

## Chapter

### 1. Literature Review of Structural Features

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#### 1.1. Introduction

The use of polymers for various applications has increased dramatically in recent years. As these substances are used in more demanding circumstances, the behavior of the polymer over long times and under extreme conditions becomes increasingly important. Nowhere is this more evident than in the area of plastics recycling.

As society and industry have become more environmentally conscious, there has been a push to eliminate waste as much as possible. Polymers are prime targets since they do not degrade as readily as some other wastes, such as paper, when landfilled, and for the fact that they make up a substantial portion of the municipal solid waste (MSW). For these reasons, recycling has become an attractive alternative to merely discarding plastics materials. However, reprocessing involves remelting the material so that it is subjected to high temperatures and shear forces necessary to form usable parts. These conditions often result in changes in the polymer's molecular weight, either through chain scission or transesterification. Consequently, properties of recycled polymers are almost universally inferior to those of "virgin" (nonrecycled) resins.

Most research dealing with reprocessing plastics has taken a very "black box" approach. Properties are measured after each processing step to determine for what type of application the material is now suitable. Little effort has been made, however, to understand what is actually happening to the polymer on a fundamental level. Conversely, many scientists have examined the degradation of polymers by subjecting them to specific time-temperature steps and monitoring some property such as sample weight or molecular weight. Clearly, this type of degradation is analogous to the thermal cycles encountered by a resin during reprocessing. Few, if any, researchers have bridged the gap between these two areas to give a clear picture of the relationship between this degradation and subsequent end-use properties. Being able to predict properties after

exposure to a certain temperature for a given time could enable more precise engineering of materials for specific applications with less possibility of failure.

This proposed study seeks to begin building this fundamental link between molecular and engineering models by carefully examining the degradation mechanisms and kinetics of a specific polymer, bisphenol A polycarbonate. This information will then be used as a tool to try and predict properties and understand long-term behavior for both recycled and virgin plastics.

In order to place the proposed research in the context of related efforts, a review of relevant literature follows. As mentioned previously, most research has focused on either structural aspects of the degradation or on property changes. Therefore, the review is organized in that manner as well. The structural section will outline one group's approach to polymer degradation including a novel technique dealing with molecular weights, will then focus specifically on the chemistry of polycarbonate degradation, and finally will highlight several analysis methods for interpreting kinetic data. The next portion will examine some specific characteristics of polycarbonate, summarizing some rheological data and looking at various relationships between molecular weight and properties such as  $T_g$  and tensile strength. Finally, the details of the proposed research project will be outlined in the last section.

## **1.2. Molecular Weight Distribution Superposition**

A recent study by Chan and Balke<sup>1,2,3</sup> took a fundamental approach to polymer thermal degradation. Polypropylene powder was placed in pyrex tubes which had been previously purged with argon gas, the powder was packed down by tapping the vials, and the open ends of the tubes were sealed using several layers of teflon tape. The tubes were then placed in a temperature-controlled fluidized bed for various times ranging from 2 minutes to 14 days to impart well-defined thermal histories. After the appropriate time, the tubes were quenched in ice water and samples taken from the center portion where

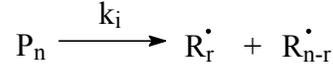
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<sup>1</sup> Chan, J. H. and S. J. Balke, *Polym. Degrad. and Stab.*, **57**, 113, 1997.

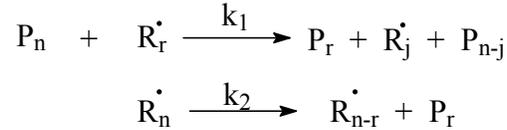
<sup>2</sup> Chan, J. H. and S. J. Balke, *Polym. Degrad. and Stab.*, **57**, 127, 1997.

heating was more uniform. Gel permeation chromatography was carefully carried out for each sample to detect any changes in molecular weights and distributions.

One of the areas of interest regarding these degraded samples was the kinetics of the degradation. In order to follow the kinetics, a comprehensive model of the various possible reactions (initiation, transfer, scission, and termination) was developed. In this model, it was assumed that initiation consists of decomposition into two free radicals:

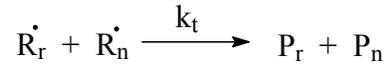


where P is polymer, R $\cdot$  is a free radical, and n and r are chain lengths. It is further assumed that chain scission is random, and that any transfer (to stabilizers, impurities, or solvents) is negligible such that



Here again, j is a chain length.

Termination by combination is taken to be negligible, especially at high temperatures. The resulting disproportionation reaction is as follows:



In these reactions,  $k_i$ ,  $k_1$ ,  $k_2$ , and  $k_t$  are the reaction rate constants.

The next step is to write the rate equations:

$$\frac{d[P_n]}{dt} = \lambda_1 - \lambda_2[P_n] \quad \text{Equation 1.2-1}$$

$$\frac{d[R_n^\cdot]}{dt} = \lambda_3 - \lambda_4[R_n^\cdot] \quad \text{Equation 1.2-2}$$

$$\lambda_1 = k_i[R^\cdot] \sum_{r=n+1}^{\infty} [P_r] + k_2 \sum_{r=n+1}^{\infty} [R_r^\cdot] + \left( k_1 \frac{\rho_0}{m_0} + k_t[R^\cdot] \right) [R_n^\cdot] \quad \text{Equation 1.2-3}$$

$$\lambda_2 = (k_1[R^\cdot] + k_i)(n-1) \quad \text{Equation 1.2-4}$$

<sup>3</sup> Chan, J. H. and S. J. Balke, *Polym. Degrad. and Stab.*, **57**, 135, 1997.

$$\lambda_3 = k_i \sum_{r=n+1}^{\infty} [P_n] + k_1 [R\cdot] \sum_{r=n+1}^{\infty} [P_n] + k_2 \sum_{r=n+1}^{\infty} [R_r\cdot] \quad \text{Equation 1.2-5}$$

$$\lambda_4 = k_1 \frac{\rho_0}{m_0} + k_t [R\cdot] + k_2 (n-1) \quad \text{Equation 1.2-6}$$

$$[R\cdot] = \sum_{r=1}^{\infty} [R_r\cdot] \quad \text{Equation 1.2-7}$$

where  $t$  is time,  $[R\cdot]$  is total free radical concentration,  $\rho_0$  is the polymer density, and  $m_0$  is monomer molecular weight.

Applying the pseudo-steady-state assumption,

$$\frac{d[R_n\cdot]}{dt} = 0 \quad \text{Equation 1.2-8}$$

where molar concentration of radicals does not change, leads to

$$[R_n\cdot] = \frac{\lambda_3}{\lambda_4} \quad \text{Equation 1.2-9}$$

and

$$[R\cdot] = \left( \frac{k_i}{k_t} \sum_{r=2}^{\infty} (r-1) [P_r] \right)^{1/2} \approx \left( \frac{k_i}{k_t} \times \frac{\rho_0}{m_0} \right)^{1/2} \quad \text{Equation 1.2-10}$$

It is also known that  $M$ , the molecular weight of polymer chains of length  $r$ , is given by

$$M = m_0 r \quad \text{Equation 1.2-11}$$

Then,  $W_N(\log M)$  is the weight fraction of polymer with  $\log M$  ranging from  $\log M$  to  $(\log M + d \log M)/d \log M$ , so that

$$W_N(\log M) = \frac{\log r^2 [P_r] m_0}{\rho_0} \quad \text{Equation 1.2-12}$$

This represents a normalized molecular weight distribution and provides a link between GPC results and the kinetics of the degradation process without imposing any assumptions regarding the initial molecular weight distributions of the samples.

However, this model still contains four parameters ( $k_i$ ,  $k_t$ ,  $k_1$ , and  $k_2$ ). It is desirable to simplify the model based on certain assumptions. One is that intramolecular transfer is much less likely than intermolecular transfer,  $k_2 \ll k_1$ . So, substituting Equation 1.2-9 into Equation 1.2-3 and Equation 1.2-4 and taking  $k_2$  as zero yields

$$\lambda_1 = (k_i + 2k_1[R\cdot]) \sum_{r=n+1}^{\infty} [P_r] \quad \text{Equation 1.2-13}$$

The next assumption is that over a small time interval  $dt$ ,  $\lambda_1$  and  $\lambda_2$  are constant. Equation 1.2-1 then becomes

$$\frac{d[P_n]}{\lambda_1 - \lambda_2[P_n]} = dt \quad \text{Equation 1.2-14}$$

Equation 1.2-14 is then integrated from  $t_1$  to  $t_2$  to give

$$[P_n]_2 = \frac{\lambda_1}{\lambda_2} - \left( \frac{\lambda_1}{\lambda_2} - [P_n]_1 \right) \exp[-\lambda_2(t_2 - t_1)] \quad \text{Equation 1.2-15}$$

which now contains only three parameters.

When further assumptions are made, even fewer parameters are needed. One is that initiation is much slower than propagation,  $k_i \ll k_1 [R\cdot]$ , which yields

$$\frac{d[P_n]}{dt} = \lambda'_1 - \lambda'_2[P_n] \quad \text{Equation 1.2-16}$$

$$\lambda'_1 = 2k'[R\cdot] \sum_{r=n+1}^{\infty} [P_r] \quad \text{Equation 1.2-17}$$

$$\lambda'_2 = k'(n-1) \quad \text{Equation 1.2-18}$$

$$k' = k_1[R\cdot] = k_1 \left( \frac{k_i}{k_t} \right)^{1/2} \left( \frac{\rho_0}{m_0} \right)^{1/2} \quad \text{Equation 1.2-19}$$

There is now a single parameter, an apparent rate constant given by

$$k_{app} = k_1 \left( \frac{k_i}{k_t} \right)^{1/2} \quad \text{Equation 1.2-20}$$

This model can be applied over the total time range in small time increments  $dt = t_2 - t_1$  and results in the final chain length distribution. Data from GPC measurements can be fit to this model, and in this manner, it is possible to obtain values for activation energy and rate constant for the degradation process.

The novel part of this study, which, to this author's knowledge, has never been reported, is the application of time-temperature superposition to molecular weight distributions. The time used for superposition is a reduced time,  $\tau$ , corresponding to a specific degree of degradation and defined as

$$\tau = kt \quad \text{Equation 1.2-21}$$

where  $k$  is the rate constant and  $t$  is the time of degradation. Equation 1.2-21 may be rewritten as

$$\tau = \tau(t, T) \quad \text{Equation 1.2-22}$$

Then, by including superpositioning, Equation 1.2-22 becomes

$$\tau(t, T) = \tau \left( \frac{1}{a_T}, T_0 \right) \quad \text{Equation 1.2-23}$$

It was found that this hypothesis of molecular weight distribution-reduced time superposition did indeed work. This was evidenced by the fact that samples which had the same  $\tau$  values, regardless of the time or temperature at which they were degraded, exhibited identical molecular weight distributions. The degree of degradation was, thus, presumably the same at equal  $\tau$ 's. This is illustrated in Figure 1.2-1. There was, however, no attempt to prepare molecular weight distribution master curves due to a limited amount of data available. It should also be noted that the foregoing treatment did not account for any possible chain branching reactions. Clearly, such a situation would complicate the analysis, necessitating changes in the equations for the reactions as well as in the GPC analysis.

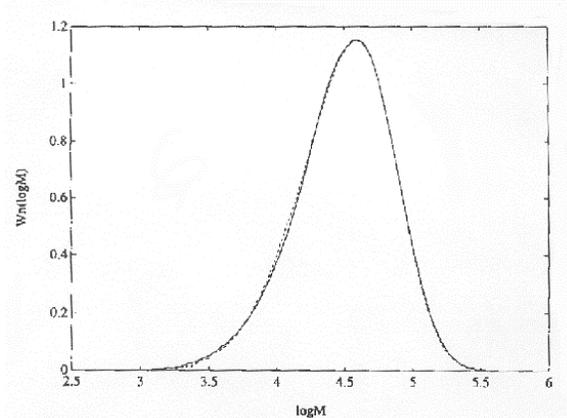


Figure 1.2-1 Comparison of two samples with different thermal histories but similar  $\tau$  values from Chan.<sup>2</sup>

While molecular weight distribution-reduced time superposition has not previously been reported, Gillen and Clough<sup>4</sup> do detail the application of time-temperature-dose rate superposition to samples which have been exposed to specified doses of radiation. While molecular weight is not explicitly dealt with, it seems quite obvious that changes in molecular weight would result from radiation. Thus, these authors are indirectly affirming the use of the molecular weight distribution superposition.

In Gillen and Clough's work, the engineering property of interest is ultimate tensile elongation,  $e$ , which has been normalized against an unaged value,  $e_0$ . Samples were tested at several levels of aging as defined by various temperatures and times. The authors point out that an Arrhenius functional form is generally used for the shift factors for chemical degradations:

$$a_T = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad \text{Equation 1.2-24}$$

To find the activation energy, first a new term, time to equivalent damage, TED, is introduced. This represents the time, at each temperature studied, where  $e/e_0$  reaches a defined value such as 50%. By plotting TED versus reciprocal time, a linear response is

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<sup>4</sup> Gillen, K. T. and R. L. Clough, *Polym. Degrad. and Stab.*, **24**, 137, 1989.

seen, and  $E_a$  can be calculated. If activation energies are equivalent for several values of  $e/e_0$ , then the same functional relationship holds and curves should be superposable over time and temperature.

To incorporate dose rates into the superposition, the dose to equivalent damage, DED, is defined analogously to the TED (i.e., the dose for  $e/e_0$  to go to 50%). One can then plot DED versus dose rate for various isotherms. A horizontal line in the graph intersects each isotherm, denoting an isodose condition. Gillen and Clough point out that “the ratio of times appropriate to two different temperatures is exactly the inverse of the ratio of the dose rates appropriate to the same two temperatures.” Therefore, finding the functional relationship for time-temperature for isodose conditions is equivalent to that between the inverse dose rate-temperature. The functional relationship posed here is of an Arrhenius form with the stipulation that  $E_a$  is independent of the isodose level and the damage level. It is as follows:

$$r = \frac{R_a}{R_c} = \exp\left[\frac{1}{T_c} - \frac{1}{T_a}\right] \quad \text{Equation 1.2-25}$$

where  $R_a$  and  $R_c$  are the dose rates and  $T_a$  and  $T_c$  are the corresponding temperatures. The authors demonstrate the successful application of this technique to the materials under study.

From these two studies, it is clear that time-temperature-molecular weight distribution superposition, which has not been widely applied, is an area that deserves closer scrutiny. It should be evident that producing master curves for these quantities would provide a powerful predictive tool for relating structural characteristics to properties of the polymer.

### 1.3. Chemistry

While the main focus of the proposed research is independent of the chemical mechanisms, that area still deserves examination. Even though polycarbonate has been studied for over 45 years, controversy still exists as to the true chemical reactions occurring during degradation. As such, and since understanding the chemistry provides a

more fundamental basis for the research, a few of the studies of polycarbonate degradation under a nitrogen atmosphere are summarized here.

