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An integral method of nonisothermal kinetic analysis

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Abstract

A new series solution for the constant heating rate Arrhenius integral is the basis of a method for determining the kinetic parameters of a single-step reaction from temperature scanning experiments. Isoconversion formulas are derived for calculating the Arrhenius activation energy and frequency factor of a reaction independent of the form of the rate law. Thermogravimetry data for pyrolysis of low density polyethylene and differential scanning calorimetry data for the phenylethynyl curing reaction were analyzed and activation energies were determined and found to agree with literature values. In contrast to existing integral methods, frequency factors for the pyrolysis and curing reaction were obtainable using the present approach without any assumptions about the reaction order or the form of the conversion function. © 1997 Elsevier Science B.V.

Keywords: Arrhenius rate constant; Differential scanning calorimetry; Kinetics; Thermal analysis; Thermogravimetry

1. Introduction

Many technologically important processes and reactions occur under nonisothermal conditions and it is often desired to calculate or predict the progress of the reaction over time during transient heating. Integral methods of nonisothermal analysis utilize cumulative values of a species concentration, heat of reaction, weight loss, etc., measured in temperature scanning experiments to extract the kinetic parameters of a reacting system and determine a suitable rate law [1–13]. These powerful methods derive from the programmable heating rate capability of modern thermal analysis equipment and are useful for calculating preconversion during the heat-up period in isothermal experiments [11], for testing reaction models over a broad temperature and conversion range [13], etc. Despite their utility integral methods have suffered from low sensitivity, a dependence on the form of the rate law, an assumption that the reaction mechanism does not change with temperature, and the somewhat cumbersome mathematics of the series approximations for the Arrhenius integral required in the analyses [3,11]. An exact solution of the Arrhenius integral is possible only for nonlinear temperature programs [3], but this capability is beyond most commercial instruments.

Since the overwhelming majority of thermal analyses are conducted at constant heating rate, the present work seeks to develop a more useful

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approximation for the Arrhenius integral under experimental conditions of a linear temperature program and extend these results to the unambiguous determination of Arrhenius kinetic parameters. It is hoped that the results of this work will aid process development of new fire-resistant thermoset resins and advance the study of polymer flammability by allowing more accurate calculation of the gasification rate in the pyrolysis zone of burning polymers [14]. Since the rate-limiting step in isothermal polymer pyrolysis is the breaking of primary chemical bonds in the molecule [15], a direct method for determining pyrolysis rate constants will facilitate the decoupling of diffusion and chemical kinetics during burning and help relate polymer structure to flammability.

2. Background

Rate laws of the type

$$\frac{d\alpha}{dt} = f(\alpha, T) \tag{1}$$

are the basis for almost all of the kinetic methods used in differential thermal analysis and differential scanning calorimetry [1–13,16]. In Eq. (1), T is the absolute temperature and

$$\alpha = \frac{C(t) - C(0)}{C(\infty) - C(0)}$$

is a fractional conversion in terms of the instantaneous, $C(t)$, initial, $C(0)$ and final, $C(\infty)$, values of a measurable reaction parameter such as a species concentration, heat of reaction, pyrolyzed mass, etc. Eq. (1) is written such that α increases with time, t. The temperature dependence of $f(\alpha,T)$ is usually assumed to reside exclusively in a rate constant, k, which has the Arrhenius form

$$k = A \exp(-E_a/RT)$$

where A is the pre-exponential or frequency factor, E_a the activation energy for the reaction, and R the universal gas constant. These assumptions lead to the generalized reaction rate law

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

If k is independent of α and $f(\alpha)$ is independent of T, separation of variables in Eq. (2) gives

$$F(\alpha) \equiv \int_{\alpha_0}^{\alpha} \frac{d\alpha'}{f(\alpha')} = \int_0^t k\, dt' = \int_0^t A e^{-E_a/RT} dt' \tag{3}$$

where primed symbols denote variables of integration. At constant temperature, $F(\alpha) = kt$, which is the basis for isothermal kinetic analyses [1,3,11,13,17]. A variety of $f(\alpha)$ have been assumed or derived for individual cases [1,4,5,13,17] such that a linear $F(\alpha)$ vs. time plot is obtained at a particular temperature having slope $k(T)$. The Arrhenius parameters A and E_a for the reaction are determined from a number of constant temperature experiments by plotting the natural logarithm of $k(T)$ vs. $1/T$ over the temperature domain of interest.

