Estimation of Kinetic Parameters During Pyrolysis from Linearized DTA Traces

LEO REICH, *Polymer Research Branch,*
Picatinny Arsenal, Dover, New Jersey 07801

Synopsis

A method which employs the linearization of DTA traces is presented for the estimation of kinetic parameters during polymer pyrolysis. By this method, two DTA traces are used, changes in mechanism with conversion may be detected, and it is not necessary to measure areas prior to evaluating activation energy and reaction order. The method is applied to polyethylene, polypropylene, and polystyrene. The agreement between observed and reported values of kinetic parameters is good. Advantages and disadvantages of the method are discussed.

INTRODUCTION

In several recent communications,[1-5] various expressions were derived for the estimation of activation energy E and reaction order n during pyrolyses from DTA traces   In all of the methods presented, it was necessary to evaluate areas under the DTA traces in order to obtain E and n.   By using an approximate method presented in this paper, whereby DTA traces are "linearized," values of E and n may be estimated without the prior evaluation of areas.   This method was applied to polyethylene (PE), polypropylene (PPr), and polystyrene (PSt).   Advantages and disadvantages of the method are given.

EXPERIMENTAL

The polymers pyrolyzed, the DTA apparatus employed, and the experimental conditions used were previously described.[2]

THEORY

By making the usual simplifying assumptions[1-5] that heat capacity terms may be neglected in comparison with other terms and that the cell constant is about equal for the reference and sample cells, we may write,

$$W_c \approx W_{0,c}(\tilde{a}/A) \tag{1a}$$

and

$$-dW_c/dT \approx W_{0,c}(\Delta T/A) \tag{1b}$$

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 validity of eqs. (1) has been strengthened by the good agreement previously obtained between observed and calculated values of a parameter K which is independent of values of E and n.[5]

From eqs. (1), the following expression is readily obtained:

$$-dW_c/W_c \approx dT \Big/ \left[\int_{T}^{T_f} \Delta T dT / \Delta T \right] \tag{2}$$

Equation (2) may be reduced to simpler form by assuming that the DTA traces obtained during polymer pyrolyses can be linearized with little error (see Fig. 1).   This assumption has been found to be good for the various polymer pyrolyses studied in this laboratory, especially on the right-hand
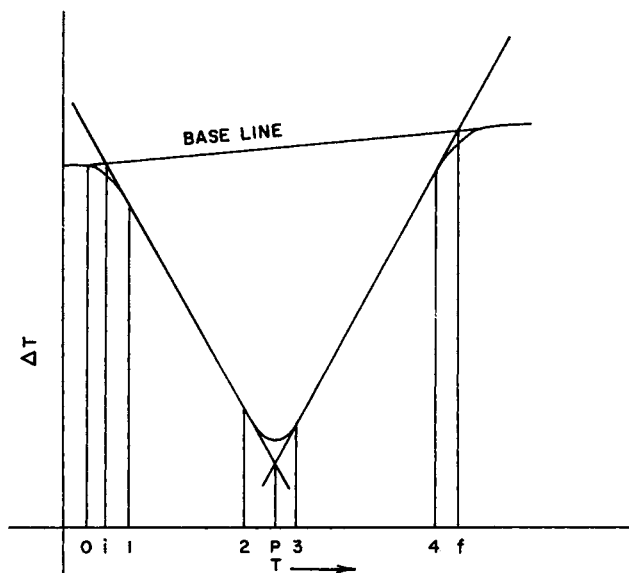

Fig. 1. Linearization of DTA traces.

side of the DTA peak (RHS).   The left-hand side of the DTA peak (LHS) is generally not as steep as the right-hand side, especially during the initial phases of the polymer degradation.   Thus, although the right-hand side may be linearized with relatively little error, it may only be possible to linearize only a small portion of the left-hand side.   Only the linearized

portions of the DTA traces should be used ($T_1 \to T_2$ and $T_3 \to T_4$ of Fig. 1) in the following method.

