

## Chapter

### 3. Kinetic Studies

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#### 3.1 Introduction

In recent years, polymers have been increasingly utilized in quite widespread applications. Along with the enhanced usage, though, comes greater likelihood of incidences of a polymeric material's loss of performance due to thermal, chemical, or mechanical degradation. In order, especially, to prevent catastrophic failures of polymeric components, it is necessary to fully understand the service environmental history of a polymeric device and its effect on material properties. One element of this history, as mentioned above, may be thermal degradation. If the rates of degradation can be accurately measured, then it becomes possible to predict material properties as they relate to the specific thermal environment. The aim of this study, then, is to develop predictive tools for material properties, based on knowledge of the environmental history, so that failures can be anticipated and hence avoided. This section of the study will focus on the elucidation of the thermal history of the sample in the form of the kinetic parameters of the degradation.

A common technique for obtaining kinetic thermal degradation parameters for polymers is thermogravimetric analysis (TGA). The apparatus consists of a microbalance within a furnace, allowing the weight of the sample to be continuously monitored while the temperature is controlled. Samples can be run either in a dynamic (temperature ramp) or an isothermal mode. Once these data are collected, analysis of the raw numbers leads to the kinetic rate parameters:  $n$ , order of reaction;  $E_a$ , activation energy; and  $A$ , preexponential factor. Several authors have proposed a variety of analysis techniques over the years, and in this chapter many of these will be applied to the data collected for polycarbonate in an attempt to select a "best" approach. Results from the different methods are compared, primarily in terms of Arrhenius parameters, and recommendations made regarding which techniques provide the more accurate representation of the physical processes.

### **3.2 Experimental**

Most studies of thermal degradation focus on unstabilized (no antioxidant package) samples of the polymer. However, one goal of this study is to achieve results which are directly applicable to an industrially processed polymer. To that end, pellets of both commercial grade Lexan® (General Electric), PC(Lex), which is a bisphenol A polycarbonate, and an unstabilized laboratory grade material, PC(Lab), also provided by General Electric, were utilized after drying overnight under vacuum and subsequent compression molding into films. These resulting samples were then stored in a dessicator to prevent moisture absorption. Pieces of these films, with a radius of approximately 6 mm and a total thickness of 0.4 mm, were then tested in a TA Instrument thermogravimetric analyzer, model 2950, in both isothermal and dynamic modes. For isothermal tests, samples were placed in the instrument and the chamber purged with nitrogen for approximately 30 minutes prior to heating. Then the furnace was ramped up in temperature to an isotherm (375, 387.5, 400, or 425°C) where the temperature was maintained until degradation was complete as determined by the leveling off of the sample weight versus time behavior. It should be noted here that the initial sample geometry is irrelevant since, at these temperatures, the sample is no longer solid and can flow. For the sake of consistency, though, all samples were circles punched out of the thin films. For dynamic tests, the furnace was ramped from 30-900°C at one of several heating rates (10, 20, 30, or 40°C/min) and punched circles of thin films were again utilized. In both cases, results of weight versus time and temperature were continuously recorded. It should also be noted that, for certain dynamic analyses, only a single thermogram was necessary to yield the desired parameters. In such a case, the thermogram with a heating rate of 10°C/min was always used.

### **3.3 Discussion**

#### **3.3.1. Isothermal Results**

As previously mentioned, thermogravimetric analysis can be divided into two broad categories, isothermal and dynamic testing. The most basic test consists of an isothermal run where the data is then fit to the standard kinetic equation:

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad \text{Eqn. 3.3.1-1}$$

where  $k(T)$  is the kinetic rate constant,  $n$  is the order of the reaction,  $t$  is time, and  $\alpha$  is a normalized fractional conversion and is defined as

$$\alpha = \frac{W(t) - W_i}{W_f - W_i} \quad \text{Eqn. 3.3.1-2}$$

where  $W(t)$  is the weight at any time  $t$ , and  $W_i$  and  $W_f$ , respectively, are the initial and final sample weights. In order to introduce a temperature dependency, the kinetic rate constant is assumed to be of the Arrhenius form:

$$k = Ae^{-E_a / RT} \quad \text{Eqn. 3.3.1-3}$$

where  $A$  is a preexponential factor,  $E_a$  is the activation energy, and  $R$  is the gas constant.

The major disadvantage of this approach is that complete degradation can require significant amounts of time (in the present case, a week to 10 days) which can introduce significant error in the modelling from ambient environmental changes. However since this approach involves no approximations and, for this study, is the closest to the actual degradation conditions, it will serve as the standard for comparison. Samples of both PC materials were degraded at each of the isothermal temperatures mentioned above, with four samples being run at the highest temperatures to ascertain the inherent error of the measurements. Raw data for each temperature are shown in Figure 3.3.1-1 and Figure 3.3.1-2.

For predictive purposes, it is possible to create an isothermal kinetic master curve by simply scaling the raw data with time. This is accomplished by dividing the time on the x axis by  $t_{1/2}$ , the time required for  $\alpha$  to reach 0.5, resulting in a collapsing of all curves onto a single curve as seen in Figure 3.3.1-3 and Figure 3.3.1-4.

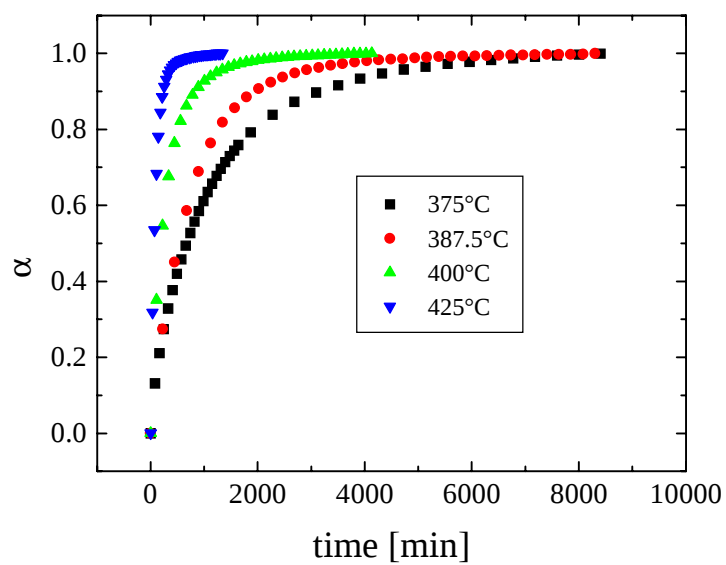


Figure 3.3.1-1 Raw data for laboratory grade polycarbonate, PC(Lab).

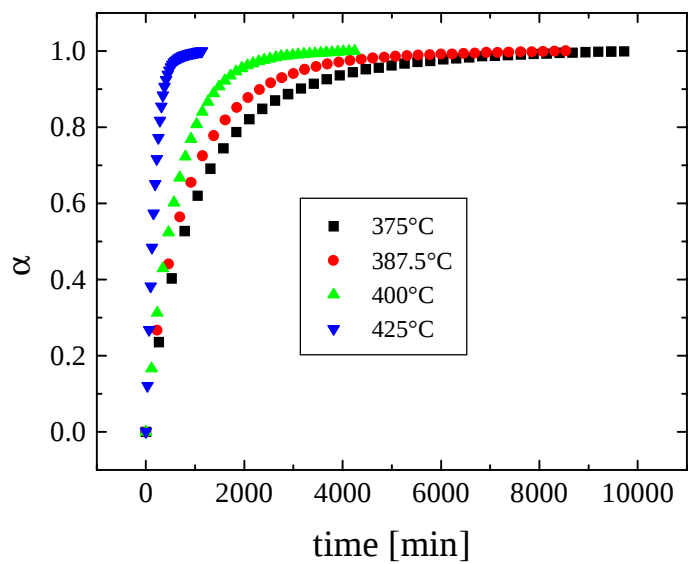


Figure 3.3.1-2 Raw data for Lexan® polycarbonate, PC(Lex).

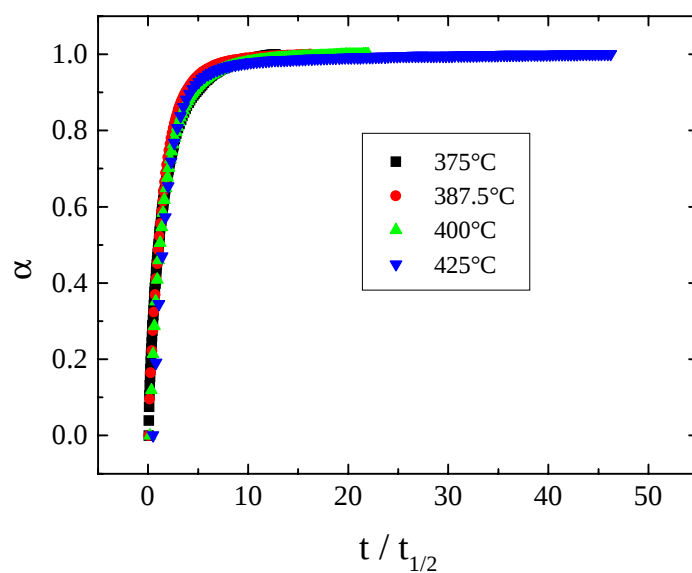


Figure 3.3.1-3 Kinetic master curve for PC(Lab).

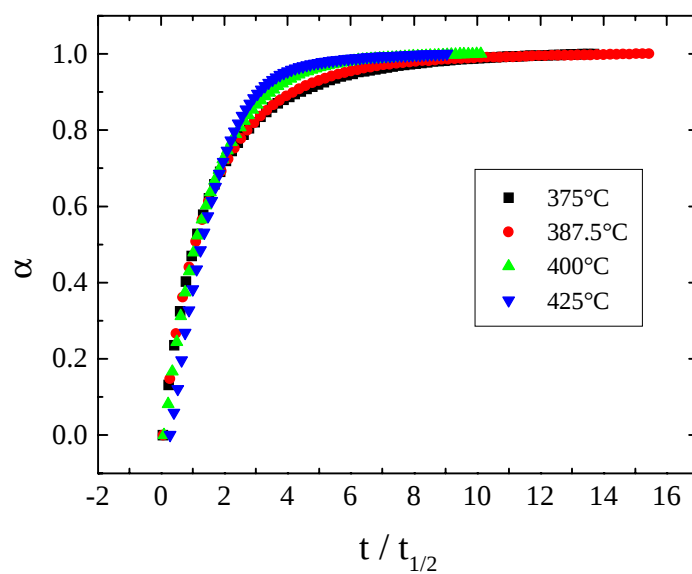


Figure 3.3.1-4 Master curve for PC(Lex).

