Application of DTA Traces to Polymer Pyrolyses

LEO REICH, *Polymer Research Branch, Picatinny Arsenal, Dover, New Jersey*

Synopsis

Various expressions are presented for the estimation of kinetic parameters during pyrolysis from DTA traces. These expressions are applied to polytetrafluoroethylene, polyethylene, polypropylene, polystyrene, isotactic poly(propylene oxide), and poly(methyl methacrylate). The results obtained are compared with reported values, and advantages and disadvantages of the various methods are given.

Introduction

In recent communications,[1,2] expressions were derived for the estimation of activation energy E and reaction order n during pyrolyses from DTA traces. These expressions were obtained by modifying expressions, utilized for the estimation of E and n from thermogravimetric traces (TGA), by means of the approximate equations,

$$W_c \approx W_{0,c}(\tilde{a}/A)$$

and

$$-dW_c/dT \approx W_{0,c}(\Delta T/A)$$

(1)

where W_c and $W_{0,c}$ denote active weight or weight fraction of polymer remaining and polymer initially present, respectively, during a pyrolysis; A represents the total area under the DTA curve; and, $\tilde{a} = A - \int_{T_0}^{T} \Delta T \, dT$, where ΔT denotes peak height. The DTA expressions were applied to DTA traces for the pyrolysis of polypropylene (PPr) and Teflon (T) (polytetrafluoroethylene). In this paper, these expressions will also be applied to various other polymers, i.e., polyethylene (PE), polystyrene (PSt), poly(methyl methacrylate) (PMMA), and isotactic poly(propylene oxide) (PPrO). Furthermore, by the utilization of eq. (1), various other TGA equations were converted into expressions suitable for the estimation of kinetic parameters from DTA traces.[2-4] All of the DTA-expressions obtained were applied to all of the polymers listed above. Advantages and disadvantages of the various methods are discussed.

Experimental

The polymers studied were of commercial grade, with the exception of PPrO. The latter polymer was synthesized in this laboratory by
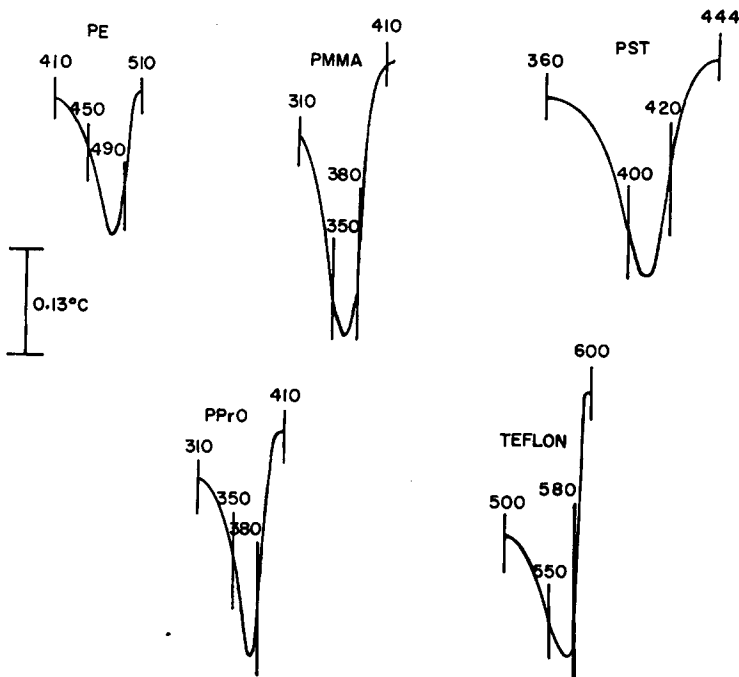
Fig. 1. DTA traces during the pyrolysis of various polymers.

R. J. Valles by means of an aluminum isopropoxide–zinc chloride catalyst system. Also, previously reported DTA data for PPr were employed.[5]

The DTA apparatus utilized consisted of an Aminco Thermoanalyzer. Generally, 9–18 mg. portions of polymer sample were "sandwiched" between sufficient alumina (Fisher Certified Reagent Grade) so that the total sample weight was 100 mg. (the sample was loosely packed). However, in order to obtain reproducible results for Teflon, it was necessary to mix the polymer thoroughly with the alumina. The latter material (100 mg.) was also used as the inert reference. The heating rates (RH) employed for the various polymers were constant and in the range of 8–8.7°C./min.; nitrogen was passed over the sample and reference at a flow rate of about 40–45 cc./min. In Figure 1 are shown DTA traces for the various polymers studied, over the temperature ranges in which they decomposed.

