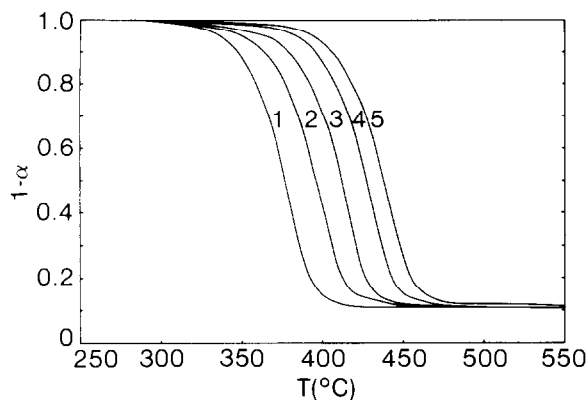


Fig. 2. Non-isothermal weight-loss curves of PET at different heating rates. $\beta(^{\circ}\text{C min}^{-1}) = 1, 0.31; 2, 1.25; 3, 2.50; 4, 5.00; 5, 10.00$.

Although the structure of the degradation process is identical at each and every heating rate, the rate of reaction is different. The maximum rate of degradation $(d\alpha/dt)_m$ shown in Table 1 reveals this clearly. From the maximum rate of $1.12 \times 10^{-4} \text{ sec}^{-1}$ at $5.17 \times 10^{-3} \text{ }^{\circ}\text{C sec}^{-1}$ the reaction rate climbs to the maximum rate of $3.50 \times 10^{-3} \text{ sec}^{-1}$ at $0.167^{\circ}\text{C sec}^{-1}$. Exhibited in Fig. 4 is the dependence of $(d\alpha/dt)_m$ on heating rate, a rapidly increasing function.

A parameter that characterizes the displacement of individual curves within the family of curves of either Fig. 2 or Fig. 3 is T_m , the temperature at which the rate of reaction peaks. Perhaps α_m is also such a parameter. Both T_m and α_m are shown in Table 1. The values of α_m show that the maximum rate of reaction at any heating rate is attained only after half of the original

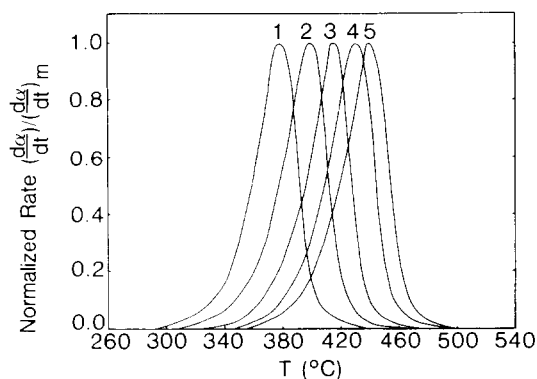


Fig. 3. Normalized rate of decomposition of PET as a function of temperature. $\beta(^{\circ}\text{C min}^{-1}) = 1, 0.31; 2, 1.25; 3, 2.50; 4, 5.00; 5, 10.00$.

TABLE I

Maximum rates of thermal decomposition of PET at different heating rates

β ($^{\circ}\text{C sec}^{-1}$)	$(d\alpha/dt)_m(\text{sec}^{-1}) \times 10^4$	$T_m(^{\circ}\text{C})$	α_m
5.17×10^{-3}	1.13	377.4	0.5170
2.08×10^{-2}	4.55	400.0	0.5740
4.17×10^{-2}	9.43	415.0	0.5566
8.33×10^{-2}	17.59	430.0	0.5477
1.67×10^{-1}	35.00	440.0	0.5350

polymer has decomposed. There is no clear trend of how α_m changes with heating rate. A reaction which peaks at 377.4°C when the heating rate is $5.17 \times 10^{-3} \text{ }^{\circ}\text{C sec}^{-1}$ shifts to 440°C when the heating rate is increased to $1.67 \times 10^{-1} \text{ }^{\circ}\text{C sec}^{-1}$ as the values of T_m indicate. Furthermore, T_m increases linearly with $\ln \beta$ as revealed in Fig. 4. One reason for the displacement in temperature, characterized by T_m , is that the true sample temperature lags behind that recorded by the instrument at higher heating rates. The origin of this is to be traced to heat transfer effects. Another possible contribution to the displacement is time-effects. Thus, at very low heating rates, dynamic TG is closer to isothermal TG than at high heating rates.

