

Kinetic Parameters in Polymer Degradation by Dynamic Thermogravimetric Analysis

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Synopsis

A new and relatively convenient procedure for obtaining kinetic parameters in the degradation of high polymers is described and the necessary experimental procedure is outlined. Results for the degradation of Teflon are compared with several previously reported methods and the agreement is found to be good. Some advantages and disadvantages of the various methods are discussed.

INTRODUCTION

In the study of the thermal degradation of polymeric materials, it is often desirable to obtain values of kinetic parameters such as the reaction order, n , and the overall activation energy, E . These values can be of great importance in the elucidation of the mechanisms involved in polymer degradation.¹ Although there are many factors which can affect the thermal stability of polymers, the E values may also be used as guides in the formulation of thermal stability indices.²

Dynamic thermogravimetric analysis (TGA) which involves variable temperature during weight loss, has been utilized to determine the above kinetic parameters for polymeric materials only rather recently. Early reported methods, using TGA, involved laborious equations and simplifying assumptions for the determination of E and n .³⁻⁵ Other relatively simpler methods, which do not utilize simplifying assumptions, have also been employed. Thus, Freeman and co-workers,⁶ Reich and co-workers,⁷ and Friedman⁸ have proposed alternate methods. However, these methods suffer from one or more disadvantages.

It is the purpose of this paper to present a novel and relatively simple method for estimating kinetic parameters in polymer degradation and to compare the results with those obtained by several other methods. New experimental techniques will also be introduced.

EXPERIMENTAL

Materials

The Teflon 7 used was obtained from du Pont. Tobolsky and co-workers⁹ have indicated that this material has a number-average molecular weight of 1.61×10^7 .

Apparatus

An American Instrument Company thermogravimetric balance (Thermograv) with continuous automatic recording was employed. Powdered samples up to 200 mg. in weight were used. The vacuum was 1 mm. Hg or less for all of the experiments.

Procedure

Besides the usual thermograms, i.e., with weight loss measured at variable temperature and constant heating rates, other types of thermograms were obtained. In one case (cf. Fig. 5) the polymer was heated at an initial rate of about 6°C./min., and after about 30% decomposition the heat input was raised so that the heating rate approached 15°C./min. In another case (cf. Fig. 6), the heating cycle was reversed. An initial high heating rate of about 16°C./min. was employed, and after about 30% decomposition the heat input was drastically reduced so that, in effect, decomposition occurred while the material was actually cooling.

RESULTS

Kinetic parameters, E and n , are listed in Table I for the thermal degradation of Teflon 7 along with various expressions employed in estimating

TABLE I
Kinetic Parameters for the Degradation of Teflon 7 Utilizing Various Expressions*

Form of equation	E , kcal./mole		n	
	Eq. no.	Calcd. Reptd.	Calcd.	Reptd.
$\Delta \log R_t = n \Delta \log W - (E/2.303R)\Delta(1/T)$	1	69-74	66-68 75 ± 4	1.0-1.16 1.02 ± 0.07
$\log R_t = \log A + (E/R) [(W_M/T_M^2 R_M^T) \log W - 1/2.303T]$	2	71-74	0.9-1.2	
$n = (W_M/T_M^2 R_M^T)(E/R)$	2a			
$\log R_t = -(E/2.303RT) + \log AW^n$ ($W = \text{constant}$)	3	66-76	1.05	
$[\Delta \log (RH)]/\Delta(1/T) = n[\Delta \log W/\Delta(1/T)] - (E/2.303R)$ ($R_T = \text{constant}$)	4	66-74	0.85-1.16 0.83 ± 0.04	
$n = (\Delta \log R_t)/(\Delta \log W)$ ($T = \text{constant}$)	4a			

* Nomenclature: A = frequency factor, E = overall activation energy, n = order of the reaction, R = gas constant, RH = rate of heating of the material, R_M^T = slope of the thermogram (dW/dT) at maximum slope, R_t = rate of decomposition, R_T = slope of primary thermogram (dW/dT), T = absolute temperature, T_M = temperature at R_M^T , W = weight of sample remaining, W_M = weight remaining at R_M^T .

these values. Equations (1), (2), and (3) have been previously reported, whereas eq. (4) is being presented for the first time, to our knowledge. The calculated values obtained from all the various expressions are in good