Much of the earliest work on the chemical mechanism of polycarbonate degradation was carried out by Davis and Golden<sup>5,6,7</sup>. They relied on such techniques as intrinsic viscosity, mass spectrometry, and gas chromatography. The caution here, though, is that their techniques mainly accounted for volatile products. Those which did not volatilize were not detected.

Their results indicate very little decomposition below 250°C. If the system is continuously evacuated so that volatile products are removed, the material undergoes branching and eventual crosslinking to form an insoluble gel. If volatiles are not removed, chain scission is observed, obeying a first order rate equation. These two modes of degradation are the result of competition between condensation and hydrolysis.

The main volatile products of polycarbonate degradation were found to be carbon dioxide and bisphenol-A, with lesser amounts of carbon monoxide, methane, phenol, diphenyl carbonate, and 2(4-hydroxyphenyl)-2-phenyl propane. The subsequent breakdown of bisphenol-A leads to ethyl phenol, isopropenylphenol, isopropylphenol, and cresol.

Bisphenol-A polycarbonate usually has either phenyl or hydroxyl as an endgroup. Initial degradation begins at the endgroup which reacts with any free hydrogen present, such as water or free hydroxyl groups. The same products are formed regardless of the endgroup present. The reactions are shown to proceed as in Figure 1.3-1, equations 1-3. The chains with  $\text{PhCO}_3^-$  endgroups give off quantitative amounts of phenol and diphenyl carbonate while those with hydroxyl endgroups evolve only trace amounts of phenol.

It is reported that the carbonate group is the major point of degradation at temperatures below 400°C, while at higher temperatures, the isopropylidene group is also susceptible to loss of a methyl radical. By studying a model compound, diphenyl carbonate, the specific reactions have been further elucidated. Below 500°C, no free-radical reactions were observed for the carbonate group, but rearrangement of the

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<sup>5</sup> Davis, A., and J. H. Golden, *J. Gas Chrom.*, **5**, 81, 1967.

<sup>6</sup> Davis, A., and J. H. Golden, *J. Chem. Soc. Part B. Phys. Org.*, n. 1-7, 45, 1968.

<sup>7</sup> Davis, A., and J. H. Golden, *J. Macromol. Sci.-Revs. Macromol. Chem.*, **C3**, 49, 1969.

carbonate moiety prevails. It has also been reported that in air at temperatures exceeding 380°C, and times longer than 15 hours, some crosslinking occurs. This is evidenced by traces of an insoluble black residue when the material is dissolved in methylene chloride.

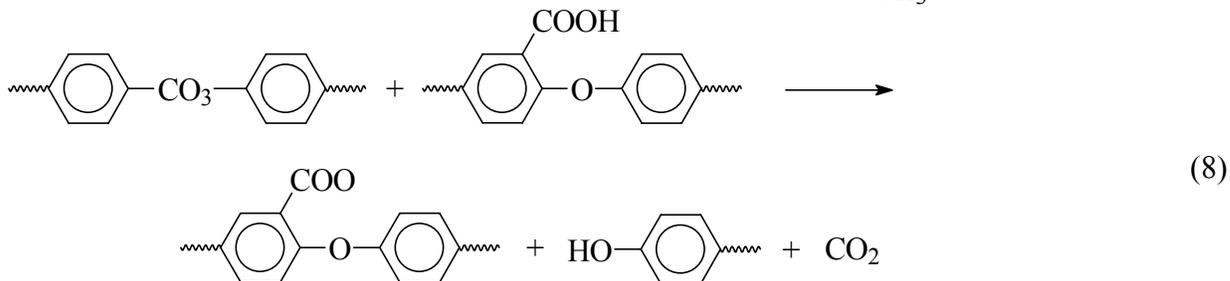
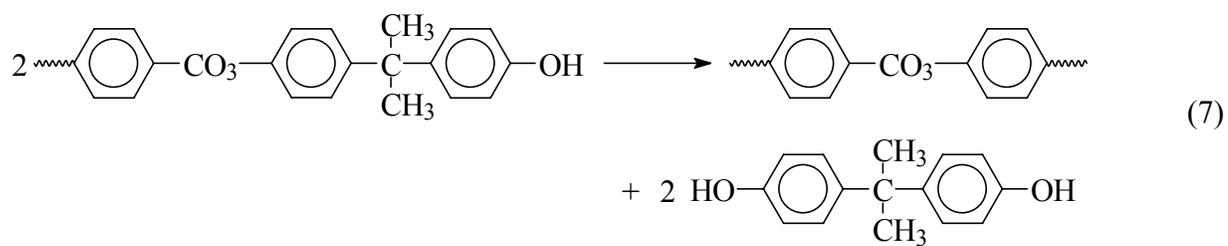
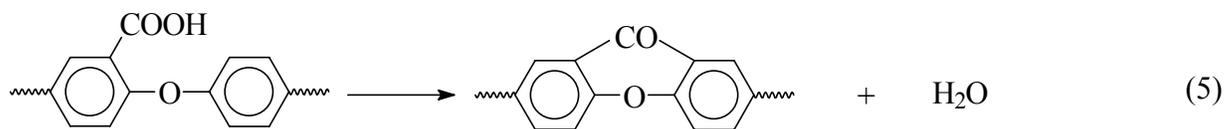
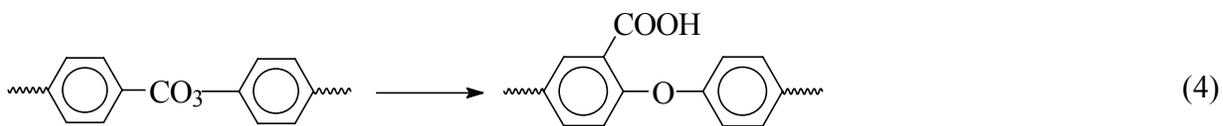
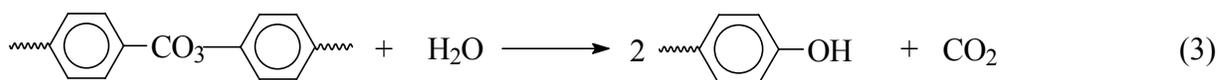
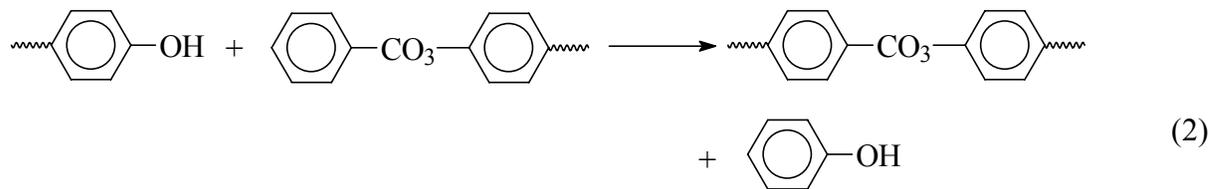
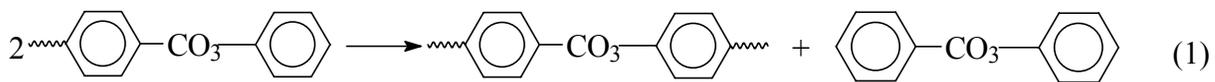


Figure 1.3-1 Davis and Golden<sup>5,6,7</sup> mechanism for polycarbonate degradation.

Using data from the model compound, Davis and Golden postulated a mechanism for BPA-PC degradation as in Figure 1.3-1, equations 4-8. In this pathway, branching can occur in (4) and (8). Gelation will only occur if 5-7 are suppressed by removal of volatiles. Otherwise, scission dominates.

Davis and Golden conclude that BPA-PC degradation is a random chain scission process occurring predominantly at the carbonate linkages. This process has also been shown to follow first order kinetics.

During the same time period, Lee<sup>8</sup> also studied the degradation of BPA-PC. From capillary rheometry, it is evident that degradation starts at temperatures above 300°C since that is where viscosity begins to drop off. Lee also employed differential thermal analysis (DTA) and determined that the degradation consisted of three stages. From mass spectrometry and vapor phase chromatography, it was found that PC first undergoes an oxidation step, as seen in Figure 1.3-2, at temperatures from 300-320°C where it is speculated that the isopropylidene group is attacked by oxygen in a free radical process. This process is retarded by employing a nitrogen atmosphere as well as by eliminating water from the sample.

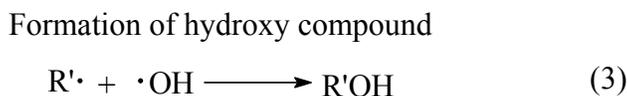
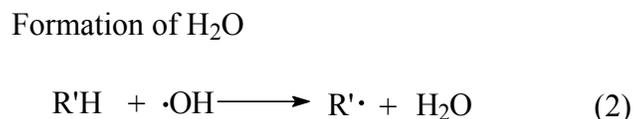


Figure 1.3-2 Lee's<sup>8</sup> degradation mechanism for PC degradation from 300-320°C.

The next step, in the range 340-380°C, is depolymerization, Figure 1.3-3, consisting of hydrolysis and alcoholysis of the carbonic ester, which is a form of ester

exchange where chains break somewhere near the middle. The hydrolysis produces CO<sub>2</sub> and either bisphenol-A (if it occurs near the chain end) or two shorter chains. Finally, at higher temperatures (480-600°C), a complex random chain scission dominates. This consists of decarboxylation, hydrolysis, hydrogen abstraction, chain scission, ether cleavage, and, under certain conditions, crosslinking. Because of the extremely high temperatures hypothesized for these reactions, they are not applicable to the proposed study and thus will not be detailed here.

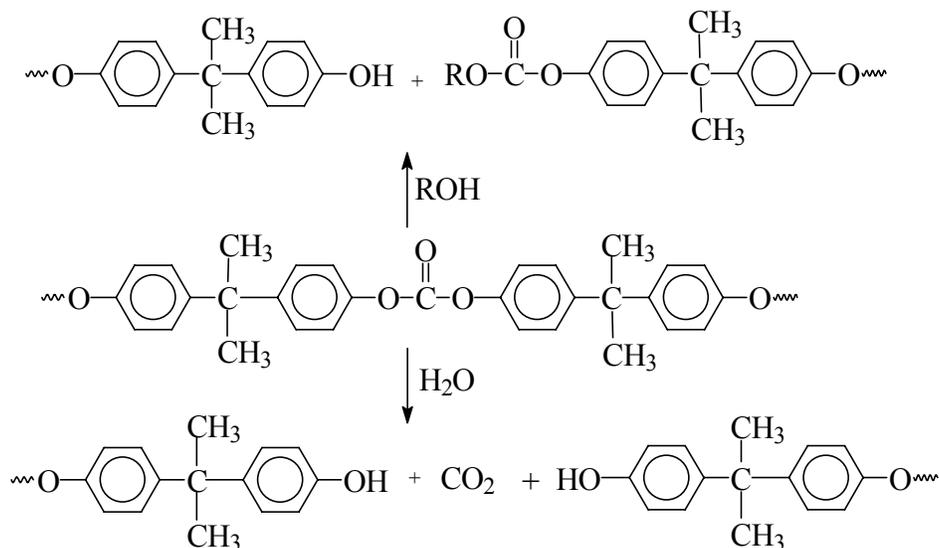


Figure 1.3-3 Lee's<sup>8</sup> degradation mechanism for 340-380°C.

Other researchers<sup>9</sup> have tried to understand the competition between scission and crosslinking of polycarbonate via mathematical models utilizing GPC data. Polycarbonate was held at 380°C for various times while the chamber was continuously evacuated. Samples were then analyzed by GPC to determine molecular weights and whether insoluble fractions were present. It was found that chain scission dominated at these conditions, but that some crosslinking did occur as evidenced by the appearance of higher molecular weights in the distribution after degradation.

It is hypothesized that the carbonate linkage in polycarbonate is the most susceptible to cleavage followed by the isopropylidene group. The ester linkage is

<sup>8</sup> Lee, L. H., *J. Polym. Sci. Part A*, **2**, 2859, 1964.

<sup>9</sup> Kuroda, S., K. Terauchi, K. Nogami, and I. Mita, *Eur. Polym. J.*, **25**, 1, 1989.

thought to be thermally stable and the site of any crosslinking. The authors present a radical reaction scheme for degradation at the isopropylidene group, and a subsequent scheme for crosslinking, which is illustrated in Figure 1.3-4.

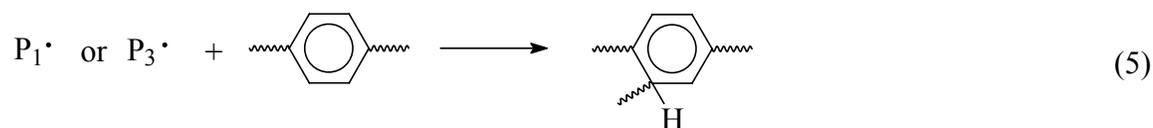
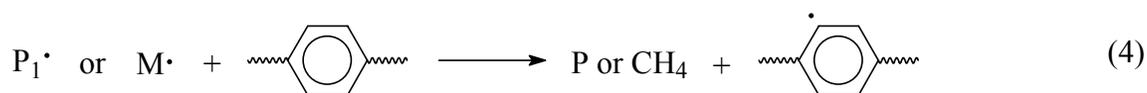
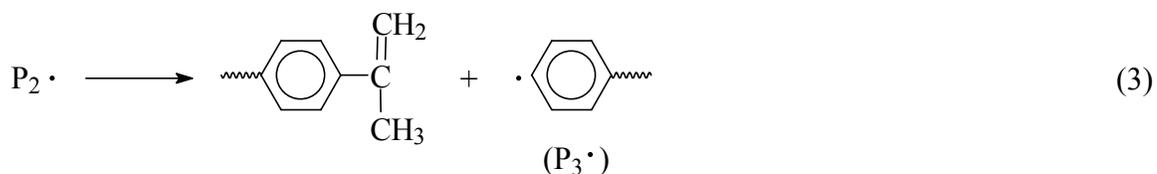
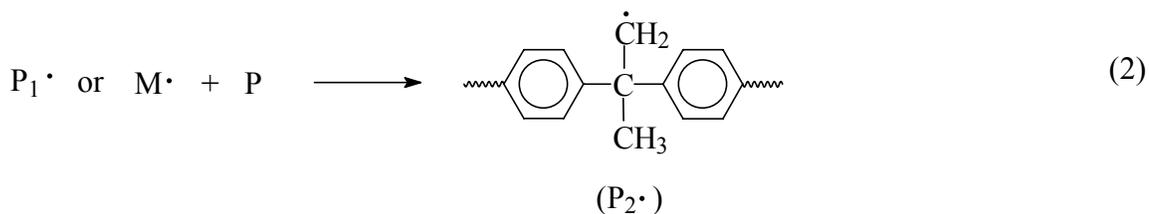
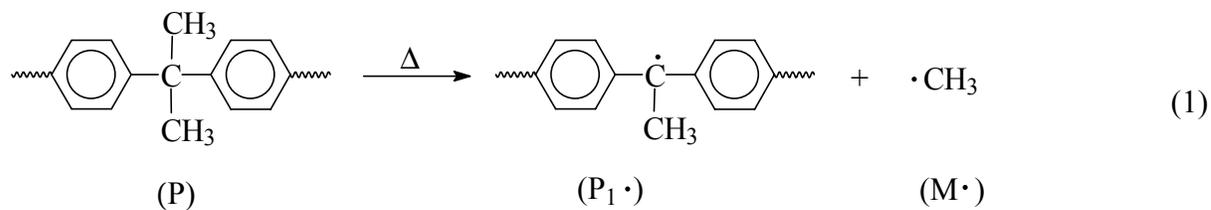


Figure 1.3-4 Kuroda's<sup>9</sup> reaction scheme for polycarbonate degradation.