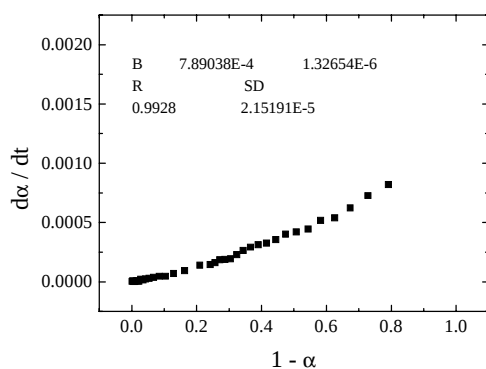
The data were then fitted to Eqn. 3.3.1-1 which resulted in values for  $n = 1$  for each temperature, a typical value for polymer degradation, and  $k$  (Figure 3.3.1-5 and Figure

3.3.1-6). The  $k$  values were then fitted to Eqn. 3.3.1-3, leading to  $E_a$  and  $A$  for the process as shown in Figure 3.3.1-7 and Figure 3.3.1-8. For the laboratory grade material, it was found that  $E_a = 190.8 \pm 14.6$  kJ/mol and  $\ln A = 28.2 \pm 2.6$ . It should be noted here that the errors shown represent, in all cases, the variance calculated from the indicated fits. The commercial polymer, PC(Lex), demonstrated nearly identical values with  $E_a = 192.0 \pm 15.7$  kJ/mol and  $\ln A = 28.0 \pm 2.8$ . It should be noted that, even though the activation energy and pre-exponential factor are nearly identical, the reaction rate constants indicate that the commercial polymer requires a longer time than the laboratory grade to reach an equivalent level of degradation, indicating that the lab grade may be an unstabilized version of polycarbonate. These numbers are slightly higher than literature values which report  $E_a = 149.3$  kJ/mol<sup>1</sup> or 153 kJ/mol with  $n = 0.8$  and  $\ln A = 21$ <sup>2</sup>. Values for the reaction rate constants,  $k$ , for PC(Lab) are shown in Table 3.3.1-1, and those for PC(Lex) are summarized in Table 3.3.1-2. These numbers will be utilized throughout the rest of this discussion in determining the rate of degradation, as will be seen in the following chapters.

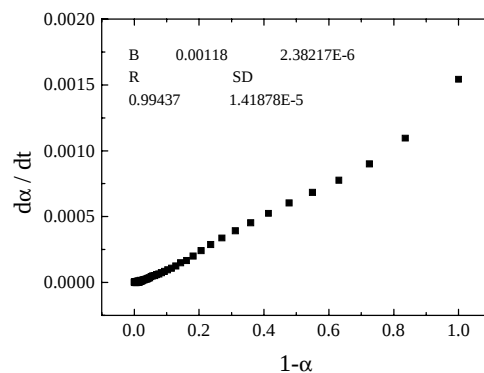
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<sup>1</sup> Knight, G. J., *British Polym. J.*, **10**, 187, 1978.

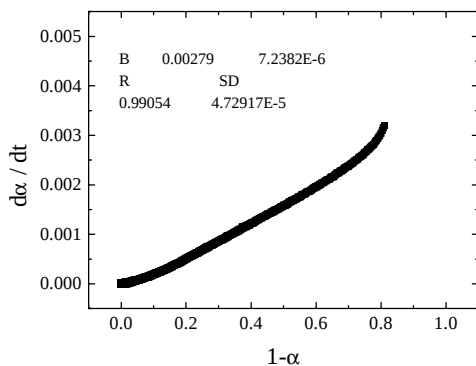
<sup>2</sup> Li, X. G. and M. R. Huang, *Polym. Int.*, **48**, 387, 1999.



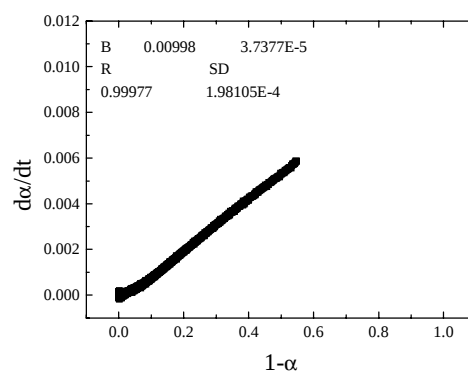
(a)



(b)



(c)



(d)

Figure 3.3.1-5 Data shown in the manner of Eqn. 3.3.1-1 for PC(Lab) at isothermal temperatures of (a) 375°C; (b) 387.5°C; (c) 400°C; (d) 425°C.

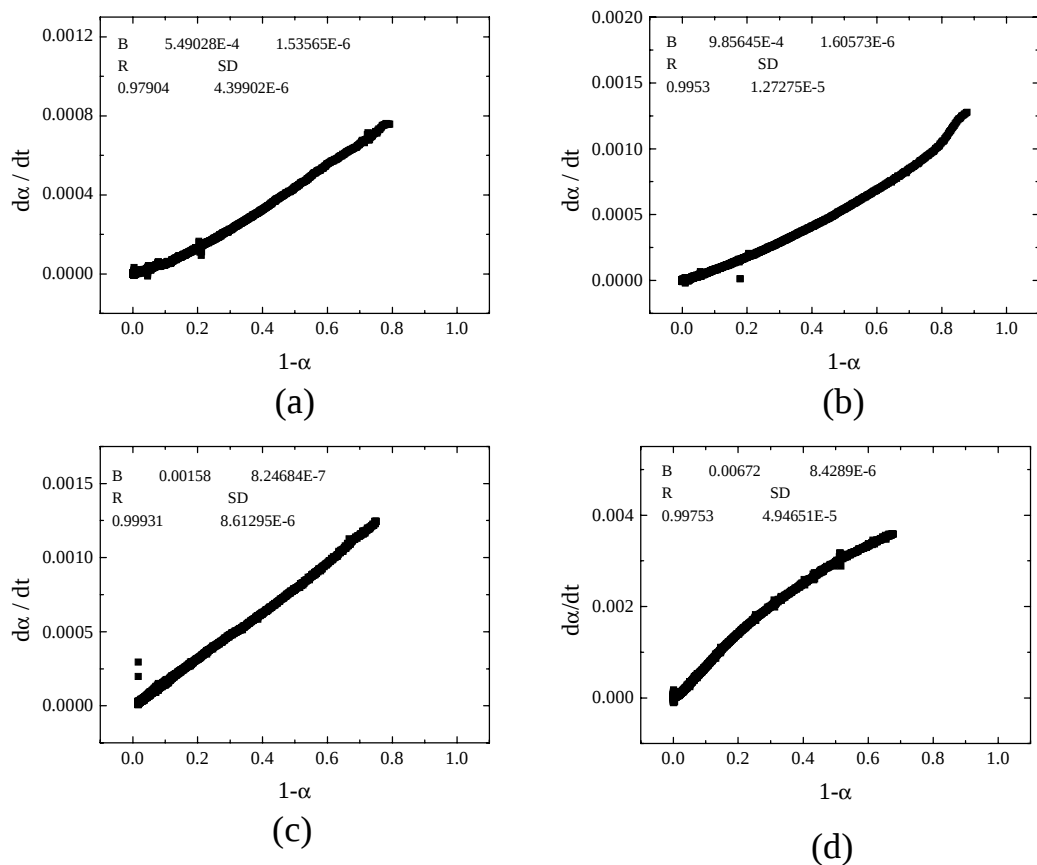


Figure 3.3.1-6 Data shown in the manner of Eqn. 3.3.1-1 for PC(Lex) at isothermal temperatures of (a) 375°C; (b) 387.5°C; (c) 400°C; (d) 425°C.

Table 3.3.1-1

Calculated Reaction Rate Constants for PC(Lab)

| Temperature [°C] | k [min <sup>-1</sup> ]                         |
|------------------|------------------------------------------------|
| 375              | $7.89 \times 10^{-4}$ ( $1.3 \times 10^{-6}$ ) |
| 387.5            | $1.18 \times 10^{-3}$ ( $2.4 \times 10^{-6}$ ) |
| 400              | $2.79 \times 10^{-3}$ ( $7.2 \times 10^{-6}$ ) |
| 425              | $9.98 \times 10^{-3}$ ( $6.4 \times 10^{-5}$ ) |
| 425              | $7.71 \times 10^{-3}$ ( $1.2 \times 10^{-5}$ ) |
| 425              | $9.27 \times 10^{-3}$ ( $1.8 \times 10^{-5}$ ) |
| 425              | $9.22 \times 10^{-3}$ ( $1.1 \times 10^{-5}$ ) |
| 425 (average)    | $9.22 \times 10^{-3}$ ( $1.1 \times 10^{-3}$ ) |

Table 3.3.1-2

Calculated Reaction Rate Constants for PC(Lex)

| Temperature [°C] | k [min <sup>-1</sup> ]                         |
|------------------|------------------------------------------------|
| 375              | $5.49 \times 10^{-4}$ ( $1.5 \times 10^{-6}$ ) |
| 387.5            | $9.86 \times 10^{-4}$ ( $1.6 \times 10^{-6}$ ) |
| 400              | $1.58 \times 10^{-3}$ ( $8.3 \times 10^{-7}$ ) |
| 425              | $6.72 \times 10^{-3}$ ( $8.4 \times 10^{-6}$ ) |
| 425              | $7.26 \times 10^{-3}$ ( $1.5 \times 10^{-5}$ ) |
| 425              | $6.54 \times 10^{-3}$ ( $1.1 \times 10^{-5}$ ) |
| 425              | $7.56 \times 10^{-3}$ ( $7.1 \times 10^{-6}$ ) |
| 425 (average)    | $7.02 \times 10^{-3}$ ( $4.7 \times 10^{-4}$ ) |

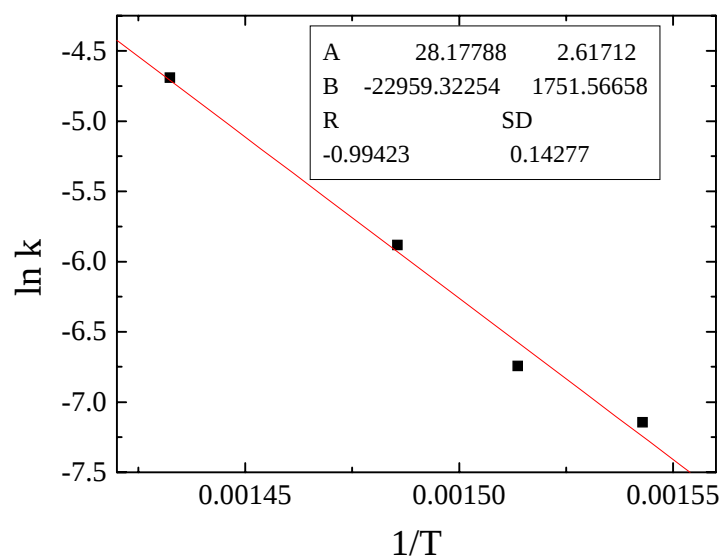


Figure 3.3.1-7 Arrhenius analysis for PC(Lab) degradation.