Kinetic parameters

The Arrhenius plots for the first-order kinetics of the thermal decomposition of PET are shown in Fig. 5. Excellent linear curves are obtained, showing that indeed the thermal degradation process follows first-order kinetics, i.e., $n = 1$. It must be mentioned that although arrival at the correct

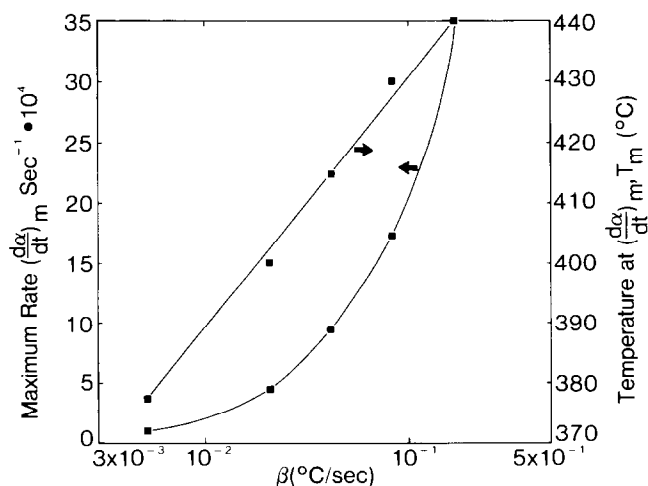


Fig. 4. Variation of maximum rate and T_m with heating rate.

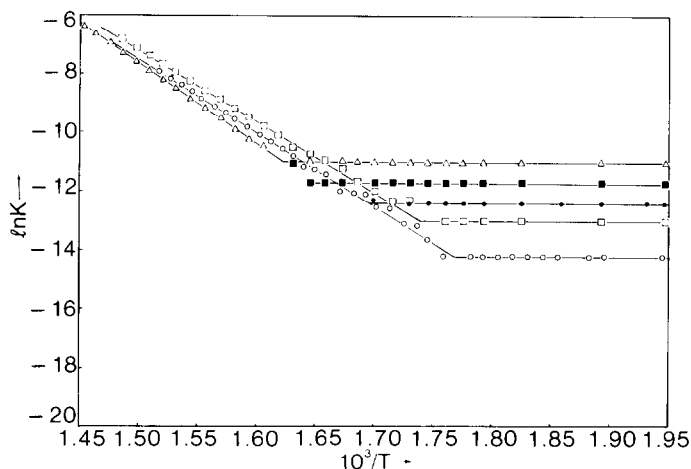


Fig. 5. Arrhenius plot for the pyrolysis of PET in nitrogen. β ($^{\circ}\text{C min}^{-1}$). Δ , 10; \blacksquare , 5.0; \bullet , 2.5; \square , 1.25; \circ , 0.31.

value of n is by trial fit, the computer program expedites the search by calculating the pair (E, A) along with their standard errors as well as by displaying the corresponding Arrhenius plots for quick view on the terminal screen/plotter. Furthermore, the least-squares fit program is very sensitive and able to discriminate well between the various values of n to within 5%. Thus trial fits at $n < 0.94$ or ≥ 1.06 are found to give unsatisfactory results in the same temperature range as that at $n = 1.0$.

An interesting feature of the Arrhenius plots of Fig. 5 is the break in each curve, separating two regions in the Arrhenius plot: a high temperature region of finite slope and a low temperature horizontal region (zero slope). For instance, at $5.17 \times 10^{-3} \text{ } ^{\circ}\text{C sec}^{-1}$ a finite slope is maintained from higher temperatures down to 295°C and then the curve levels off (to avoid over-crowding in Fig. 5, the finite slope region of two intermediate heating rates has been omitted). At the highest heating rate ($0.167^{\circ}\text{C sec}^{-1}$) the break point is 340°C . An immediate consequence of the segmented Arrhenius plot is that though order of reaction is the same, the other kinetic parameters, i.e., E and A , are different in each region. Implications of this for the estimation of isothermal kinetics are discussed in another section.

