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### Kinetics and Gaseous Products of Thermal Decomposition of Polymers

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## Kinetics and Gaseous Products of Thermal Decomposition of Polymers\*

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The application of polymers at ever-increasing temperatures has given impetus to research on the chemistry of thermal decomposition. In recent years polymers have been used for a variety of high-temperature applications, such as cooking vessels, motor insulation, and re-entry vehicle heat shields. Interest in chemistry of decomposition has been found in such industries as tobacco and grinding-wheels. Because of the vast number of polymers that are available and the variety of applications thousands of papers have appeared in the literature. Rather than give a complete review the purpose of this paper is to give a brief survey of topics that have been emphasized in the author's research, namely kinetics, mechanisms, and gaseous decomposition products at elevated temperatures.

In classical kinetic studies one usually carries out a reaction at constant temperature and measures the appearance of products and disappearance of reactants as a function of time. Substances of comparatively simple structure are generally studied, and standard measuring techniques are usually adequate. Because of the nature of polymeric molecules one is often uncertain of the precise structure of the original polymer sample and of the residue as decomposition progresses. Molecular weight, size distribution, structure of chain ends, existence of branches, presence of weak

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links, and inclusion of impurities may have a profound influence. While it is possible to measure or to approximate some of these parameters for some linear polymers, cross-linked or char-forming polymers are much harder to handle. Control of preparation can be an important consideration. It is often possible to promote irreversible decomposition during preparation. Different portions of the same piece may have different compositions. The surface of a sample may be quite different from the interior, especially if it is prepared in the presence of oxygen or if an entrained product must escape during polymerization. Opportunities for changing the composition are available during grinding, a process that is often used to prepare samples for degradation studies. It is not uncommon to utilize poorly characterized off-the-shelf samples. The present author has had to use such samples from time to time. The availability of standard pure samples would greatly aid research in this field.

Sample size is an extremely important consideration. Diffusion-controlled weight loss and secondary chemical reactions due to retention of primary decomposition compounds may have a strong influence on the results. It is customary to examine the effect of film thickness or particle size in kinetics studies. The usual criterion is given by choosing dimensions that are below a size at which the rate of loss of weight is influenced by the size. In a study of pyrolysis of poly(methyl methacrylate) and polystyrene Barlow et al. (1) found that film thicknesses of less than 250 and 400 Å, respectively, were required for the rate of loss of weight to

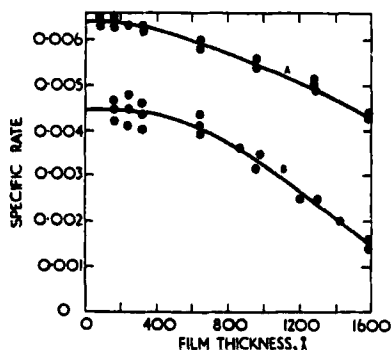
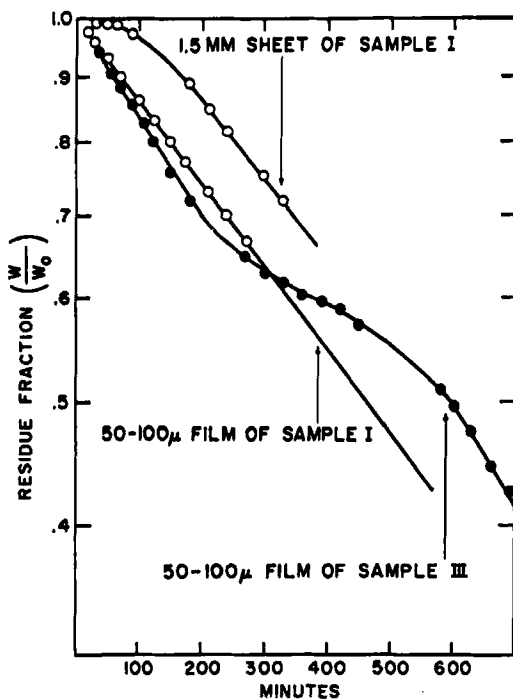


FIG. 1. Dependence of rate of degradation on sample thickness for poly(methyl methacrylate) (A) and polystyrene (B); multiply ordinate scale by 10 for (B). [From (1); courtesy of Gordon & Breach Science Publishers, Inc., New York.]

be independent of film thickness (Fig. 1). The rate of loss of weight was slower for thicker films. Siegle et al. (2) found that films of polytetrafluoroethylene that were initially thicker than 4 mils started to decompose at a slower rate than the thinner films but eventually reached the same rate (Fig. 2). These authors also found that, if the thin films fused and agglomerated, the rate of loss of weight could be retarded for the period that it took the film to become sufficiently thin, owing to degradation. The differences in thickness of a factor of more than 1,000 for these different polymers is striking. It could, perhaps, be related to the morphology of the polymers or to a surface effect for the very thin polymers. Jones and Moyles (3) (Fig. 3) found that pyrolysis of polystyrene samples in the microgram range produced only styrene monomer, while milligram samples that were pyrolyzed under the same conditions produced significant quantities of dimer and trimer in



**FIG. 2.** Effect of film thickness on rate of degradation of polytetrafluoroethylene; polymer III has very low initial melt viscosity and flowed into a compact mass after about 180 min. [From (2); courtesy of John Wiley & Sons, Inc., New York.]

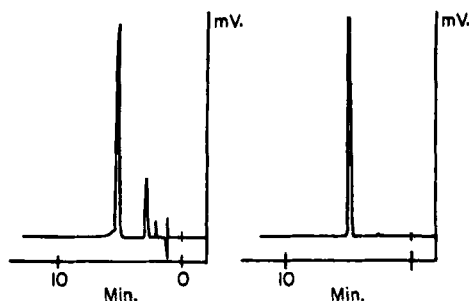


FIG. 3. Pyrolysis chromatograms for milligram (left) and microgram (right) quantities of polystyrene under similar conditions. [From (3); courtesy of *Nature* and the authors, C. E. Roland Jones and A. F. Moyles.]

addition to monomer. Even if small particles are used, they should be so distributed that they do not agglomerate if they melt, and they should not be placed in a mound. The latter provides an opportunity for secondary reactions by collision of primary decomposition products with other solid particles.