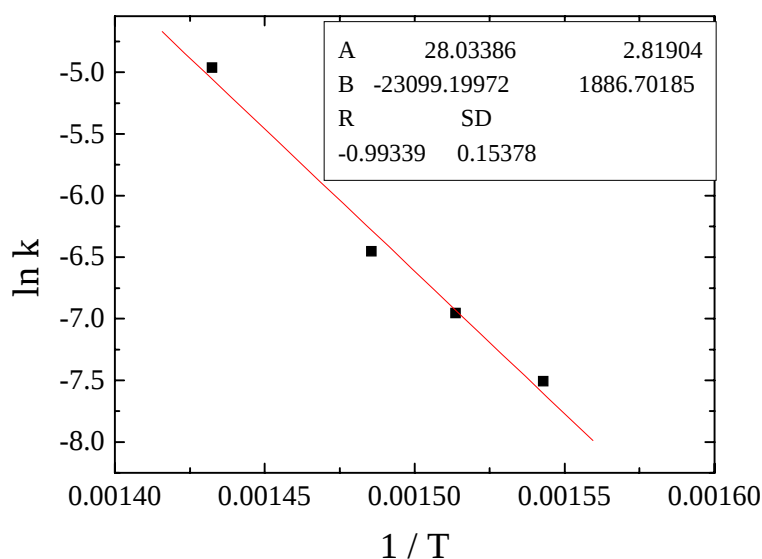


Figure 3.3.1-8 Arrhenius analysis for PC(Lex) degradation.

Another isothermal degradation analysis technique utilized in this present study is the stationary point method of Klaric<sup>3</sup>. The stationary point,  $S(t_m, V_{max})$  is defined as the maximum of the curve  $(d\alpha/dt)$  versus  $t$  where  $\alpha$  is now defined as

$$\alpha = \frac{W_i - W(t)}{W_i} \quad \text{Eqn. 3.3.1-4}$$

The activation energy can then be found from the slope  $(= -E_a / R)$  of the plot of  $\ln V_{max}$  versus  $(1/T)$  for several different isothermal temperatures. This technique was applied to isothermal data for both grades of polycarbonate with the results shown in Figure 3.3.1-9 and Figure 3.3.1-10. The fit for PC(Lex) leads to an activation energy of  $424.5 \pm 100.3$  kJ/mol. This value is of the correct order of magnitude, but the large error and high value relative to the standard isothermal fit cast doubt on the reliability of this technique. Furthermore, when the method is applied to PC(Lab), the “fit” is even worse resulting in  $E_a = 3.4 \pm 19.3$  kJ/mol which is clearly not acceptable. One possible source of this error may be related to the type of reaction occurring. In his study, Klaric was examining an

<sup>3</sup> Klaric, I., U. Roje, and T. Kovacic, *J. Therm. Anal.*, **45**, 1373, 1995.

autocatalytic process which exhibits an induction time before degradation begins. Polycarbonate degradation, however, demonstrates no such phenomena, and, thus, maxima in the derivative curve are less obvious. This is illustrated in Figure 3.3.1-11 where it is particularly difficult to determine maxima at the lowest temperatures. Outcomes such as these tend to discredit the Klaric method, at least for the system being studied here.

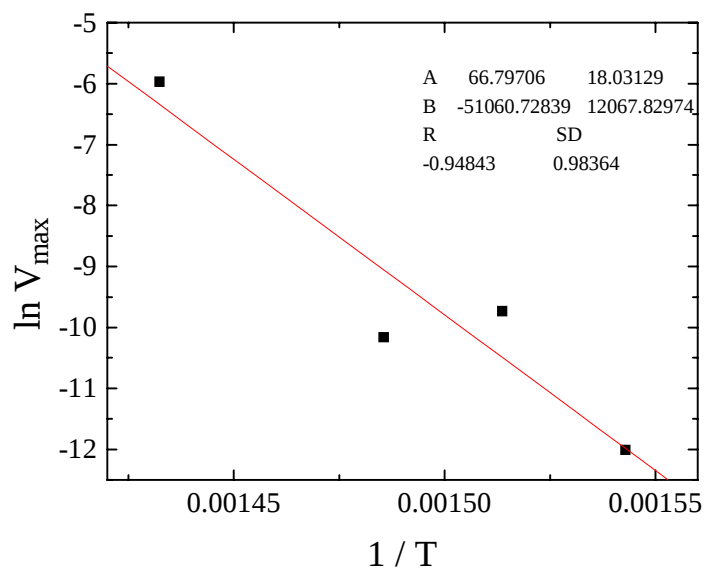


Figure 3.3.1-9 Klaric's method applied to PC(Lex).

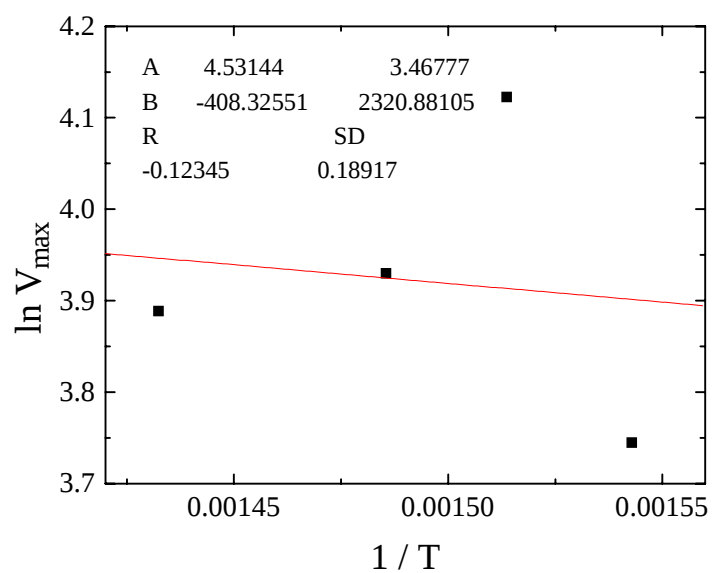


Figure 3.3.1-10 Klaric's method applied to PC(Lab).

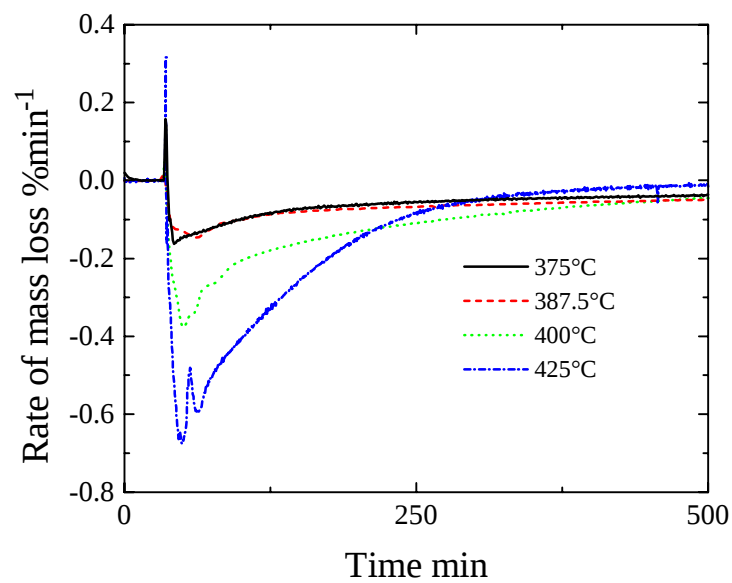


Figure 3.3.1-11 Derivative curves for PC(Lab).

MacCallum and Schoff<sup>4</sup> reported that plotting  $t/P$  versus  $1/t$  for thermal degradation studies, where  $1-P = W/W_i$ , leads to a straight line with slope and intercept related to  $k$  and  $n$ . However, their method only applies to reactions with order other than 1, and thus does not apply to the present situation. When these quantities are plotted for Lexan, Figure 3.3.1-12, the slope is found to be undefined serving as confirmation that the order for this material is indeed 1.

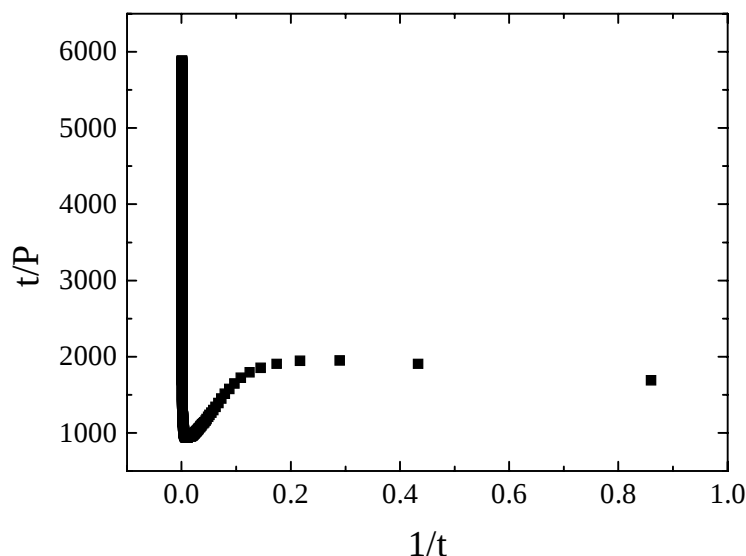


Figure 3.3.1-12 MacCallum and Schoff's method applied to PC(Lex).

Further work was carried out by MacCallum<sup>5</sup> to show that, for fixed values of  $\alpha$  (where  $\alpha = (W_i - W) / W_i$ ), a plot of the logarithm of time versus reciprocal temperatures gives a linear result with slopes related to  $E_a$ . If one then plots the resulting intercepts at various isothermal temperatures versus  $\alpha$  and extrapolates to zero conversion,  $A$  is obtained. This technique has been applied to both grades of PC with results as seen in Figure 3.3.1-13(a)-(d). For PC(Lab),  $E_a = 180.5 \pm 3.9$  kJ/mol and  $\ln A = 21.9 \pm 0.2$  while  $E_a = 147.0 \pm 9.8$  kJ/mol and  $\ln A = 18.0 \pm 0.7$  for PC(Lex). The values for activation energy are of the same order of magnitude (slightly lower) than those calculated from the

<sup>4</sup> MacCallum, J. R. and C. K. Schoff, *Polym. Lett.*, **9**, 395, 1971.

<sup>5</sup> MacCallum, J. R., in *Comprehensive Polymer Science: The Synthesis, Characterization, Reactions and Applications of Polymers*, Vol. I, p. 903, Geoffrey Allen and John C. Bevington, Ed., Pergamon Press,

standard method. The preexponential factor, though, is significantly lower via this method. By choosing more values for  $\alpha$  is may be possible to achieve better results.