Recent work in the area of PC degradation has benefited from more sophisticated analytical techniques. These newer methods allow for analysis of volatile as well as nonvolatile degradation products, which has led to a better understanding of the mechanisms. However, the polymer community is still far from agreement, as evidenced by the work of McNeill and Rincon and Montaudo and Puglisi.

McNeill and Rincon<sup>10,11</sup> have utilized a battery of techniques to elucidate the mechanism of polycarbonate degradation. In addition to TGA and DSC, the authors have also made use of thermal volatilization analysis (TVA), subambient TVA (SATVA), infrared spectroscopy, and gas chromatography-mass spectrometry (GC-MS). The main technique used, TVA, was carried out at both a heating rate of 10°C/min and at isothermal temperatures in a continuously evacuated system. This produces three types of products: condensable volatile products (-196°C), cold ring fraction (CRF), consisting of tar and wax which is volatile at degradation temperatures but not at room temperature, and involatile solid residue. Condensable materials go on to SATVA where fractions are analyzed by spectrometry. CRF products are analyzed by IR, NMR, or MS, with direct pyrolysis-MS (DPMS) being used in some cases to confirm results. The authors stress the necessity of using this slow heating rate in order to accurately determine degradation temperatures and products. Thus, DPMS is only used as a secondary technique.

The authors point out that phenol is an early degradation product (see Figure 1.3-5), as is cyclic dimer produced by the radical depolymerization which involves scission at isopropylidene. Scheme 2 (Figure 1.3-6) consists of homolytic scission at the carbonate linkage and produces bisphenol A. Next, Scheme 3 in Figure 1.3-7 explains the production of p-cresol and p-ethyl phenol from homolytic reactions involving migration of methyl groups. Finally, hydrogen abstraction after homolysis in the methyl group is illustrated in Scheme 4, Figure 1.3-8, a reaction which could lead to crosslinking. Scission and methyl-group migration produces p-vinyl phenol and p-cresol.

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<sup>10</sup> McNeill, I. C., and A. Rincon, *Polym. Degrad. and Stab.*, **31**, 163, 1991.

<sup>11</sup> McNeill, I. C., and A. Rincon, *Polym. Degrad. and Stab.*, **39**, 13, 1993.

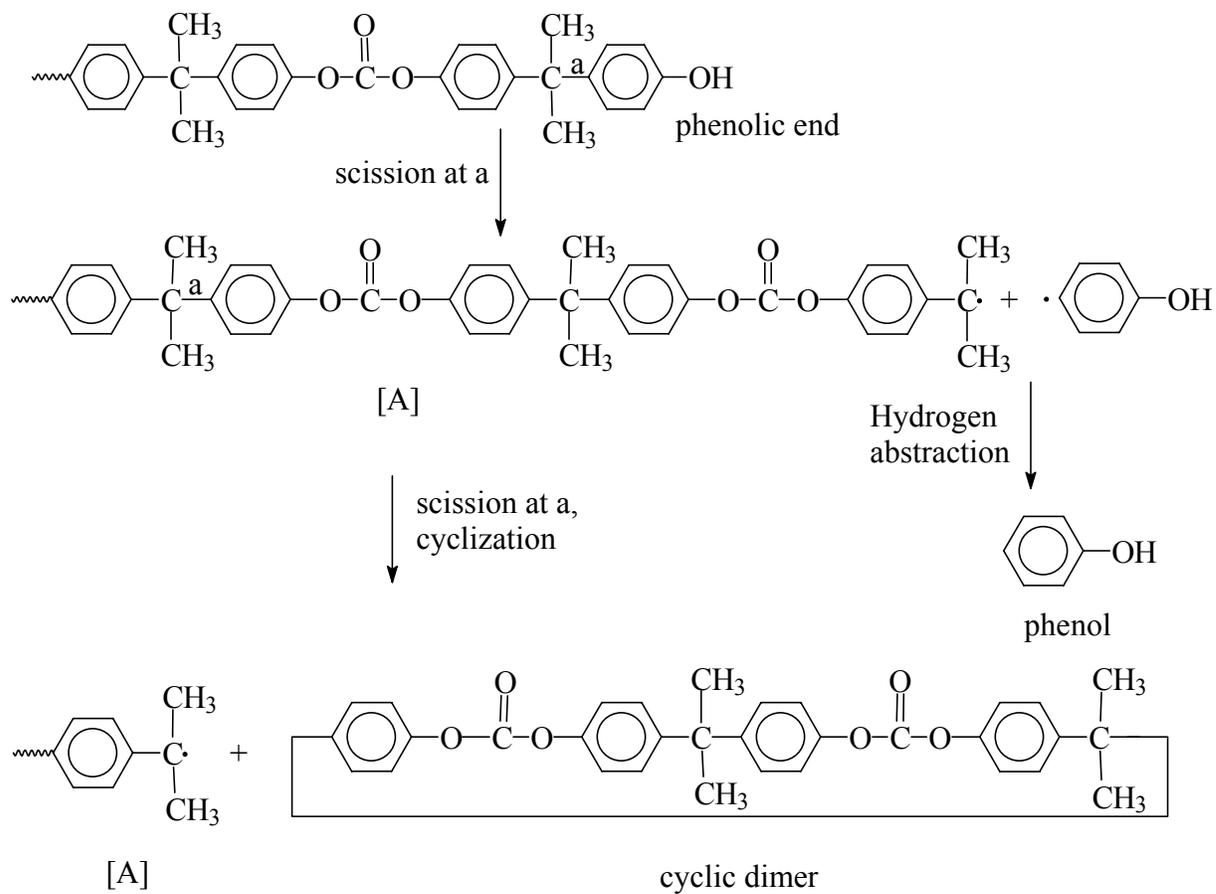


Figure 1.3-5 McNeill and Rincon's<sup>10,11</sup> Scheme I for polycarbonate degradation.

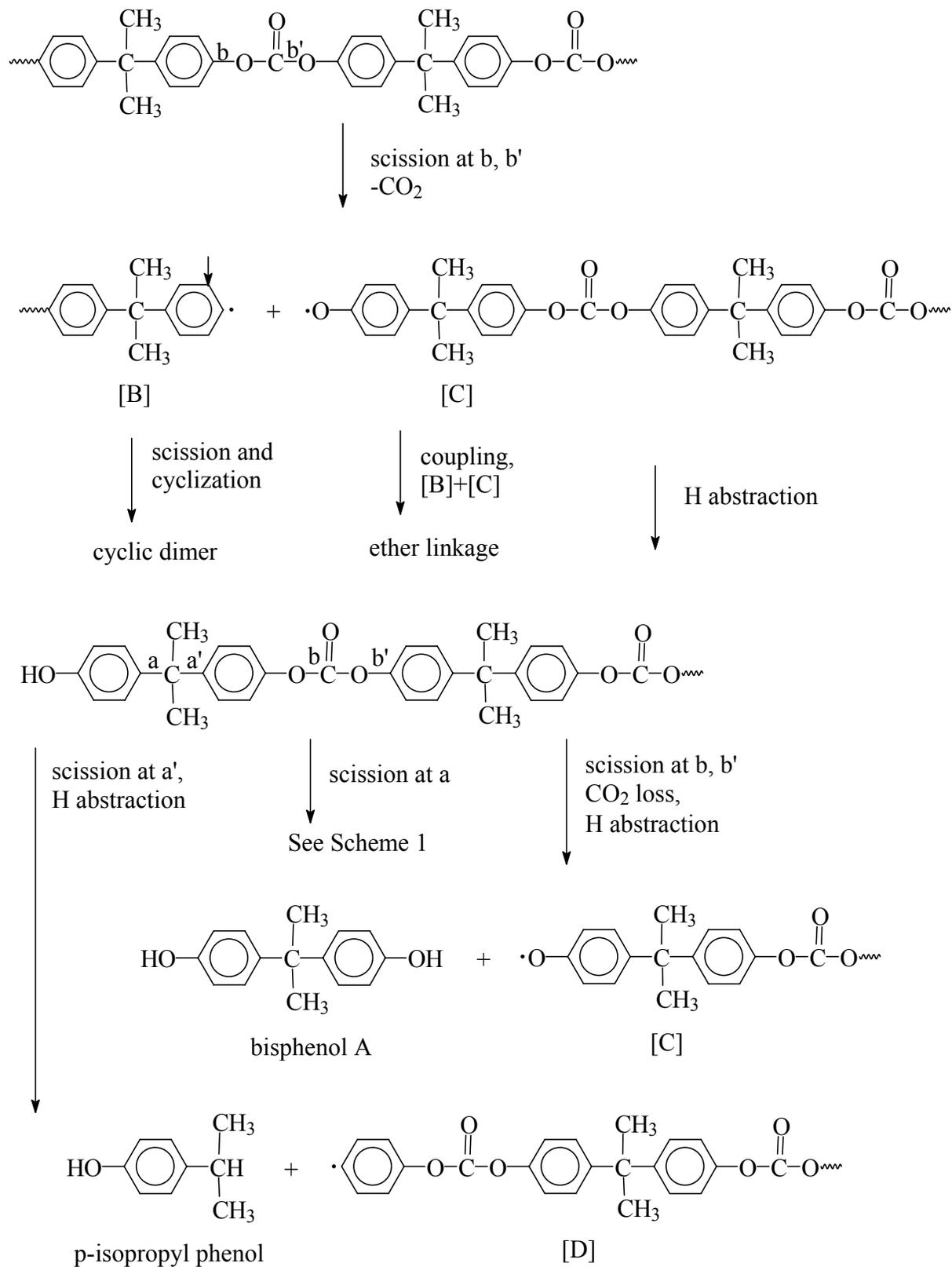


Figure 1.3-6 McNeill and Rincon's<sup>10,11</sup> Scheme II for polycarbonate degradation.



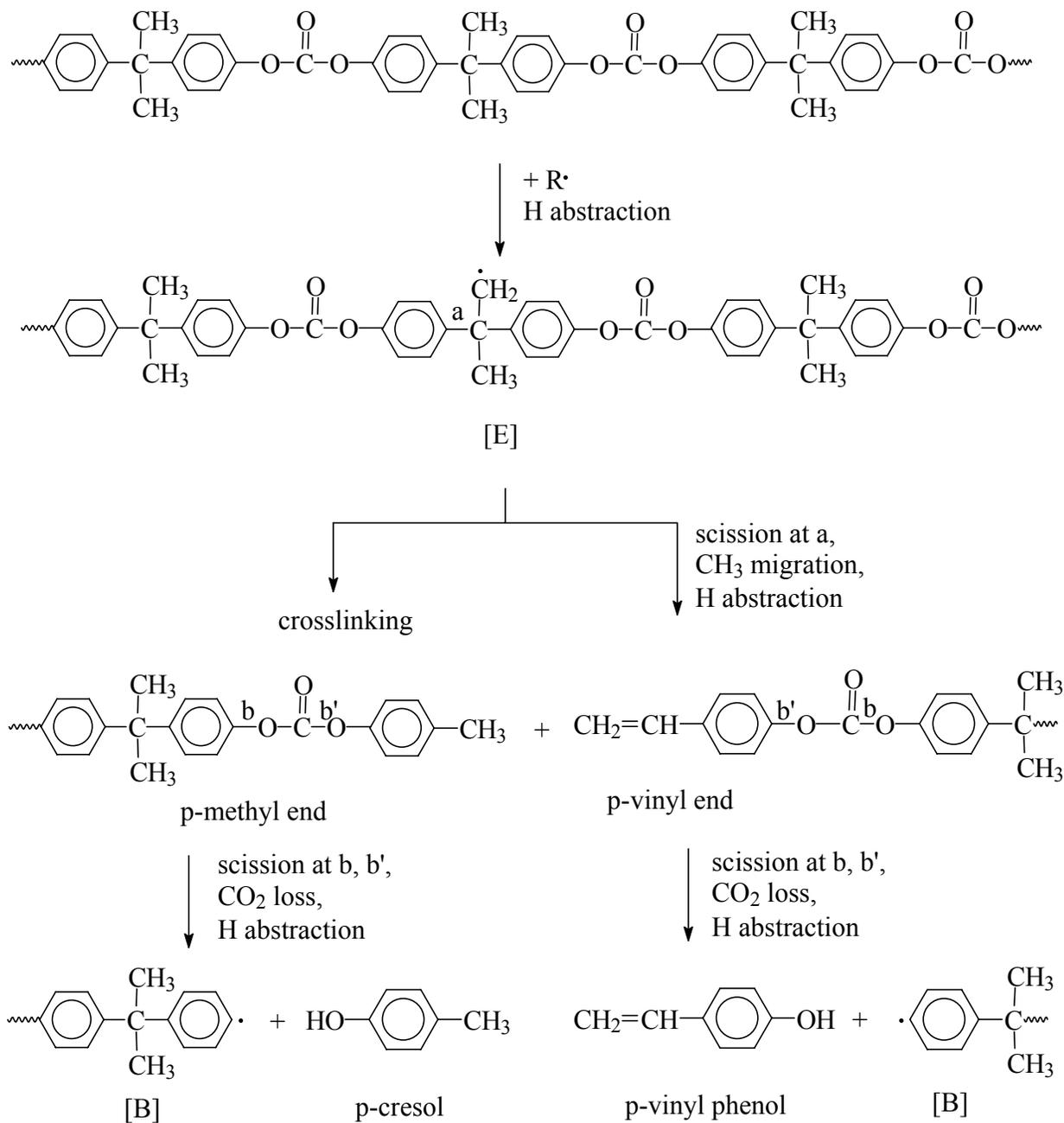


Figure 1.3-8 McNeill and Rincon's<sup>10,11</sup> Scheme IV for polycarbonate degradation.

While acknowledging that this degradation is quite sensitive to the presence of oxygen and water, the authors also point out the presence of non-volatile degradation products (cold ring fraction, CRF) at temperatures lower than those postulated by Davis and Golden. They rule out the possibility of ester interchange and also determine that, at

the lowest temperatures, hydrolysis at the carbonate linkage is not occurring. The reaction schemes account for all the products seen in their results and in those of Davis and Golden, as well as the reported crosslinking reaction which occurs under certain conditions. McNeill and Rincon conclude that the degradation can largely be explained by hydrolysis reactions, as per Davis and Golden, but that several complex events occur at different temperatures which complicate the decomposition substantially.