Results and Discussion

For convenience, the various expressions employed to estimate kinetic parameters from DTA traces are given in eqs. (1)–(7).

$$\left.\begin{array}{ll} F(T) = \left(\dfrac{\tilde{a}_1}{\tilde{a}_2}\right) \dfrac{\log\,(A/\tilde{a})_1}{\log\,(A/\tilde{a})_2} & \text{For } n = 1 \\[2em] F(T) = \left(\dfrac{\tilde{a}_1}{\tilde{a}_2}\right)^n \dfrac{1 - (\tilde{a}/A)_1{}^{(1-n)}}{1 - (\tilde{a}/A)_2{}^{(1-n)}} & \text{For } n \neq 1 \end{array}\right\} \qquad (2a)$$

where $F(T) \equiv (T_1/T_2)^2(\Delta T_1/\Delta T_2)$.

$$(E/R) = T^2\Delta T/[\tilde{a}\ln(A/\tilde{a})] \qquad\qquad \Big\} \quad \text{For } n = 1$$

$$(E/R) = \{[(1 - n)T^2\Delta T]/A\}/(\tilde{a}/A)^n[1 - (\tilde{a}/A)^{(1-n)}]\} \quad \text{For } n \neq 1 \qquad (2b)$$

$$\Delta \log(\Delta T) = n\Delta\log\tilde{a} - (E/2.3R)\Delta(1/T) \qquad\qquad (3)$$

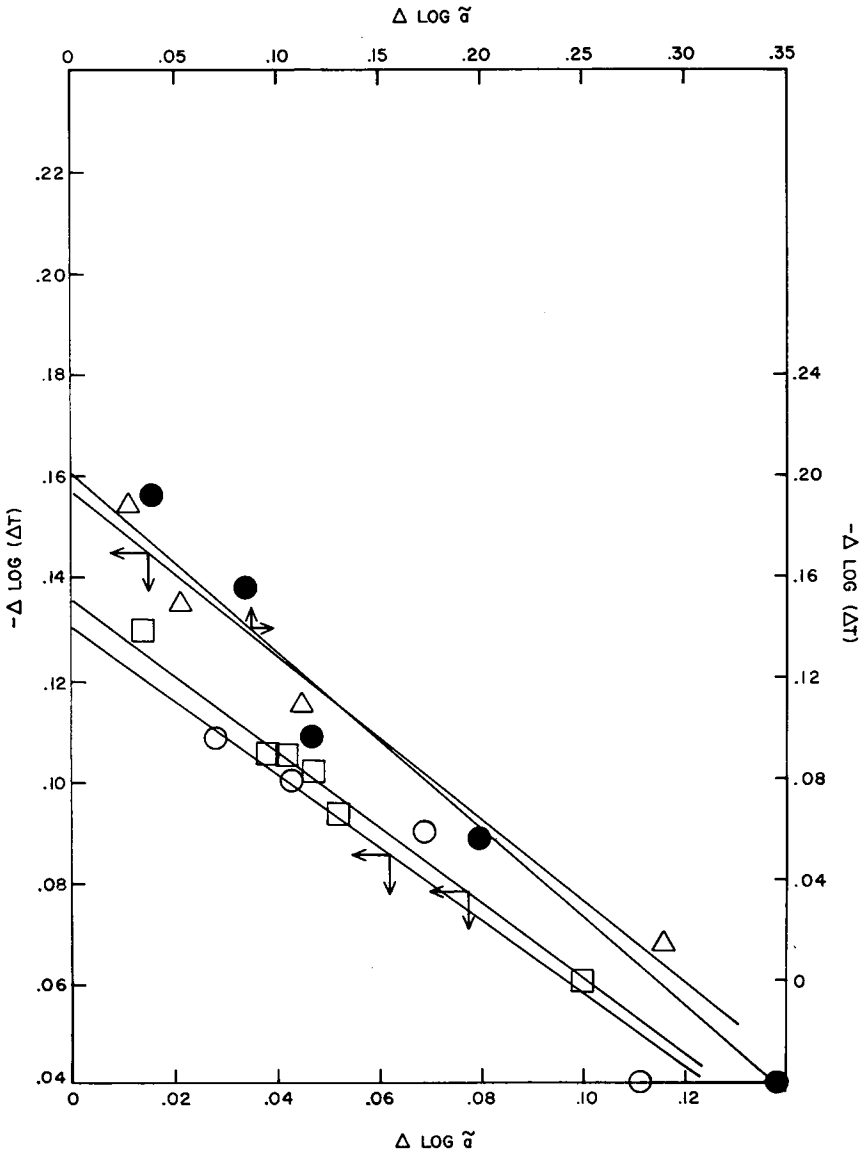$$\ln(a/AT^2) = -E/RT + \ln[ZR/E(\text{RH})] \quad \text{For } (2RT/E) \ll 1 \qquad (4)$$