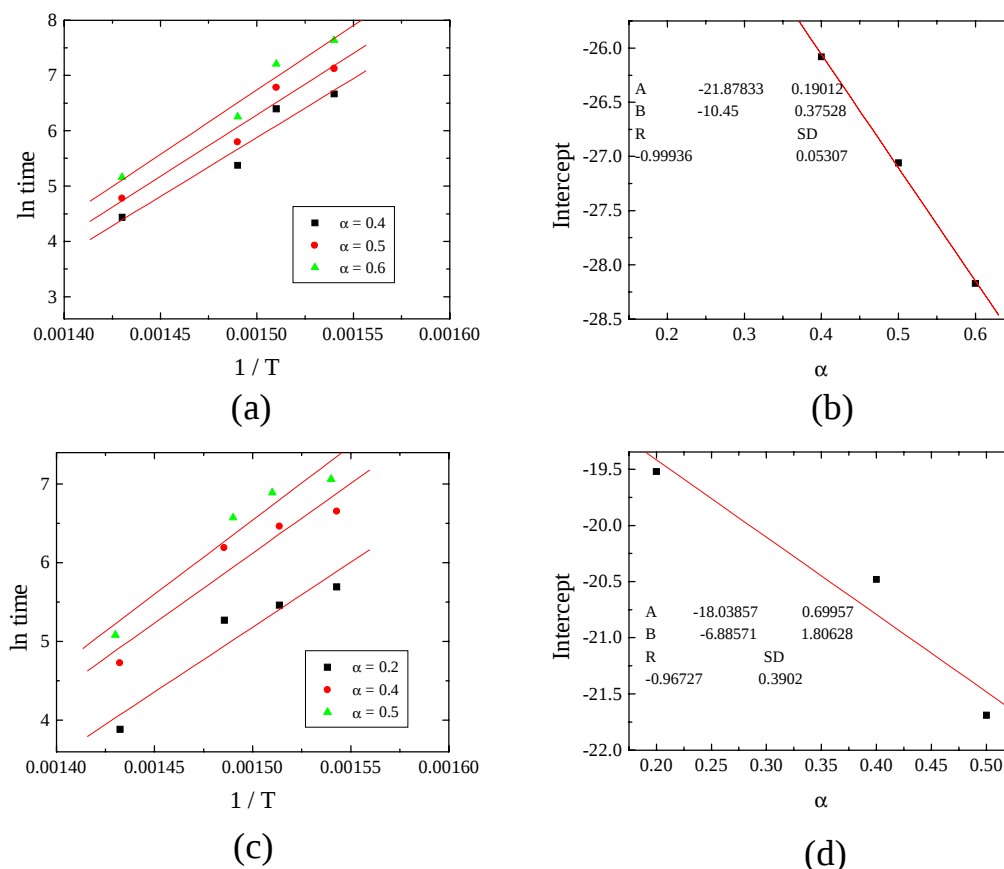


Figure 3.3.1-13 MacCallum's method applied to both PC grades: (a) and (b) PC(Lab); (c) and (d) PC(Lex).

The analytical methods for degradation kinetics espoused by both Criado<sup>6</sup> and Judd and Norris<sup>7</sup> were not applied to the present case, as justified by the following: the former method relies on tabulated data to determine the mechanism of the decomposition which is irrelevant to this study; while the latter technique does address the kinetic parameters in question here, but applies to solid state reactions. Here, polycarbonate is being degraded at temperatures in excess of 300°C, well above the glass transition

Oxford, 1989.

<sup>6</sup> Criado, J. M., *J. Therm. Anal.*, **21**, 155, 1981.

<sup>7</sup> Judd, M. D. and A. C. Norris, *J. Therm. Anal.*, **5**, 179, 1973.

temperature for the material. Thus, these samples are not in the solid state, but are fluid, and the use of this model would be inappropriate.

Other techniques which were discounted for the purposes of this study included those of Chatterjee<sup>8</sup> and Rozycki<sup>9,10</sup>. Chatterjee's method was shown to be in error as discussed in the literature review. Rozycki's technique relies on a complex computer program. Since a main drawback of the standard method is the length of time needed to complete the testing, it was reasoned that adding additional time to that with programming was not consistent with the objectives of this thesis.

Of the isothermal analysis methods discussed, only a few were actually applicable to the polycarbonate data, and these yielded widely varying values for  $n$ ,  $E_a$ , and  $A$ . Results from these, as well as the standard analysis, which serves as the baseline here, are summarized in Table 3.3.1-3.

Table 3.3.1-3

Summary of Results from Isothermal Methods

| Method    | $E_a$ [kJ/mol] |               | $\ln A$ [ln min <sup>-1</sup> ] |            | $n$     |         |
|-----------|----------------|---------------|---------------------------------|------------|---------|---------|
|           | PC(Lab)        | PC(Lex)       | PC(Lab)                         | PC(Lex)    | PC(Lab) | PC(Lex) |
| Standard  | 190.9 (14.6)   | 192.0 (15.7)  | 28.2 (2.6)                      | 28.0 (2.8) | 1       | 1       |
| Klaric    | 3.4 (19.3)     | 424.5 (100.3) | ---                             | ---        | ---     | ---     |
| MacCallum | 180.5 (3.9)    | 147.0 (9.8)   | 21.9 (0.2)                      | 18.0 (0.7) | ---     | ---     |

### 3.3.2. Dynamic Methods

Since a major detriment of the isothermal techniques is the total length of time required, many researchers have turned to dynamic TGA profiles where the temperature is programmed to a specific heating rate. These offer the advantage that tests are usually quite rapid, on the order of minutes or hours instead of days. In some cases, all necessary parameters can be calculated from a single TGA trace, alleviating errors which may arise when multiple samples are required. However, many of these methods are unwieldy and difficult to apply, and the results have been significantly different than those calculated by the standard isothermal technique.

<sup>8</sup> Chatterjee, P. K., *J. Polym. Sci., Part A*, **3**, 4253, 1965.

<sup>9</sup> Rozycki, C. and M Maciejewski, *Thermochim. Acta*, **96**, 91, 1985.

<sup>10</sup> Rozycki, C. and M Maciejewski, *Thermochim. Acta*, **122**, 339, 1987.

One of the most commonly used methods is that of Freeman and Carroll<sup>11</sup>. This involves choosing equal temperature intervals,  $\Delta(1/T)$ , running dynamic sweeps, and then plotting  $\Delta\log(-dW/dt)$  versus  $\Delta\log W$ . The slope of the resulting line yields  $n$  and the intercept is related to  $E_a$ . Results of this approach for both grades of polycarbonate at a heating rate of 10°C/min are shown in Figure 3.3.2-1. From this methodology it can be concluded that  $E_a = 200.0 \pm 74.3$  kJ/mol with an order of reaction of  $1.18 \pm 0.09$  for PC(Lex), while PC(Lab) exhibits an  $E_a = 360.4 \pm 180.0$  kJ/mol with an order of reaction of  $0.94 \pm 0.24$ . Within the error of the measurement, these results agree quite well with those found with the standard isothermal method. However, it should be pointed out that the errors are indeed quite substantial and that the method is rather unwieldy to apply to data. Presumably, it would be possible to develop some program to analyze the data, but without such a tool in existence, a significant amount of effort is required for answers. Still, the possibility of obtaining these data with a single TGA trace could outweigh these difficulties.

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<sup>11</sup> Freeman, E. S. and B. Carroll, *J. Phys. Chem.*, **62**, 394, 1958.

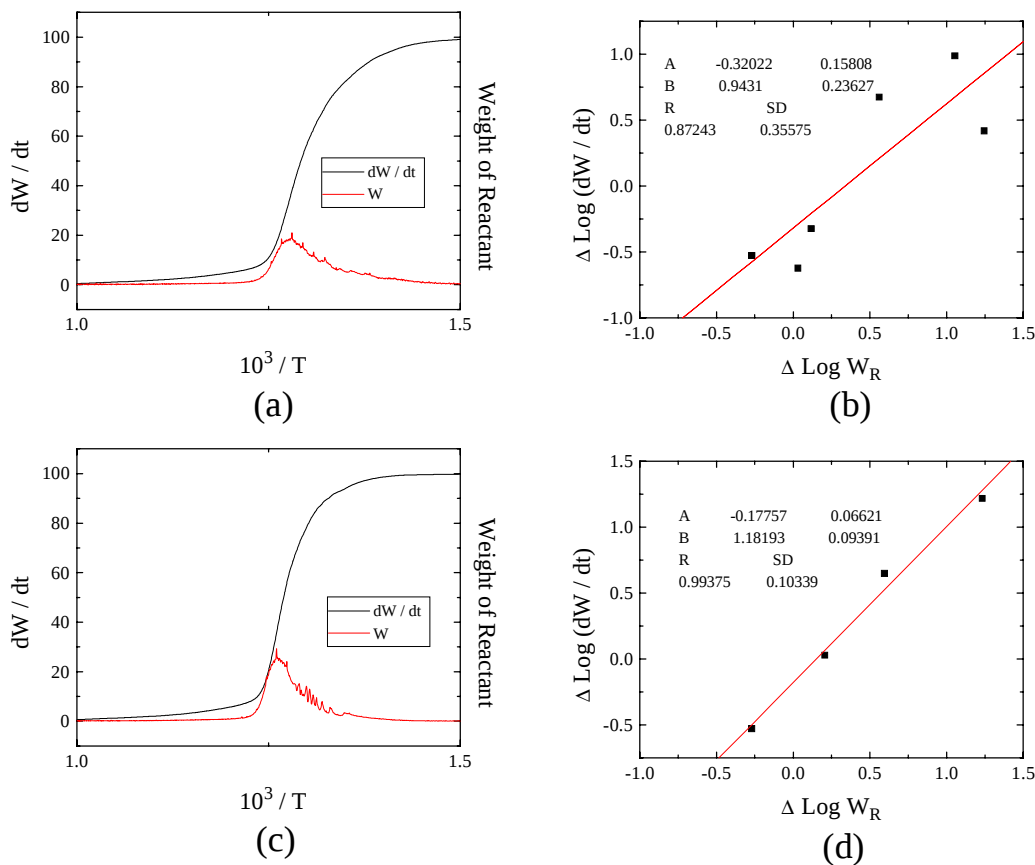


Figure 3.3.2-1 Results of the Freeman-Carroll method for: (a) and (b) PC(Lab); and (c) and (d) PC(Lex).

Another method of analyzing thermal degradation data, developed independently by Fuoss<sup>12</sup> and by Reich<sup>13</sup>, focuses on the inflection point, which is the point where the reaction rate is maximum. While this technique requires only a single thermogram, it has the disadvantage that the order of the reaction must be known *a priori*. For the purposes of the present study,  $n$  is known to be 1 and this method can be applied. The activation energy can be found quite simply from the expression

$$E_a = \frac{-\left[nRT^2\left(\frac{dW}{dT}\right)_{\max}\right]}{W_{\max}} \quad \text{Eqn. 3.3.2-1}$$

<sup>12</sup> Fuoss, R. M., I. O. Salyer, and H. S. Wilson, *J. Polym. Sci., Part A*, **2**, 3147, 1964.