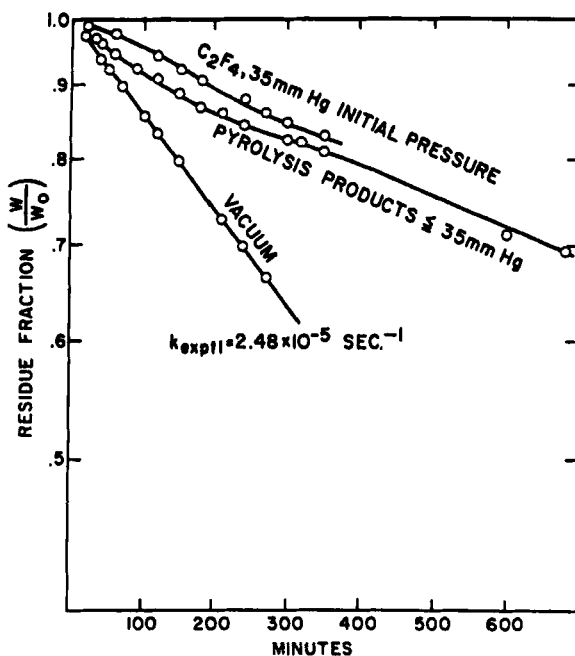


FIG. 4. Pyrolysis of polytetrafluoroethylene films in the presence of tetrafluoroethylene and pyrolysis products. [From (2); courtesy of John Wiley & Sons, Inc., New York.]

TABLE I

Composition of Liquid Fraction from Pyrolysis of Polymethylene  
in a Vacuum and in Helium (5)<sup>a</sup>

| Component                              | Weight percentage of total volatiles |                  |                  |                  |                   |                   |
|--|--------------------------------------|------------------|------------------|------------------|-------------------|-------------------|
|  | 500°C,<br>vacuum                     | 500°C,<br>helium | 800°C,<br>vacuum | 800°C,<br>helium | 1200°C,<br>vacuum | 1200°C,<br>helium |
| CH <sub>4</sub>                        | —                                    | —                | —                | 0.2              | 3.1               | 0.1               |
| C <sub>2</sub> H <sub>2</sub>          | —                                    | —                | —                | 0.4              | 2.9               | 0.6               |
| C <sub>2</sub> H <sub>4</sub>          | —                                    | 2.1              | 5.4              | 11.9             | 22.3              | 16.2              |
| C <sub>2</sub> H <sub>6</sub>          | 0.1                                  | 0.8              | 0.3              | 2.2              | 0.8               | 1.5               |
| C <sub>3</sub> H <sub>4</sub>          | 0.1                                  | 0.1              | 0.2              | 0.2              | 2.1               | —                 |
| C <sub>3</sub> H <sub>6</sub>          | 0.1                                  | 2.2              | 2.8              | 5.8              | 6.4               | 3.9               |
| C <sub>3</sub> H <sub>8</sub>          | 0.2                                  | 0.8              | —                | 0.6              | 0.4               | —                 |
| C <sub>4</sub> H <sub>2</sub>          | —                                    | 0.3              | —                | 0.3              | —                 | 0.3               |
| C <sub>4</sub> H <sub>6</sub>          | 0.3                                  | 0.5              | 0.9              | 1.7              | 5.4               | 1.3               |
| C <sub>4</sub> H <sub>8</sub>          | 0.2                                  | 1.5              | 3.9              | 3.6              | 2.4               | 0.7               |
| C <sub>4</sub> H <sub>10</sub>         | 0.1                                  | 0.3              | 0.4              | 0.3              | —                 | —                 |
| C <sub>5</sub> to C <sub>9</sub> incl. | 4.8                                  | 8.5              | 8.1              | 16.7             | 1.9               | 13.8              |

<sup>a</sup> This table is reproduced by courtesy of the *SPE Journal*.

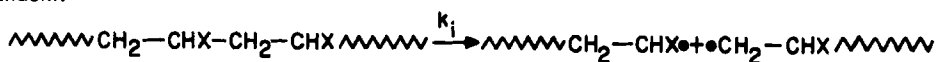
The chemical environment in which a polymer will be used influences its decomposition. Oxygen often has a profound effect. Conley (4) has carried out extensive investigations of the role of oxygen in the decomposition of condensation polymers. The influence of inert gases is different from that of vacuum, as may be seen from the results of pyrolysis of polymethylene in vacuum and helium, as carried out by Madorsky (5) (Table 1). In vacuum the primary decomposition product is rapidly pumped away from the hot reaction zone, before it can undergo extensive further degradation. In the presence of an inert gas the primary decomposition products may undergo further homogeneous reactions as a result of collisions with hot inert gas molecules or may be altered by heterogeneous reactions, if they are reflected back to the hot surface of the sample. The presence or absence of decomposition gases will affect kinetic measurements in cases in which reversible reactions occur. This was demonstrated by Siegle et al. (2) in comparing the rate of pyrolysis of polytetrafluoroethylene in vacuum and in the presence of tetrafluoroethylene monomer and decomposition products (Fig. 4).

The mechanisms and kinetics of decomposition of vinyl polymers have been studied more thoroughly than those of any other family.

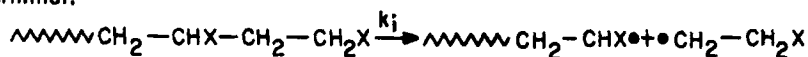
A variety of structures have been pyrolyzed by many scientists and with a variety of techniques. Grassie (6) has done particularly significant research in this field. Poly(methyl methacrylate) and polytetrafluoroethylene, which pyrolyze to form nearly 100% monomer, have been studied more extensively than any of the other polymers. Lesser conversion to monomer, even 0% in some cases, has been observed in the case of other polymers. For total conversion to monomer the results of experiments have been explained on the basis of depolymerization, that is, the reverse of the polymerization mechanism (7), as follows:

### Initiation

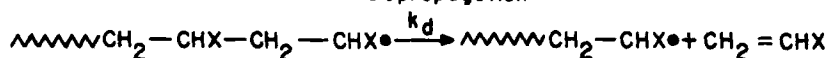
Random:



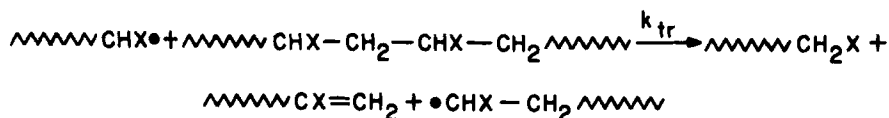
Terminal:



### Depropagation



### Transfer

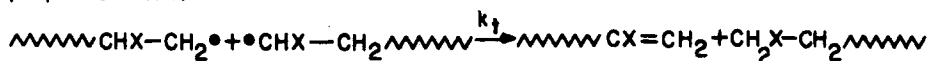


### Termination

Recombination:



Disproportionation:



Many mathematical treatments of these reactions have been attempted during the past fifteen years, including elaborate computer treatments and the effect of various molecular-weight distributions. The following rather simple equations will be used to illustrate the types of relationship that may be used and the mathematical consequences (8).