Contrary to the conclusions of McNeill and Rincon, Montaudo and Puglisi<sup>12,13,14</sup> take the opposing view. While agreeing on the sensitivity of PC to water, they espouse the view that intramolecular ester exchange, an ionic process, is the initial degradation step. Both groups do, however, agree that cyclic oligomer is a major product.

Montaudo and Puglisi rely primarily on direct pyrolysis-MS (DPMS), but also utilize thermogravimetry, inherent viscosity, FAB-MS, isothermal pyrolysis, and aminolysis of the pyrolysis residue. The DPMS measurements were made from 100-700°C at a heating rate of 10°C/min. Results are again organized into reaction schemes. As shown in Figure 1.3-9, reaction (a), PC undergoes intramolecular exchange to yield cyclic oligomers followed in (b) by hydrolytic cleavage of the carbonate group. Next, in (c), carbon dioxide elimination occurs, then disproportionation, (d), of the bisphenol A unit, and finally isomerization of the carbonate group (e). An alternative isomerization reaction is illustrated in Scheme II, Figure 1.3-10, which yields xanthone units and fluorenone units.

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<sup>12</sup> Montaudo, G. and C. Puglisi, in *Developments in Polymer Degradation*, N. Grassie, ED., Elsevier, London, p. 35, 1987.

<sup>13</sup> Montaudo, G. and C. Puglisi, *Poly. Degrad. and Stab.*, **37**, 91, 1992.

<sup>14</sup> Puglisi, C., L. Sturiale, and G. Montaudo, *Macro.*, **32**, 2194, 1999.

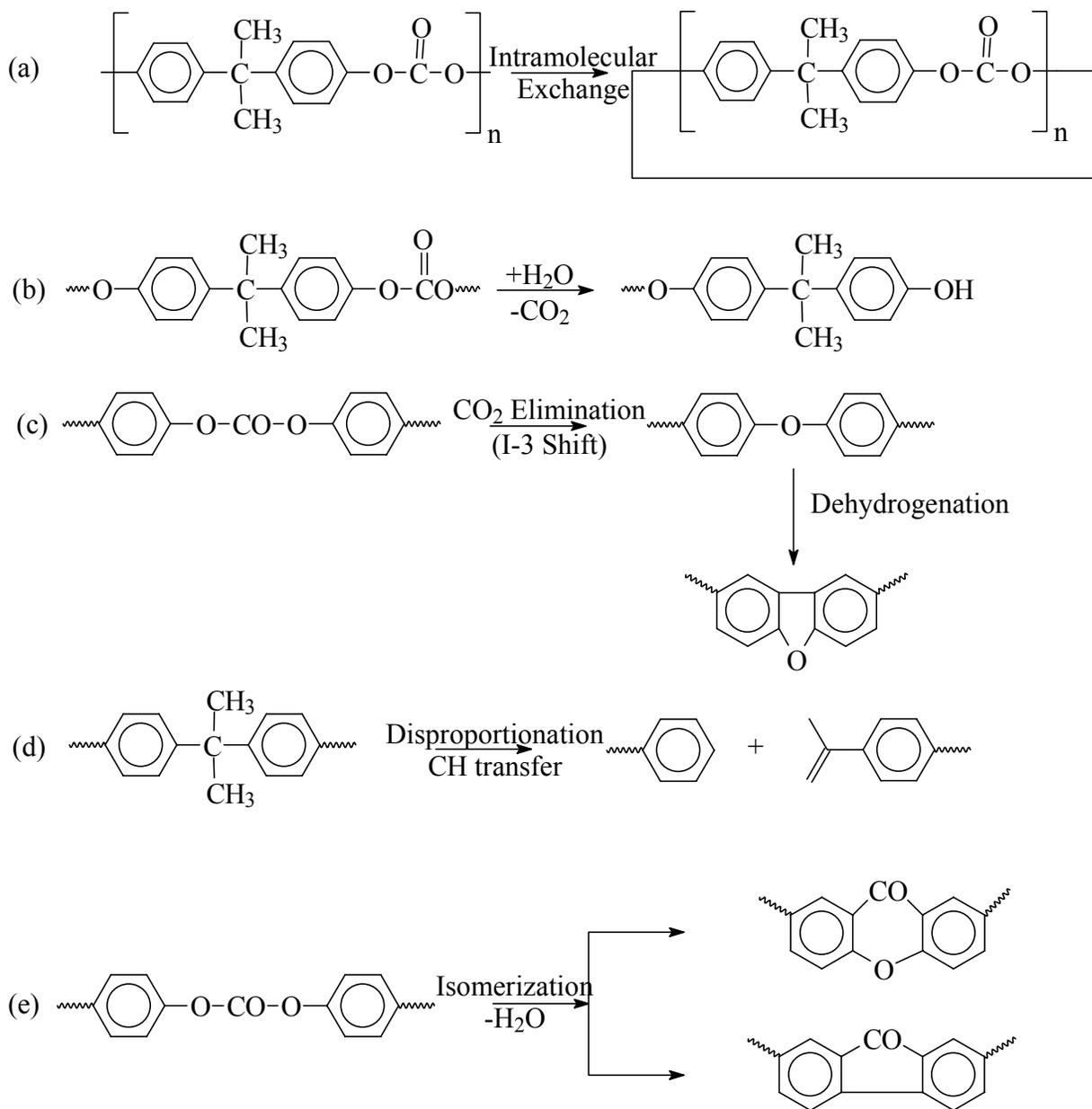


Figure 1.3-9 Montaudou and Puglisi's<sup>12,13,14</sup> Scheme I for polycarbonate degradation.

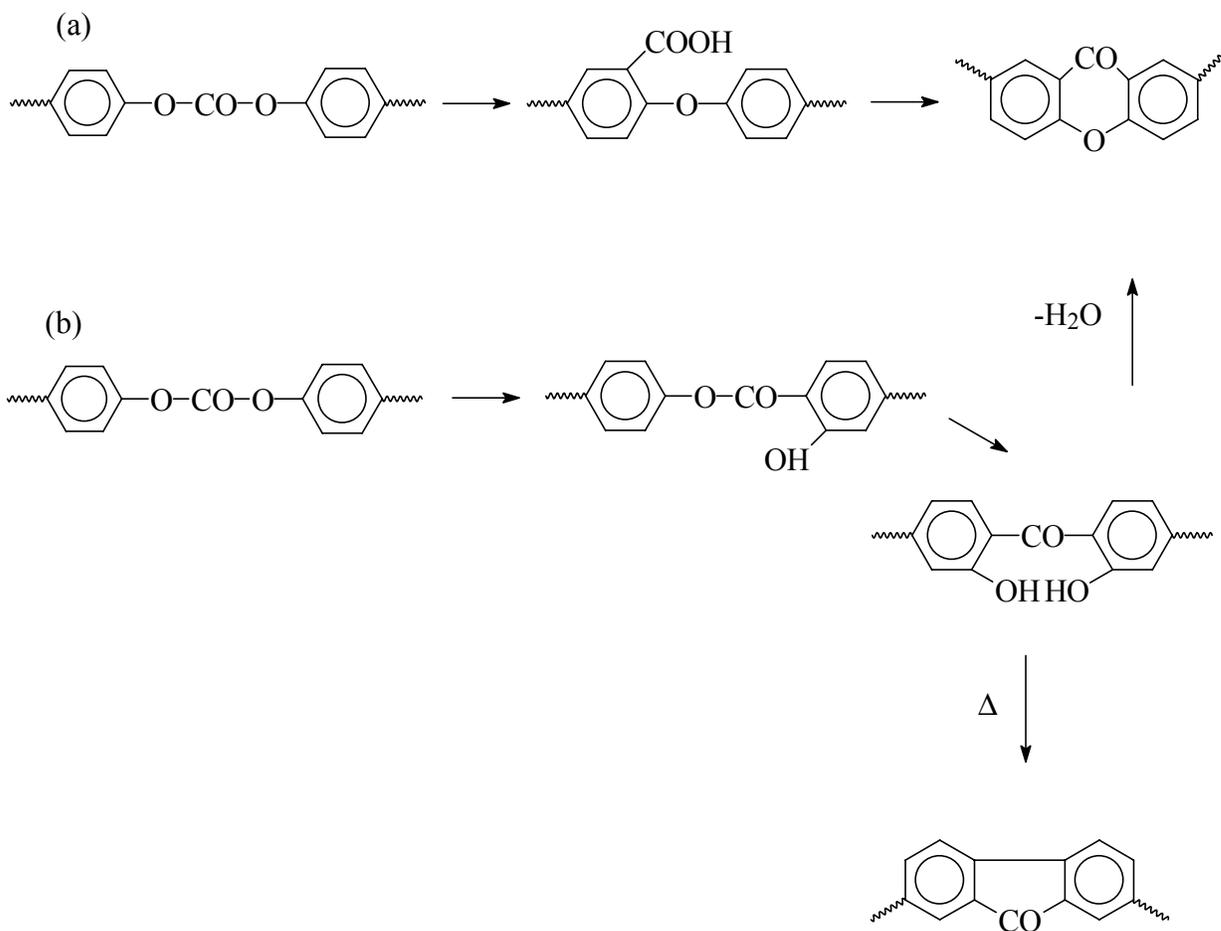


Figure 1.3-10 Montaudo and Puglisi's<sup>12,13,14</sup> Scheme II for polycarbonate degradation.

The authors comment that water and carbon dioxide evolution occurs all during the pyrolysis and forms ether bridges by decarboxylation and, through hydrolysis, phenolic end groups. Molecular rearrangements and structural decomposition occur at higher (500-700°C) temperatures and form linear open chain molecules. Disproportionation of isopropylidene yields phenyl and isopropylidene end groups. Dehydrogenation of ether units leads to dibenzofuran products, while isomerization and condensation result in xanthone and fluorenone units. Long ether/xanthone sequences can undergo aromatization and crosslinking.

In more recent investigations, researchers<sup>15</sup> used matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) as an additional tool to investigate polycarbonate degradation. After undergoing degradation at a set temperature and time, residue was dissolved in an appropriate solvent and MALDI was performed. This technique allows closer monitoring of relative amounts of species produced during pyrolysis but which are not volatile at that degradation temperature. The authors found this method to be a good complement to their previous results with the MALDI data reinforcing their proposed reaction schemes.

Clearly, the results of these two research groups are quite contradictory. While some of the same products are generated, the proposed routes are very different. Montaudo argues that the mechanism of McNeill assumes an inert carbonate group and a radical recombination reaction at high temperature, an unlikely scenario. McNeill postulates that Montaudo's use of DPMS gives misleading results because secondary reactions are not prevented with this method. One group espoused a radical mechanism while the other is convinced of an ionic pathway. Obviously, the mechanism of PC degradation is still an area open to research and speculation.

Other workers have used various other techniques to study polycarbonate degradation. The first use of infrared spectroscopy as such a tool was reported relatively recently by Politou and coworkers.<sup>16</sup> According to the authors, several factors have hindered this type of study on PC, the main one being the complexity of the polymer and its degradation as well as the presence of overlapping bands in both cases. Furthermore, they report that PC turns opaque and optically black at even early stages of degradation, making conventional IR quite difficult. For these reasons, they relied on photothermal beam deflection spectroscopy (PBDS). In addition to a scan of the initial material, scans were taken of PC degraded under dynamic vacuum at various temperatures ranging from 340-750°C.

At the lowest temperatures studied (pyrolysis near 340°C), very few spectral changes occurred. It is reported that after an initial critical heating period of three hours, the extent of the degradation is fairly unaffected by the heating time. The changes that

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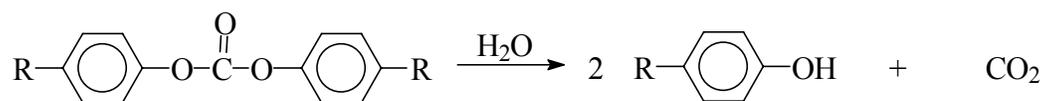
<sup>15</sup> Puglisi, C., F. Samperi, S. Carroccio, and G. Montaudo, *Macro.*, **32**, 8821, 1999.

were observed included a decrease in intensity of the 771  $\text{cm}^{-1}$  band and near-elimination of the 713  $\text{cm}^{-1}$  band, which are both related to monosubstituted aromatic rings. These changes are consistent with the removal of phenyl end groups and the evolution of oligomer which was initially present or produced during pyrolysis. The authors argue that these results support the work of Davis and Golden<sup>5,6,7</sup> and of Lee<sup>8</sup> where random hydrolysis of the carbonate group followed by condensation are the first stages of degradation.

Abbas<sup>17,18</sup> has also devoted time to studying the degradation of PC, but from a processing point of view. He examined both melt polymerized (broader molecular weight distribution) and interfacially polymerized PC. Utilizing TGA under flowing nitrogen, weight loss was monitored at isothermal conditions of 290, 350, and 365°C for one hour. He reports that at 290°C, even though no weight loss is detected, some samples are insoluble indicating crosslinking has occurred. It is concluded that the broader molecular weight distribution sample has a higher tendency towards crosslinking.

In order to more closely reproduce processing conditions, PC was also degraded in a capillary rheometer barrel in the temperature range 300-330°C for up to 80 minutes. Because the polydispersity, as measured by GPC, does not tend towards 2 at the highest degradations, Abbas concludes that the process is non-random. He also reports an activation energy for the reaction. Abbas<sup>19</sup> has also carried his work further by studying degradation of PC under injection molding conditions. This process, however, imparts mechanical as well as thermal degradation and thus will not be discussed here.

Pryde and Hellman<sup>20</sup> examined hydrolysis of PC by holding a sample at 125°C in the presence of steam for various times. Relying on the fact that hydrolysis of an aromatic ester produces two molecules of phenol:



<sup>16</sup> Politou, A. S., C. Marterra, and M. J. D. Low, *Carbon*, **28**, 529, 1990.

<sup>17</sup> Abbas, K. B., *Preprints of Short Communications Presented at IUPAC MAKRO Mainz*, 641, 1979.

<sup>18</sup> Abbas, K. B., *Polymer*, **21**, 936, 1980.

<sup>19</sup> Abbas, K. B., *Polym. Engr. Sci.*, **20**, 376, 1980.

<sup>20</sup> Pryde, C. A. and M. Y. Hellman, *J. Appl. Polym. Sci.*, **25**, 2573, 1980.

they found they could monitor the hydrolysis of PC by watching the growth of the –OH (3605 cm<sup>-1</sup>) peak via FTIR.

Mass spectrometry has also been used to elucidate a mechanism for PC degradation.<sup>21</sup> Samples were heated at a rate of 10°C/min. The results indicate that intramolecular ester exchange dominates and leads to cyclic oligomer species. Hydrolytic cleavage of the cyclic dimer and trimer produces open chain structures. This agrees with the mechanism suggested by Montaudo and Puglisi.<sup>12-14</sup>

Li and Huang<sup>22</sup> applied high-resolution TGA (HRTG) to the study of PC degradation. With no drying of the sample, HRTG was carried out under a nitrogen or air flow at an initial heating rate of 50°C/min from 25-900°C. The authors claim to see one major degradation step and two minor ones for a nitrogen atmosphere, and different results in air, as one would expect. Kinetic data analysis is carried out according to several researchers including Freeman-Carroll and Friedman (see Section 1.3) and yields values for activation energy in the range 153-155 kJ/mol, reaction order, n, of 0.8, and ln A (where A is the preexponential factor) = 21 min<sup>-1</sup> for the primary reaction occurring from 400-480°C.