<sup>13</sup> Reich, L., H. T. Lee, and D. W. Levi, *Polymer Letters*, **1**, 535, 1963.

where  $W_{\max}$  and  $T_{\max}$  are the weight and temperature at the inflection point, respectively, and  $\left(\frac{dW}{dT}\right)_{\max}$  is the slope at that point. The pre-exponential factor is then found from

$$A = -\left(\frac{\beta}{W_{\max}}\right)\left(\frac{dW}{dT}\right)_{\max} e^{E_a/RT_{\max}} \quad \text{Eqn. 3.3.2-2}$$

where  $\beta$  is the heating rate of the experiment. When this method is applied to both sets of data, the result is  $E_a = 428.7$  kJ/mol and  $A = 1.37 \times 10^{28}$  for PC(Lex) and  $E_a = 278.2$  kJ/mol and  $A = 2.23 \times 10^{18}$  for PC(Lab). While the values for the activation energy are slightly elevated relative to those for the standard method, a large discrepancy exists in the pre-exponential factor where the values are many orders of magnitude different. It should also be noted that the values reported by Fuoss for this parameter were also high relative to those generally seen for polymer degradation. This leads one to believe that, while this technique may be good for an approximation of  $E_a$ , it should not be used to calculate  $A$  with any degree of certainty.

In further work, Reich<sup>14</sup> also developed a method whereby one could change the heating rate of the dynamic test when a specified conversion was reached during the experiment. However, the way in which the instrument in use for the present study was designed, such a change would be very difficult to carry out-this method was not applied.

Van Krevelen's<sup>15</sup> method makes use of a mathematical approximation for the exponential term from the Arrhenius expression. Then plotting  $\ln I$ , a constant defined in Chapter 1, Equation 1.3-41, which, for reactions of order one is  $\ln W$ , versus  $\ln T$  should yield a line with slope related to  $E_a$  and intercept to  $A$ . The result of such a fit is shown in Figure 3.3.2-2 for PC(Lab) and in Figure 3.3.2-3 for PC(Lex). The PC(Lab) parameters are very close to the standard values with  $E_a = 190.2$  kJ/mol and  $A = 1.48 \times 10^{12}$ . The fit for the commercial grade, though, is somewhat low in comparison to the standard with  $E_a = 164.0$  kJ/mol and  $A = 3.6 \times 10^9$ . The fact that the results for the lab grade material seem so accurate lends support to the validity of this method even though a mathematical approximation is utilized.

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<sup>14</sup> Reich, L., H. T. Lee, and D. W. Levi, *J. Appl. Polym. Sci.*, **9**, 351, 1965.

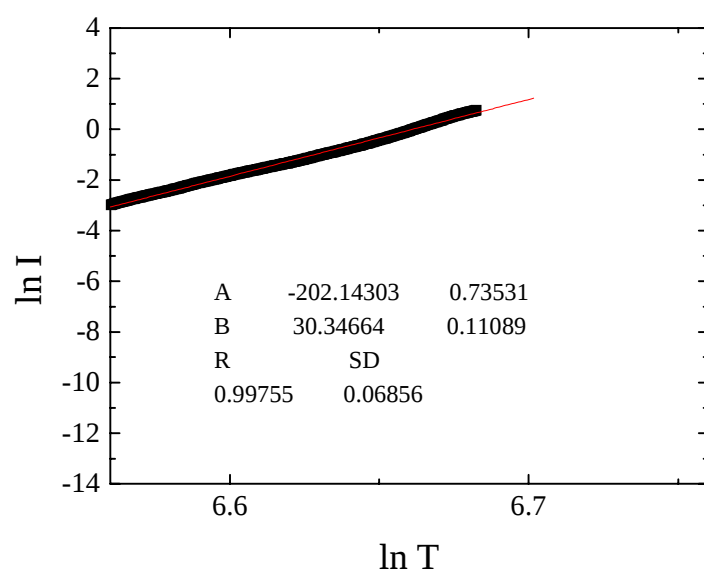


Figure 3.3.2-2 PC(Lab) analyzed according to the method of Van Krevelen.

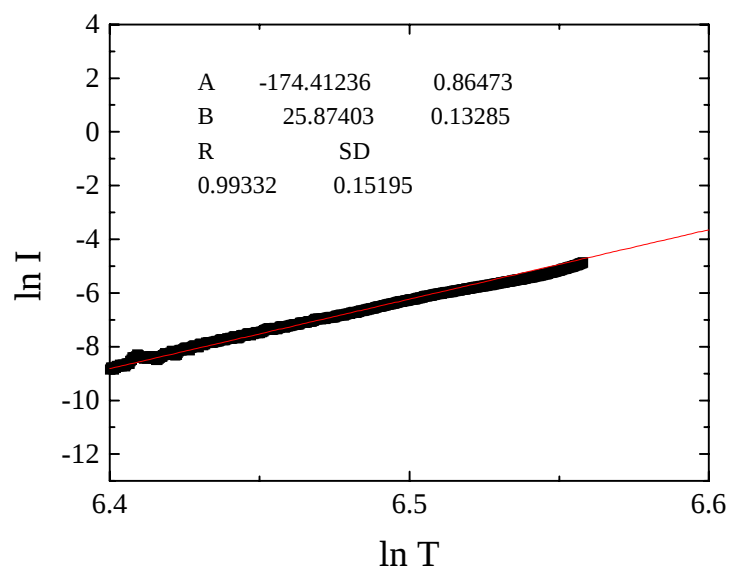


Figure 3.3.2-3 PC(Lex) analyzed according to the method of Van Krevelen.

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<sup>15</sup> Van Krevelen, D. W., C. Van Heerden, and F. J. Huntjens, *Fuel*, **30**, 253, 1951.

Horowitz and Metzger<sup>16,17</sup> developed a TGA analysis scheme, initially intended for the case where all products are gaseous. However, for the situation, as in the present study, where some residual solid remains from a first order reaction, modifications are made. For instance, they define a term,  $c$ , such that

$$c = \frac{w_i - w_f}{w(t) - w_f} \quad \text{Eqn. 3.3.2-3}$$

and another quantity,  $\theta$ , which is equal to  $T - T_s$  where  $T_s$  is the temperature where  $c = 1/e$ . Then, a plot of  $\ln \ln 1/c$  versus  $\theta$  results in a line with slope related to the activation energy and intercept of  $A$ . As with the previous technique, the results for PC(Lab) agree reasonably well with the standard values with  $E_a = 218.6 \pm 0.8$  kJ/mol and  $A = 1.7 \times 10^{14}$ . For PC(Lex), though, the values are higher than expected with  $E_a = 298.0 \pm 1.2$  kJ/mol and  $A = 2.4 \times 10^{19}$ . The fits themselves are illustrated in Figure 3.3.2-4 and Figure 3.3.2-5.

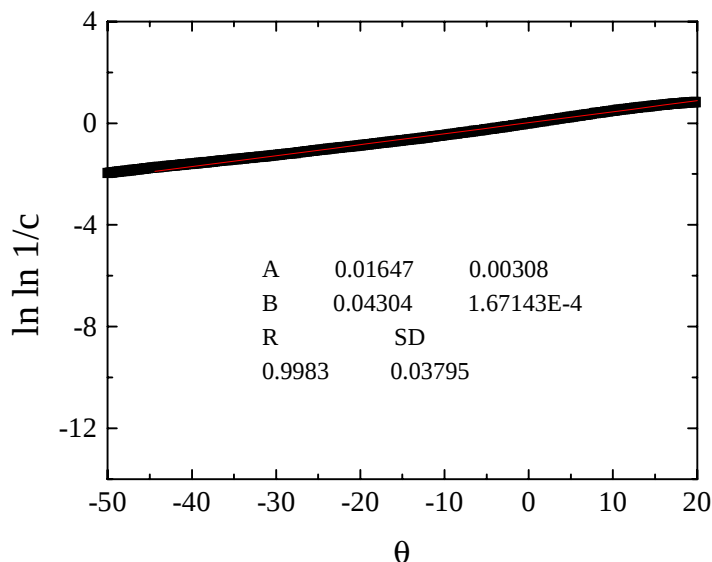


Figure 3.3.2-4 PC(Lab) analyzed according to the method of Horowitz and Metzger.

<sup>16</sup> Horowitz, H. H., and G. Metzger, *Anal. Chem.*, **35**, 1464, 1963.

<sup>17</sup> Horowitz, H. H., and G. Metzger, *Fuel*, **42**, 418, 1963.

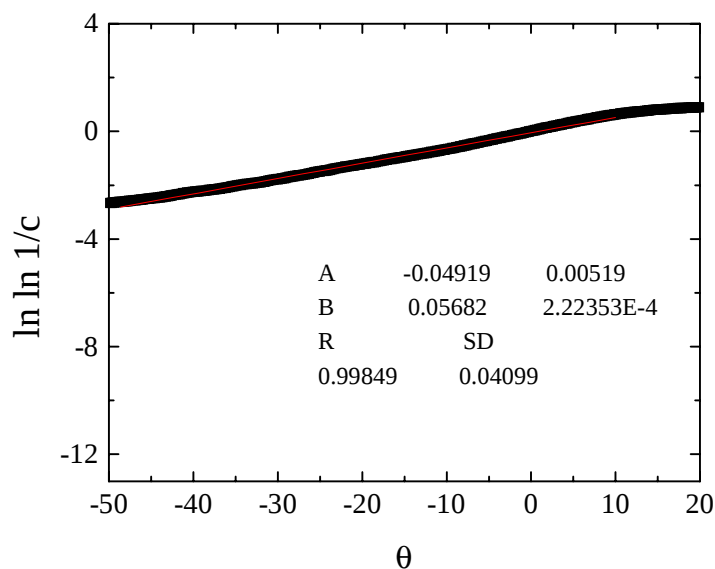


Figure 3.3.2-5 PC(Lex) analyzed according to the method of Horowitz and Metzger.

Another fairly complicated approach to TGA degradation studies, which requires thermograms at several heating rates, was offered by Friedman<sup>18,19</sup>. To apply the technique, several values are first chosen for  $W/W_0$  where  $W$  is the sample weight and  $W_0$  is the initial weight. Next, a plot of  $-\frac{1}{W_0} \frac{dW}{dt}$  versus  $1/T$  yields a linear fit with slope  $-E_a/R$  and intercept  $\ln [A f(W/W_0)]$ . Elucidation of  $A$  requires averaging values of  $\ln [A f(W/W_0)]$  at each value of  $W/W_0$  and then plotting those values against  $\ln \left[ \frac{W - W_f}{W_0} \right]$ . The result should be a line with slope of  $n$  and intercept equal to  $\ln A$ .