Random initiation:

$$d[R]/dt = 2k_i(2N - 1)[P] \approx 4k_iN[P]$$

where  $[R]$  and  $[P]$  are the concentrations of radical and polymer molecules, respectively,  $N$  is the degree of polymerization, and  $t$  is the time.

Terminal initiation:

$$d[R]/dt = 2k_i[P]$$

Depropagation:

$$(1/V)(dM/dt) = k_d[R]$$

where  $V$  is the volume and  $M$  is moles of monomer.

Termination:

$$-d[R]/dt = 2k_t[R]^2$$

The consequences of this treatment for a variety of combinations are shown below.

Random initiation, complete unzipping:

$$-dw/dt = 2k_iNw$$

where  $w$  is the weight of polymer. In this case the kinetic chain length is always greater than the molecular chain length. The rate of degradation is first-order in weight and is proportional to the molecular weight of the sample. If the sample is monodisperse, its molecular weight will remain constant throughout decomposition and will suddenly drop to zero at the end. If the molecule sizes are distributed, initiation will tend to start in the longer molecules initially, and the molecular weight of the sample will tend to drop throughout pyrolysis.

Terminal initiation, complete unzipping:

$$-dw/dt = 2k_t w$$



The kinetic chain length is always greater than the molecular chain length in this case. The rate is first-order in sample weight and is independent of the molecular weight. The molecular-weight distribution tends to remain unchanged during degradation.

Random initiation, bimolecular termination

$$-dw/dt = k_d(2k_t m/Dk_i)^{1/2} w$$

where  $m$  is the molecular weight of monomer and  $D$  is the density of polymer. In this case the molecular weight of sample is always greater than the kinetic chain length. The rate is first-order in sample weight and is independent of molecular weight in this case as in terminal initiation, complete unzipping. The molecular weight reduces as depolymerization progresses. The rate of molecular-weight reduction is greater for disproportionation than for recombination.

Terminal initiation, bimolecular termination

$$-dw/dt = k_d(k_t m/DNk_i)^{1/2} w$$

In this case the molecular weight is always greater than the kinetic chain length. While the rate is first-order in sample weight, it is inversely proportional to the square root of molecular weight. If termination is by disproportionation, the molecular weight will decrease as pyrolysis progresses. If recombination is favored, the molecular weight may increase, decrease, or remain unchanged, depending on the relative sizes of the kinetic and molecular chain lengths.

Current thought on the pyrolysis of polytetrafluoroethylene (2,9) tends to support random initiation, partial depropagation, and bimolecular termination by disproportionation. The decomposition of poly(methyl methacrylate) is thought to be somewhat more complicated (10). At temperatures below 270°C initiation occurs at unsaturated chain ends. Partial unzipping occurs, except where the kinetic chain length is longer than the molecular chain. Termination is by disproportionation. When the temperature is above 300°C, an additional mechanism comes into play; that is, random initiation occurs in addition to the above reactions.

In recent years there has been a trend toward the use of linear rates of temperature rise in addition to isothermal heating. The principal techniques that incorporate such heating for polymers

are thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Several monographs (11,12) provide comprehensive descriptions of apparatus, techniques, and evaluations of these many other methods of thermal analysis. In TGA sample weight is recorded continually with an automatic recording balance. Thermograms for a series of polysiloxanes are shown in Fig. 5.

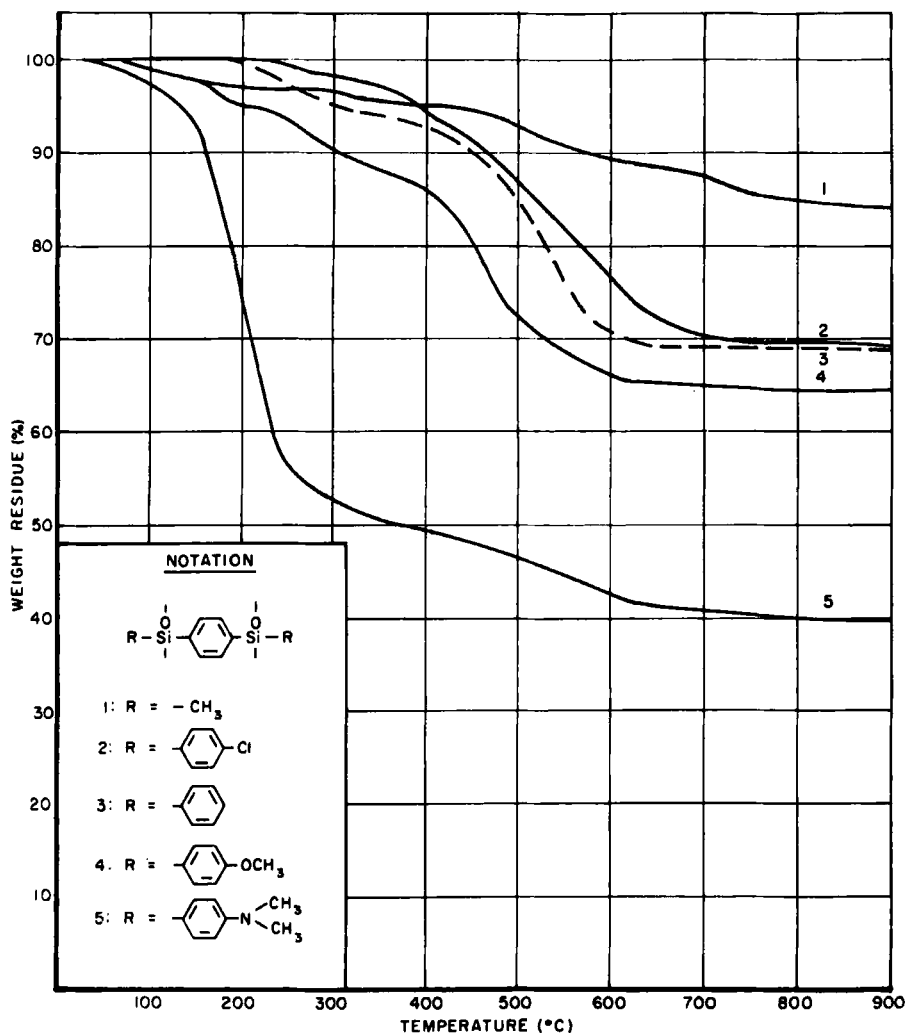


FIG. 5. Thermogravimetric curves for polysiloxanes. [From (13); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