These authors conclude that the carbonate bond is initially cleaved and can then initiate breakdown of other bonds. This is based upon the bond dissociation energies for the various bonds in PC. The carbonate C-O bond is reported here to have an energy of 330 kJ/mol, while the isopropylidene C-C bond is 346 kJ/mol. This small difference in energies may serve to complicate the reactions such that any conclusions drawn here are invalid.

Numerous researchers have reported values for the kinetic parameters associated with polycarbonate degradation. Knight<sup>23</sup> used TGA in both dynamic (2°C/min) and isothermal modes in both air and nitrogen. For BPA-PC, in the range 268-339°C, activation energies are as shown:

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<sup>21</sup> Foti, S., M. Giuffrida, P. Maravigna, and G. Montaudo, *J. Polym. Sci. Polym. Chem.*, **21**, 1567, 1983.

<sup>22</sup> Li, X. G. and M. R. Huang, *Polym. Intl.*, **48**, 387, 1999.

<sup>23</sup> Knight, G. J., *British Polym. J.*, **10**, 187, 1978.

5-10% weight loss	10-15%	15-20%	20-25%	25-30%	30-35%
123 kJ/mol	123	132	172	171	175

When BPA-PC is heated at 350°C under vacuum, considerable degradation occurs via a free radical process<sup>24</sup>. The average molecular weight drops off drastically but is accompanied by some degree of crosslinking. Intermolecular reesterification also occurs, which results in an evening out of the fractional polymer composition and evolution of CO<sub>2</sub>.

In summary, it is clear that views on polycarbonate degradation mechanisms are diverse. It is evident that this small field is still quite active, and there are really no generally accepted routes. It should again be stressed that chemical mechanism elucidation is not the goal of the proposed research. However, further study in this area is certainly warranted.

#### 1.4. Kinetics

When studying thermal degradation, clearly the kinetics of the process are of paramount importance. If the equations for kinetics are known, predicting the degree of degradation after a given time at a specific temperature is a simple process. This portion of the review focuses on methods to elucidate these equations.

Kinetic studies of materials degradation have been carried out for many years using numerous techniques to analyze the data. Most often, thermogravimetric analysis (TGA) is the experimental method of choice and the only technique to be explored here. TGA involves placing a sample of polymer on a microbalance within a furnace and monitoring the weight of the sample during some temperature program.

It is generally accepted that materials degradation obeys the basic equation

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad \text{Equation 1.4-1}$$

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<sup>24</sup> Yakubovich, Y. A., G. Y. Gordon, L. I. Maslennikova, E. M. Grobman, K. I. Tret'yakova, and N. I. Kokoreva, *J. Polym. Sci.*, **55**, 251, 1961.

where  $k$  is the reaction rate constant,  $n$  is the order of the reaction, and  $\alpha$  is the normalized weight loss, defined as follows:

$$\alpha = \frac{W(t) - W_i}{W_i - W_f} \quad \text{Equation 1.4-2}$$

In Equation 1.4-2,  $W(t)$  is the weight at time  $t$  and  $W_i$  is the initial and  $W_f$  the final weight of the sample. The temperature dependence in Equation 1.4-1 enters through the reaction rate term  $k$  which is assumed to be of the Arrhenius form:

$$k = Ae^{-E_a/RT} \quad \text{Equation 1.4-3}$$

where  $A$  is the pre-exponential factor,  $E_a$  is some activation energy, and  $R$  is the gas constant.

Perhaps the simplest way to analyze isothermal (or static) thermogravimetric data is to fit it to Equation 1.4-1. This would result in values for  $k$  and  $n$ . Repeating at several temperatures leads to a spectrum for  $k(T)$  which, via Equation 1.4-3, can be used to calculate values for  $A$  and  $E_a$  for the reaction.

Another isothermal technique is the so-called “stationary point method” reported by Klaric and coworkers.<sup>25</sup> They also started with the standard kinetic equations (Equation 1.4-1 and Equation 1.4-3) but defined  $\alpha$  as  $W_i - W/W_i$ . The stationary point is  $S(t_m, V_{\max})$  where  $V_{\max}$  is simply  $(d\alpha/dt)_{\max}$ . This point is defined on the curve of  $(d\alpha/dt)$  versus  $t$  as the point where the rate reaches a maximum, or  $(d^2\alpha/dt^2)$  is zero. At the same time, the inflection point  $P(t_m, \alpha_m)$  is defined for the curve of  $\alpha$  versus  $t$  as the point where the degradation rate is at a maximum. Then, the activation energy can be found from either

$$\frac{d \ln V_{\max}}{d(1/T)} = \frac{d \ln k}{d(1/T)} = -\frac{E_a}{R} \quad \text{Equation 1.4-4}$$

or

$$\frac{d \ln t_m}{d(1/T)} = \frac{d \ln t}{d(1/T)} = \frac{E_a}{R} \quad \text{Equation 1.4-5}$$

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<sup>25</sup> Klaric, I., U. Roje, and T. Kovacic, *J. Therm. Anal.*, **45**, 1373, 1995.

Clearly, this method presents a simple procedure for finding the activation energy for a degradation process. However, that is indeed the only kinetic parameter which is derived. It should be noted here, though, that this is one of the few techniques that attempt to analyze isothermal data and in that way does contribute to the body of information on kinetic methods.

MacCallum and Schoff<sup>26</sup> also use a slightly different nomenclature for their technique. They begin with the integrated form of a generalized rate expression for an nth order reaction with  $n \neq 1$ :

$$(1 - P)^{1-n} = 1 + (n - 1)kt \quad \text{Equation 1.4-6}$$

where  $t$  is the time when the reaction reaches a fractional conversion  $P$ , and  $k$  and  $n$  are as previously defined. In the case of polymer degradation,  $1-P=W/W_0$ , and the left-hand-side of Equation 1.4-6 can be expanded in a series and terms greater than  $P^2$  dropped to give

$$\frac{1}{k} + \frac{nP}{2k} = \frac{t}{P} \quad \text{Equation 1.4-7}$$

Using this form, a plot of  $P$  versus  $t/P$  should yield a straight line whose slope and intercept lead to  $k$  and  $n$ . However, this expression was found to be unsatisfactory for values of  $P > 0.25$ . In order to expand the applicability, the authors rearranged Equation 1.4-7 to give

$$\frac{1}{k} = \frac{t}{\left[ P \left( 1 + \frac{nP}{2} \right) \right]} \quad \text{Equation 1.4-8}$$

Another series expansion is used for the term  $\left( 1 + \frac{nP}{2} \right)^{-1}$ , and again terms of order greater than  $P^2$  are dropped:

$$\frac{t}{P} = \frac{1}{k} + \frac{n}{2t} \quad \text{Equation 1.4-9}$$

Thus, a plot of  $t/P$  versus  $t^{-1}$  should lead to order of reaction,  $n$ , and rate constant,  $k$ .

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<sup>26</sup> MacCallum, J. R. and C. K. Schoff, *Polym. Lett.*, **9**, 395, 1971.

The authors find this expression to give much more satisfactory results than Equation 1.4-7, but others<sup>27</sup> report that, due to the approximations made in this derivation, this expression should still only be utilized for  $P < 0.30$ .

MacCallum<sup>28</sup> later developed another method for analysis of isothermal degradation. He defines  $\alpha$  as  $(W_i - W) / W_i$ . Then,

$$-\frac{d(1-\alpha)}{dt} = kf(1-\alpha) \quad \text{Equation 1.4-10}$$

The rate constant,  $k$ , is defined just as in Equation 1.4-3. The form of  $f(1-\alpha)$  is not being proposed, but its integrated form will be taken as  $F(1-\alpha)$ . Then, integration of Equation 1.4-10 leads to

$$F(1-\alpha) = kt \quad \text{Equation 1.4-11}$$

Over a temperature range,  $F(1-\alpha)$  should be constant for a given value of  $\alpha$ . Then Equation 1.4-11 can be rewritten as

$$\frac{E_a}{RT} + \ln[F(1-\alpha)] - \ln A = \ln t \quad \text{Equation 1.4-12}$$

Plotting the logarithm of time against the reciprocal temperature at fixed values of  $\alpha$  should yield a straight line with slope proportional to the activation energy. If one then plots the intercepts at various temperatures versus  $\alpha$ , extrapolation to zero conversion yields  $A$  as shown:

$$\text{Intercept} = \ln[F(1-\alpha)] - \ln A \quad \text{Equation 1.4-13}$$

It should be noted here that these expressions apply only to a single-step degradation reaction. The presence of multiple steps would necessitate changes in the mathematics. Furthermore, the main disadvantage of this method is the need for multiple samples to be run at several temperatures, potentially introducing errors into the analysis.

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<sup>27</sup> Judd, M. D. and A. C. Norris, *J. Therm. Anal.*, **5**, 179, 1973.

<sup>28</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, Oxford, 1989.

Yet another isothermal method was proposed by Criado.<sup>29</sup> Beginning with the standard kinetic equations, Equation 1.4-1 and Equation 1.4-3, the author then points out that, at the maximum reaction rate, the following equation holds:

$$\frac{d^2\alpha}{dt^2} = k \cdot f'(\alpha_{\max}) \cdot \left( \frac{d\alpha}{dt} \right)_{\max} = 0 \quad \text{Equation 1.4-14}$$

and hence,

$$f'(\alpha_{\max}) = 0 \quad \text{Equation 1.4-15}$$

It should be noted that Equation 1.4-15 holds independently of the values of  $k$  and  $T$ . Criado tabulates some values for  $\alpha_{\max}$  and the corresponding values for  $f(\alpha)$ . According to this information, by calculating  $\alpha_{\max}$ , one could get an idea of the mechanism of the thermal decomposition reaction for certain types of reactions (i.e., one following the Prout-Tompkins or the Avrami-Erofeev mechanisms). For certain other types of mechanisms, however, uncertainties will arise and this method should be used only with extreme caution.

Another technique for analysis of isothermal data for a solid state reaction was reported on by Judd and Norris.<sup>27</sup> It begins with a standard kinetic equation in a slightly different formulation:

$$-\frac{d(a-x)}{dt} = k(a-x)^n \quad \text{Equation 1.4-16}$$

where  $a$  is the original concentration of reactant and  $x$  is the amount reacted in time  $t$ . Integrating Equation 1.4-16 leads to

$$-\int_a^{a-x} \frac{d(a-x)}{(a-x)^n} = k \int_0^t dt \quad \text{Equation 1.4-17}$$

Using the Mampel Intermediate Law, this integration yields

$$1 - (1-\alpha)^{1/n'} = kt + b \quad \text{Equation 1.4-18}$$

where  $1-x/a = \alpha$ , and  $b$  is a constant. The reaction order  $n'$  is related to  $n$  by

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<sup>29</sup> Criado, J. M., *J. Therm. Anal.*, **21**, 155, 1981.

$$n' = \frac{1}{1-n} \quad \text{Equation 1.4-19}$$

Substituting Equation 1.4-18 and Equation 1.4-19 into Equation 1.4-16 results in

$$-\frac{d(1-\alpha)}{dt} = \frac{k}{1/n'} (1-\alpha)^{1-1/n'} \quad \text{Equation 1.4-20}$$

If one then replaces  $k/(1/n')$  by  $k''$ , Equation 1.4-20 becomes

$$-\frac{d(1-\alpha)}{dt} = k'' (1-\alpha)^{1-1/n'} \quad \text{Equation 1.4-21}$$

Taking the logarithm of both sides leads to

$$\log\left(-\frac{d(1-\alpha)}{dt}\right) = \left(1 - \frac{1}{n'}\right) \log(1-\alpha) + \text{constant} \quad \text{Equation 1.4-22}$$

Thus, a plot of  $\log\left(-\frac{d(1-\alpha)}{dt}\right)$  versus  $\log(1-\alpha)$  will lead to a linear result with slope  $1-1/n'$ , and thus the order of the reaction.

While this method can be applied to the entire decomposition range, it is a difference-difference procedure. This means that differences are taken between successive values of  $(1-\alpha)$ . Thus, an error in a single value of  $\alpha$  will then be propagated to two values of  $d(1-\alpha)/dt$ . Any scatter in these values will then lead to uncertainties in the determination of the reaction order.

Judd and Norris suggest another technique to alleviate the error mentioned above. They begin with the equation

$$\alpha = 1 - (1 - kt(1-n))^{1/(1-n)} \quad \text{Equation 1.4-23}$$

They recommend that values for  $n$  and  $k$  are best found from a least squares fit of the data such that the sum of the squares of the differences between the observed and calculated values of  $\alpha$  are at a minimum.

Chatterjee<sup>30</sup> proposes another isothermal method. He also begins with the basic kinetic equations Equation 1.4-1 and Equation 1.4-3), but frames them in terms of weight remaining at time  $t$ , represented by  $W$ :

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<sup>30</sup> Chatterjee, P. K., *J. Polym. Sci., Part A*, **3**, 4253, 1965.

$$-\frac{dW}{dt} = AW^n e^{-E_a/RT} \quad \text{Equation 1.4-24}$$

He then hypothesizes that one route of gathering kinetic data is to start with two different initial sample weights. Then Equation 1.4-24

, in logarithmic form, becomes:

$$\begin{aligned} n \log W_1 - \log \left( -\frac{dW}{dt} \right)_1 &= \frac{E_a}{2.303RT} - C \\ n \log W_2 - \log \left( -\frac{dW}{dt} \right)_2 &= \frac{E_a}{2.303RT} - C \end{aligned} \quad \text{Equation 1.4-25}$$

The constant, C, is the same in both terms above and can thus be disregarded. Taking ratios leads to

$$n = \frac{\log \left( -\frac{dW}{dt} \right)_1 - \log \left( -\frac{dW}{dt} \right)_2}{\log W_1 - \log W_2} \quad \text{Equation 1.4-26}$$

$W_i$  and  $(dW/dt)_i$  can be determined at specific temperatures from each set of curves. Once n is found, it is then possible to plot  $n \log W - \log \left( -\frac{dW}{dt} \right)$  versus  $1/T$ .

The slope is  $E_a/2.303 R$  and the intercept is  $\log A$ .

In a followup to Chatterjee's paper, Broido<sup>31</sup> challenges the entire premise of this method. According to Broido, this method implies that the rate of decomposition depends on the amount of starting material, which clearly cannot be the case. The reason for this inconsistency is Chatterjee's use of weight instead of weight fraction. The Arrhenius equation requires W to be an intensive quantity such as concentration or mole fraction. Thus, this method is invalid, but serves to remind the reader that inaccuracies can and do occasionally get published in the scientific literature.