Case 1: Right-Hand Side of Peak

Due to linearization, we may write

$$\int_{T}^{T_f} \Delta T dT = (\Delta T)_{av.} \int_{T}^{T_f} dT \tag{3}$$

where,

$$(\Delta T)_{av.} = \Delta T/2$$

Upon substituting eq. (3) into eq. (2) and integrating, there is obtained

$$-\int_{W_{0,c}}^{W_c} dW_c/W_c = \int_{T_0}^{T} 2dT/(T_f - T) \tag{4}$$

or

$$W_c = W_{0,c}[(T_f - T)/(T_f - T_0)]^2 \tag{4b}$$

Case 2: Left-Hand Side of Peak

From the definition of $\bar{a}$ previously given, and due to linearization,

$$\int_{T}^{T_f} \Delta T dT \Big/ \Delta T = \int_{T_i}^{T_f} \Delta T dT \Big/ \Delta T - \int_{T_i}^{T} \Delta T dT \Big/ \Delta T \tag{5}$$

The extreme right-hand member of eq. (5) becomes [cf. eq. (3)] $(T - T_i)/2$. The first term on the right-hand side of eq. (5) becomes $(\Delta T_p/2\Delta T) \int_{T_i}^{T_f} dT$. Letting $\Delta T = z\Delta T_p$, eq. (5) becomes

$$\int_{T}^{T_f} \Delta T dT/\Delta T = [(T_f - T_i)/2z] - (T - T_i)/2 \tag{6}$$

Upon substituting eq. (6) into eq. (2), there is obtained

$$-\int_{W_{0,c}}^{W_c} dW_c/W_c = \int_{T_i}^{T} 2zdT/[(T_f - T_i) + z(T_i - T)] \tag{7}$$

Since $z = \Delta T/\Delta T_p = (T - T_i)/(T_p - T_i)$, eq. (7) becomes, after integration and rearrangement,

$$W_c = W_{0,c}[T_f - T_i - z(T - T_i)]/(T_f - T_i) \tag{8}$$

Estimation of n

We may write, employing the Arrhenius equation,

$$-dW_c/dT = [Z/(RH)]e^{-E/RT}W_c^n \tag{9}$$

From eqs. (1), (9), and either (4a) or (8), the eqs. (10a) and (11a) are obtained for the right- and left-hand sides of the DTA peak, respectively,

$$\Delta T = [Z/(\mathrm{RH})]e^{-E/RT}W_{0,c}{}^{n-1} A [(T_f - T)/(T_f - T_0)]^{2n} \quad (10a)$$

and

$$\Delta T = [Z/(\mathrm{RH})]e^{-E/RT}W_{0,c}{}^{n-1} A [(T_f - T_i) - z(T - T_i)/(T_f - T_i)]^{n} \quad (11a)$$

By using two heating rates, $(\mathrm{RH})_1$ and $(\mathrm{RH})_2$, and employing isothermals, eqs. (10a) and (11a) may be converted into eqs. (10b) and (11b), respectively:

$$\log \frac{\Delta T_1}{\Delta T_2} = 2n \log \left[\frac{(T_f - T)_1}{(T_f - T)_2} \right] + \log K_1 \quad (10b)$$

where

$$K_1 = \frac{(\mathrm{RH})_2}{(\mathrm{RH})_1} \left(\frac{A_1}{A_2} \right) \left(\frac{W_{0,c,1}}{W_{0,c,2}} \right)^{n-1} \left[\frac{(T_f - T_0)_2}{(T_f - T_0)_1} \right]^{2n}$$

$$\log \frac{\Delta T_1}{\Delta T_2} = n \log \left[\frac{(T_f - T_i)_1 - z_1(T - T_i)_1}{(T_f - T_i)_2 - z_2(T - T_i)_2} \right] + \log K_2 \quad (11b)$$

where

$$K_2 = \frac{(\mathrm{RH})_2}{(\mathrm{RH})_1} \left(\frac{A_1}{A_2} \right) \left(\frac{W_{0,c,1}}{W_{0,c,2}} \right)^{n-1} \left[\frac{(T_f - T_i)_2}{(T_f - T_i)_1} \right]^{n}$$