Fig. 2. Plots for determination of kinetic parameters from eq. (3): (O) PMMA; (△) PE; (□) PPrO; (●) Teflon.

TABLE I.   Application of Equations (2)–(6) to Various Polymers

| Material | Eq. no. | E, kcal./mole | | n | |
		Calcd.	Reptd.	Calcd.	Reptd.
Benzenedi-	2	28 ± 0.7	28.3[a]	1.03 ± 0.04	1[a,b]
azonium	3	30	28.7[b]	1.1	
Chloride	4	$25\frac{1}{2}$		—	
(aq. soln.)	5	$25\frac{1}{2}$		—	
	6	35		—	
	7	$29\frac{1}{2}$		1.2	
PPr	2	58 ± 2	58[c]	0.89 ± 0.08	1 (over a limited
	3	54	55[d]	0.73	conversion
	4	50	62.5[e]	—	range)[e]
	5	54	65[f]	—	
	6	61		—	
	7	57		0.95	
PE	2	73 ± 1	67 ± 5[g]	0.88 ± 0.03	1 (over a limited
	3	76	72 (linear)[c]	0.82	conversion
	4	74	64 (branched)[c]	—	range)[c,g]
	5	74		—	
	6	74		—	
	7	72		1.0	
PMMA	2	48 ± 1	30–52[h]	1.05 ± 0.10	≈ 1[c]
	3	46	56[i]	0.75	
	4	55		—	
	5	46		—	
	6	56		—	
	7	54		1.5	

<div align="right">(continued)</div>

where Z denotes frequency factor and R is the gas constant.

$$\ln[(a - a_i)/A] = -E/RT + \ln[Z(T - T_i)W_{0,c}^{(n-1)}/(\mathrm{RH})]$$

$$\text{For } (T - T_i) = \text{constant} \qquad (5)$$

$$\log A_u = [(E/RT_a) + 3]\log T + \log B \qquad (6)$$

where

$$A_u = \int_0^T (a/A)dT$$

$$B = \{(ZW_0^{(n-1)}R)/E(\mathrm{RH})[(E/RT_a) + 3]\}(1/eT_a)^{E/RT_a}$$

and T_a denotes an average temperature over the temperature range studied; and

$$\log (\Delta T) = (E/R)(K \log \tilde{a} - 1/2.3T)$$

$$+ (E/R)K \log (W_0/A) + \log [ZA/(\mathrm{RH})W_0] \qquad (7a)$$

$$n = K(E/R) \qquad (7b)$$

where, $K \equiv (\tilde{a}/\Delta T)_{\mathrm{M}}(1/T_{\mathrm{M}})^2$

TABLE I (*continued*)

Material	Eq. no.	E, kcal./mole		n	
		Calcd.	Reptd.	Calcd.	Reptd.
PPrO	2	55 ± 1	45[j]	1.0 ± 0.10	1 (over a limited
	3	49		0.8	conversion
	4	53		—	range)[j]
	5	46		—	
	6	53		—	
	7	54		1.2	
Teflon	2	71 ± 4	67, 69[i]	0.78 ± 0.02	(1.02 + 0.07)[l]
	3	64	66–68[k]	0.73	(0.85–1.16)[i]
	4	74	74 ± 4[l]	—	
	5	64		—	
	6	≈100		—	
	7	72		0.94	
PSt	2	78 ± 2	60 ± 5[g]	0.97 ± 0.06	1 (over a limited
	3	—	74, 77[i]	—	conversion
	4	74		—	range)[g]
	5	73		—	
	6	≈100		—	
	7	90		1.3	

[a] Data of Borchardt.[6]
[b] Data of Reed et al.[7]
[c] Data of Madorsky.[8]
[d] Data of Moiseev et al.[9]
[e] Data of Bresler et al.[10]
[f] Data of Davis et al.[11]
[g] Data of Anderson and Freeman.[12]
[h] Data of Madorsky.[13]
[i] Data of Fuoss et al.[14]
[j] Data of Madorsky and Straus.[15]
[k] Data of Doyle.[16]
[l] Data of Anderson.[17]

and the subscript M denotes values of the appropriate terms at the maximum value of ΔT.