These were reported by Ehlers (13) and were obtained in a Chevenard Thermobalance in a nitrogen atmosphere at a rate of 150°C/hr. TGA thermograms show processes only when there is a change of weight. It is possible to determine such factors as temperature range and extent of certain decomposition processes and extent volatilization. It is also possible to determine the relative thermal stabilities of polymers, especially when they are part of the same family and decompose in a similar way. In DTA the temperature differences between a sample and reference standard are measured while the latter is heated linearly. If sufficient sensitivity is available, it is possible to detect all endo- and exothermic processes, regardless of whether the weight changes or not. Figure 6 shows two DTA thermograms that were obtained for polychlorotrifluoroethylene by Doyle (14). TGA for the same polymer is also shown on the same figure.

Since TGA and DTA give decomposition data as a function of time and temperature, they have been assumed to be a rather efficient source of kinetic data. Although DTA has not been used very frequently, many papers have been written on kinetic analysis of TGA. Most treatments use some form of the equation

$$-dw/dt = A \exp(-\Delta E/RT)f(w)$$

where  $A$  and  $\Delta E$  are the pre-exponential factor and activation-energy terms of the rate constant, respectively,  $R$  is the gas constant,  $T$  is absolute temperature, and  $f(w)$  is some function of the sample weight and is usually assumed to have the form  $w^n$  for polymers that volatilize completely. For polymers that leave a residue  $f(w)$  is related to instantaneous sample weight and the final weight of residue. For the heating rate  $dT/dt = \rho$  the kinetic equation may be written

$$-dw/f(w) = (A/\rho) \exp(-\Delta E/RT) dT$$

The kinetic parameters are obtained by a variety of derivative and integral methods. The temperature term of the kinetic equation may be integrated to give

$$\int_{T_0}^T \exp(-\Delta E/RT) dT = T \exp(-\Delta E/RT) - T_0 \exp(-\Delta E/RT) + (\Delta E/R) \left[ \int_{v_0}^{\infty} (e^{-v}/v) dv - \int_v^{\infty} (e^{-v}/v) dv \right]$$

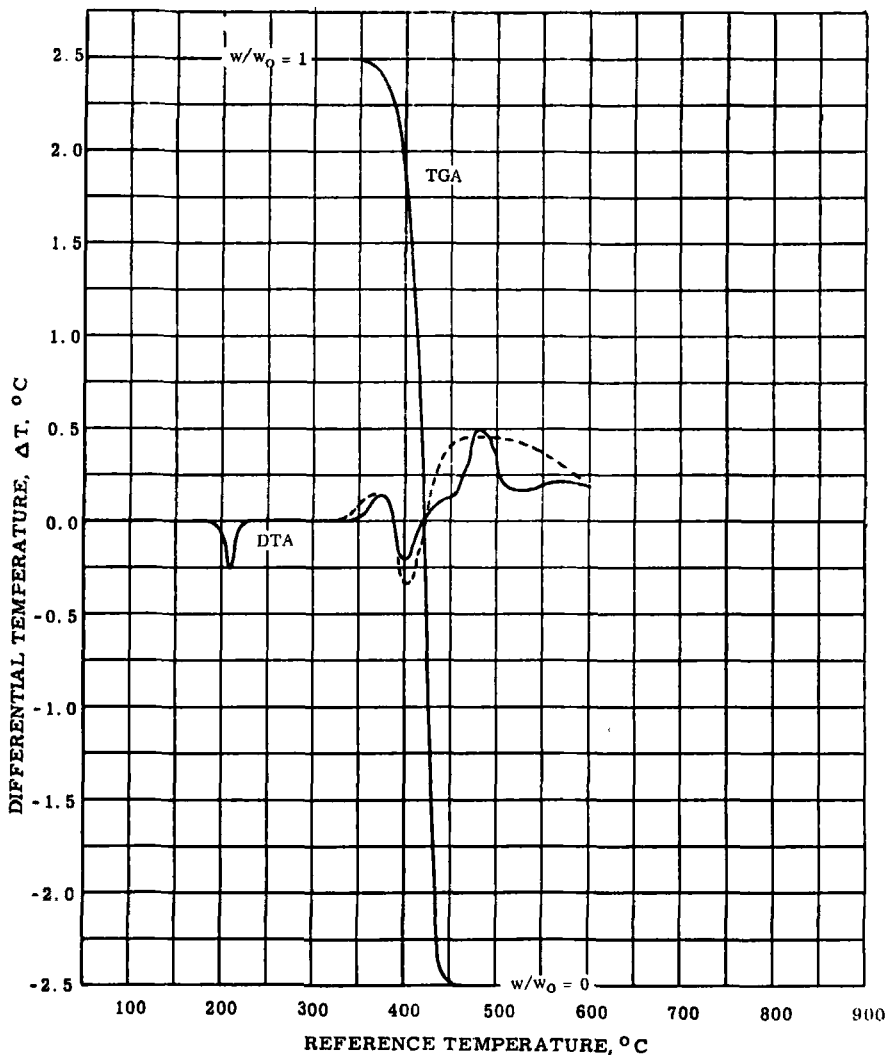


FIG. 6. Thermogravimetric and differential thermal analysis curves for polychlorotrifluoroethylene. [From (14); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

where  $v = \Delta E/RT$  and  $v_0 = \Delta E/RT_0$ . The integral containing  $v$  is known as the exponential integral. It is tabulated in several references, but that by Vallet (15) is the most comprehensive and is convenient to use. Since  $\Delta E$  and  $T$  appear in several parts of the

equation, including exponents, analytical use of the integral is awkward. Several authors (16-18) have employed approximate integrals effectively.\*