Estimation of E

Once the reaction order n has been evaluated by means of eqs. (10b) and/or (11b) (K_1 and K_2 may also be determined), values of E may be obtained by utilizing eqs. (10a) and/or (11a). Thus, for the right-hand side of the peak,

$$\log \Delta T - 2n \log (T_f - T) = -E/2.3RT$$
$$+ \log \left[(W_{0,c})^{n-1} \frac{ZA}{(\mathrm{RH})} \left(\frac{1}{T_f - T_0} \right)^{2n} \right] \quad (12)$$

and for the left-hand side of the peak,

$$\log \Delta T - n \log \left[\frac{(T_f - T_i) - z(T - T_i)}{(T_f - T_i)} \right] = -E/2.3RT$$
$$+ \log \left[(W_{0,c})^{n-1} \frac{ZA}{(\mathrm{RH})} \left(\frac{1}{T_f - T_i} \right)^{n} \right] \quad (13)$$

RESULTS AND DISCUSSION

In Table I are listed values of n, E (average), K_1, and K_2 for the various polymers investigated. The agreement between observed and either reported or calculated values is good and gives credence to the validity of the linearization method employed.

Values of n were estimated by utilizing either eq. (10b) (right-hand side of peak) or eq. (11b) (left-hand side of peak), and corresponding plots are shown in Figure 2. Values of E were estimated from eq. (12) (right-hand
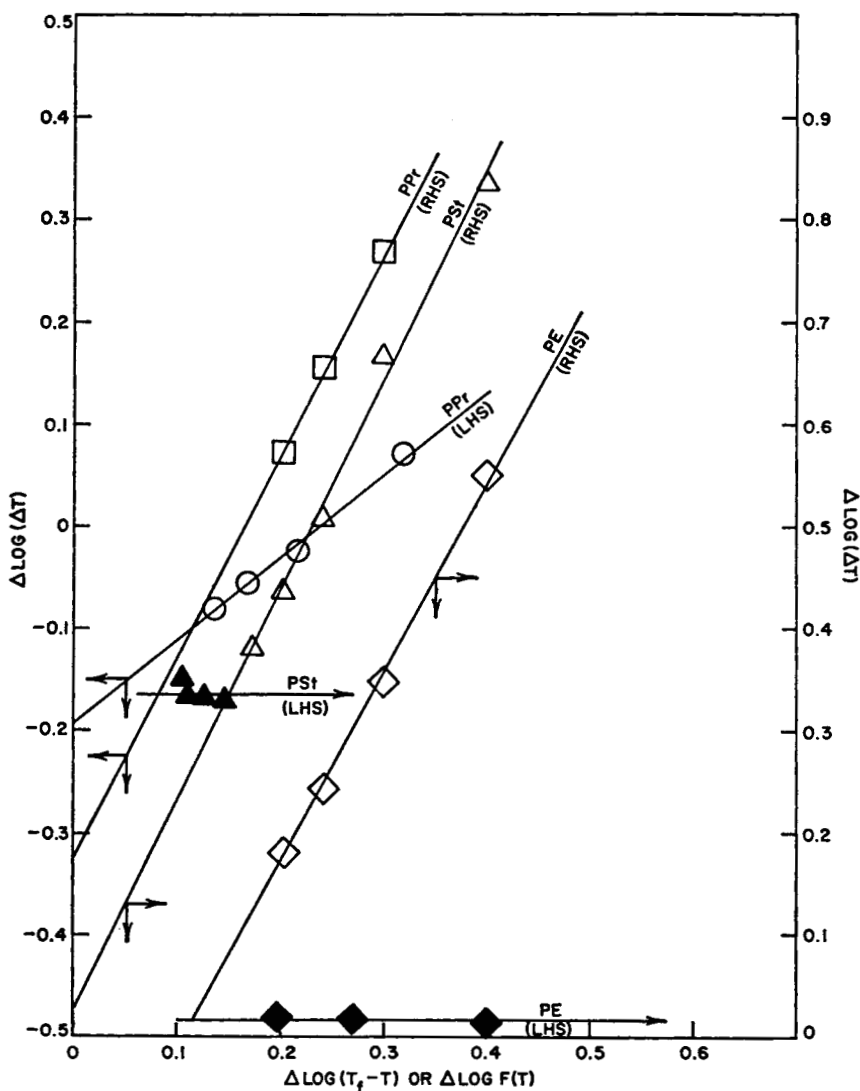