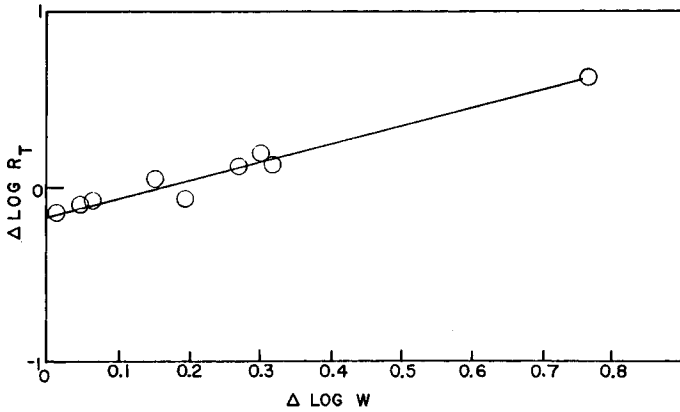


Fig. 1. Plot for determination of kinetic parameters for Teflon by eq. (1). $RH = 6^{\circ}\text{C./min.}$

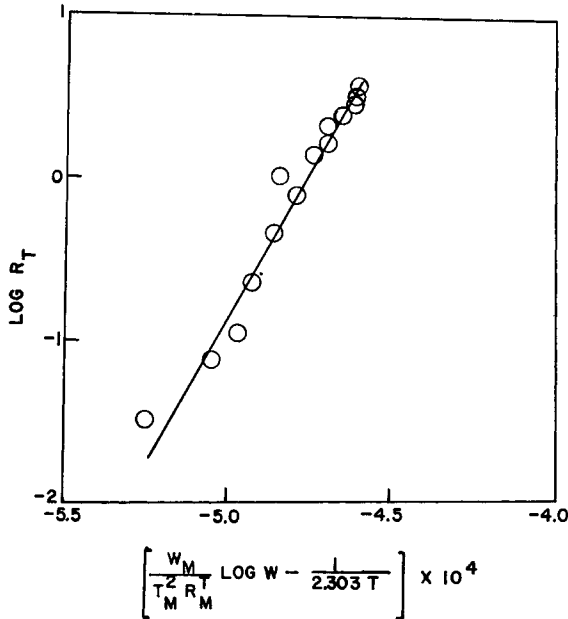


Fig. 2. Plot for determination of E for Teflon by eq. (2). $RH = 6^{\circ}\text{C./min.}$

agreement with previously reported values.^{10,11} A typical plot which utilizes eq. (1) is shown in Figure 1. In this plot, the slope affords the value for n while the intercept yields the value for E . Another typical plot which employs eq. (2) is shown in Figure 2. The value for E may be obtained from the slope of the line. Then n may be calculated utilizing eq. (2a) in Table I. Equation (3) was employed in obtaining Figure 3. Each line represents a different percent decomposition and the lines should be parallel. An average value for E can be obtained from the slopes of these

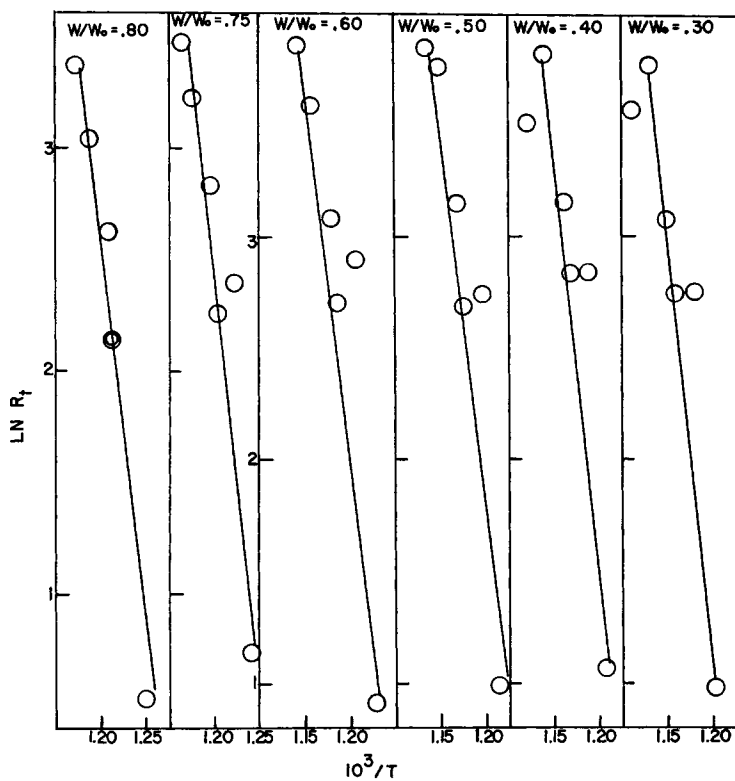


Fig. 3. Plots for determination of E for Teflon by eq. (3).