The isothermal procedure based on Eq. (2) requires a priori knowledge of $F(\alpha)$ and the measured kinetic parameters are valid only for the temperature range examined. Usually $f(\alpha)$ and, therefore, $F(\alpha)$, are not known prior to the experiment so various methods have been proposed to allow determination of E_a and $f(\alpha)$ separately or in combination from a series of temperature-scanning experiments at different constant heating rates [1–3,6–13]. For a constant heating rate, $dT/dt = \beta$, Eq. (3) can be written as follows:

$$F(\alpha) = \frac{A}{\beta} \int_{T_0}^{T} e^{-E_a/RT'} dT' \tag{4}$$

where the sample temperature is uniform but changes linearly from T_0 to T over the time interval $(0,t)$. Application of nonisothermal or integral methods to experimental data requires evaluating the exponential temperature (Arrhenius) integral on the right-hand side of Eq. (4). Unfortunately, the Arrhenius integral has no exact solution, hence numerical or approximate solutions are required.

Series solutions for the Arrhenius integral can be expressed as a polynomial, $p(x)$, where, $x = -E_a/RT$, so that Eq. (4) takes the form

$$F(\alpha) \equiv \frac{AE_a}{\beta R} \int_{x_0}^{x} \frac{e^{x'}}{x'^2} dx' = \frac{AE_a}{\beta R} p(x') \Big|_{x_0}^{x} \tag{5}$$

Several of these series solutions have been derived, and Flynn and Wall provide an excellent review [3].

Typical of the series solutions for the Arrhenius integral is an asymptotic expansion of the exponential integral after a single integration-by-parts [18], i.e.,

$$p(x) = \frac{e^x}{x^2}\left[1 + \frac{2!}{x} + \frac{3!}{x^2} + \frac{4!}{x^3} \dots\right] \tag{6}$$

and Schlomilch's expansion [19]

$$p(x) = \frac{e^x}{x(x-1)}\left[1 - \frac{1}{2-x} + \frac{2}{(2-x)(3-x)} - \frac{4}{(2-x)(3-x)(4-x)} + \dots\right] \tag{7}$$

A property of these integral expansions is that the difference between the true value of the function and the sum of a finite number of terms in the series is essentially of the order of magnitude of the last term retained. This requires that either $-x > 30$, or that a few terms be retained in the series expansions for $-x < 10$, to achieve an accuracy greater than 95%. An empirical equation for $p(x)$ was proposed by Doyle [6],

$$p(x) = 7.03 \times 10^{-3} e^{xB(x)} \tag{8}$$

where $B(x)$ ranges from 1.195 to 1.034 over the domain, $-60 < x < -10$. An average value, $B(x) = 1.052$, is often used in integral methods of thermal analysis [2,3,6,8,11,13].

3. Arrhenius integral approximation

The intractability of multiterm series approximations, required for accurate evaluation of the Arrhenius integral, has limited the utility of integral methods for quantitative kinetic analysis. The following derivation leads to a simple, semi-analytic result which provides better accuracy than any previous single-term approximation of the constant heating-rate Arrhenius temperature integral.

Let us begin by defining a new variable, $y = e^x/x^2$, so that Eq. (4) becomes

$$F(\alpha) = \frac{AE_a}{\beta R}\int_{y_0}^{y} f(y')\mathrm{d}y' \tag{9}$$

with, $f(y) = x/(x-2)$. A single integration-by-parts gives

$$F(\alpha) = \frac{AE_a}{\beta R}\left\{\left[\frac{e^{x'}}{x'(x'-2)}\right]\Bigg|_{x_0}^{x} + 2\int_{x_0}^{x}\frac{e^{x'}\mathrm{d}x'}{x'^2(x'-2)^2}\right\} \tag{10}$$

Repeated integration-by-parts transforms the right-hand side of Eq. (10) to

$$F(\alpha) = \frac{AE_a}{\beta R}\frac{e^{x'}}{x'(x'-2)}\left[1 + \frac{2}{x'(x'-2)} + \frac{8}{x'(x'-2)^2} + O(x'^{-4}) + O(x'^{-5}) + \dots\right]\Bigg|_{x_0}^{x} \tag{11}$$

which contains a new series solution for the Arrhenius integral as follows:

$$p(x) = \frac{e^x}{x(x-2)}\left[1 + \frac{2}{x(x-2)} + \frac{8}{x(x-2)^2} + O(x^{-4}) + O(x^{-5}) + \dots\right] \tag{12}$$

The first term of Eq. (12), $p(x) = e^x/(x(x-2))$, is identical to the first two terms of the Schlomilch expansion (Eq. (7)).