The graphical fits for this technique are shown in Figure 3.3.2-6. The activation energies calculated in this manner are  $186.1 \pm 42.2$  kJ/mol for PC(Lex) and  $153.3 \pm 18.7$  kJ/mol for PC(Lab). Orders of reaction seem quite unreasonable with values of  $-19$  and  $-15$ , respectively. The natural logarithm of the pre-exponential factors can be calculated as

<sup>18</sup> Friedman, H. L., *Polym. Preprints*, **4**, 662, 1963.

<sup>19</sup> Friedman, H. L., *J. Poly., Sci., Part C*, **6**, 183, 1964.

15.0 and 13.9 which are several orders of magnitude lower than the standard value of approximately  $\ln A = 28$  for both materials.

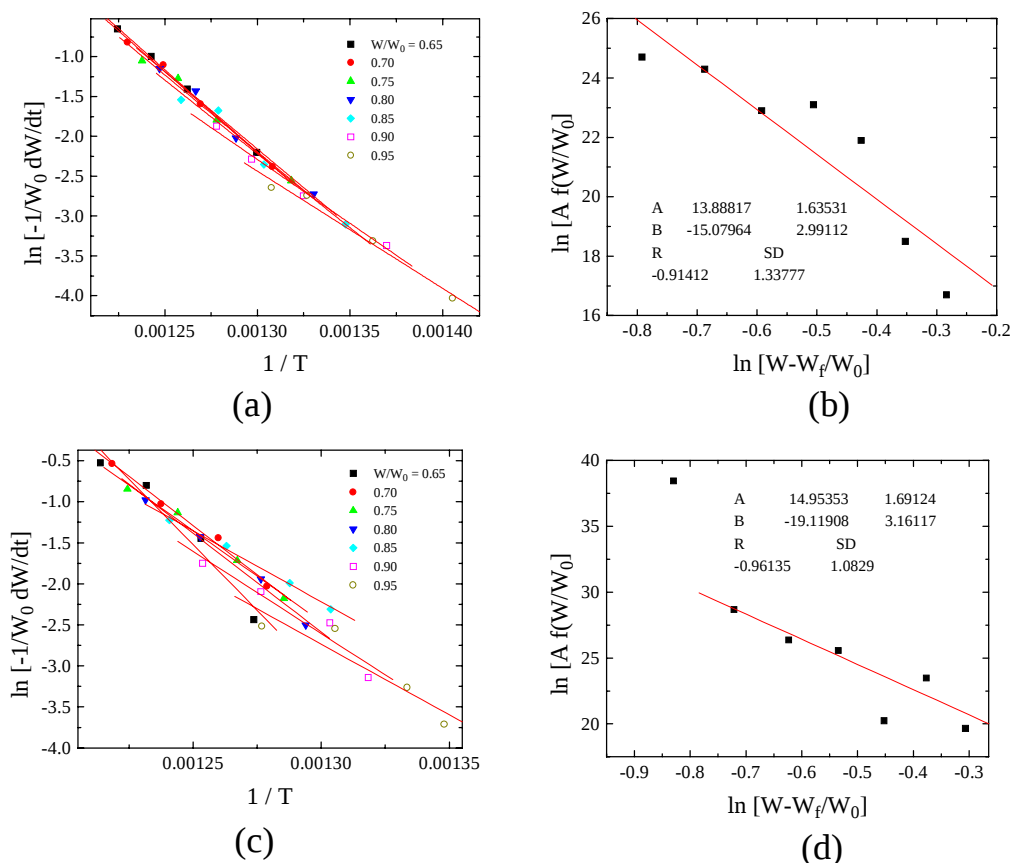


Figure 3.3.2-6 Application of Friedman's method to: (a) and (b) PC(Lab); and (c) and (d) PC(Lex).

Some authors have attempted to describe the thermogram from a purely mathematical viewpoint, as could be done with any geometric shape, and then relate the constants from this fit to the activation energy and the pre-exponential factor. Doyle<sup>20,21</sup> proposes such a method, but the complexity involved obviates any usefulness it may have. Calculation of the kinetic parameters requires successive approximations, which is so labor intensive that the technique was not applied to the data of the present study.

<sup>20</sup> Doyle, C. D., *J. Appl. Polym. Sci.*, **5**, 285, 1961.

<sup>21</sup> Doyle, C. D., *J. Appl. Polym. Sci.*, **6**, 639, 1962.

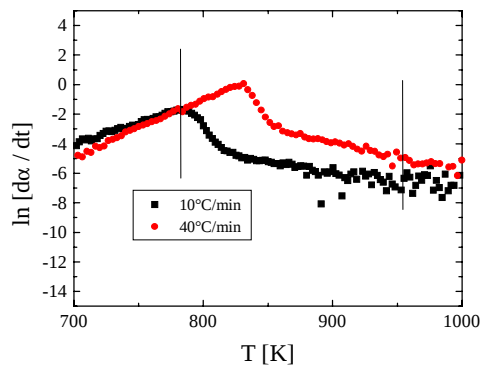
Another graphical technique was developed by Reich, Lee, and Levi<sup>22,23,24</sup>. Their procedure requires two thermograms of the same material but at different heating rates. The areas between these thermograms are related to the kinetic parameters. When one plots  $\ln R_t (=d\alpha/dt)$  versus temperature and measures the area between the curves for the two heating rates a value for  $A_R$  is accessible. Similarly, plotting  $\ln W$  versus  $T$  leads to  $A_W$ . It is reported that the reaction order,  $n$ , is simply the ratio of these two quantities,  $A_R/A_W$ . The next step is to plot  $[\ln R_t - n \ln W]$  versus reciprocal temperature which leads to a line with slope  $-E_a/R$  and intercept  $\ln A$ . This method was applied to both grades of PC at heating rates of 10°C/min and 40°C/min. The reaction orders are significantly higher than unity found with the standard method. For PC(Lab),  $n = 4.1$ , and  $n = 6.2$  for PC(Lex). The other parameters for PC(Lab) were  $E_a = 184.0 \pm 2.1$  kJ/mol and  $\ln A = 19.2 \pm 0.4$ , and  $E_a = 304.3 \pm 3.5$  kJ/mol and  $\ln A = 30.2 \pm 0.6$  for PC(Lex). The graphical results are illustrated in Figure 3.3.2-7.

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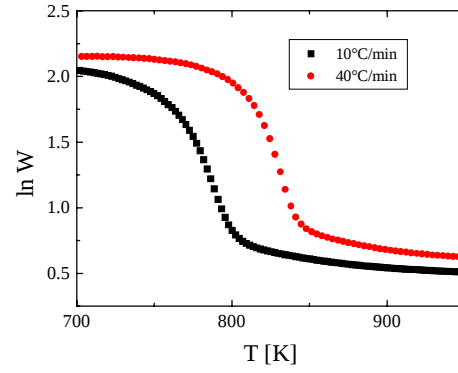
<sup>22</sup> Reich, L. and D. W. Levi, *J. Poly. Sci., Part B*, **2**, 1109, 1964.

<sup>23</sup> Levi, D. W., L. Reich, and H. T. Lee, *Polym. Engr. Sci.*, **5**, 135, 1965.

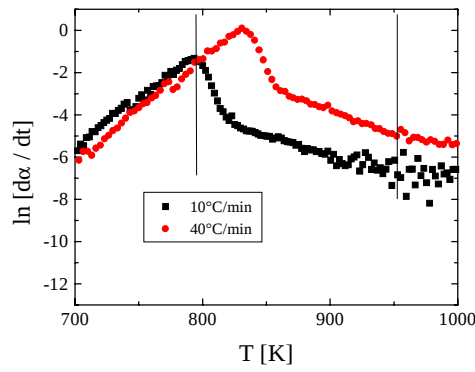
<sup>24</sup> Reich, L. and D. W. Levi, *Macromol. Rev.*, **1**, p. 188 Ed. A. Peterlin, M. Goodman, S. Okamura, B. H. Zimm, H. F. Mark, Wiley, NY, 1967.



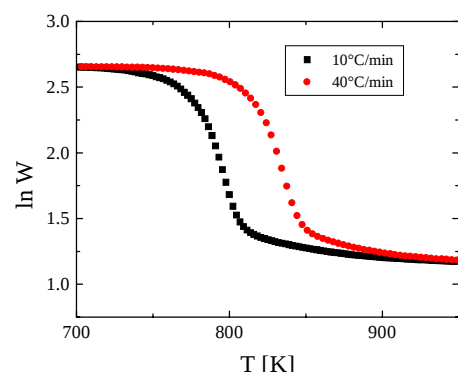
(a)



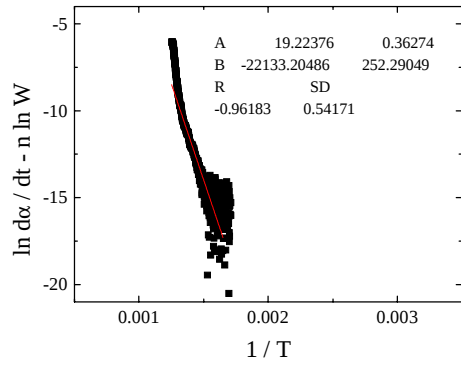
(b)



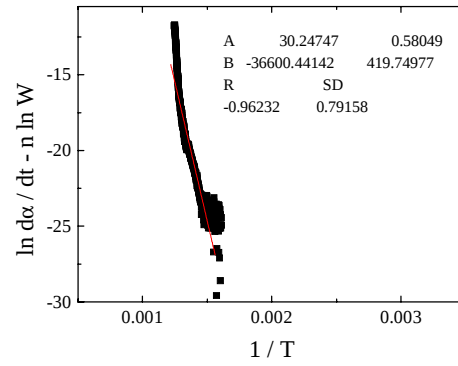
(c)



(d)



(e)



(f)

Figure 3.3.2-7 Reich's method applied to PC. (a) and (b):  $A_R$  and  $A_W$  for PC(Lab); (c) and (d):  $A_R$  and  $A_W$  for PC(Lex); (e) linear fit for PC(Lab); (f) linear fit for PC(Lex).