A wide variety of derivative methods have been developed, the most frequently used being that developed by Freeman and Carroll

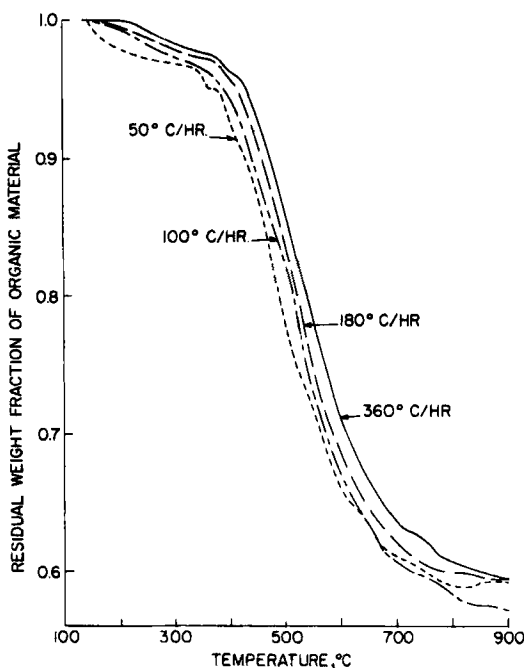


FIG. 7. Thermogravimetric-analysis curves for a phenolic plastic at various heating rates. [From (22); courtesy of John Wiley & Sons, Inc., New York.]

(21). These workers used the equation

$$\Delta \ln (-dw_r/dt)/\Delta \ln w_r = -(\Delta(1/T)/\Delta \ln w_r)(\Delta E/R) + n$$

where  $w_r$  is the weight of the reactive portion of the sample;  $[\Delta \ln (-dw_r/dt)/\Delta \ln w_r]$  is plotted against  $[\Delta(1/T)/\Delta \ln w_r]$ . If a straight line results, the slope is  $-\Delta E/R$  and the intercept is  $n$ . A different type of derivative treatment is based on intercomparison of TGA curves obtained at linear rates of temperature rise (22,23). The method developed by Friedman (22) is based on the logarithm-

\* Two very recent papers (19,20) extended Doyle's (17) approximate integration to multiple linear heating rates.

mic treatment of the kinetic equation, giving

$$\ln(-dw/dt) = \ln[A \times f(w)] - \Delta E/RT$$

where  $f(w)$  is assumed to be constant at constant  $w$  (that is, the chemical composition of the solid is dependent only on the weight).

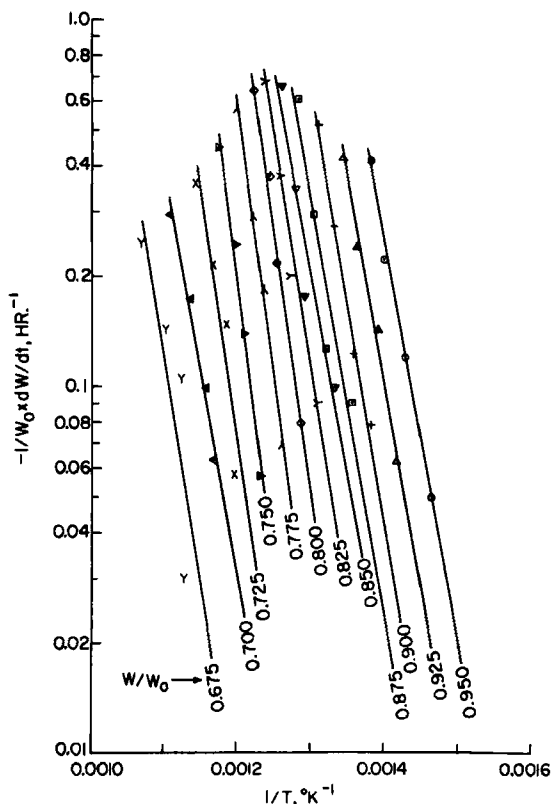


FIG. 8. Arrhenius-type plots for determining kinetic parameters from data in Fig. 7. [From (22); courtesy of John Wiley & Sons, Inc., New York.]

The  $\ln(-dw/dt)$  is plotted against  $1/T$  for various weights. The slope is  $-\Delta E/R$  and the intercept is  $\ln[A \times f(w)]$ . The TGA curves are shown for a phenolic resin in Fig. 7. The Arrhenius-type plots are shown in Fig. 8.  $A$  and  $n$  were determined by assuming  $f(w) = (w - w_f)^n$ , where  $w_f$  was the final weight of char. Multiplying by  $A$  and taking logarithms gives

$$\ln[A \times f(w)] = \ln A + n \ln(w - w_f)$$

The  $\ln [A \times f(w)]$  was plotted against  $\ln (w - w_f)$ . The slope was  $n$  and the intercept was  $\ln A$ . Anderson (23) employed the equation

$$-dw/dt = A \exp(-\Delta E/RT)w^n$$

which is well established for polytetrafluoroethylene, a polymer that leaves no residue. By using three different heating rates it was possible to determine a very consistent set of values for the three unknowns  $A$ ,  $\Delta E$ , and  $n$  over the complete range of weights from small to nearly complete degradation. A third derivative method is based on the fact that  $d^2w/dt^2 = 0$  at the maximal rate of loss of weight (22,24). Then  $\Delta E$  may be determined from the equation

$$\Delta E = -(nRT_m^2/w_m)(dw/dT)_m$$

where the subscript  $m$  represents the point at which the rate of loss of weight is at a maximum.

