KINETIC CONSTANTS OF POLYMERIC MATERIALS
FROM THERMOGRAVIMETRIC DATA

S. R. Urzendowski* and A. H. Guenther

Air Force Weapons Laboratory, Kirtland Air Force Base, Albuquerque, New Mexico, U.S.A.

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The thermal decomposition of polytetrafluoroethylene (TFE, Teflon), high and low density polyethylene (HDP and LDP), Delrin Acetal (DA), AVCO Phenolic Fiberglass (APFG), and carbon phenolic (CP), were studied by a thermogravimetric technique which utilized a constant heating rate. Loss in sample weight was recorded as a function of time or temperature from room temperature to approximately 700°. Reaction orders were established from logarithmic rate versus temperature plots. Arrhenius frequency factors and overall activation energies were determined from computerized integrations of the appropriate rate equations in which the results were treated on the basis of first-order reaction mechanisms for specific temperature regions. Zero-order mechanisms were estimated by the usual graphical methods.

The development of new polymers and the optimum use of existing polymeric materials in modern aerospace technology depend not only on a knowledge of the thermal decomposition mechanisms and the influence of molecular structure on thermal stability but also on the environmental test conditions under which degradation occurs. It is known [1] that polymers which tend to vaporize completely at sufficiently high temperature indicate scissions occurring primarily in the backbone of the chain. Polymers which on prolonged heating form a more or less carbonaceous residue indicate scissions occurring primarily between the carbon of the backbone and the side chain groups which result in the formation of double bonds. By comparison polymers that are highly cross-linked are usually converted into a partially carbonized residue.

By a dynamic thermogravimetric technique, the polymeric samples were weighed and the weight recorded continuously and automatically as a function of the temperature attained by the sample while it was being heated in a stream of nitrogen or under vacuum while the temperature rose at a linear rate of 5 degrees per minute. The resulting thermogravimetric curve disclosed the threshold temperature for active pyrolysis, the range of temperature within which most of the pyrolysis occurred, and the yield of char (or extent of volatilization) when pyrolysis neared completion. Kinetic parameters such as reaction rates, k, Arrhenius frequency factors, Z, and activation energies, E, were determined from the thermogravi-

* Presently at the University of Albuquerque, Albuquerque, New Mexico.

metric data in order to define the utility of these polymeric materials at high temperatures and to correlate stability with chemical structure. Results were compared to static thermogravimetric analysis [2, 3] wherein the sample weight was recorded as a function of time at constant temperature for a series of temperatures from above the threshold temperature for active pyrolysis to a temperature at which pyrolysis became inconveniently rapid.

Experimental

Apparatus and procedure

The instrument employed in this study [4] measured the weight of a material as a function of temperature or time and has a temperature capability to 1200°.

Samples (8 − 10 mg in weight) were suspended directly on a quartz beam balance and heated at a rate of 5−10°/min in an atmosphere of dry nitrogen (flow rate (14−28 l/hr) or under vacuum conditions (10^{-4} to 10^{-5} torr) by means of a vacuum pump. The balance mechanism and the shielded thermocouple situated directly above the sample permitted accurate weight and temperature measurements so that recorded curves indicating weight loss versus temperature were readily obtained. The use of a constant heating rate permitted simplified calculations by recourse to weight loss as the variable as a function of time. Zero time was designated as that point at which departure from the baseline was first noted.

The data obtained from the resulting weight loss curve and its derivative were used to evaluate the kinetics of decomposition. The solution of the requisite equations was obtained from a digital reduction program of thermal formulations proposed by Schempf et al. [5] which accepted sample weight, W, and sample temperature, T, as a function of time, t. The computer program makes use of a least squares polynomial fit of the time-sample weight values according to the following equation:

$$W = \sum_{i=0}^{n} K_{(i+1)} t^{(i)} \tag{1}$$

where n is the desired polynomial order, K the coefficient of the polynomial, and t the time. The precision of the computer fit of the TG curve was ±0.2 mg. The reading accuracy for sample weight was 0.1 mg. Once the appropriate relation was obtained for the experimental curve, the computer differentiated the curve and determined the slope using the raw input data. The specific rate constant, k, was then obtained from

$$k = \frac{- \sum_{i=0}^{n-1} [i + 1] K_{(i+2)} t^{(i)}}{\sum_{i=0}^{n} K_{(i+1)} t^{(1)}} = \frac{dW/dt}{W} \tag{2}$$

and is the overall rate constant for the degradation reaction. After determining the values for the Arrhenius plot of log k vs $1000/T$ for the desired first-order temperature region a least squares fit on these points was accomplished and the activation energy for the reaction was calculated from:

$$-\frac{E}{2.303R} = \frac{\sum^{N_i} (1000/T_i)\,(\log k_i) - [\sum^{N_i} 1000/T_i]\,[\sum^{N_i} \log k_i]/N_i}{\sum^{N_i} (1000/T_i)^2 - [\sum^{N_i} (1000/T_i)]^2/N_i} \qquad (3)$$

where N_i is the number of the time–temperature data points available. The Arrhenius frequency factor Z was calculated in a straightforward manner from the following relationship:

$$\log Z = \frac{\sum^{N_i} \log k_i + E/2.303R\,[\sum^{N_i} (1000/T_i)]}{N_i} \qquad (4)$$

Finally the program automatically plotted the TG output data in graphical form.