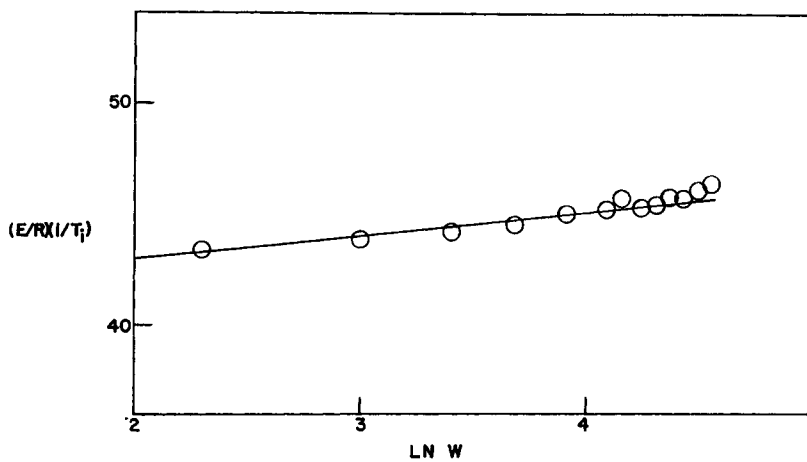


Fig. 4. Plot for determination of n for Teflon by eq. (3).

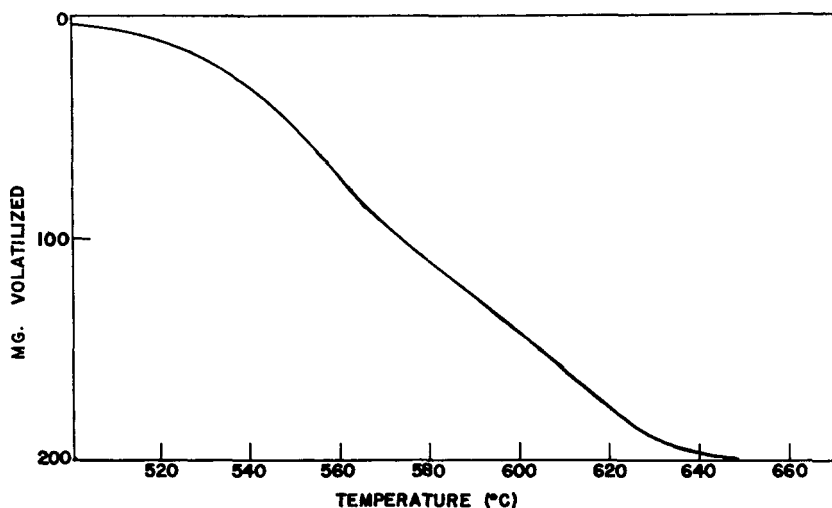


Fig. 5. Variable heating rate thermogram for Teflon.

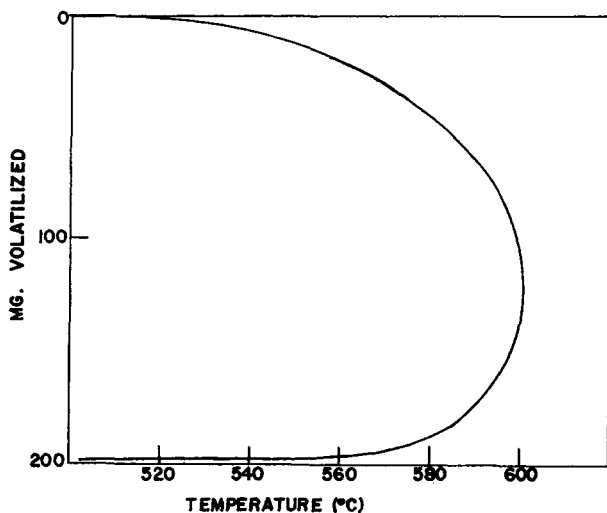


Fig. 6. Variable heating rate thermogram for Teflon.

lines. Then a plot of the intercepts versus $\log W$ will afford the value for n (cf. Fig. 4).

The novel eq. (4) was employed by using Figures 5 and 6. This method consisted of obtaining pairs of values of (RH) , T , and W from sections of these curves which gave equal values of $R_T (dW/dT)$. Then, appropriate plots, as shown in Figures 7 and 8, provided lines whose slopes afforded values for n and whose intercepts yielded values for E . The value for n was checked independently by constructing an isotherm on Figure 6 and by substituting these values into eq. (4a). Four such isotherms were