For the normal temperature ranges and activation energies of scanning thermal analysis the lower limit in Eq. (11) can be neglected since, $-x_0 \gg -x$. Moreover, since $-x \geq 10$ (typically), only the first term of Eq. (11) need be retained

$$F(\alpha) \approx \frac{AE_a}{\beta R}\frac{e^x}{x(x-2)} = \frac{ART^2}{\beta(E_a + 2RT)}e^{-E_a/RT} \tag{13}$$

By way of comparison, Doyle's approximation (Eq. (8)) leads to the single-term result

$$F(\alpha) \approx 7.03 \times 10^{-3}\frac{AE_a}{\beta R}e^{-1.052\,E_a/RT} \tag{14}$$

while the first term of the asymptotic expansion (Eq. (7)) gives

$$F(\alpha) \approx \frac{AE_a}{\beta R}\frac{e^x}{x^2} = \frac{ART^2}{\beta E_a}e^{-E_a/RT} \tag{15}$$

Eq. (13) differs from Eq. (15) by the factor $2RT$ in the denominator. Because of their simplicity, Eqs. (14)

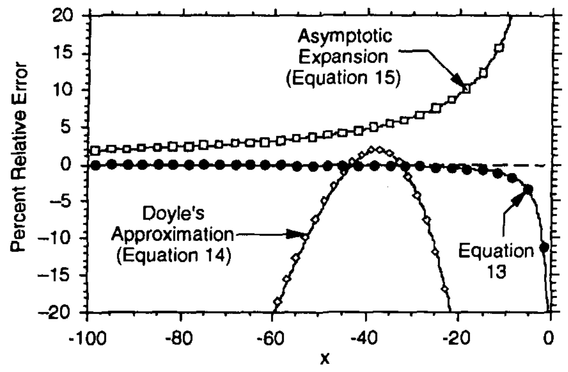

Fig. 1. Percent relative error vs. $x = -E_a/RT$ for Eqs. (13)–(15) as approximations for the Arrhenius integral.</fig

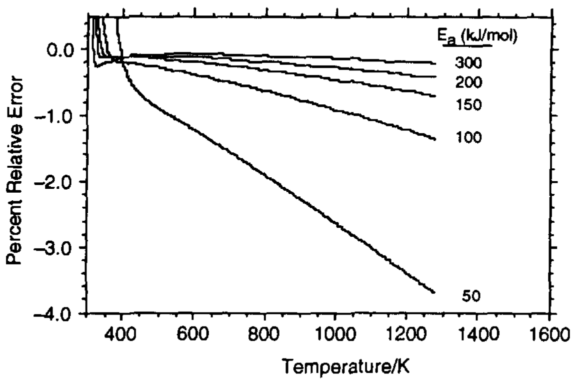

Fig. 2. Percent relative error vs. temperature for Eq. (13) with $E_a = 50$, 100, 150, 200, and 300 kJ mol^{-1}.

and (15) are commonly used in integral methods of thermal analysis [1–3,6–8,11–13].

The relative percent error associated with the use of Doyle's approximation (Eq. (14)) and the single-term asymptotic expansion (Eq. (15)) as solutions of the Arrhenius integral for a physically realistic domain of x are plotted in Fig. 1 along with the error for the present result, Eq. (13). The 'exact' value of the Arrhenius integral used for the error calculation was obtained by double precision numerical integration of Eq. (4) using the trapezoidal rule with a step size of 0.5 K between the limits of $T_0 = 300$ K and T. Fig. 1 shows that Eq. (13) is significantly more accurate than either of the single-term approximations, Eq. (14) or Eq. (15), as a solution of the Arrhenius integral. Eq. (13) under-predicts the true value of the Arrhenius integral by less than 1% over the domain $-x \geq 10$ normally encountered in experimental studies. Comparable accuracy requires at least three terms of the asymptotic expansion or the first two terms of the Schlomilch expansion [20].