In some more recent work, Rozycki et al.<sup>32,33</sup> take a more general approach by not assigning  $f(\alpha) = (1-\alpha)^n$ . They began, again, with the standard kinetic equations, but in integral form:

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<sup>31</sup> Broido, A., *Polym. Lett.*, **6**, 349, 1968.

<sup>32</sup> Rozycki, C. and M Maciejewski, *Thermochim. Acta*, **96**, 91, 1985.

<sup>33</sup> Rozycki, C. and M Maciejewski, *Thermochim. Acta*, **122**, 339, 1987.

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T) \int_0^t dt \quad \text{Equation 1.4-27}$$

The left-hand-side is named  $g(\alpha)$ , and  $k(T)$  is, in the usual fashion, taken as an Arrhenius relationship. Then,

$$g(\alpha) = k(T)t = Ae^{-E_a/RT} \quad \text{Equation 1.4-28}$$

The authors next define a reduced time,

$$t_{\text{red}} = \frac{t}{t_{0.5}} \quad \text{Equation 1.4-29}$$

where  $t_{0.5}$  is the time where  $\alpha = 0.5$ . One can then plot  $\alpha$  versus  $t_{\text{red}}$ . Rozycki also notes that changing the time scale of Equation 1.4-28 leads to

$$g(\alpha) = B \left( \frac{t}{t_{0.5}} \right) \quad \text{Equation 1.4-30}$$

where  $B$  is a constant dependent on the value of  $g(\alpha)$ . Values of  $g(\alpha)$ , along with  $B$ , have been tabulated. Using a graphical method, one can plot the experimental data and compare it to the theoretical plot of  $\alpha$  versus  $t_{\text{red}}$  for various  $g(\alpha)$  functions. Whichever curve most closely matches the experimental data is then taken as  $g(\alpha)$ .

Rozycki et al. continue by describing a computer program for less subjective determination of  $g(\alpha)$ . Based upon the complexity, however, it does not appear to offer any distinct advantages over other methods, and thus will not be covered here.

In general, isothermal methods suffer in relation to dynamic methods in that comparatively large amounts of data are required. Furthermore, a new sample is utilized for each test, which introduces additional error into the measurement. If the reaction proceeds relatively quickly, some of the material may have reacted during the span of time the sample was being heated to the isothermal temperature. Finally, this technique does not provide information about the kinetics of degradation over a continuous temperature region, but only at discrete stages.<sup>34</sup>

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<sup>34</sup> Reich, L. and D. W. Levi, *Macromol. Rev.*, **1**, p. 173 Ed. A. Peterlin, M. Goodman, S. Okamura, B. H. Zimm, H. F. Mark, Wiley, NY, 1967.

To negate some of these issues, researchers usually turn to dynamic (non-isothermal) TGA techniques. An example of such a technique is that of Freeman and Carroll<sup>35</sup> who applied a non-isothermal thermogravimetric technique to the degradation of calcium oxalate monohydrate. They assumed a non-reversing reaction where a reactant, P, goes to a solid product and a volatile gas:



They wrote a general rate expression for this reaction

$$-\frac{dW}{dT} = \frac{A}{\beta} e^{-E_a/RT} W^n \quad \text{Equation 1.4-32}$$

where W is the weight of P remaining and  $\beta$  is the heating rate. Using a single TGA trace, Equation 1.4-32 can be applied at two points on the curve. Then the results can be subtracted to yield

$$\Delta \log\left(\frac{-dW}{dt}\right) = n\Delta \log W - \frac{E_a}{2.303R} \Delta \frac{1}{T} \quad \text{Equation 1.4-33}$$

If equal reciprocal temperature intervals are chosen (i.e.,  $\Delta(1/T)$  is held constant), a plot of  $\Delta \log\left(\frac{-dW}{dt}\right)$  versus  $\Delta \log W$  will be linear.

Anderson and Freeman<sup>36</sup> applied this method to study the degradation of polystyrene and polyethylene. First, they plotted the derivatives of the thermogram ( $dW/dt$ ) and of W versus  $1/T$ . Then, an interval for  $\Delta(1/T)$  was chosen and values for  $\Delta \log\left(\frac{-dW}{dt}\right)$  and  $\Delta \log W$  were read off the thermogram to create another plot. At constant  $\Delta(1/T)$ , a plot of  $\Delta \log\left(\frac{-dW}{dt}\right)$  versus  $\Delta \log W$  was made. The slopes yields n and the intercept is related to  $E_a$ .

This method requires only a single thermogram and also allows study over a continuous temperature range. However, such a technique suffers in that it requires

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<sup>35</sup> Freeman, E. S. and B. Carroll, *J. Phys. Chem.*, **62**, 394, 1958.

<sup>36</sup> Anderson, D. A. and E. S. Freeman, *J. Polym. Sci.*, **54**, 253, 1961.

slopes in steep areas of the thermogram. This introduces substantial error in the analysis of the kinetic parameters which may make determination of the constants imprecise.<sup>37,38</sup>

Other researchers<sup>39,40</sup> have analyzed thermograms by concentrating on the inflection point of the curve where the second derivative goes to zero. The first step is to maximize the rate by differentiating Equation 1.4-32 with respect to temperature and setting the result equal to zero. Then, for an nth order reaction,

$$E_a = \frac{-\left[ nRT^2 \left( \frac{dW}{dT} \right)_{\max} \right]}{W_{\max}} \quad \text{Equation 1.4-34}$$

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. Once a value for  $E_a$  is calculated, one can then find a value for  $n$ , the order of the reaction:

$$n = \left( \frac{W_{\max}}{T_{\max}^2} \right) \left( \frac{1}{(dW/dT)_{\max}} \right) \left( \frac{E_a}{R} \right) \quad \text{Equation 1.4-35}$$

and for the pre-exponential factor,  $A$ :

$$A = -\left( \frac{\beta}{W_{\max}} \right) \left( \frac{dW}{dT} \right)_{\max} e^{E_a/RT_{\max}} \quad \text{Equation 1.4-36}$$

where  $\beta$  is the heating rate chosen for the experiment.

This method was used, with some success, to study the thermal degradation of Teflon.<sup>41</sup> The results of this study agreed well with other reported values for kinetic constants.

The advantage of this method is the ease of application as well as the fact that no mathematical approximations are involved. It is also reported that the calculated constants apply to the entire TGA trace, meaning that the method satisfactorily represents

<sup>37</sup> Reich, L. and D. W. Levi, *Macromol. Rev.*, **1**, p. 173 Ed. A. Peterlin, M. Goodman, S. Okamura, B. H. Zimm, H. F. Mark, Wiley, NY, 1967.

<sup>38</sup> Flynn, J. H. and L. A. Wall, *J. Res. Natl. Bur. Stds.*, **70A**, 487, 1966.

<sup>39</sup> Levi, D. W., L. Reich, and H. T. Lee, *Polym. Engng. Sci.*, **5**, 135, 1965.

<sup>40</sup> Fuoss, R. M., I. O. Salyer, and H. S. Wilson, *J. Polym. Sci., Part A*, **2**, 3147, 1964.

the kinetics of the degradation over the entire temperature range. Levi points out, though, that the method is not nearly as precise at calculating values for  $n$  as for  $E_a$  due to scatter in the data, and that an ancillary method would be preferable for the determination of reaction order.

Another technique in dynamic thermogravimetry is that of variable heating rate. Reich and coworkers<sup>42</sup> developed this novel method for calculating  $n$  and  $E_a$ . They began heating a sample at a set rate and then, after a specified conversion was reached, changed the heating rate. This second heating rate could be higher than the initial rate, but the researchers found the method more useful if the second rate was so drastically lower that the sample was effectively degrading during cooling.

The next step was to obtain pairs of values of heating rate ( $\beta$ ), temperature, and weight of sample  $W$  from segments of the thermogram where  $(dW/dT)$  is the same. Using the equation

$$[\Delta \log(\beta)] / \Delta \left( \frac{1}{T} \right) = n \left[ \Delta \log W / \Delta \left( \frac{1}{T} \right) \right] - \frac{E_a}{2.303R} \quad \text{Equation 1.4-37}$$

one can plot  $[\Delta \log(\beta)] / \Delta(1/T)$  versus  $\Delta \log W / \Delta(1/T)$  producing a line where the slope is  $n$  and the intercept gives  $E_a$ .

The advantage of choosing the second heating rate to be lower than the first relates to the value of  $n$ . One can check the value by constructing an isotherm and substituting values in

$$n = (\Delta \log \left( \frac{dW}{dt} \right)) / (\Delta \log W) \quad \text{Equation 1.4-38}$$

to check for consistency. With this choice of  $\beta_1 > \beta_2$  comes the necessity that the resulting thermogram be unsymmetrical and distinctly curved at both ends as seen in Figure 1.4-1.

<sup>41</sup> Reich, L., H. T. Lee, and D. W. Levi, *Polymer Letters*, **1**, 535, 1963.

<sup>42</sup> Reich, L., H. T. Lee, and D. W. Levi, *J. Appl. Polym. Sci.*, **9**, 351, 1965.

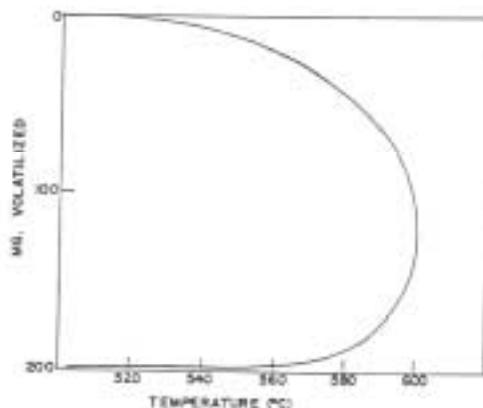


Figure 1.4-1 Variable heating rate thermogram for Teflon.<sup>42</sup>

Overall, advantages of this method include the need for only a single thermogram, less scatter in the data, and, according to the authors, less labor than some of the other methods. Knowing at what conversion to change the heating rates could present some difficulties and constitutes a disadvantage, as does the necessity for the unsymmetrical thermogram.

Van Krevelen et al.,<sup>43</sup> were some of the first researchers to study the pyrolysis of organic compounds. They use an approximation for the exponential term in Equation 1.4-3:

$$e^{-E_a/RT} \approx \left( \frac{T}{eT_m} \right)^{E_a/T_m} \quad \text{Equation 1.4-39}$$

where  $T_m$  is the temperature where a maximum reaction rate is reached. When this approximation is substituted into the standard kinetic equation (Equation 1.4-1) and then integrated, the result is

$$\ln \int_{W_0}^{W_0} \frac{dW}{W^n} = \ln \left[ \frac{A}{\beta} \left( \frac{1}{eT_m} \right)^{E/RT_m} \left( \frac{E}{RT_m} + 1 \right) \right] + \left( \frac{E}{RT_m} + 1 \right) \ln T \quad \text{Equation 1.4-40}$$

The right-hand side of Equation 1.4-40 can be taken as a constant,  $I$ , resulting in:

$$\int_{W_0}^{W_0} \frac{dW}{W^n} = I \quad \text{Equation 1.4-41}$$

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<sup>43</sup> van Krevelen, D. W., C. Van Heerden, and F. J. Huntjens, *Fuel*, **30**, 253, 1951.

If a value of  $n$  is known or assumed, a plot of  $\ln I$  versus  $\ln T$  should then yield a straight line if the assumed value for  $n$  is correct. This line's slope would be proportional to  $E_a$  and its intercept to  $A$ . The authors report that, depending on the value of  $n$ ,  $I$  can take on one of the following quantities:

$$\begin{aligned} I &= 1 - W & n &= 0 \\ I &= -\ln W & n &= 1 \\ I &= \frac{1}{W} - 1 & n &= 2 \end{aligned} \quad \text{Equation 1.4-42}$$

The main disadvantage of this method is the need for  $n$  to be known *a priori*. If  $n$  is indeed known, it offers the advantages of the ability to check  $n$  (by the linearity of the line from Equation 1.4-40) and a single thermogram to find both  $E_a$  and  $A$ .

Horowitz and Metzger<sup>44,45</sup> define terms slightly differently in their method. For any pyrolysis where all products are gases, they maintain that pseudo-first order kinetics apply. This is due to the fact that their reaction order,  $n$ , applies to concentrations and not weights of reactants. For such a case, concentration is constant and one can write

$$\ln \frac{W_0}{W} = \int_0^T \frac{A}{\beta} e^{-E_a/RT} dT \quad \text{Equation 1.4-43}$$

The authors define some terms in order to integrate Equation 1.4-43:  $W/W_0 = 1/e$  at the temperature  $T_s$  and  $\theta = T - T_s$ .

The next step is applying some mathematical approximations:

$$\frac{1}{T} \approx \left(1 - \frac{\theta}{T_s}\right) \frac{1}{T_s} \quad \text{since } \frac{\theta}{T_s} \ll 1 \quad \text{Equation 1.4-44}$$

If this is substituted into Equation 1.4-43 along with the new terms, one finds

$$\ln \ln \left( \frac{W}{W_0} \right) = \frac{E_a \theta}{RT_s^2} \quad \text{Equation 1.4-45}$$

and

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<sup>44</sup> Horowitz, H. H., and G. Metzger, *Anal. Chem.*, **35**, 1464, 1963.

<sup>45</sup> Horowitz, H. H., and G. Metzger, *Fuel*, **42**, 418, 1963.

$$\ln\left(\frac{ART_s^2}{E\beta}\right) = \frac{E_a}{RT_s} \quad \text{Equation 1.4-46}$$

From Equation 1.4-45, plotting  $\ln \ln (W/W_0)$  versus  $\theta$  should give a straight line with slope proportional to  $E_a$ . This value, along with Equation 1.4-46, yields a result for  $A$ . Note that this result applies only to a single-reaction pyrolysis that results in only gaseous products.

The authors deal with some other cases, such as when only a fraction of the total weight is volatilized. These special cases become quite complex, essentially negating their usefulness in polymer degradation.

While this method is applicable to many degradation conditions, it also suffers some disadvantages. A strong one is the need for the reaction order,  $n$ , to be known beforehand. Also, many assumptions are inherent in this method, so it should only be applied to a narrow temperature range. To its credit, though, it does not require measurement of slopes in steep areas of the thermogram, as do some methods mentioned above.

The method of Doyle<sup>46,47</sup> views the thermogram as a geometric object which, like any other, can be described by mathematical equations. The technique begins with the standard equation in a more general form:

$$-\frac{d\alpha}{dT} = \frac{Af(\alpha)e^{-E_a/RT}}{\beta} \quad \text{Equation 1.4-47}$$

This can then be integrated, taking  $A$  and  $E_a$  as constants, to yield

$$\int_{\alpha_1}^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad \text{Equation 1.4-48}$$

Doyle goes on to show that  $g(\alpha)$  has the following form:

$$g(\alpha) = \frac{AE_a}{\beta R} \left( \frac{e^{-x}}{x} - \int_x^{\infty} \frac{e^{-u}}{u} du \right) = \frac{AE_a}{\beta R} p(x) \quad \text{Equation 1.4-49}$$

A simpler approximation of the form is given:

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<sup>46</sup> Doyle, C. D., *J. Appl. Polym. Sci.*, **5**, 285, 1961.