Kinetic parameters, E and n, are listed in Table I for the thermal degradation of various polymers and of benzenediazonium chloride (BDC) (aqueous solution) along with the various equations employed in estimating these values. The latter material was also utilized, since it represents a relatively "ideal" case[1] and offers a means whereby the accuracy of the various equations may be judged. Previously reported DTA data for BDC were used.[6]

Values of E and n were obtained from the various equations as follows. Prior to determining E from eq. (2b), it is necessary to estimate n. From eq. (2a), it can be seen that $F(T)$ may be plotted as a function of n for various values of $(\tilde{a}_1/A)$ and $(\tilde{a}_2/A)$.[1] Then, values of the sample temperature T and the peak height ΔT are obtained, where $(\tilde{a}/A)$ possesses the desired value on the thermogram. After a few rapid trial-and-error trac-

ings of the thermogram with a planimeter, values of T and ΔT correspond-
ing to two desired values of $(\tilde{a}/A)$ may be readily obtained. From the
values of T and ΔT, $F(T)$ may be calculated, and n may be subsequently
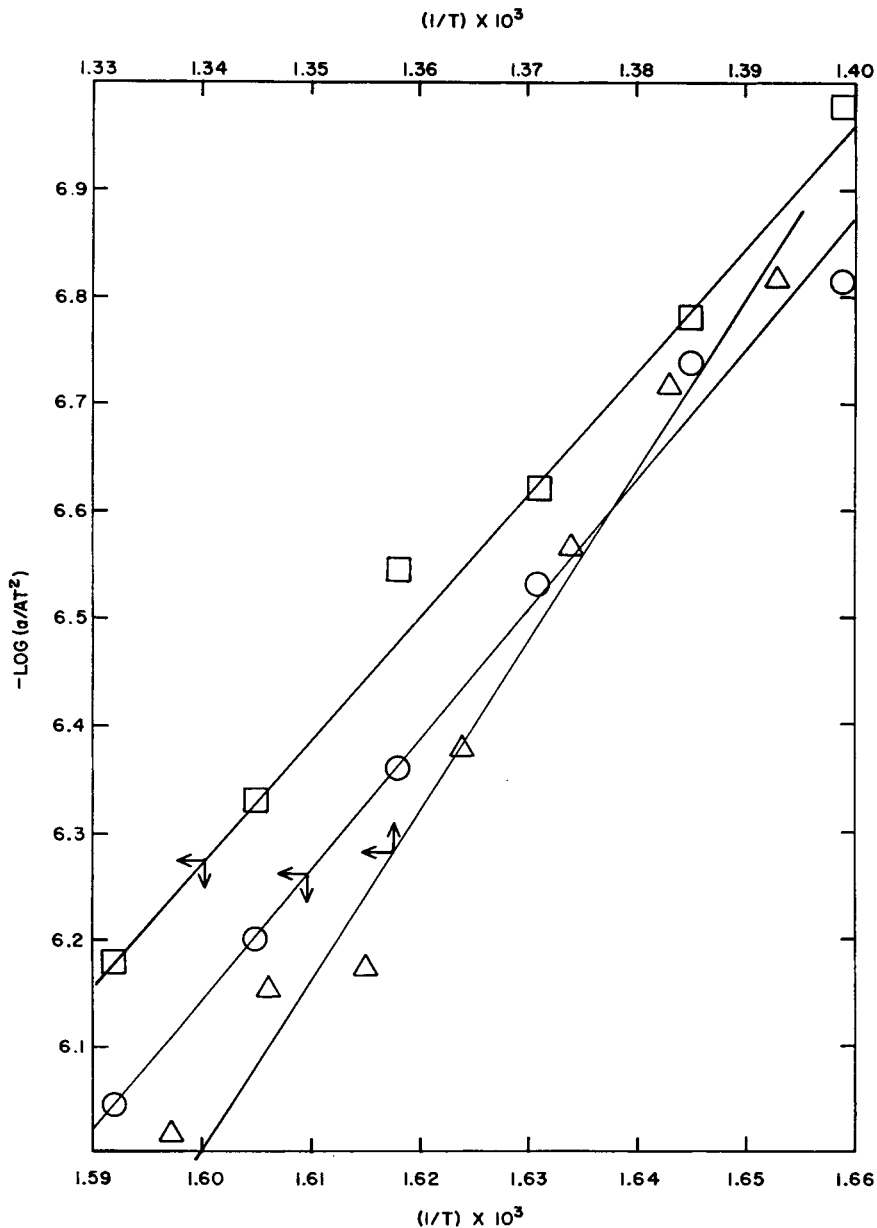determined from the preconstructed plot of $F(T)$ versus n. After n has