Fig. 2. Estimation of reaction order for PE, PPr, and PSt by eqs. (10b) and (11b). $F(T) \equiv T_f - T_i - z(T - T_i).$

TABLE I
Values of Parameters by Linearization Method

Polymer	n Obsd.	n Reptd.	E, kcal./mole Obsd.	E, kcal./mole Reptd.	K_1 Obsd.	K_1 Calcd.	K_2 Obsd.	K_2 Calcd.
PE	0.93 (RHS)	1.18 (35–95% conversion)[a]	76	67 ± 5,[a] 73 ± 1[b]	0.71	0.76	1.0	1.0
	0.0 (LHS)	>0 (3–15% conversion)[a]	58	61[a]				
PPr	1.0 (RHS)	1 (over a limited conversion range)[c]	56	58[c]	0.47	0.47	0.64	0.65
PSt	0.9 (LHS)							
	1.0 (RHS)	1 (15–95% conversion)[a]	74	74, 77[d]	1.1	1.2	2.1	2.1
	0.0 (LHS)	0 (up to 10% conversion)[a]	64	46[a]				

[a] Data of Anderson and Freeman.[6]
[b] Data of Reich.[2]
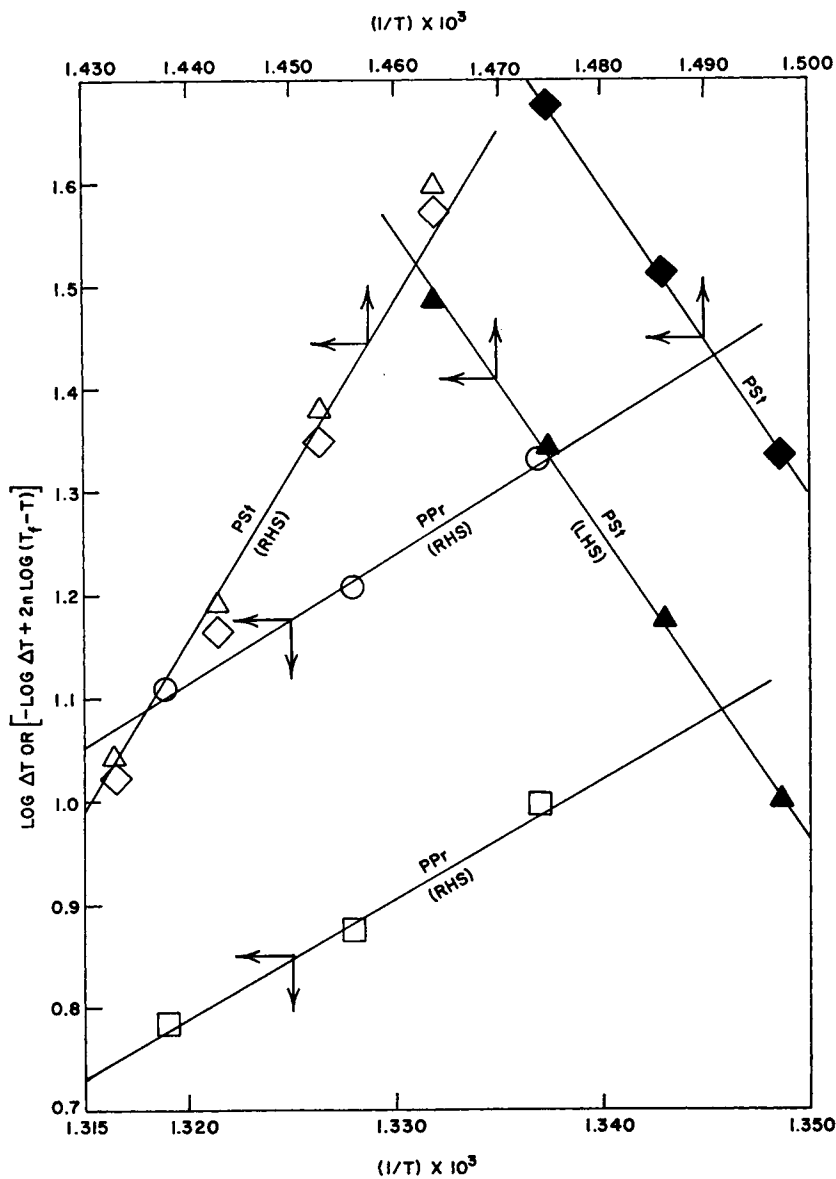[c] Data of Madorsky.[7]
[d] Data of Fuoss et al.[8]