Fig. 2 is a plot of the percent relative error vs. temperature using Eq. (13) to approximate the Arrhenius integral for a range of activation energies. An accuracy of greater than 99% is obtained for $E_a \geq 100$ kJ/mol over the temperature range normally examined in scanning thermal analyses. The positive catastrophe in Fig. 2 at low temperatures is the result of neglecting the lower limit of integration in arriving at Eq. (13), which becomes significant as T approaches T_0

4. Kinetic parameters from constant heating-rate experiments

The determination of both A and E_a from isothermal or nonisothermal experiments requires a priori knowledge of $f(\alpha)$ or $F(\alpha)$. A common functional form for $f(\alpha)$ is an arbitrary (nth) order reaction [1,3–13,17,18] which allows an analytic solution for $F(\alpha)$ and provides an additional fitting parameter – the reaction order, n. However, while A and E_a have physical significance [14] their numerical values and the reaction order determined from three-parameter fits of nth-order kinetics to conversion data is questionable except in the case of a well-defined reaction mechanism [3]. To circumvent the need to assume nth-order reaction kinetics to extract kinetic parameters, isoconversion methods [2,8,11] have been developed which utilize temperature and heating rate data at a fixed value of α and, thus, presumably, a fixed value of $F(\alpha)$. This eliminates the need to assume a functional form for $F(\alpha)$ to determine the activation energy of the reaction but precludes simultaneous determination of the frequency factor. Typical of the isoconversion methods is an iterative technique for determining E_a directly from conversion vs. temperature data at different heating rates proposed by Wall [2]. The method is based on Doyle's approximation of the Arrhenius integral (Eq. (14)) which can be differentiated to give

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}\frac{1}{T(\alpha)}} \approx -B(x)\frac{E_a}{R}$$

where $T(\alpha)$ is the temperature corresponding to a specific degree of conversion at a particular heating rate. The method requires successive approximations of E_a as the empirical coefficient $B(x)$ is incremented for each new value of $E_a/RT(\alpha)$. The activation energy thus determined is independent of $F(\alpha)$ to the extent that the assumptions used to obtain Eqs. (1)–(4) are valid but the method is time consuming without computerized data analysis and is empirically based [1,3].

An analogous but more direct method for determining E_a from constant heating-rate experiments without any assumptions about the form of $f(\alpha)$ or it's integral $F(\alpha)$ follows from Eq. (13). Taking the natural logarithms of Eq. (13)

$$\ln[F(\alpha)] = \ln A - \ln\beta - \ln\frac{1}{T(\alpha)} - \ln(2-x) + x \tag{16}$$

where $x = x(\alpha) = -E_a/RT(\alpha)$. If $F(\alpha)$ and A are independent of temperature and β is treated as a continuous variable, Eq. (16) can be 'differentiated' with respect to the reciprocal isoconversion temperature, $1/T(\alpha)$,

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}(1/T(\alpha))} = -T(\alpha)\left[2 - x - \frac{2}{2-x}\right] \tag{17}$$

The $2/(2-x)$ term on the right-hand side of Eq. (17) can be neglected since it accounts for less than two percent of the bracketed quantity for $-x \geq 10$. The slope of a plot of heating rate vs. the reciprocal temperature at any fixed conversion is therefore

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}(1/T(\alpha))} = -\left[\frac{E_a}{R} + 2T(\alpha)\right] \tag{18}$$

from which the activation energy at a particular conversion is

$$E_a(\alpha) = -R\left[\frac{\mathrm{d}\ln\beta}{\mathrm{d}1/T(\alpha)} + 2T(\alpha)\right] \tag{19}$$

If the activation energy of the reaction is known (e.g., from Eq. (19)) and β, $T(\alpha)$ data are available, then Eq. (16) is a single equation with two unknowns, A and $F(\alpha)$. Determination of a unique value for the frequency factor, A, from Eq. (16) therefore requires a numerical value for $F(\alpha)$. If $F(\alpha)$ satisfies the usual condition for the normalized conversion integral $F(\alpha) = 1$ at $\alpha = 1$ (c.f., Refs. [3,17]), then $\ln[F(\alpha)] = 0$ at completion of the reaction and Eq. (13) becomes for $T(\alpha = 1) \equiv T(1)$

$$\ln[F(1)] \equiv 0 = \ln[A] - \ln[\beta] - \ln\left[\frac{1}{T(1)}\right] - \ln\left[2 + \frac{E_a}{RT(1)}\right] - \frac{E_a}{RT(1)} \tag{20}$$

from which

$$\ln\left[\frac{\beta}{T(1)}\right] = \ln[A] - \left\{\ln[2 + E_a/RT(1)] + \frac{E_a}{RT(1)}\right\} \tag{21}$$