Fig. 3. Plots for determination of kinetic parameters from eq. (4):   (O) PMMA; ($\triangle$)
PE; ($\square$) PPrO.

been determined, a value of E may be calculated for each ratio, $(\bar{a}/A)$, by means of eq. (2b). The average values of E and n estimated by means of eq. (2) and listed in Table I represent the grand mean ($\pm$ the grand mean deviation) for various values of $(\bar{a}/A)$ obtained from at least two runs. From Table I, it can be observed that the reported values of E and n for
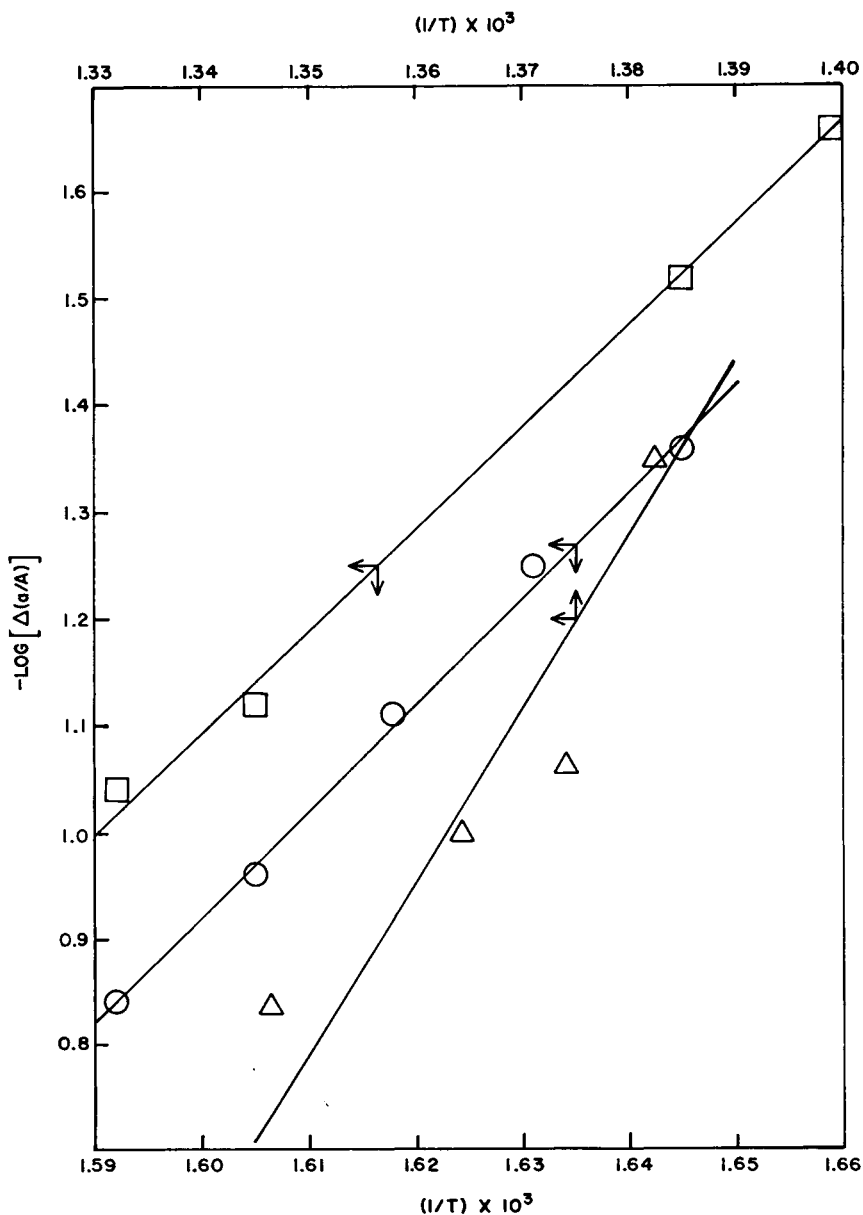