Reich<sup>25</sup> also developed another approach for data treatment of the type in which we are interested. In this technique, a quantity  $S$  is defined as

$$S = \frac{dW_C}{d(1/T)} \quad \text{Eqn. 3.3.2-4}$$

$$W_{0,C} = W_0 - W_R$$

$$W_C = W - W_R$$

where  $W_R$  is the weight fraction remaining after pyrolysis is complete and  $W$  is the sample weight fraction at time  $t$ . To apply the method, first an order of reaction must be estimated. This can be accomplished using a theoretical plot which features  $n$  versus  $S_1/S_2$  for various values of  $W_1/W_2$  (where  $W_1$  and  $W_2$  are different fractional conversions and  $S_1$  and  $S_2$  are each calculated according to these conversions). After determination of  $n$ ,  $E_a$  is found from

$$\frac{E_a}{R} = \frac{S}{[W_C \ln(W_{0,C} / W_C)]} \quad \text{if } n = 1 \quad \text{Eqn. 3.3.2-5}$$

$$\frac{E_a}{R} = \frac{S(1-n)}{W_C^n (W_{0,C}^{(1-n)} - W_C^{(1-n)})} \quad \text{for } n \neq 1$$

Finally,  $A$  is calculated from

$$\log A = \log \left\{ [S(RH) / W^n \left( \frac{1}{T} \right)^2] \right\} + \frac{E_a}{2.3RT} \quad \text{Eqn. 3.3.2-6}$$

Application of this procedure leads to a value of 0.35 for the reaction order for both grades of PC. PC(Lex) is found to exhibit  $E_a = 241.5$  kJ/mol and  $\ln A = 39.6$ , while PC(Lab) was calculated to have  $E_a = 171.6$  kJ/mol and  $\ln A = 29.0$ . The activation energy values are close to those calculated from the standard method as is the pre-exponential factor for the lab grade polymer. The reaction orders are somewhat low but are certainly more reasonable than those calculated from most other methods. While this approach requires a bit of trial and error approximation, the results seem to be fairly accurate, and the speed of obtaining the data (with a single thermogram) further favors the technique.

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<sup>25</sup> Reich, L. *J. Appl. Polym. Sci.*, **9**, 3033, 1965.

A popular “isoconversional” method was developed first by Flynn and Wall<sup>26,27,28</sup> and then extended by Ozawa<sup>29,30,31,32</sup>. This procedure involves plotting the logarithm of  $\beta$  (heating rate) versus  $1/T$  for fixed values of conversion,  $\alpha$ , with the resulting line having slope proportional to  $E_a$ . Ozawa reports that it is possible to also derive values for both  $A$  and  $n$  from an extension of this technique, but such a proposition is so complex that it was not attempted for the data of the present study.

To apply this “isoconversional” method, heating rates of 10, 20, 30, and 40°C/min were chosen, as were conversions of  $\alpha = 0.6, 0.7, 0.8$ , and  $0.9$ . Graphs of the data are shown in Figure 3.3.2-8 and Figure 3.3.2-9, and from these, the activation energies were found to be  $385.2 \pm 22.3$  kJ/mol for PC(Lab) and  $433.0 \pm 5.0$  kJ/mol for PC(Lex). One advantage of this method is that any changes in the mechanism of the degradation are immediately apparent as variations in the slope for different conversions. In this case, the slopes appear relatively constant, implying no such changes in mechanism over the entire conversion range studied. This technique suffers, though, in that several specimens are required, leading to potential sample-to-sample error, and in the high values it yields for the activation energy.

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<sup>26</sup> Flynn, J. H. and L. A. Wall, *J. Res. Natl. Bur. Stds.*, **70A**, 504, 1966.

<sup>27</sup> Flynn, J. H. and L. A. Wall, *Polym. Lett.*, **4**, 323, 1966.

<sup>28</sup> Flynn, J. H., *J. Therm. Anal.*, **27**, 95, 1983.

<sup>29</sup> Ozawa, T., *Bull. Chem. Soc. Japan*, **38**, 1881, 1965.

<sup>30</sup> Ozawa, T., *J. Therm. Anal.*, **2**, 301, 1970.

<sup>31</sup> Ozawa, T., *J. Therm. Anal.*, **31**, 301, 1986.

<sup>32</sup> Ozawa, T., *J. Therm. Anal.*, **37**, 1299, 1991.

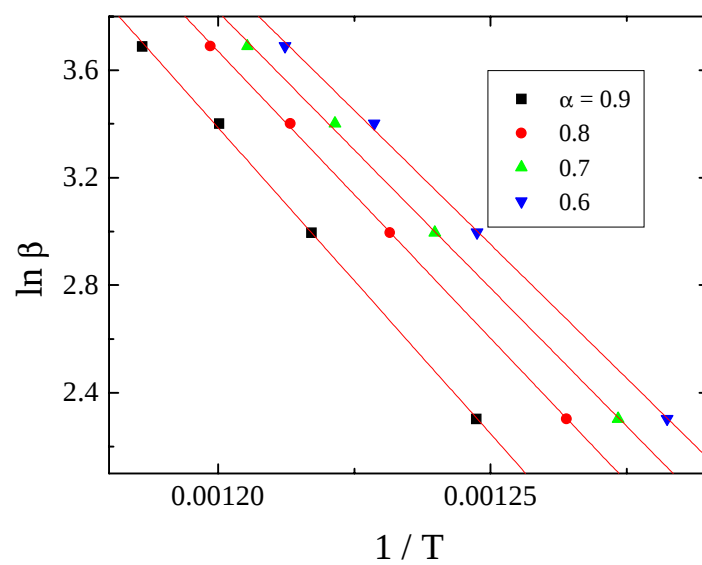


Figure 3.3.2-8 PC(Lab) as plotted via Ozawa's technique.

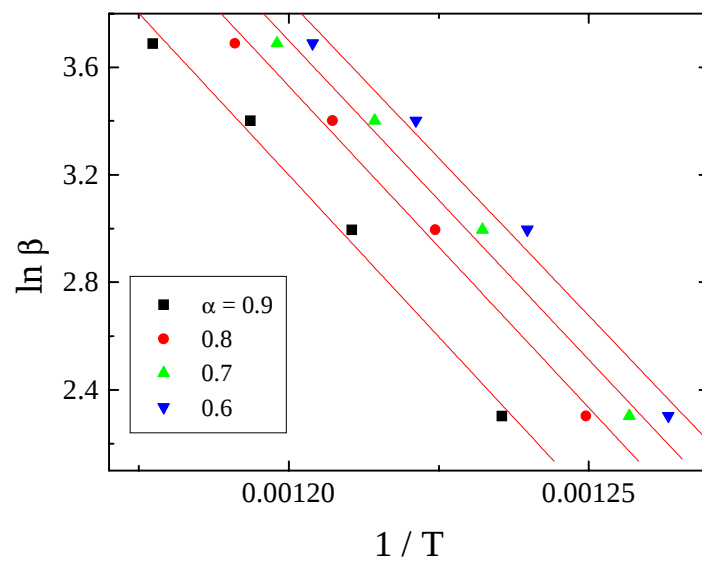


Figure 3.3.2-9 PC(Lex) as plotted via Ozawa's technique.

Flynn<sup>3334</sup> was also involved with an entirely different approach which applies at low conversions,  $\alpha \leq 0.05$ . It was shown that plotting  $T^2 \left( \frac{d\alpha}{dT} \right)$  versus  $\alpha$  resulted in a line with slope approximately  $\frac{E_a}{R} + 2T_i$  for small conversions and where  $T_i$  is the initial temperature. After  $E_a$  is found, a plot of  $\ln \frac{d\alpha}{dt} + \frac{E_a}{RT}$  versus  $\ln (1-\alpha)$  yields a line with slope of  $n$  and intercept equal to  $\ln A$ . The results of these two fits are illustrated for both PC grades in Figure 3.3.2-10. According to this technique, PC(Lex) has an activation energy of  $272.6 \pm 2.6$  kJ/mol,  $\ln A = 41.1 \pm 0.01$ , and  $n = 5.8 \pm 0.3$ . Similarly, PC(Lab) exhibits  $E_a = 189.9 \pm 2.7$  kJ/mol,  $\ln A = 43.1 \pm 0.04$ , and  $n = 9.9 \pm 1.3$ . While the values for activation energy are comparable to the standard ones, both the pre-exponential factor and the reaction order results are higher than with other techniques. As with several of the other techniques, then, this one is convenient for predicting activation energy, but further results could be inaccurate.

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<sup>33</sup> Flynn, J. H. and L. A. Wall, *Polym. Lett.*, **5**, 191, 1967.

<sup>34</sup> Flynn, J. H. and B. Dickens, *ACS Symp. Series*, **95**, *Durability of Macromolecular Materials*, Washington, DC, 1979.

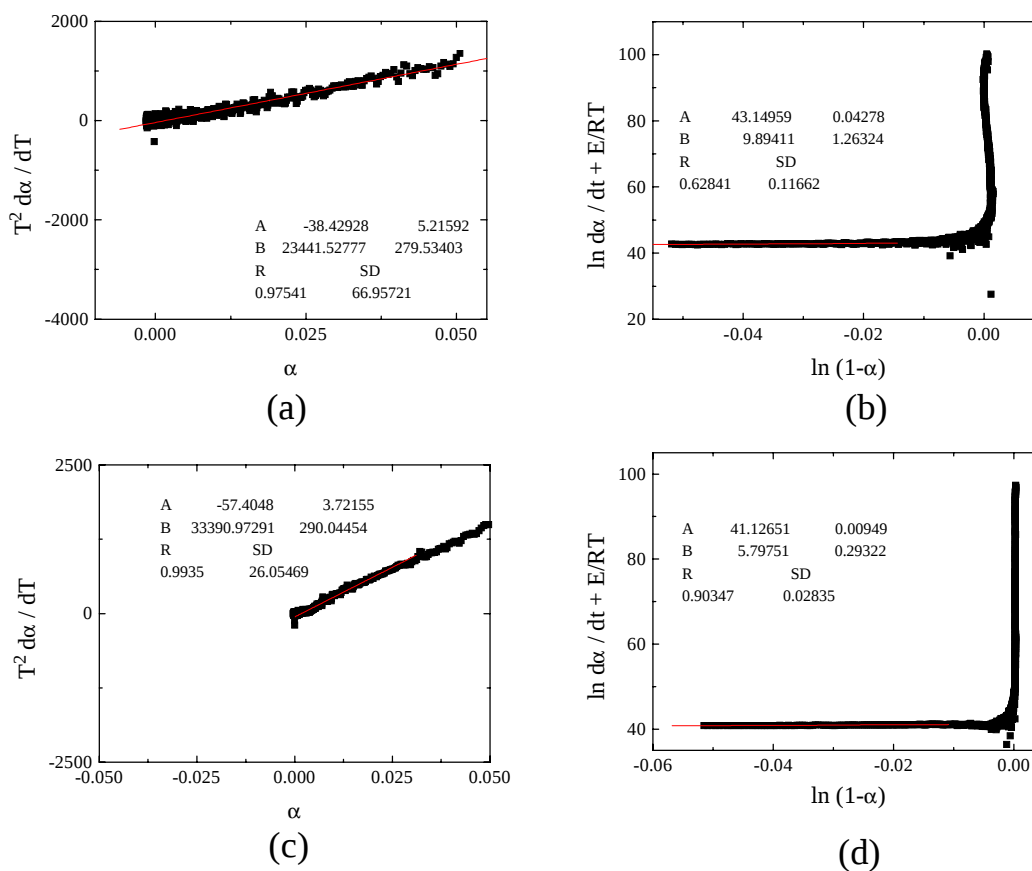


Figure 3.3.2-10 Flynn's procedure applied to: (a) and (b) PC(Lab); and (c) and (d) PC(Lex).