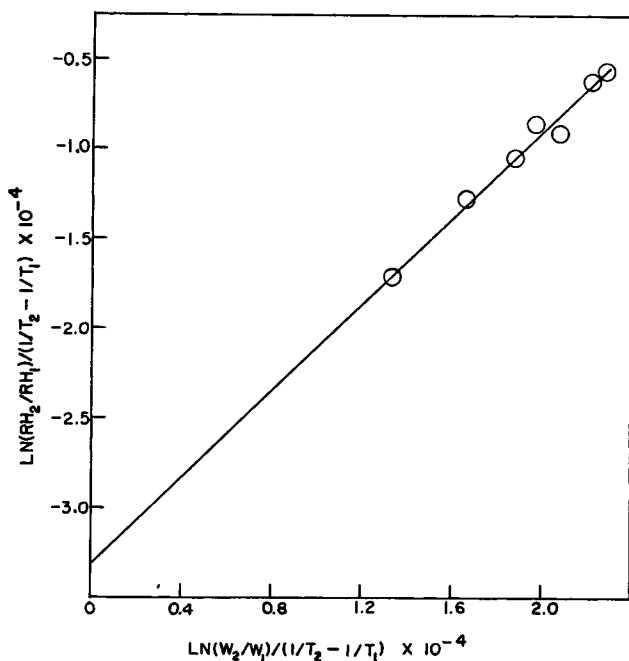


Fig. 7. Plot for obtaining kinetic parameters for Teflon by eq. (4). Data from Fig. 5.

constructed, and the value of n was found to be 0.83 ± 0.04 , which agrees with the value 0.85 obtained from Figure 8.

DISCUSSION

All the expressions listed in Table I are based upon the assumption that the Arrhenius equation is valid for the degradation process. Also, the values obtained for E and n by these expressions are in good agreement with one another. However, the first three equations listed in Table I suffer from several disadvantages. Thus, eq. (1) is somewhat laborious to use and often leads to considerable scatter in the derived data. Similar statements can be made for eq. (2). Moreover, this latter equation is limited to values for $n \neq 0$. Although eq. (3) can be used to determine values of kinetic parameters at various degrees of conversion (and thus to determine whether any change in kinetic order or mechanism has occurred), several thermograms at various heating rates are required. Moreover, at least two separate plots are required (see Figs. 3 and 4) in order to determine values for E and n .

Equations (4) and (4a) appear to offer certain distinct advantages. These include: (a) only one thermogram need be obtained, (b) the value for n may be readily checked from a thermogram as shown in Fig. 6, (c) the method can indicate whether the kinetic order has changed at various

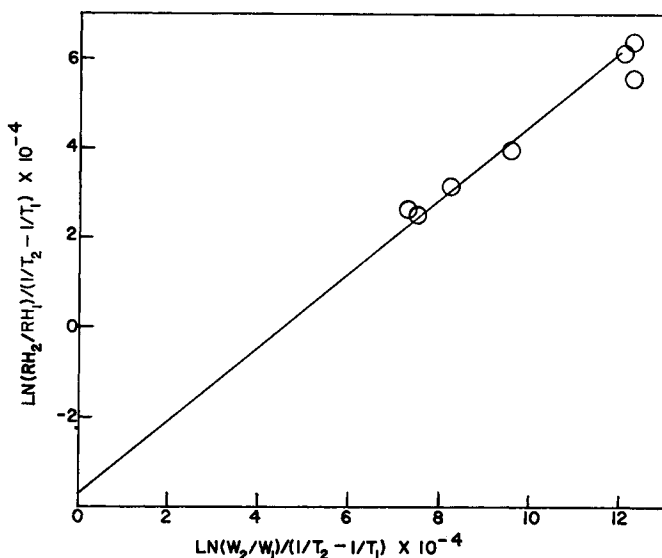


Fig. 8. Plot for obtaining kinetic parameters for Teflon by eq. (4). Data from Fig. 6.

conversions, (d) the corresponding plots tend to show less scatter of derived data, and (e) the amount of labor involved in utilizing this expression is not as great. Nevertheless, it should be indicated that the thermogram in Figure 6 is preferred over that in Figure 5. This is because the former allows a check of the value of n and also does not employ primary data which are as close to the extremities of the thermogram. Such data near the extremities are subject to a greater possibility of error. It may also be noted that when a thermogram such as in Figure 6 is obtained, experimental conditions should be such that the resulting curve is unsymmetrical but shows distinct curvature on both sides. Otherwise, it will be difficult, if not impossible, to utilize eq. (4).

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Résumé

On décrit une nouvelle méthode assez pratique pour obtenir des paramètres cinétiques dans la dégradation des polymères de haut poids moléculaire, et on donne la procédure expérimentale nécessaire. On compare les résultats de la dégradation du teflon avec les différentes méthodes antérieures, et on a trouvé un bon accord. On discute de certains avantages et désavantages des différentes méthodes.

Zusammenfassung

Ein neues und verhältnismässig bequemes Verfahren zur Gewinnung der kinetischen Parameter beim Abbau Hochpolymerer wird beschrieben und die erforderliche Versuchstechnik angegeben. Ergebnisse beim Abbau von Teflon werden mit einigen früher beschriebenen Methoden verglichen und gute Übereinstimmung festgestellt. Gewisse Vor- und Nachteile der verschiedenen Methoden werden diskutiert.

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