Fig. 4. Plots for determination of kinetic parameters from eq. (5): (O) PMMA; ($\triangle$) PE; ($\square$) PPrO.
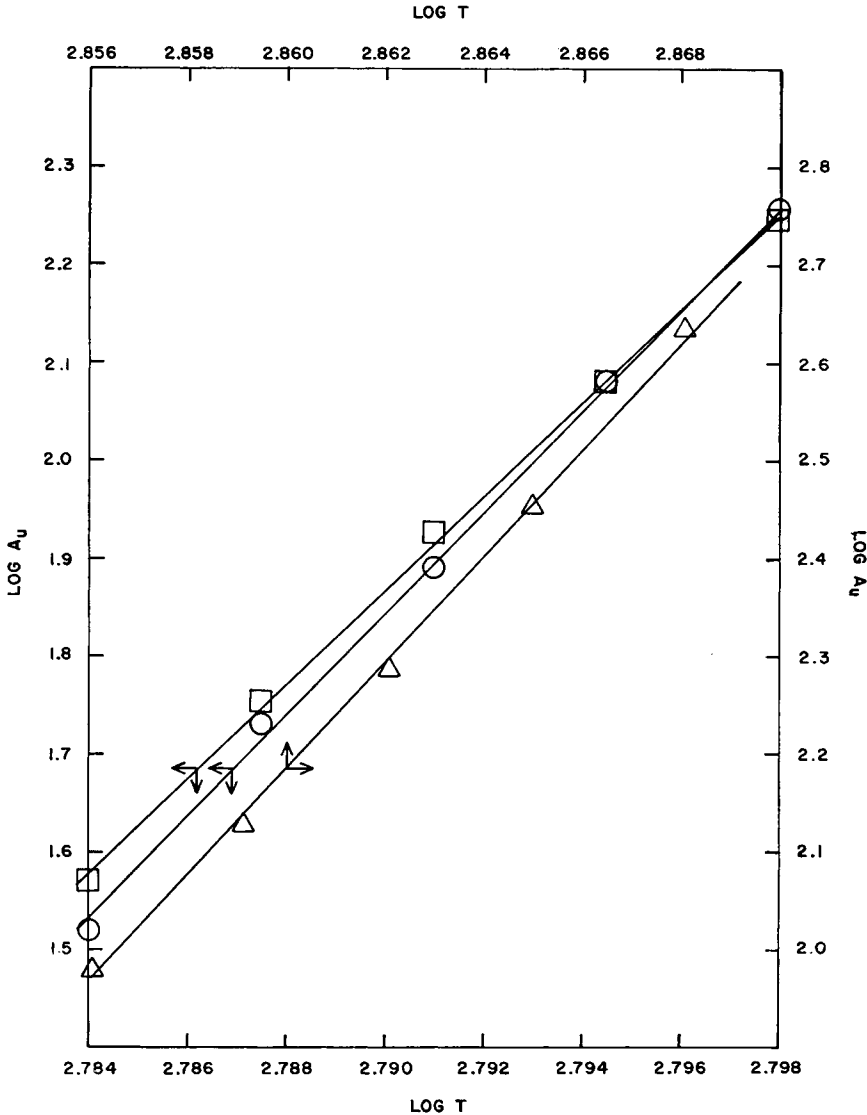
Fig. 5. Plots for determination of kinetic parameters from eq. (6): (O) PMMA; (△) PE: (□) PPrO.

the various materials listed agree well, in general, with those values estimated by means of eq. (2).