<sup>47</sup> Doyle, C. D., *J. Appl. Polym. Sci.*, **6**, 639, 1962.

$$g(\alpha) = \frac{A' E_a e^{-x}}{\beta R x^2} \quad \text{Equation 1.4-50}$$

where  $x = E_a/RT$ . However, if the reaction is zero order or first order,  $g(\alpha)$  has simplified forms:

$$\begin{aligned} g(\alpha) &= 1 - \alpha & n &= 0 \\ g(\alpha) &= -\ln \alpha & n &= 1 \end{aligned} \quad \text{Equation 1.4-51}$$

Doyle then uses these equations to fit the thermogram and produce values for the kinetic parameters.

It is evident that this method involves significantly more mathematics than several other methods. By choosing more sophisticated equations, one can easily fit the data. However, it becomes unclear whether constants derived in this manner have any physical meaning, or what that meaning might be. Upon application to previously studied materials, octamethylcyclotetrasiloxane and polytetrafluoroethylene (PTFE), this method yields results which agree with reported values. However, it provides no real advantages over simpler techniques but presents a far more complicated method of application.

Yet another method is that developed by Friedman.<sup>48,49</sup> He starts with

$$-\frac{1}{W_0} \frac{dW}{dt} = A e^{-E_a/RT} f\left(\frac{W}{W_0}\right) \quad \text{Equation 1.4-52}$$

where  $W$  is the weight of organic material,  $W_0$  is the original weight,  $t$  is in hours,  $A$  in  $\text{hr}^{-1}$ ,  $E_a$  in  $\text{cal/mol}$ ,  $R = 1.987 \text{ cal/mol K}$ , and  $T$  in  $\text{K}$ .  $f(W/W_0)$  is some function of the weight of the organic material and assumed constant for a given value of  $W/W_0$ . Taking the logarithm of both sides of Equation 1.4-52 yields

$$\ln\left(\frac{1}{W_0} \frac{dW}{dt}\right) = \ln A + \ln f\left(\frac{W}{W_0}\right) - \frac{E_a}{RT} \quad \text{Equation 1.4-53}$$

Several values are chosen for  $W/W_0$ . Then a plot of  $-\frac{1}{W_0} \frac{dW}{dt}$  versus  $1/T$  is made. The slope yields  $-E_a/R$  and the intercept is  $\ln [A f(W/W_0)]$ . In order to find  $A$ , the average

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<sup>48</sup> Friedman, H. L., *Polym. Preprints*, **4**, 662, 1963.

<sup>49</sup> Friedman, H. L., *J. Poly., Sci., Part C*, **6**, 183, 1964.

value for  $E_a$  and experimental parameters are substituted into Equation 1.4-53 to yield several values for  $\ln [A f (W/W_0)]$ . Average values for  $\ln [A f (W/W_0)]$  at each value of  $W/W_0$  can then be found and plotted as in Figure 1.4-2. This plot can then be fit to the equation

$$f\left(\frac{W}{W_0}\right) = \left[\frac{W - W_f}{W_0}\right]^n \quad \text{Equation 1.4-54}$$

where  $W - W_f$  represents the amount of material available for degradation at time  $t$ . Combining Equation 1.4-54 and Equation 1.4-52 and taking the logarithm leads to

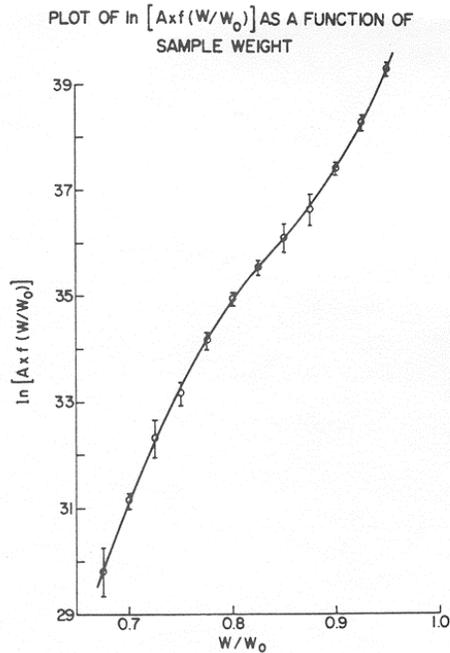


Figure 1.4-2 Illustration of Friedman's method.<sup>49</sup>

$$\ln \left[ A \cdot f \left( \frac{W}{W_0} \right) \right] = \ln A + n \ln \left[ \frac{W - W_f}{W_0} \right] \quad \text{Equation 1.4-55}$$

From this equation, a plot of  $\ln [A f (W/W_0)]$  versus  $\ln \left[ \frac{W - W_f}{W_0} \right]$  will yield a straight line with slope  $n$  and intercept  $\ln A$ .

The advantage of this method is that, since several values of  $E_a$  are calculated, any change in the kinetics of the degradation would be evident in changes in  $E_a$ . However,

since various heating rates are required, so too are several samples which could lead to errors. Furthermore, the technique for calculating A and n seems quite laborious and includes so many steps that it would seem errors would be common.

Reich and Levi,<sup>50,51,52</sup> along with Lee, developed a graphical method for analyzing TGA data. In this technique, two thermograms of the same material at different heating rates are used. First, definition of a new term,  $R_t = (d\alpha/dt)$ , is necessary. Combining this quantity with Equation 1.4-32 yields

$$\int_1^2 \ln R_t T^x dT - \int_1^2 \ln R'_t T^x dT = n \left[ \int_1^2 \ln W T^x dT - \int_1^2 \ln W' T^x dT \right] \quad \text{Equation 1.4-56}$$

The temperature limits for the two thermograms are the same. The variable x is an arbitrary constant and can be chosen to be zero. In that case,

$$n = \frac{A_R}{A_W}$$

$$A_R = \int_1^2 \ln R_t dT - \int_1^2 \ln R'_t dT \quad \text{Equation 1.4-57}$$

$$A_W = \int_1^2 \ln W dT - \int_1^2 \ln W' dT$$

$A_R$  and  $A_W$  are found graphically by measuring the appropriate areas between the two heating rate curves as seen in Figure 1.4-3 and Figure 1.4-4. Then, using the equation

$$\ln R_t = \ln A - \frac{E_a}{RT} + n \ln W \quad \text{Equation 1.4-58}$$

one may also calculate  $E_a$  and A.

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<sup>50</sup> Reich, L. and D. W. Levi, *J. Poly. Sci., Part B*, **2**, 1109, 1964.  
<sup>51</sup> Levi, D. W, L. Reich, and H. T. Lee, *Polym. Engr. Sci.*, **5**, 135, 1965.  
<sup>52</sup> Reich, L. and D. W. Levi, *Macromol. Rev.*, **1**, p. 188 Ed. A. Peterlin, M. Goodman, S. Okamora, B. H. Zimm, H. F. Mark, Wiley, NY, 1967.

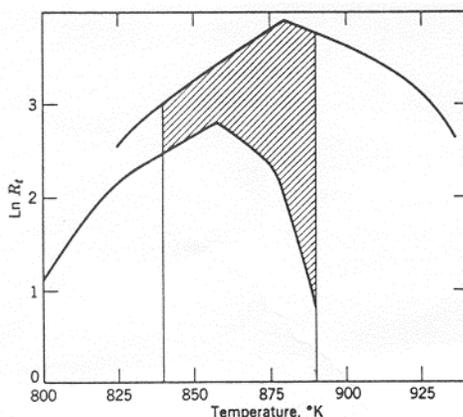


Figure 1.4-3 Curves for graphical estimation of  $A_R$  for Teflon at heating rates of  $6^\circ\text{C}/\text{min}$  and  $18^\circ\text{C}/\text{min}$ .<sup>52</sup>

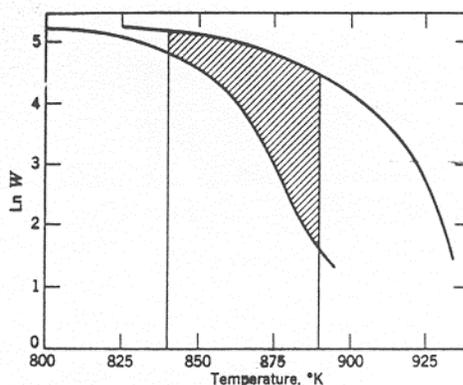


Figure 1.4-4 Curves for graphical estimation of  $A_W$  for Teflon at heating rates of  $6^\circ\text{C}/\text{min}$  and  $18^\circ\text{C}/\text{min}$ .<sup>52</sup>

This method allows a check on the reaction order since, by taking different temperature ranges, or several different heating rates, one can calculate several values for  $n$  and compare them. In general, values for the kinetic parameters obtained by this method are reported to agree well with other literature values. However, this method does require more than one heating rate, and thus more than one sample, which could cause uncertainty in the data.

Another technique proposed by Reich<sup>53</sup> begins with the expression

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<sup>53</sup> Reich, L. *J. Appl. Polym. Sci.*, **9**, 3033, 1965.

$$R_T = \frac{A}{\beta} e^{-E_a/RT} W^n \quad \text{Equation 1.4-59}$$

where  $R_T$  is the slope of the thermogram ( $d\alpha/dT$ ),  $\beta$  is the heating rate, and  $W$  is the weight fraction of material remaining. If some amount of material,  $W_R$ , remains after pyrolysis,  $W$  goes to  $W_C$ :

$$W_C = W - W_R \quad \text{Equation 1.4-60}$$

The next step is to expand Equation 1.4-59 in an asymptotic series, taking  $2RT/E_a \ll 1$ , which is a good assumption for polymer degradation, to yield

$$-\int_{W_0}^W dW / W^n = \frac{A}{\beta} \frac{RT^2}{E_a} a^{-E_a/RT} \quad \text{Equation 1.4-61}$$

combining Equation 1.4-61 with Equation 1.4-59 leads to

$$\frac{E_a}{R} = \frac{S}{[W_C \ln(W_{0,C} / W_C)]} \quad \text{if } n = 1 \quad \text{Equation 1.4-62}$$

or

$$\frac{E_a}{R} = \frac{S(1-n)}{W_C^n (W_{0,C}^{(1-n)} - W_C^{(1-n)})} \quad \text{for } n \neq 1 \quad \text{Equation 1.4-63}$$

In Equation 1.4-62 and Equation 1.4-63,

$$S = \frac{dW_C}{d(1/T)} \quad \text{Equation 1.4-64}$$

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

From Equation 1.4-62 and Equation 1.4-63, one can show that

$$\frac{S_1}{S_2} = \frac{W_{1,C}}{W_{2,C}} \frac{\log\left(\frac{W_{0,C}}{W_{1,C}}\right)}{\log\left(\frac{W_{0,C}}{W_{2,C}}\right)} \quad n = 1$$

Equation 1.4-65

$$\frac{S_1}{S_2} = \left(\frac{W_{1,C}}{W_{2,C}}\right)^n \frac{\left[1 - \left(\frac{W_{1,C}}{W_{0,C}}\right)^{(1-n)}\right]}{\left[1 - \left(\frac{W_{2,C}}{W_{0,C}}\right)^{(1-n)}\right]} \quad n \neq 1$$

In order to utilize this method, the first step is to estimate a value for  $n$ . Reich developed a theoretical plot, Figure 1.4-5, of  $n$  versus  $S_1/S_2$  for various values of  $W_1/W_2$  or  $W_{1,C}/W_{2,C}$  and  $W_R$ . This figure can be used to estimate  $n$  from a thermogram.

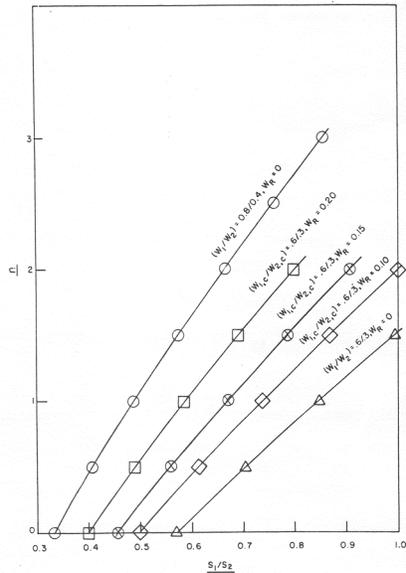


Figure 1.4-5 Theoretical plots of reaction order  $n$  versus  $S_1/S_2$  for various values of  $W_1/W_2$  or  $W_{1,c}/W_{2,c}$  and  $W_R$ .<sup>42</sup>

Once  $n$  is determined, the values can be substituted into Equation 1.4-62 and Equation 1.4-63 to find  $E_a$ . Finally, a value for the preexponential factor,  $A$ , may be determined from the following:

$$\log A = \log \left\{ [S(\beta)/W^n] \left( \frac{1}{T} \right)^2 \right\} + \frac{E_a}{2.3RT} \quad \text{Equation 1.4-66}$$

Reich employed this method for the degradation of Teflon and found it satisfactory. Values agreed with those reported previously.

It should be noted that, while acceptable results have been reported with this method, it does involve some mathematical approximations. Further, sequential estimations are required. If  $n$  is estimated poorly, values calculated for  $E_a$  and  $A$  are certain to be adversely affected. As such, care should be taken when applying this method.

Ozawa's technique<sup>54</sup>, the so-called "isoconversional method," is an extension of Doyle's procedure. Ozawa first postulates that the weight fraction of the degrading polymer is a function of a structural quantity which for macromolecules is the fraction of broken bonds. This structural factor is called  $x$ , and it follows the equation

$$-\frac{dx}{dt} = Ae^{-E_a/RT} g(x) \quad \text{Equation 1.4-67}$$

He defines  $x_0$  as the value of  $x$  at time  $t = t_0$  and then integrates:

$$-\int_{x_0}^x \frac{dx}{g(x)} = A \int_{t_0}^t e^{-E_a/RT} dt \quad \text{Equation 1.4-68}$$

At a constant heating rate,  $\beta$ , the change in  $x$  goes to

$$-\int_{x_0}^x \frac{dx}{g(x)} = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad \text{Equation 1.4-69}$$

where  $T = T_0$  at  $t = t_0$ . At low temperatures, the reaction rate is usually quite slow, leading to the approximation

$$\int_{T_0}^T e^{-E_a/RT} dT = \int_0^T e^{-E_a/RT} dT \quad \text{Equation 1.4-70}$$

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<sup>54</sup> Ozawa, T., *Bull. Chem. Soc. Japan*, **38**, 1881, 1965.