Although these and many more elaborate methods have been developed for the kinetic analysis of TGA, the writer is not certain that the quality of the data that have been obtained in the laboratory warrants the degree of sophistication. Table 2 lists kinetic parameters that various authors have obtained for isothermal vacuum pyrolysis of polytetrafluoroethylene, and Table 3 lists similar parameters for TGA vacuum pyrolysis. Of the isothermal measure-

TABLE 2  
Kinetic Parameters Observed for Isothermal Vacuum Pyrolysis  
of Polytetrafluoroethylene

| Workers                               | Ref. | Technique                 | Weight, mg                     | A, sec <sup>-1</sup>  | $\Delta E$ , kcal/<br>mole |
|---------------------------------------|------|---------------------------|--------------------------------|-----------------------|----------------------------|
| Madorsky, Hart,<br>Straus, and Sedlak | 25   | Manometric<br>gravimetric | 5 to 345<br>6 to 7             | $4.7 \times 10^{18}$  | 80.5                       |
| Siegle, Muus,<br>Lin and Larsen       | 2    | Manometric<br>gravimetric | Not re-<br>ported <sup>a</sup> | $3 \times 10^{19}$    | 83                         |
| Wright                                | 26   | Gravimetric               | 5 to 10                        | —                     | 76                         |
| Reich, Lee,<br>and Levi               | 27   | Gravimetric               | <200                           | $1.6 \times 10^{18b}$ | 79 <sup>b</sup>            |
| Rosen and<br>Melveger                 | 28   | Torsion-<br>effusion      | 50 to 150                      | $1.9 \times 10^{17}$  | $77 \pm 7$                 |

<sup>a</sup> Films, 50 to 100  $\mu$  thick.

<sup>b</sup> Approximate measurement, calculation by Friedman.

**TABLE 3**  
Kinetic Parameters Observed for Thermogravimetric Vacuum  
Pyrolysis of Polytetrafluoroethylene

| Workers                 | Ref. | Weight, mg | A, sec <sup>-1</sup> | ΔE, kcal/mole |
|-------------------------|------|------------|----------------------|---------------|
| Doyle <sup>a</sup>      | 17   | 200        | $8 \times 10^{14}$   | 67            |
| Anderson                | 29   | 10         | —                    | $75 \pm 4$    |
| Farmer                  | 30   | 100        | $1.4 \times 10^{14}$ | 69            |
| Reich, Lee,<br>and Levi | 27   | < 200      | —                    | $72 \pm 2$    |
| Anderson                | 23   | 9 to 11.5  | $6.7 \times 10^{18}$ | 77            |

<sup>a</sup> Nitrogen atmosphere.

ments those of Madorsky et al. (25) and Siegle et al. (2) are thought to be the most significant, for the measurements were made by two different techniques, and a wide range of initial molecular weights was employed. Note that the pre-exponential factors are about  $10^{18}$  sec<sup>-1</sup> and the activation energies are about 80 kcal. The TGA kinetic parameters tend to be lower. The following discussion of TGA errors is general and may only be partly applicable to polytetrafluoroethylene and other polymers that decompose via comparatively simple mechanisms.

Only weight loss is determined in TGA measurements. If consecutive or competing reactions occur and overlap, then the weight measurement may not resolve the reactions. Unless sufficient separation occurs, kinetic analysis is problematic. Although direct temperature monitoring and regulation methods have been described (31) and are available in at least one commercial instrument (32), few kinetic TGA measurements have been made with such apparatus. Exo- and endothermic reactions cause the sample temperature to depart from that which is desired. Large temperature deviations have been demonstrated (33). In addition, temperature variations are present within the sample, being greatest for the largest samples. In fact, these differences make DTA measurements possible. Since temperature effects have an exponential effect in kinetics, they are particularly significant. Of course, the use of large samples or particles and inert atmospheres would tend to have the same types of effect in TGA as in other methods, as was described earlier. Other types of error may occur in any type of vacuum gravimetry. Momentum transfer may tend to make



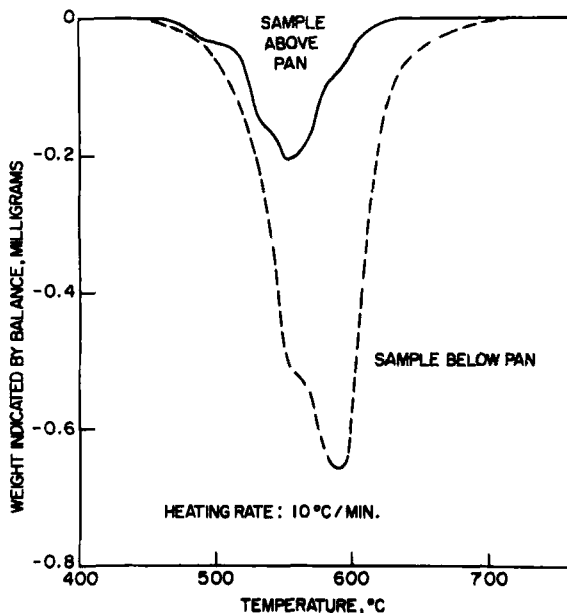


FIG. 9. Effect of heating polytetrafluorethylene samples above and below empty thermobalance pan. [From (34); courtesy of *Analytical Chemistry*.]

the sample appear to be heavier as a result of high-velocity evolution of pyrolysis gases from the sample pan. Aerodynamic drag of pyrolysis gases as they are pumped away from the vicinity of the sample may produce significant errors. Friedman (34) observed such aerodynamic effects by heating 1-mil-thick samples of polytetrafluorethylene, weighing about 7 mg, both above and below an empty sample pan, as may be seen in Fig. 9. The pan was supported by a wire that was suspended from above, and the pumping port was also in this position. Although drag along the support wire occurred in each case, the greater effect was obtained from the pan acting as a sail when the sample was heated below the pan. These effects are very dependent on the geometry of the thermobalance heating chamber, sample suspension, pumping speed, and rate of evolution of products.

Thus it is reasonable that isothermal measurements give different kinetic parameters from those of TGA measurements, as in the case of polytetrafluorethylene. The good agreement between the isothermal values and Anderson's (23) TGA values may appear to

contradict this argument; the present writer, however, believes that this may be due to the method of kinetic analysis. Anderson's kinetic treatment, as was discussed earlier, was based on inter-comparison of TGA measurements that were obtained at different linear rates of heating. Since the various errors would tend to be in the same direction for each of the runs, they may have tended to compensate for each other in the kinetic treatment and may well indicate that this technique could be expected to provide superior kinetic parameters from TGA measurements.

Mass spectrometric thermal analysis (MTA), as was first described by Langer and Gohlke (35) and has since been applied to polymers by Friedman (36) and Shulman (37), has been used for overcoming some of the problems of TGA. In MTA pyrolysis gases are analyzed continually with a time-of-flight mass spectrometer, as polymer samples are heated through linear rates of temperature rise. Its main benefits are that temperature is controlled directly and that evolution of individual products is readily resolved.