Fig. 3. Estimation of activation energy for PPr and PSt by eqs. (12) and (13): ($\triangle$, $\blacktriangle$) (RH) = 8.6°C./min.; ($\lozenge$, $\blacklozenge$) (RH) = 15.2°C./min.; (O) (RH) = 17.1°C./min.; ($\square$) (RH) = 10.4°C./min.

side of peak) and eq. (13) (left-hand side of peak), and corresponding plots are shown in Figures 3 and 4. After n had been determined, values of K_1 and K_2 were calculated from eqs. (10b) and (11b), respectively. It should be noted that when the right-hand side of the peak is utilized (the linearization is good), it is not necessary that the left-hand side of the
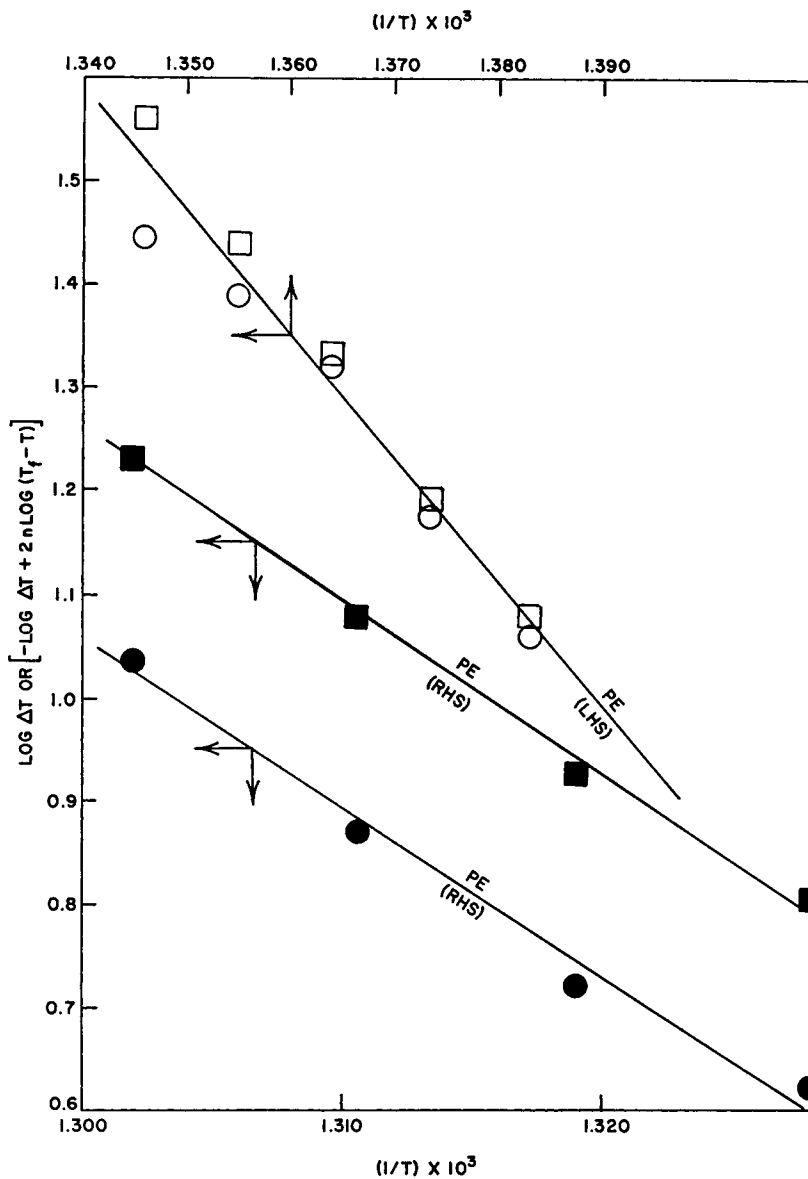
$(1/T) \times 10^3$