The pair of first-order kinetic parameters (E, A) calculated from the finite slope regions of Fig. 5 are shown in Table 2. The indicated error in the activation energy is one standard deviation from the mean. In general, both E and A increase with increasing heating rate. The dependence of E on β is shown in Fig. 6 where it is seen that the activation energy increased from 48.1 to $55.6 \text{ kcal mole}^{-1}$ over the heating rate range. The kinetic compensation effect [12,13] according to which increase in E due to heating rate is compensated by a corresponding increase in A such that a linear relationship

TABLE 2

First-order kinetic parameters for thermal decomposition of PET

β ($^{\circ}\text{C sec}^{-1}$)	E (kcal mole $^{-1}$)	A (sec $^{-1}$)	k_0 (sec $^{-1}$)
5.17×10^{-3}	48.14 ± 0.75	3.16×10^{12}	6.81×10^{-7}
2.08×10^{-2}	47.74 ± 0.67	3.19×10^{12}	2.19×10^{-6}
4.17×10^{-2}	52.15 ± 0.67	7.14×10^{13}	4.24×10^{-6}
8.33×10^{-2}	53.94 ± 0.60	2.19×10^{14}	8.38×10^{-6}
1.67×10^{-1}	55.56 ± 0.39	7.84×10^{14}	1.67×10^{-5}

exists between $\log A$ and E holds for PET decomposition. The (E, A) data in Table 2 all fit in a straight line represented by $\log A = 0.306E - 2.028$. For comparison purposes the activation energy was calculated by the method of isoconversional analysis. Figure 7 shows the plot of $\log \beta$ vs. $1/T$ giving straight lines at each constant conversion. The values of E calculated by this method are shown in Table 3 and range from 41.5 ± 5.4 kcal mol $^{-1}$ at $\alpha = 0.05$ to 49.2 ± 2.9 kcal mole $^{-1}$ at $\alpha = 0.80$. Deviations from the mean values of E are considerably higher than those calculated by the single heating rate method shown in Table 2.

Explanation of the observed variation of kinetic parameters with heating rate is to be sought from the coupling of physical processes and chemical processes as shown in a larger context of the kinetics of heterogeneous reactions [14]. In the case of polymer decomposition, and PET pyrolysis in particular, the chemical processes are primarily bond-breaking with consequent production of many gaseous products which in turn give rise to high concentration differences between the reaction front and the inert fluid

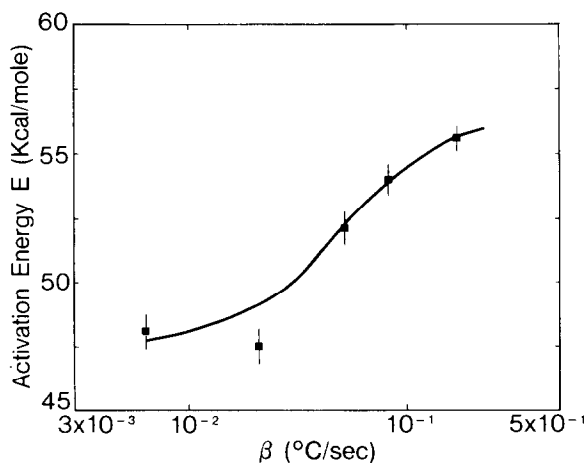


Fig. 6. Activation energy vs. heating rate.