From eq. (3), it can be seen that when $\Delta(1/T)$ is maintained constant, a plot of $\Delta \log (\Delta T)$ versus $\Delta \log \tilde{a}$ should yield a linear relationship whose slope will afford a value of n and whose intercept a value of E. Such a plot is depicted in Figure 2 for various polymers. Although the agreement between calculated and reported values of E and n appear to be satisfactory, due to considerable scattering of derived data, it was not possible
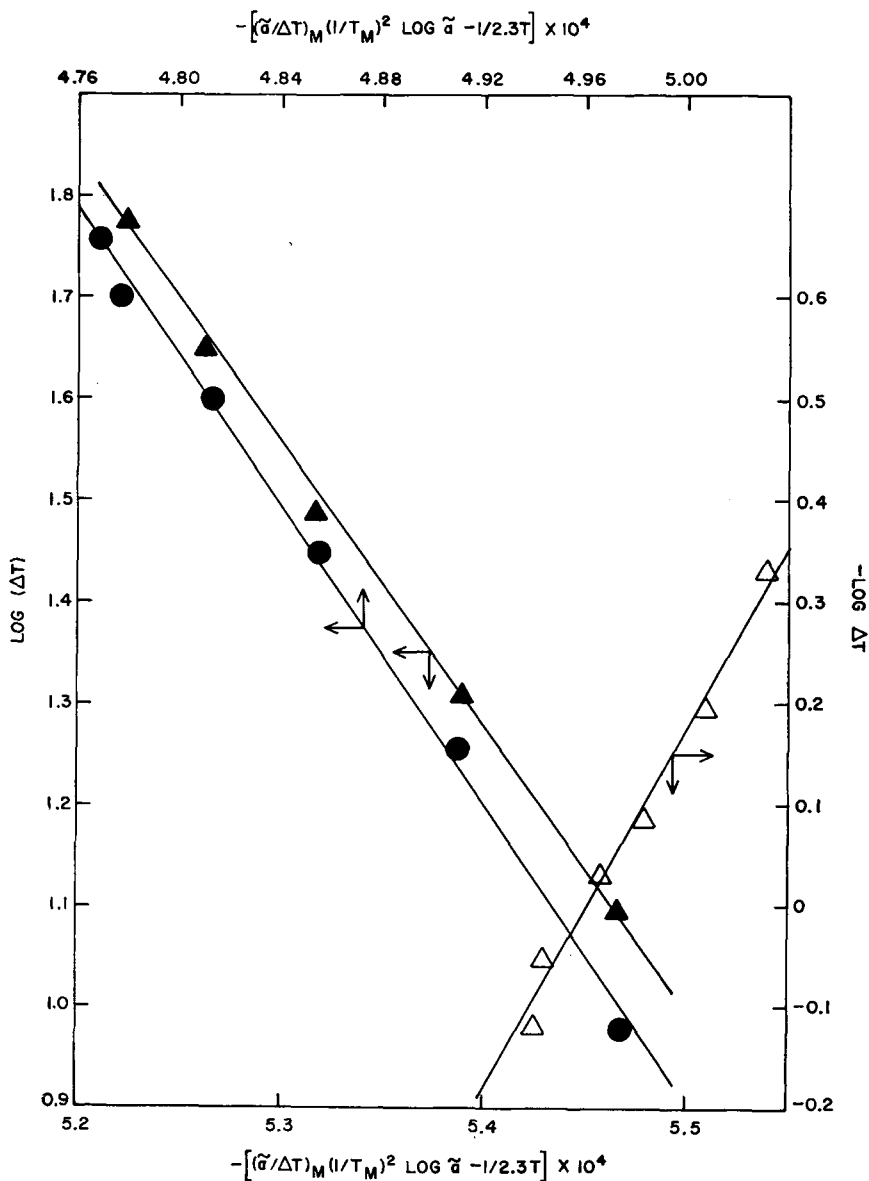
Fig. 6. Plots for determination of kinetic parameters from eq. (7): (●) Teflon; (△) PE; (▲) PPr.