Following from the work of van Krevelen<sup>15</sup> and Horowitz and Metzger<sup>16,17</sup>, Broido<sup>35</sup> developed a more complicated technique which involves the use of tabulated values and an assumed reaction order. Because of the difficulties inherent in this type of approach, this method was not applied to the present data.

A very simple TGA degradation data model was put forth by Coats and Redfern.<sup>36</sup> They show that a plot of  $\ln \alpha/T^2$  versus  $1/T$  should yield a line with slope related to  $E_a$  for small  $\alpha$  ( $< 0.3$ ). These fits, for lab grade and commercial Lexan, are shown in Figure 3.3.2-11 and Figure 3.3.2-12. While the data plotted in such a manner does indeed show linear response as required, the values for the activation energy are extremely low at 15.2

<sup>35</sup> Broido, A., *J. Polym. Sci, Part A-2*, **7**, 1761, 1969.

<sup>36</sup> Coats, A. W. and J. P. Redfern, *Polym. Lett.*, **3**, 917, 1965.

$\pm 0.3$  kJ/mol (PC(Lex)) and  $15.6 \pm 0.3$  kJ/mol (PC(Lab)). Application of this technique, then, while simple, does not seem to produce accurate results.

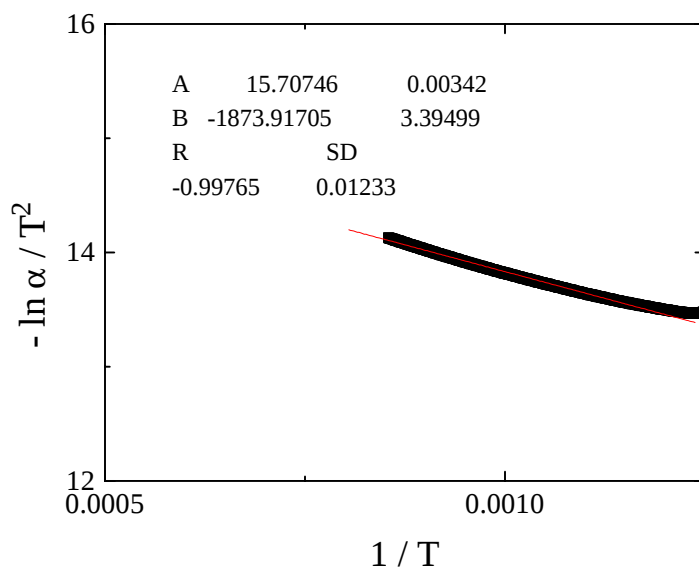


Figure 3.3.2-11 Coats and Redfern's method applied to PC(Lab).

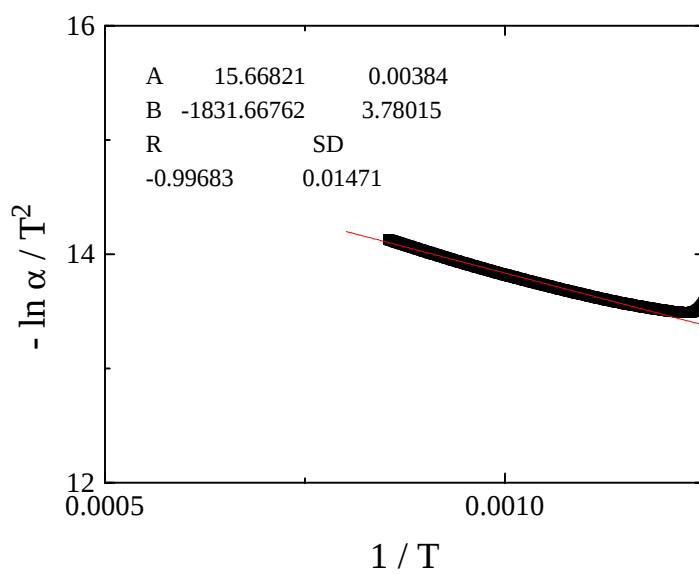


Figure 3.3.2-12 Coats and Redfern's method applied to PC(Lex).

Another simple method, proposed recently by Tagle and Diaz<sup>37,38</sup>, involves plotting  $F = \ln \left[ \frac{-(d\alpha/dT)}{(1-\alpha)^n} \right]$  versus  $1/T$ . When the reaction order is taken to be unity, the resultant line has a slope proportional to  $E_a$  and an intercept related to  $A$ . Such graphs are illustrated in Figure 3.3.2-13 and Figure 3.3.2-14 for both PC polymers. For PC(Lab),  $E_a = 179.0 \pm 1.0 \text{ kJ/mol}$  and  $\ln A = 26.6 \pm 0.2$ . PC(Lex) yields values of  $E_a = 247.0 \pm 1.6 \text{ kJ/mol}$  and  $\ln A = 36.6 \pm 0.3$ . These values compare quite well with those of the standard isothermal method, and that fact, combined with the ease of application of the technique, makes it an attractive option.

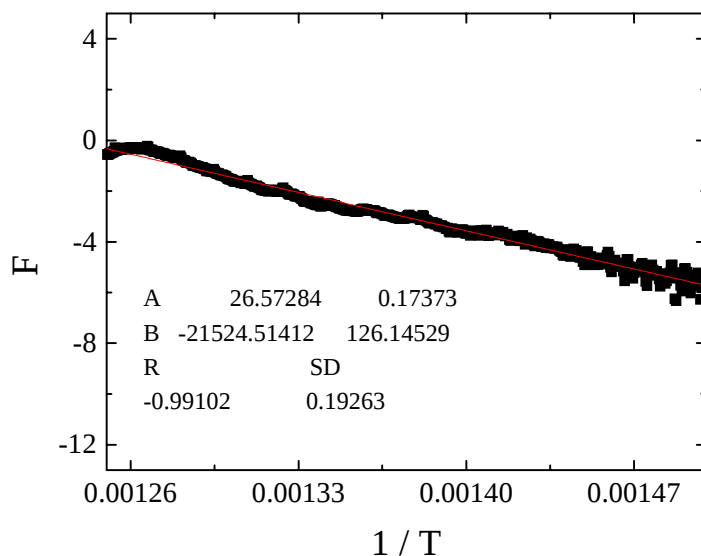


Figure 3.3.2-13 PC(Lab) analyzed according to Tagle's method.

<sup>37</sup> Tagle, L. H. and Diaz, F. R., *Thermochim. Acta*, **160**, 161, 1990.

<sup>38</sup> Tagle, L. H. and Diaz, F. R., *Intern. J. Polym. Mater.*, **26**, 207, 1994.

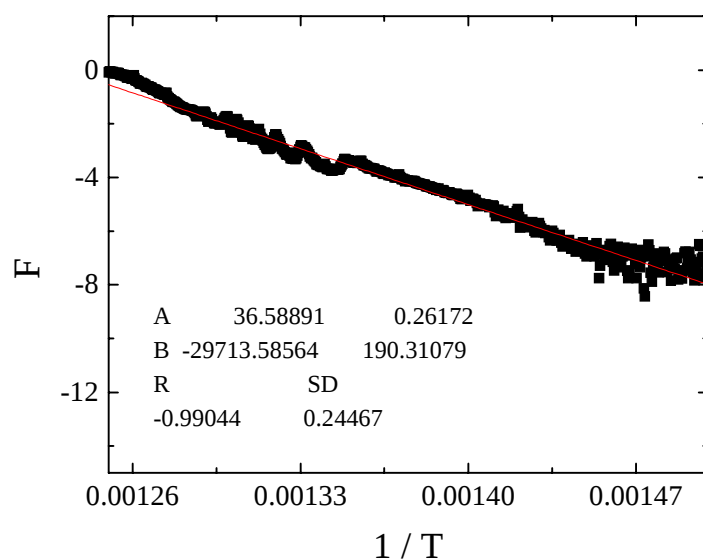


Figure 3.3.2-14 PC(Lex) analyzed according to Tagle's method.

In summary, numerous dynamic analysis methods were applied to both the laboratory grade and commercial grade polycarbonates. The resulting parameters are summarized in Table 3.3.2-1.

Table 3.3.2-1

Summary of Results from Dynamic Analyses for both Polycarbonates

| Method       | E <sub>a</sub> [kJ/mol] |              | ln A [ln min <sup>-1</sup> ] |            | n          |            |
|--------------|-------------------------|--------------|------------------------------|------------|------------|------------|
|              | PC(Lab)                 | PC(Lex)      | PC(Lab)                      | PC(Lex)    | PC(Lab)    | PC(Lex)    |
| Freeman      | 360.4                   | 200.0 (74.3) | ---                          | ---        | 0.94 (0.2) | 1.18 (0.1) |
| Fuoss/Reich  | 278.2                   | 428.7        | 42.2                         | 64.8       | ---        | ---        |
| van Krevelen | 190.2                   | 164.0        | 28.0                         | 22.0       | 1*         | 1*         |
| Horowitz     | 218.6 (0.8)             | 298.0 (1.2)  | 32.8                         | 44.6       | 1*         | 1*         |
| Friedman     | 153.3 (18.7)            | 186.1 (42.2) | 13.9                         | 15.0       | -15        | -19        |
| Reich/Lee    | 194.0 (2.1)             | 304.3 (3.5)  | 19.2 (0.4)                   | 30.2 (0.6) | 4.1        | 6.2        |
| Reich        | 171.6                   | 241.5        | 29.0                         | 39.6       | 0.35       | 0.35       |
| Flynn/Ozawa  | 385.2 (22.3)            | 433.0 (5.0)  | ---                          | ---        | ---        | ---        |
| Flynn        | 189.9 (2.7)             | 272.6 (2.6)  | 43.1                         | 41.1       | 9.9 (1.3)  | 5.8 (0.3)  |
| Coats        | 15.6 (0.3)              | 15.2 (0.3)   | ---                          | ---        | ---        | ---        |
| Tagle        | 179.0 (1.0)             | 247.0 (1.6)  | 26.6 (0.2)                   | 36.6 (0.3) | ---        | ---        |

\*assumed value

### 3.4 Summary

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From the many examples just outlined, it is clear that application of different analytical techniques to two grades of bisphenol A polycarbonate result in broadly varying parameters for pre-exponential factor and reaction rate constant. One observation from the data obtained in this study is that the majority of the methods, whether isothermal or dynamic, result in activation energies which are comparable to those from the standard procedure. In terms of agreement with the values obtained from the standard scheme, dynamic techniques proposed by Freeman, van Krevelen, and Tagle seem to provide the closest matches. It is worth noting, however, that none of these procedures yield values for all three parameters of interest. Thus, for serious kinetic study, the standard isothermal technique is still the recommended method.