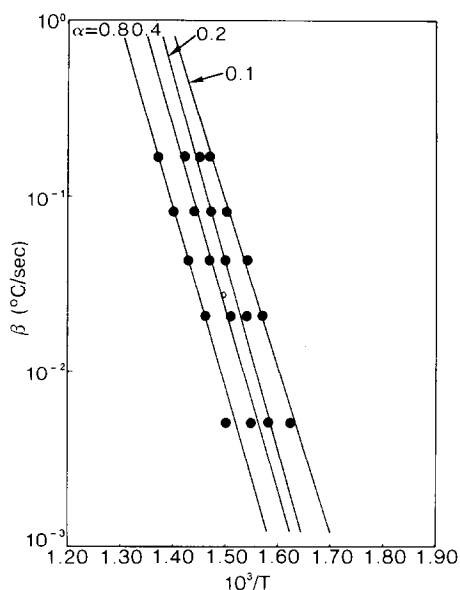


Fig. 7. Isoconversional analysis: heating rate vs. $1/T$.

atmosphere. Thus mass transfer effects would be significant and should depend on the extent of the decomposition reaction since the porous ash layer grows with progress of the reaction front. Similarly, heat transfer effects are not to be neglected considering the fairly large sample size (volume) and the poor thermal conductivity of polymeric materials. Though separating the effects of heat and mass transfer from each other may be difficult in non-isothermal polymer decomposition experiments, it is possible to separate these physical processes from the chemical processes through

TABLE 3

Activation energy from isoconversional analysis of PET degradation kinetics

α	$E(\text{kcal}/\text{mole}^{-1})$
0.05	41.5 ± 5.4
0.07	43.3 ± 3.7
0.10	44.8 ± 3.7
0.20	47.3 ± 3.3
0.30	47.3 ± 3.3
0.40	47.3 ± 3.3
0.50	48.9 ± 1.5
0.60	48.9 ± 1.5
0.70	48.9 ± 1.5
0.80	49.2 ± 2.9

correlational studies of experimental conditions in dynamic thermogravimetry.

Estimation of isothermal kinetics

One, 5, and 10% lifetime (t_α , $\alpha = 0.01, 0.05, 0.10$) of PET at 75, 100, 200 and 300°C are shown in Tables 4–6. These values of lifetime were calculated using the kinetic parameters of Table 2 by a subroutine within the main computer program. At any temperature the calculated lifetime is seen to depend strongly on the heating rate, t_α decreases with decreasing β . For example, at 75°C in Table 4 the 1% lifetime drops from 3.21×10^{10} years to 1.73×10^8 years when the heating rate is lowered from $0.167^\circ\text{C sec}^{-1}$ to $5.17 \times 10^{-1} \text{ }^\circ\text{C sec}^{-1}$, a factor of 186 times decrease. However, note that the ratio $t_\alpha(\beta_2)/t_\alpha(\beta_1)$, where $\beta_1 < \beta_2$, is not constant with temperature. In fact the ratio for $\beta_1 = 5.17 \times 10^{-3}$ and $\beta_2 = 0.167^\circ\text{C sec}^{-1}$ is 186, 91, 11, and 3 at 75, 100, 200, and 300°C, respectively, for 1% decomposition. It is noteworthy that similar calculations of t_α at higher temperatures ($T > 300^\circ\text{C}$) showed no variation with heating rate. Thus the effect of heating rate on isothermal

TABLE 4

One percent lifetime of PET at different temperatures and heating rates

$\beta(^\circ\text{C sec}^{-1})$	$t_\alpha = 0.01$ (years)			
	75°C	100°C	200°C	300°C
5.17×10^{-3}	1.726×10^8	1.624×10^6	1.766	2.318×10^{-4}
2.08×10^{-2}	9.697×10^7	9.480×10^5	1.154	1.629×10^{-4}
4.17×10^{-2}	2.540×10^9	1.620×10^7	5.605	3.490×10^{-4}
8.33×10^{-2}	1.106×10^{10}	5.928×10^7	12.31	5.495×10^{-4}
1.67×10^{-1}	3.208×10^{10}	1.470×10^8	19.23	6.355×10^{-4}