to obtain values for PSt (cf. Table I).   Equation (4) was employed in obtaining Figure 3, which depicts some of the plots that were constructed. From the slopes of the various linear relationships obtained, values of E were estimated.   Based upon the value of E obtained for BDC, it would appear that values of E obtained from eq. (4) should tend to be on the low side.   This propensity would also be predicted, based upon the derivation

employed.[3] The derivation neglected certain terms, and this should lead
to lower values of E.   Also, eq. (4) should be valid only at low conversions.
Although a somewhat lower value of E was obtained for PPr, eq. (4) yielded
values of E for the other polymers which were not low.   Similar consider-
ations apply to eq. (5).   Based upon its derivation,[2] it should apply only
at low conversions and should tend to afford somewhat lower values of E.
Although this tendency may be observed in the case of BDC, it is not readily
apparent for the other materials studied.   This may be due to the small
scatter of derived data, which may exert a relatively large effect on the
value of E obtained.   [The same may be stated for eq. (4).]   Equation
(5) was utilized to construct the plots, shown in Figure 4 for some of the
polymers studied.   In the derivation[2] of eq. (6), simplifying assumptions
were made which limited the application of eq. (6) to low conversions.
Also, over the conversion range employed, an average temperature T_a
was assumed, such that over the temperature range utilized, the value of
the ratio, T/T_a, was close to unity.   In the application of eq. (6), it is im-
portant to ascertain accurately the value of T at which $(\tilde{a}/A) = 0$; other-
wise, relatively large errors in E may result.   Equation (6) was employed
to construct Figure 5, which depicts plots for some of the polymers studied.
From Table I, it can be seen that, based upon the value of E obtained for
BDC by means of eq. (6), values of E for the polymers studied may tend
to be on the high side.   This propensity can be readily observed for T,
PSt, and PPr.   Equation (7a) was utilized to construct Figure 6.   From
the slopes of the linear relationships obtained, values of E can be estimated
[log (ΔT) and log $\tilde{a}$ may be expressed in arbitrary units].   Then, by means
of eq. (7b), corresponding values of n may be ascertained.   From the rela-
tively high value of n obtained for BDC by means of eqs. (7), it might be
anticipated that this value may tend to be high for the polymers studied.
This propensity may readily be observed for PMMA and PSt and may, in
part, be due to the sensitive dependence of n upon values of E and K [cf. eq.
(7b)].   As in the case of eq. (6), eq. (7) yielded a high value of E for PSt.

   All the expressions listed previously are based upon the assumption that
the Arrhenius equation is valid for the degradation process.   It has also
been assumed that heat capacity terms are negligible in comparison with
other terms and that the cell constants for the sample and reference cells
are about equal.   The latter assumptions lead to eq. (1).[1,6,7]   Furthermore,
it has been assumed that there is no change in the degradation mechanism
during the pyrolysis and that diffusion barriers are negligible.

   Although eqs. (4) and (5) provide values of E for the various polymers
studied which are in reasonably satisfactory agreement with reported
values, they suffer from several disadvantages: (a) they do not provide
values of n;   (b) they often lead to considerable scatter in the derived data;
(c) they are limited to low conversions.   Equations (2), (3), and (7) also
gave reasonably satisfactory values of E (and n) in comparison with re-
ported values.   However, eq. (3) suffers from disadvantage (b) mentioned
earlier and because of this, it was not possible to apply eq. (3) to PSt.

Equation (7) is limited to values of $n \neq 0$. (However, very few cases of polymer pyrolyses would be anticipated wherein the value of n would be exactly equal to zero.) Also, values of n, obtained by means of eg. (7), tend to be high, as indicated previously. Equation (2) appears to be the most reliable for obtaining values of E and n. Nevertheless, it does suffer from the disadvantage that it involves trial-and-error procedures. However, with a little experience, these procedures do not require much time and effort.

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Résumé

Des expressions diverses sont présentées pour l'estimation des paramètres cinétiques on cours de pyrolyse au départ de traces d'analyse thermique différentielle. Ces expressions sont appliquées au polytétrafluoroéthylène, au polyéthylène, au polypropylène, au polystyrène, l'oxyde polypropylène isotactique, et au polyméthacrylate de méthyle. Les résultats obtenus sont comparés aux valeurs rapportées et les avantages et désavantages de ces diverses méthodes sont indiqués.

Zusammenfassung

Verschiedene Ausdrücke zur Bestimmung der kinetischen Parameter während der Pyrolyse aus DTA-Kurven werden angegeben. Diese Ausdrücke werden auf Polytetrafluoräthylen, Polyäthylen, Polypropylen, isotaktisches Poly(propylenoxyd) sowie Poly(methylmethacrylat) angewendet. Die erhaltenen Ergebnisse werden mit Literaturwerten verglichen, und die Vor- und Nachteile der verschiedenen Methoden erörtert.