The pyrolysis apparatus that is currently being used by the present writer is shown in Fig. 10. The furnace tube may be baked out in advance of pyrolysis. Magnet manipulation is employed to put the sample into proper position and to place the thermocouple tip in the sample crucible after bake-out is completed. Current studies are being carried out for a series of polybenzimidazoles. Samples 1 mg in weight are heated from room temperature to 1000°C at a rate of 10°C/min. All the pyrolysis gases are taken into the mass spectrometer through a leak that contains 821 holes

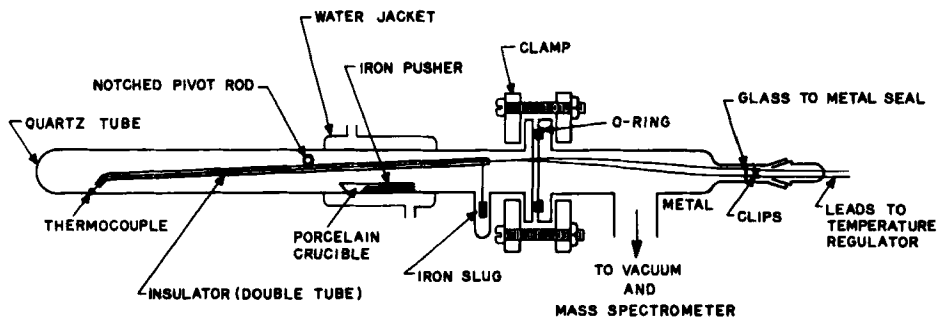


FIG. 10. Mass spectrometric-thermal analysis pyrolysis vacuum system. [From (36); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

2 mil in diameter. The leak plate is about 1 m from the pyrolysis zone. The pyrolysis gases are permitted to cool to room temperature by collision with the walls for accurate analysis, since the mass spectrometer sensitivity and fragmentation pattern are influenced by temperature. Secondary reactions and some condensation could occur in the cool zone, but the use of small samples and low pressures should help to reduce such effects.

The following spectra were obtained from pyrolysis of four polybenzimidazoles in a slightly different pyrolysis apparatus, without bake-out, where 10-mg samples were heated at a rate of  $16\frac{2}{3}^{\circ}\text{C}/\text{min}$ . The polymers were poly-2,6-(*m*-phenylene)diimidazobenzene, its *p*-phenylene analogue, poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole, and its *p*-phenylene analogue (I, II, III, and IV, respectively, in Figs. 11, 12, and 13). The mass spectra are plotted as ion intensity versus temperature for *m/e* 27, 94, and 128 (Figs. 11, 12, and 13, respectively). In these figures *m/e* 27 represents hydrogen cyanide and is a major product, *m/e* 94 represents phenol, which is a condensation product of polymerization rather than a pyrolysis product (note the difference in yields for the various

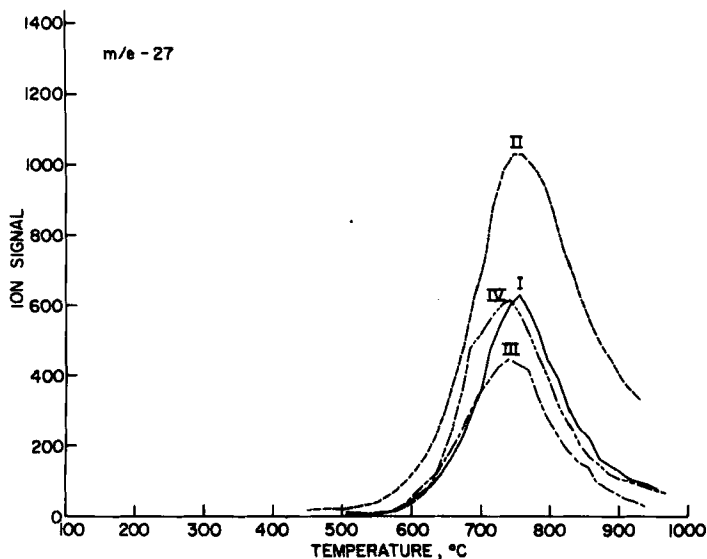


FIG. 11. Polybenzimidazole mass spectrometric-thermal analysis curves for *m/e* 27. [From (36); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

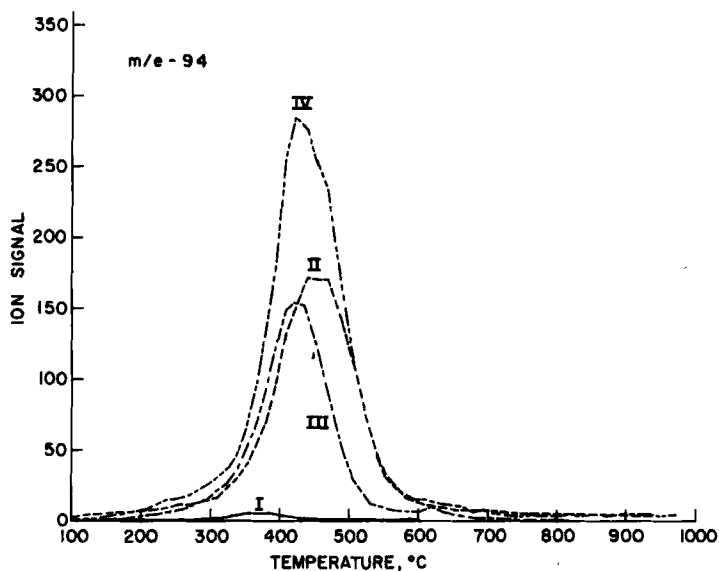


FIG. 12. Polybenzimidazole mass spectrometric thermal analysis curves for  $m/e$  94. [From (36); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