The frequency factor can be calculated by direct substitution of E_a and β, $T(1)$ data pairs into Eq. (21) after some rearrangement.

$$A = \frac{\beta\{E_a + 2RT(1)\}}{RT(1)^2}\mathrm{e}^{E_a/RT(1)} \tag{22}$$

Alternatively, E_a may be used as a fitting parameter in Eq. (21) to obtain unit negative slope in a plot of $\ln[\beta/T(1)]$ vs. $\{\ln[2 + E_a/RT(1)] + E_a/RT(1)\}$, yielding ln [A] as the intercept. The unit slope method allows simultaneous determination of both the global activation energy and frequency factor of an arbitrary single-step reaction from a few temperature scanning experiments without any assumptions about the reaction order or the functional form of $f(\alpha)$.

From the definition of the Arrhenius rate constant and Eq. (22) it follows that

$$k[T(1)] \equiv A\exp[-E_a/RT(1)] = \frac{\beta\{E_a + 2RT(1)\}}{RT(1)^2} \tag{23}$$

The reaction rate constant at temperature $T(1)$ is directly calculable from E_a and the β, $T(1)$ data pairs obtained in temperature scanning experiments.

5. Experimental

5.1. Polyethylene pyrolysis

Table 1 is a compilation of fractional mass-loss temperatures $T(\alpha)$ obtained in our laboratory for

Table 1
Heating rate and fractional mass loss temperatures for pyrolysis of low-density polyethylene

Heating rate, β K min^{-1}	$T(0.01)$ K	$T(0.02)$ K	$T(0.05)$ K	$T(0.10)$ K	$T(0.20)$ K	$T(0.50)$ K	$T(1.0)$ K
5	639	655	680	695	711	726	762
10	658	678	699	715	730	749	779
20	673	691	712	726	740	761	792
40	689	706	727	741	756	776	808
60	699	713	734	749	764	784	821
80	709	723	744	758	773	793	833

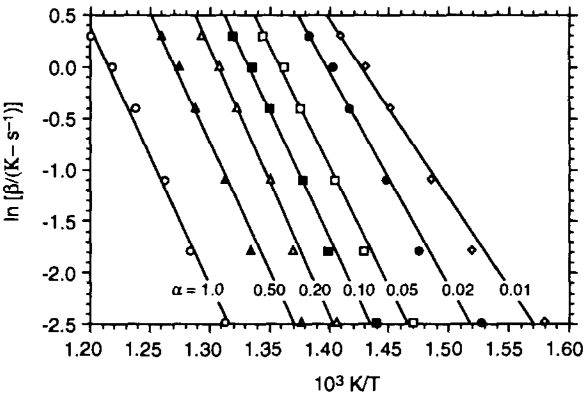

Fig. 3. Plot of natural logarithm of heating rate vs. the reciprocal temperature for volatile fractions, $\alpha = 0.01, 0.02, 0.05, 0.10, 0.20, 0.50$, and 1.0 for low molecular weight, low-density polyethylene.

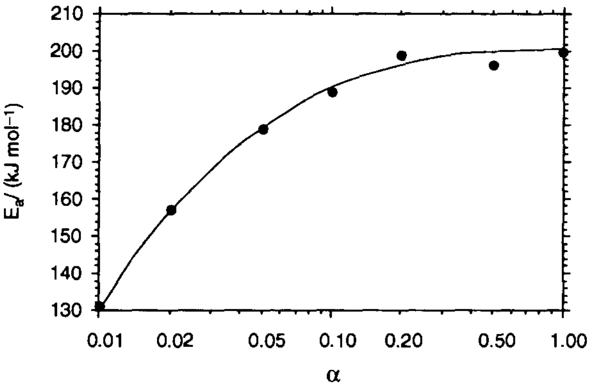

Fig. 4. Activation energy vs. fractional weight loss for low-density polyethylene calculated from Eq. (19).