In Equation 1.4-48 and Equation 1.4-49, Doyle<sup>46,47</sup> showed that the right hand side of Equation 1.4-70 is expressed by the tabulated function  $p(x)$ . Substituting this into Equation 1.4-70,

$$\frac{E_a}{R} p\left(\frac{E_a}{RT}\right) = \int_0^T e^{-E_a/RT} dT \quad \text{Equation 1.4-71}$$

For a constant  $\alpha$ , the left hand side of Equation 1.4-69 is constant independent of  $\beta$ . So, if  $\alpha$  goes to a given value at  $T_1$  and heating rate  $\beta_1$ , and the same value at  $T_2$  and  $\beta_2$ , one can write

$$\frac{AE_a}{\beta_1 R} p\left(\frac{E_a}{RT_1}\right) = \frac{AE_a}{\beta_2 R} p\left(\frac{E_a}{RT_2}\right) = \dots \quad \text{Equation 1.4-72}$$

One can also use an approximation for  $p(x)$ :

$$\frac{d \log \beta}{d \frac{1}{T}} \cong 0.457 \frac{E_a}{R} \quad \text{Equation 1.4-73}$$

So plotting the logarithm of  $\beta$  versus  $1/T$  for a given  $\alpha$  should yield a straight line with slope proportional to  $E_a$ .

The next step is to set up a theoretical master curve of  $1-\alpha$  versus  $\log \frac{AE_a}{\beta R} p(x)$  for discrete values of  $n$  such as  $n=0, 1, 2, 3$ . The experimental master curve is prepared by superposing the  $\log \beta$  versus  $1/T$  curves by shifting them horizontally. From values of  $\alpha$  and  $T$  on this curve, one can construct a plot of  $1-\alpha$  versus  $\log \frac{AE_a}{\beta R} p(x)$  which can then be matched to the theoretical curve of the appropriate reaction order by shifting  $\log A$  horizontally. The amount of the shift is  $A$ . Thus,  $A$  is now known, and the reaction order, which must be assumed, is confirmed.

Flynn and Wall<sup>55</sup> report that this method is one of the most widely applicable techniques developed. Even so, Ozawa<sup>56,57,58</sup> extended and modified this method slightly

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<sup>55</sup> Flynn, J. H. and L. A. Wall, *J. Res. Natl. Bur. Stds.*, **70A**, 504, 1966.

<sup>56</sup> Ozawa, T., *J. Therm. Anal.*, **2**, 301, 1970.

<sup>57</sup> Ozawa, T., *J. Therm. Anal.*, **31**, 301, 1986.

to further broaden its application area. He has used this method, with some success, on the degradation of calcium oxalate and nylon 6, as well as the thermal shrinkage of polycarbonate. Values agree well with those reported in the literature.

Elucidation of  $E_a$  is quite simple by Ozawa's method and presents the added advantage that any change of mechanism is obvious by changes in the slopes of the lines at different conversions. However, multiple heating rates require several samples, therefore possibly introducing errors. Furthermore, calculating a value for  $A$  is rather complex, and finding  $n$  requires a sort of trial-and-error procedure, factors which work to this method's disadvantage.

Flynn and Wall<sup>59</sup> independently developed this same method in 1966, but stopped short of proposing a scheme for finding  $A$  and  $n$ , merely suggesting a method for calculating  $E_a$ . They offered a more detailed analysis of their technique some years later,<sup>60</sup> discussing the errors introduced by utilizing Doyle's approximation, and a way to improve the calculation consisting of a tabulated correction factor,  $F(x)$ .

Another group of researchers<sup>61</sup> also worked on eliminating some of the error associated with the isoconversional method. Instead of using tabulated values as previously proposed, Opfermann and Kaiserberger suggest using computer-aided analysis to generate the  $F(x)$  factor. It was found empirically that

$$F(x) = a_0 \left( 1 + \frac{a_1 + x}{1 + a_2x + a_3x^2} \right) \quad \text{Equation 1.4-74}$$

where  $a_0 = 0.94961$ ,  $a_1 = 7.770439$ ,  $a_2 = 4.56082$ , and  $a_3 = 0.48843$ . The authors report very small errors associated with this empirical equation and high precision with  $r > 0.99999$ . They also report an equation for the  $p(x)$  term found in the isoconversional method:

$$p(x) = \frac{e^{-x}}{x} \left( \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \right) \quad \text{Equation 1.4-75}$$

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<sup>58</sup> Ozawa, T., *J. Therm. Anal.*, **37**, 1299, 1991.

<sup>59</sup> Flynn, J. H. and L. A. Wall, *Polym. Lett.*, **4**, 323, 1966.

<sup>60</sup> Flynn, J. H., *J. Therm. Anal.*, **27**, 95, 1983.

<sup>61</sup> Opfermann, J. and E. Kaiserberger, *Thermochim. Acta*, **203**, 167, 1992.

As with any technique with so many parameters, care should be taken in assigning importance to them. In general, more parameters yield a better fit, but with less physical significance behind the values. Such may be the case in this instance, and results should be treated with caution.

Flynn and coworkers<sup>62,63</sup> also developed an entirely different method. They begin with the standard rate equation, Equation 1.4-1 combined with Equation 1.4-3. For this technique, interest is in the slope at low conversions ( $\alpha \leq 0.05$ ), so the next step involves differentiating the rate equation with respect to  $\alpha$ :

$$\frac{d}{d\alpha} \left( \frac{d\alpha}{dt} \right) = \frac{d}{d\alpha} \left( \beta \frac{d\alpha}{dT} \right) = \beta \frac{d}{d\alpha} \left( \frac{d\alpha}{dT} \right) + \frac{d\alpha}{dT} \frac{d\beta}{d\alpha} = \beta \frac{E_a}{RT^2} + \frac{f'(\alpha)}{f(\alpha)} \frac{d\alpha}{dT} \quad \text{Equation 1.4-76}$$

where

$$\frac{f'(\alpha)}{f(\alpha)} = \frac{-n}{1-\alpha} \quad \text{Equation 1.4-77}$$

For a constant heating rate  $\beta$ , one finds

$$\frac{d}{d\alpha} \left( \frac{d\alpha}{dT} \right) = \frac{E_a}{RT^2} - \frac{n}{1-\alpha} \frac{d\alpha}{dT} \quad \text{Equation 1.4-78}$$

If one then plots  $T^2 \left( \frac{d\alpha}{dT} \right) = \frac{-d\alpha}{d(1/T)}$  versus  $\alpha$ , the slope becomes  $\frac{E_a}{R} + 2T + \frac{n}{1-\alpha} \frac{d\alpha}{d(1/T)}$ . At low conversions, one may approximate the incremental slope by

$$\Delta \left( T^2 \frac{d\alpha}{dT} \right) / \Delta\alpha \approx \frac{E_a}{R} + 2T \quad \text{Equation 1.4-79}$$

Once  $E_a$  is calculated by the aforementioned procedure, one can plot  $\ln \frac{d\alpha}{dt} + \frac{E_a}{RT}$  versus  $\ln(1-\alpha)$  which should have an initial slope of  $n$  and an intercept of  $\ln A$ .

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<sup>62</sup> Flynn, J. H. and L. A. Wall, *Polym. Lett.*, **5**, 191, 1967.

<sup>63</sup> Flynn, J. H. and B. Dickens, *ACS Symp. Series*, **95**, *Durability of Macromolecular Materials*, Washington, DC, 1979.

The advantages of Flynn's procedure are many. Firstly, only a single sample is required, alleviating error from multiple samples. Because this method is concerned only with small extents of reaction, one can ignore the form of the dependence of the rate of reaction on the extent of reaction. Finally, the manner in which the slope changes can help the experimenter infer other information about the degradation. For example, if the slope increases with increasing  $\alpha$ , then the reaction is autocatalytic. If the opposite is true (slope decreases with increasing  $\alpha$ ), the reaction follows a positive reaction order. Zero-order kinetics are implied if the slope is independent of  $\alpha$ .

Drawbacks also exist for Flynn's technique. Primarily, the extent of conversion term is present in both quantities being plotted, so one must use especial care in choosing the beginning of the polymer degradation. Furthermore, any volatiles, such as monomer, solvent, or plasticizer, which may be present in the sample need to be minimized in a pretreatment step since the the initial rate of weight loss is very dependent on these sorts of contaminants. This is also true for any residual catalyst, antioxidants, stabilizers, etc., which may also affect initial weight-loss rates.

Broido,<sup>64</sup> instead of developing a new approach of analysis, refines the existing techniques of van Krevelen<sup>43</sup> and of Horowitz and Metzger.<sup>44,45</sup> He begins with the standard rate equation, as in Equation 1.4-1 and Equation 1.4-3, but with a slight modification. His expressions are in terms of  $y = 1 - \alpha$ . Therefore,

$$\frac{dy}{dt} = -ky^n \quad \text{Equation 1.4-80}$$

Next, a temperature ramp is defined as

$$T = T_0 + \beta t \quad \text{Equation 1.4-81}$$

Then, substituting Equation 1.4-81 into Equation 1.4-80

yields

$$\frac{dy}{y^n} = -\frac{A}{\beta} e^{-E_a/RT} dT \quad \text{Equation 1.4-82}$$

Integration leads to

$$\int_y^1 \frac{dy}{y^n} = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad \text{Equation 1.4-83}$$

Broido solves the integration on the left-hand-side of Equation 1.4-83 by assuming a first-order reaction,  $n = 1$ , so the term becomes  $\ln(1/y)$ . The right-hand-side of Equation 1.4-83 presents difficulties. Both van Krevelen and Horowitz and Metzger used approximations to solve this term. Broido resorts to a substitution of  $z = E_a / RT$  such that the term becomes

$$J(z) = \int_z^\infty z^{-2} e^{-z} dz = z^{-2} e^{-z} S(z) \quad \text{Equation 1.4-84}$$

Values for  $J(z)$  and  $S(z)$  have been tabulated. Broido concludes that, for  $n=1$ ,

$$\ln y = -\frac{AE_a}{\beta R} J(z) \quad \text{Equation 1.4-85}$$

The advantage of this method, according to the author, is that this approximation is much more accurate than that of either van Krevelen or Horowitz and Metzger. However, it also necessitates assumption of a reaction order and reliance on cumbersome tables for calculations. This technique does not seem to offer any real advantages over many others, and indeed may be a poor choice.

Another procedure, that of Coats and Redfern,<sup>65</sup> begins in a similar manner to the previous method of Broido.<sup>64</sup> However, in this instance, equations are carried out in terms of  $\alpha$ . So, starting with the standard rate equations (Equation 1.4-1 and Equation 1.4-3) and integrating leads to

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^T e^{-E_a/RT} dT \quad \text{Equation 1.4-86}$$

The authors report that the right-hand-side of Equation 1.4-86 has been found to be

$$\frac{A}{\beta} \int_0^T e^{-E/RT} dT = \frac{ART^2}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) e^{-E_a/RT} \quad \text{Equation 1.4-87}$$

In order to get values for the left-hand-side of Equation 1.4-86, a series expansion is carried out:

<sup>64</sup> Broido, A., *J. Polym. Sci, Part A-2*, **7**, 1761, 1969.

<sup>65</sup> Coats, A. W. and J. P. Redfern, *Polym. Lett.*, **3**, 917, 1965.

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \alpha + \frac{n\alpha^2}{2} + n(n+1)\frac{\alpha^3}{6} + \dots \quad \text{Equation 1.4-88}$$

For values of  $\alpha \leq 0.3$ , one can neglect  $\alpha^2$  and higher terms in the series to yield

$$\alpha = \frac{ART^2}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) e^{-E_a/RT} \quad \text{Equation 1.4-89}$$

Combining terms leads to

$$\ln \frac{\alpha}{T^2} = \ln \left( \frac{AR}{\beta E_a} \right) \left( 1 - \frac{2RT}{E_a} \right) - \frac{E_a}{RT} \quad \text{Equation 1.4-90}$$

Using Equation 1.4-90

, it is evident that plotting  $\ln \alpha/T^2$  versus  $1/T$  should give a linear result. The slope is simply  $-E_a/R$  because, at small  $\alpha$  or for  $n=0$ , the term  $\ln \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right)$  should be essentially constant.

The authors applied this method to the degradation of PTFE with satisfactory results. One large advantage of this method is its simplicity. It is very easily applied to the data. However, caution should be taken when using this procedure since certain limitations, such as small  $\alpha$  and no change of mechanism, apply. Overall, this technique would probably be useful for obtaining preliminary values for kinetic parameters, particularly in the early stages of the degradation.

A very basic method has been used in recent years by Tagle and Diaz.<sup>66,67</sup> It begins with the basic equations which Tagle and Diaz rewrite in terms of temperature rather than time. Then, they rearrange and take the logarithm leading to

$$F = \ln \left[ \frac{-(d\alpha/dT)}{(1-\alpha)^n} \right] = \ln A - \frac{E_a}{RT} \quad \text{Equation 1.4-91}$$

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<sup>66</sup> Tagle, L. H. and Diaz, F. R., *Thermochim. Acta*, **160**, 161, 1990.

<sup>67</sup> Tagle, L. H. and Diaz, F. R., *Intern. J. Polym. Mater.*, **26**, 207, 1994.

Again, plotting  $F$  versus  $1/T$  yields a straight line with slope proportional to  $E_a$  and intercept related to  $A$ . The authors have applied this method to degradation of various polycarbonates with some success. The ease of applying this technique cast it in a favorable light.

Some authors question the standard kinetic equations, calling into doubt their applicability except in very limited circumstances. Shlensky<sup>68</sup> proposes that the kinetic equations which should be in use are

$$\frac{d\omega}{dt} = -k(\omega - \omega_\infty)^n + \omega'_{inst}(T) \quad \text{Equation 1.4-92}$$

and

$$k = k_0 \left( 1 + \frac{\beta}{\beta_0} \right) e^{-E_a/RT} \quad \text{Equation 1.4-93}$$

with terms defined as follows:  $\omega$  = relative mass of sample residue (weight / initial weight);  $\omega_\infty$  = relative mass during equilibrium heating (infinitely slowly);  $\omega_{inst}$  = relative mass at instantaneous heating (infinitely quickly); and  $\beta_0$  = parameter which for many polymers is about 1 K/s.

According to the author, while traditional kinetic parameters ( $E_a$ ,  $A$ , and  $n$ ) fit data at a specific set of conditions (heating rate, for example), an entirely new set of parameters are necessary to describe the curve at a different experimental condition (heating rate). Shlensky's method reportedly overcomes this deficiency. However, this method has not been widely used in more recent kinetic studies, leading one to believe that the traditional methodologies are adequate for the current engineering needs.

From this overview, it is evident that methods to analyze kinetic data are limited only by the imagination of researchers. Certain techniques, though, are relied upon more heavily in newer research. These include the methods of Freeman and Carroll, Friedman, and Ozawa. The prevalence of these procedures tends to corroborate their utility in polymer degradation. Dynamic tests are generally faster to conduct, so techniques to analyze the resulting data would be preferred. Those which demonstrate the greatest ease of application include Tagle's and van Krevelen's. However, neither of these methods

result in values for the order of reaction, so it would either have to be assumed or calculated via some other technique.

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<sup>68</sup> Shlensky, O. F., *J. Therm. Anal.*, **28**, 421, 1983.