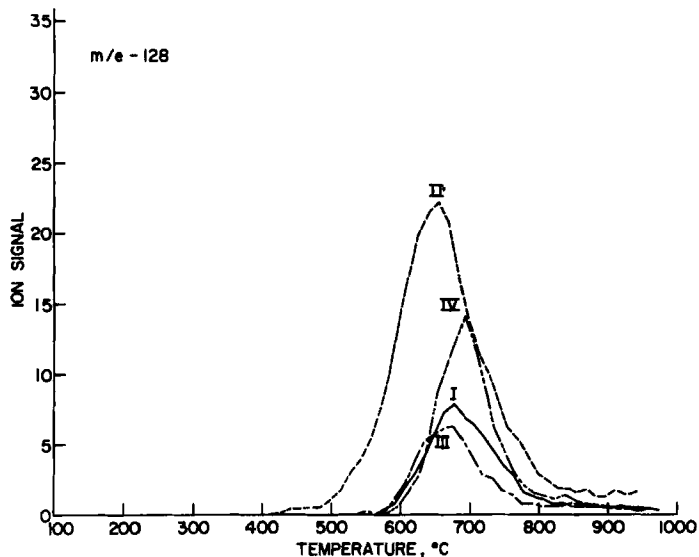


FIG. 13. Polybenzimidazole mass spectrometric thermal analysis curves for  $m/e$  128. [From (36); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

polymers, indicating differences in extent of cure), and  $m/e$  128 represents phthalonitrile and/or terephthalonitrile, which is a minor pyrolysis product. These polymers were found to produce about fifteen different products, and the resulting TGA curves were very complex, in contrast to the smooth and well-resolved MTA curves.

Since an enormous quantity of data is produced in a polymer pyrolysis experiment, much data-processing effort is needed for even a single run. The automatic data-collecting system shown in Fig. 14 has recently been developed and installed in the writer's laboratory. The system will eventually be used for obtaining computerized qualitative and quantitative analysis.

Mass spectrometry, gas chromatography, and optical spectroscopy are most often applied to chemical analysis of decomposition products. The use of a single technique is not usually completely successful. If the mass spectrometer is used alone, it is sometimes difficult to obtain a completely unambiguous qualitative and quantitative analysis, especially if a large number of products are produced. MTA has overcome this difficulty by producing a large number of independent but interrelated spectra as a function of temperature (time). Several different columns are sometimes needed to perform a complete separation of products by gas chromatography. Since retention time is not an absolute qualitative indicator, a number of laboratories have coupled mass spectrometers to the effluent of the gas chromatograph, so that qualitative identification could be assured. Infrared absorption spectroscopy may help to identify products that might otherwise be missed. Great care must be exercised if cold traps are employed or if products are to be stored prior to analysis, because chemical reactions between products occur in some cases. Physical properties, such as pressure, may be measured in those cases in which single volatile products are formed.

The use of polymers at very high temperatures, such as in ablating heat shields, has presented some very interesting and difficult problems. Since these polymers usually form char layers at their surfaces, primary decomposition products will undergo homogeneous and heterogeneous reactions as they travel from the lower temperature region beneath the surface to the ever-hotter and partly and completely decomposed material near or at the surface. The effects of such transpiration have been demonstrated

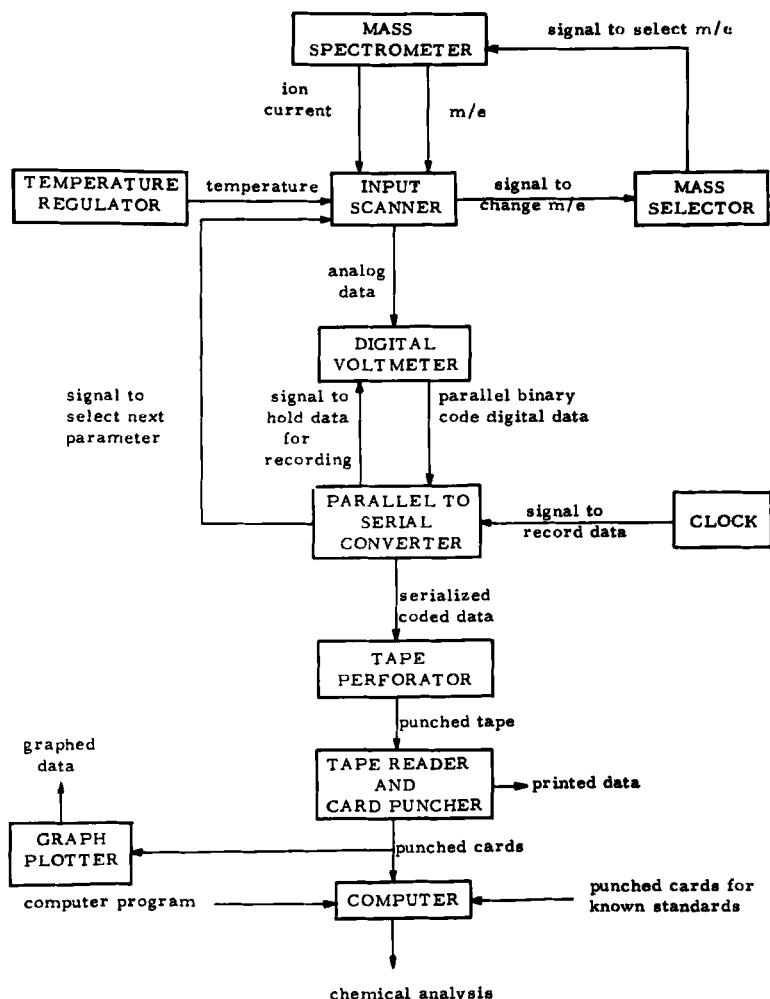


FIG. 14. Automatic data-collection system for mass spectrometric thermal analysis. [From (36); courtesy of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory.]

by Barry and Gaulin (38). Thus, it is clear that many different chemical reactions are concurrent. This simplified picture excludes the further complication of the presence of very hot atmosphere gases at the surface of the vehicle. It is certain that many transitory species, such as atoms and free radicals, are present in many zones. Since no single experiment can simulate all aspects

of re-entry heating, solutions to this problem have been obtained by combining theoretical models, as developed by the aerodynamicist (39), with knowledge gained from experiments that simulate parts of re-entry heating. Arc-image furnace (40-43), flash lamp (44-46), plasma torch (40,42), and chemical flame heating (47) have been used together with other techniques. In many cases sample temperatures are difficult to control or measure. Because of the speed and complexity of the reactions it is very difficult to obtain direct measurements of kinetic relationships at the high temperatures.

Thus, it is clear that, although much has been done in advancing the state of knowledge of the chemistry of thermal decomposition of polymers, much remains to be done. Because of the prospects of ever-increasing applications one may expect much research effort to go into this area in coming years.

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