anaerobic pyrolysis of (3–5) mg samples of low-density polyethylene ($M_w \approx 35000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 4.5$, $\rho = 906\ \mathrm{kg\ m^{-3}}$, Aldrich Chemical) under nitrogen flowing at $0.10\ \mathrm{l\ min^{-1}}$ in a thermogravimetric analyzer (Perkin–Elmer TGA-7) at constant heating rates $\beta = 5$, 10, 20, 40, 60, and 80 K min^{-1}. Fig. 3 is a composite of the data in Table 1 plotted as $\ln[\beta]$ vs. $1/T(\alpha)$ for volatile fractions $\alpha = 0.01, 0.02, 0.05, 0.10, 0.20, 0.50$, and 1.00. High correlation coefficients ($r^2 > 0.98$) were obtained for all of the linear regression curves of $\ln[\beta]$ vs. $1/T(\alpha)$ and the slopes at each conversion were used in Eq. (19) to calculate the activation energies plotted in Fig. 4 vs. fractional conversion. Individual values for the activation energy at each conversion, calculated by Eq. (19), were within ±0.2% of the mean value plotted in Fig. 4, indicating that E_a determined by this method is effectively independent of heating rate.

The variation in activation energy with weight loss observed in Fig. 4 for low molecular weight, low-density polyethylene suggests the possibility of consecutive thermal degradation reactions or a single-step reaction with a distribution of activation energies over the conversion domain. Alternatively, $F(\alpha)$ or A may be temperature dependent so that their derivatives with respect to $1/T$ are non-zero as was assumed in deriving Eq. (19). The relatively constant value, $E_a \approx 200\ \mathrm{kJ\ mol^{-1}}$, for conversions above about twenty percent in Fig. 4 is within the range of literature values, $E_a = 192 - 263\ \mathrm{kJ\ mol^{-1}}$ reported for this polymer under these experimental conditions [21].

Fig. 5 is a plot of the data in Table 1 according to Eq. (21) for the low-density polyethylene of this study. Unit negative slope in Fig. 5 was obtained for $E_a = 200\ \mathrm{kJ\ mol^{-1}}$ in agreement with the method of Eq. (19) and Fig. 4. The correlation coefficient for

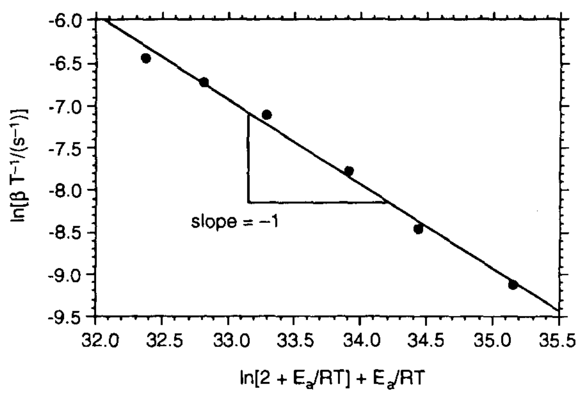

Fig. 5. Plot of $\ln[\beta/T]$ vs. $\{\ln[2+E_a/RT]+E_a/RT\}$ for thermal degradation of low-density polyethylene at complete conversion according to Eq. (21) with $E_a = 200\,\text{kJ mol}^{-1}$.

the linear regression curve was $r^2 = 0.99$. The intercept of the linear plot in Fig. 5 is, $26.039 = \ln[A]$ from which $A = 2.0\times10^{11}\,\text{s}^{-1}$, a typical value for the frequency factor or pre-exponential term in polymer thermal degradation [13].

5.2. Phenylethynyl curing reaction

The present integral method of nonisothermal kinetic analysis was also applied to differential scanning calorimetry data for the curing reaction exotherm of phenylethynyl-terminated imide oligomers obtained by Hinkley [22,23]. These phenylethynyl curing experiments were conducted on ≈7 mg samples of the oligomer in a differential scanning calorimeter (Shimadzu DSC-50) at heating rates of 5, 20, 40, 60, and 80 K min^{-1}. Samples of fine powder were contained in open platinum pans purged with nitrogen at a flow rate of $0.03\,\text{l min}^{-1}$ during the temperature scanning experiments. Fractional conversion, α, was calculated as the cumulative heat of reaction up to a particular temperature in the scanning experiments divided by the total heat of reaction at the incipient temperature of complete reaction according to standard methods [24]. Linear baselines were assumed.