Fig. 4. Estimation of activation energy for PE by eqs. (12) and (13): (O, ●) (RH) =
8.7°C./min.; (□, ■) (RH) = 16.1°C./min.

peak show good linearity. However, when the left-hand side of the peak
is used (shows good linearity), the right-hand side of the peak must also
possess good linearity. Thus, it may be seen that there are more limita-
tions in employing the left-hand than the right-hand side of the peak.
However, where possible, the former should be used to check the latter.
In this connection, data from the left-hand side of the peak for PPr was

used to check the value of n of unity obtained from the right-hand side of the peak. In the cases of PE and PSt, analysis of the left-hand side of the peak gave values of n of about zero (low polymer conversions), whereas analysis of right-hand side of the peak gave values of n of about unity (high polymer conversions).

Anderson and Freeman[6] have reported that in the thermal decomposition of PE in vacuum the value of n was essentially unity and $E = 67 \pm 5$ kcal./mole over a conversion range of 35–95% (from thermogravimetric experiments). However, over 3–15% reaction, $E = 61$ kcal./mole, and this region appeared to involve a transition from zero- to first-order kinetics. The latter stage of the PE pyrolysis (3–15%) was attributed to end chain cleavage while the 35–95% stage was ascribed to random rupture of carbon–carbon bonds. They also observed a similar behavior in the case of PSt. Thus, up to 10% conversion, E and n were 46 kcal./mole and zero, respectively; over 15–95% reaction, E and n were found to possess values of 60 ± 5 kcal./mole and unity, respectively. The lower conversion stage was attributed to the splitting off of styrene monomer. These results indicated that there were two degradation mechanisms, one predominant at low temperatures and the other at high temperatures.

Advantages of the method employed in this paper for estimating E and n are: (1) changes in n (and E) with conversion may be detected; (2) it is not necessary to measure areas prior to determining n (and E). Disadvantages are: (1) two DTA traces are required; (2) it may be difficult at times to readily obtain two DTA traces for the same material at two different heating rates which overlap sufficiently so that the method can be employed.

References

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Résumé

Une méthode utilisant la linéarisation des traces d'analyse thermique différentielle est présentée pour l'estimation des paramètres cinétiques ou cours de la pyrolyse de polymères. Grâce à cette méthode, deux traces DTA sont utilisées, des changements de mécanismes avec le degré de conversion peuvent être détectés et il n'est pas nécéssaire de mesurer la surface avant d'évaluer l'énergie d'activation ni l'ordre de réaction. La méthode est appliquée au polyéthylène, polypropylène et polystyrène. L'accord entre les valeurs observées et rapportées des paramètres cinétiques est bon. Les avantages et désavantages de cette méthode sont soumis à discussion.

Zusammenfassung

Eine Methode mit Verwendung der Linearisierung von DTA Kurven wird zur Bestimmung der kinetischen Parameter bei der Polymerpyrolyse angegeben. Bei dieser Methode werden zwei DTA Kurven benützt und es können Anderungen des Mechanismus mit dem Umsatz erkannt werden. Es ist nicht notwendig, zur Bestimmung von Aktivierungsenergie und Reaktionsordnung Flächen auszumessen. Die Methode wird auf Polyäthylen, Polypropylen uns Polystyrol angewendet. Es besteht gute Ubereinstimmung zwischen den beobachteten Werten und Literaturwerten für die kinetischen Parameter. Vorund Nachteile der Methode werden diskutiert.