TABLE 5

Five percent lifetime of PET at different temperature and heating rates

$\beta(^\circ\text{C sec}^{-1})$	$t_\alpha = 0.05$ (years)			
	75°	100°C	200°C	300°C
5.17×10^{-3}	8.807×10^8	8.288×10^6	9.016	1.183×10^{-3}
2.08×10^{-2}	4.949×10^8	4.839×10^6	5.889	8.314×10^{-4}
4.17×10^{-2}	1.297×10^{10}	8.268×10^7	28.61	1.781×10^{-3}
8.33×10^{-2}	5.645×10^{10}	3.026×10^8	62.82	2.805×10^{-3}
1.67×10^{-1}	1.637×10^{11}	7.502×10^8	98.13	3.244×10^{-3}

TABLE 6

Ten percent lifetime of PET at different temperatures and heating rates

β ($^{\circ}\text{C sec}^{-1}$)	$t_{\alpha} = 0.10$ (years)			
	75 $^{\circ}\text{C}$	100 $^{\circ}\text{C}$	200 $^{\circ}\text{C}$	300 $^{\circ}\text{C}$
5.17×10^{-3}	1.809×10^9	1.702×10^7	18.52	2.430×10^{-3}
2.08×10^{-2}	1.017×10^9	9.939×10^6	12.10	1.708×10^{-3}
4.17×10^{-2}	2.663×10^{10}	1.698×10^8	58.77	3.659×10^{-3}
8.33×10^{-2}	1.159×10^{11}	6.215×10^8	129.0	5.761×10^{-3}
1.67×10^{-1}	3.363×10^{11}	1.379×10^9	201.6	5.964×10^{-3}

kinetics estimated from non-isothermal kinetic parameters is restricted to low temperature; the lower the temperature the stronger the effect of heating rate, as expected. Similar behavior of lifetime estimates has previously been observed in polymer decomposition [9]. Furthermore, for $T > 300^{\circ}\text{C}$, we have observed good agreement between isothermal experimental data and calculated values.

The difference in the dependence of estimated isothermal kinetics on heating rate at low ($< 300^{\circ}\text{C}$) and high temperatures is a consequence of the observed break in the Arrhenius plot of Fig. 5. In the zero slope region the apparent rate constant k_0 is indeed constant with temperature. However, note that $\ln k_0$ is a linear function of $\ln \beta$, or $k_0 = 10^{-4}\beta$, as revealed in Fig. 8. Clearly when kinetic parameters (E, A) obtained from the finite slope region are used to calculate isothermal kinetics at low temperatures, i.e., below the break point in the Arrhenius plot (generally about 300°C), an invalid extrapolation is performed, for polymer chain scission and depoly-

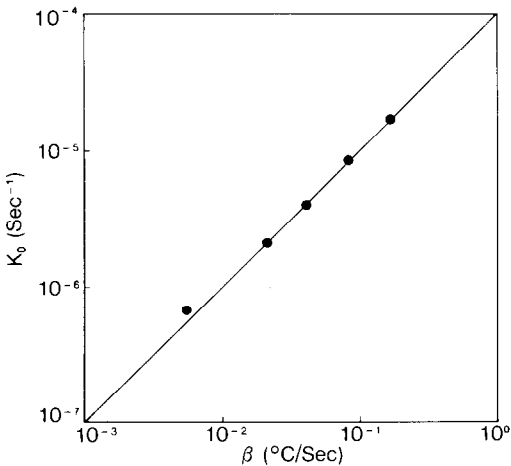


Fig. 8. Specific rate constant vs. heating rate.

merization at low temperature may have a totally different mechanism, and thus, kinetics.

CONCLUSIONS

A rapid computer analysis of thermogravimetric weight-loss data and differential kinetic models has provided kinetic parameters of non-isothermal decomposition of polyethylene terephthalate films in inert atmosphere. The effect of heating rate on observed kinetics was investigated in the range 10^{-3} – 10^{-1} °C sec⁻¹. The variation of kinetic parameters with heating rate was attributed to coupling of physical transport processes with chemical reactions.

Estimates of low temperature (< 300°C) isothermal kinetics of PET films were shown to depend strongly on the heating rate employed in dynamic thermogravimetry whereas estimates at high temperature were independent of heating rate.

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