Hinkley's analysis of these data using Wall's [2] iso-conversion method and Doyle's integral approximation (Eq. (14)) for $\alpha = 0.10, 0.30, 0.50, 0.90$, yielded an average activation energy for the phenylethynyl curing reaction, $E_a = 139.0\pm3.3\,\text{kJ mol}^{-1}$. However, for this activation energy and temperature range $x = -E_a/RT \approx -(139\,\text{kJ mol}^{-1})/(8.314\,\text{J mol}^{-1}\,\text{K}^{-1})$ $(800\text{ K}) = -21$ and the more accurate empirical constant $B(x) = 1.098$ [2] should have been used in Eq. (14) in place of the average $B(x) = 1.052$. This single iteration of $B(x)$, according to Wall [2], improves the activation energy estimate for the phenylethynyl curing reaction to $E_a = 133.2\pm 3.2\,\text{kJ mol}^{-1}$ which agrees well with studies by other investigators who had found $E_a = 132.3$ and $152.8\,\text{kJ mol}^{-1}$ for the curing reaction of phenylethynyl-terminated model compounds [25]. Attempts by Hinkley to determine a single frequency factor for the phenylethynyl curing reaction were unsuccessful due to the presence of both $F(\alpha)$ and A in Eq. (14). Hinkley assumed nth order kinetics with $n = 3/2$ and used the β-independent conversion value $\alpha \approx 0.48$ at the peak reaction-rate temperature to obtain a numerical value for $F(\alpha = 0.48)$. Substituting $F(0.48)$ into Eq. (14) resulted in a range of frequency factors, $A = 10^5$ to $10^9\,\text{s}^{-1}$ for the phenylethynyl curing reaction.

Phenylethynyl curing data at complete conversion, not published in the original work, were kindly provided by Hinkley [23] and are given in Table 2. Analysis of these data using Eq. (19) with the best-fit slope of the linear regression of $\ln[\beta]$ vs. $1/T(1)$ gives an average $E_a = 132.8\pm0.6\,\text{kJ mol}^{-1}$. Substituting $E_a = 132.8\,\text{kJ mol}^{-1}$ into Eq. (22) gives $A = 9.8\pm0.8\times10^6\,\text{s}^{-1}$ for the five data pairs. By comparison, the unit negative slope method at total conversion (Eq. (21)) plotted in Fig. 6 gives $E_a = 133.4\,\text{kJ mol}^{-1}$ and $A = 10.7\times10^6\,\text{s}^{-1}$ with a correlation coefficient $r^2 = 0.992$. These activation energies for the phenylethynyl curing reaction determined from Eqs. (19) and (21) are self-consistent and in quantitative agreement with the published values, while the frequency factors for this reaction determined from Eqs. (21) and (22)

Table 2
Heating rate and incipient completion temperatures for phenylethynyl curing reaction [23]

$\beta/(\text{K min}^{-1})$	5	20	40	60	80
$T(\alpha=1)/K$	726	778	795	810	821

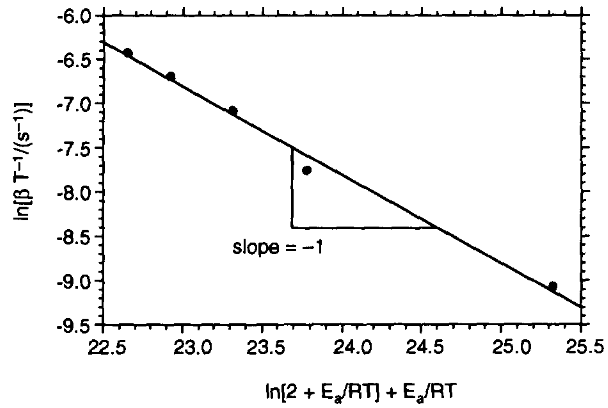

Fig. 6. Plot of $\ln[\beta/T]$ vs. $\{\ln[2+E_a/RT]+E_a/RT\}$ for cure of phenylethynyl-terminated imide oligomer at complete conversion according to Eq. (21) with $E_a = 133\,kJ\,mol^{-1}$

are well within the estimated range for this Arrhenius parameter.

6. Conclusions

A new series solution provides an accurate single-term approximation for the constant heating-rate Arrhenius integral which can be used to determine the activation energy and frequency factor of an arbitrary, single-step reaction from a series of temperature scanning experiments. Assumptions about the form of the rate law are not necessary for applying the present integral method to the analysis of non-isothermal reaction data. Agreement of the calculated Arrhenius activation energy and frequency factor for polyethylene pyrolysis and ethynyl curing reactions with literature values demonstrates the general utility of the present approach for determining kinetic parameters of single-step reactions from constant heating-rate experiments. Determination of a physically meaningful reaction-rate law from isothermal experiments is possible since the Arrhenius rate constant at complete conversion can now be obtained independently of any assumptions about reaction order, or the form of the conversion function.

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