Materials studied

The polytetrafluoroethylene sample used (Teflon, TFE) [6] was a highly crystalline linear polymer with a density of 2.186 g/cm³. Elemental analysis by the manufacturer indicated 76.0 per cent fluorine and 24.0 per cent carbon by weight.

High density polyethylene (HDP) [6] was a thermoplastic resin of very long, nearly branch-free chains. Elemental analysis [6] indicated 86.0 per cent carbon and 14.0 per cent hydrogen with a measured density of 0.967 g/cm³.

Low density polyethylene (LDP) [6] was of lower molecular weight than the high density formulation. The specific differences in physical properties between these two materials were greatly influenced by the density (crystallinity) and the molecular weight (melting point) which were the results of the increased branching present in the low density polymer. The sample studied had a measured density of 0.922 g/cm³.

Delrin Acetal (DA) [6] was a highly crystalline, stable form of polymerized formaldehyde (super polyoxymethylene), which exhibited high tensile strength, rigidity, and creep resistance, over a wide temperature range. The material employed a mean density of 1.51 g/cm³.

The phenolic fiberglass sample used (APFG) [7] was a phenolformaldehyde thermosetting resin laminated with glass fibers. The fibers formed a regular weave pattern with the resin binder resulting in a measured density of 1.71 g/cm³.

The prepregnated carbon phenolic used (CP) [8] contained cloth filaments which appeared to be uniaxially orientated. Specification data include: density, 1.48 g/cm³; resin, 34 per cent by weight, reinforcement, 66 per cent by weight; elemental analysis, 90.8 per cent carbon, 0.7 per cent nitrogen, 2.1 per cent hydrogen and 6.5 per cent oxygen.

Results and discussion

The dynamic thermogravimetric weight versus temperature curves obtained for the preceding polymers are shown in Fig. 1. The curves disclose the threshold temperatures for active pyrolysis as well as the temperature ranges in which the major part of the degradations occurred. These curves were obtained from programmed linear thermogravimetric (TG) rate records (in vacuo) indicating the continuously decreasing weight of the sample as it is heated at a constant rate. Similar curves were obtained for the samples heated in a stream of flowing nitro-
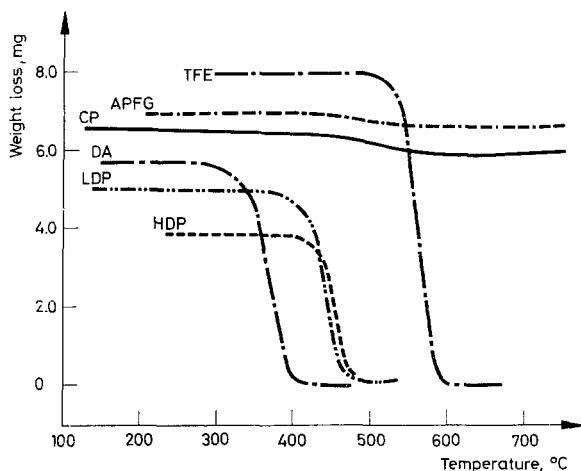

Fig. 1. Thermogravimetric curves for the polymers studied

gen (28 l/hr). In agreement with results obtained by Vassalo [9] pyrolyses of polymers in nitrogen occurred approximately 10 degrees higher than those in vacuum. These observed higher decomposition temperatures may be due in part to the fact that the gaseous atmosphere may cause a pressure dependence upon the decomposition temperatures. This pressure dependence could also account for differences observed for the Arrhenius frequency factor, Z, and the activation energies, E (Table 1), calculated both in an atmosphere of nitrogen and in vacuo.

For comparative purposes graphs of per cent conversion versus temperature are shown in Fig. 2. The average total conversion (volatilization) for a specific time interval was calculated in per cent of the original sample weight. The total average conversion for this interval was then plotted as a function of temperature. In most cases the plots were straight lines throughout most of their course, being suggestive of first-order mechanisms. By extrapolating the straight line portions of the plots to zero conversion the initial rates were obtained.

The relative thermal stability of the polymers studied follow the order:

$$DA < LDP < HDP < TFE < APFG \approx CP \qquad (5)$$

which illustrates the greater stability of the reinforced or laminated polymers. This greater stability was evident from the large amount of residue as well as the higher maximum temperature pyrolysis regions observed for these materials.
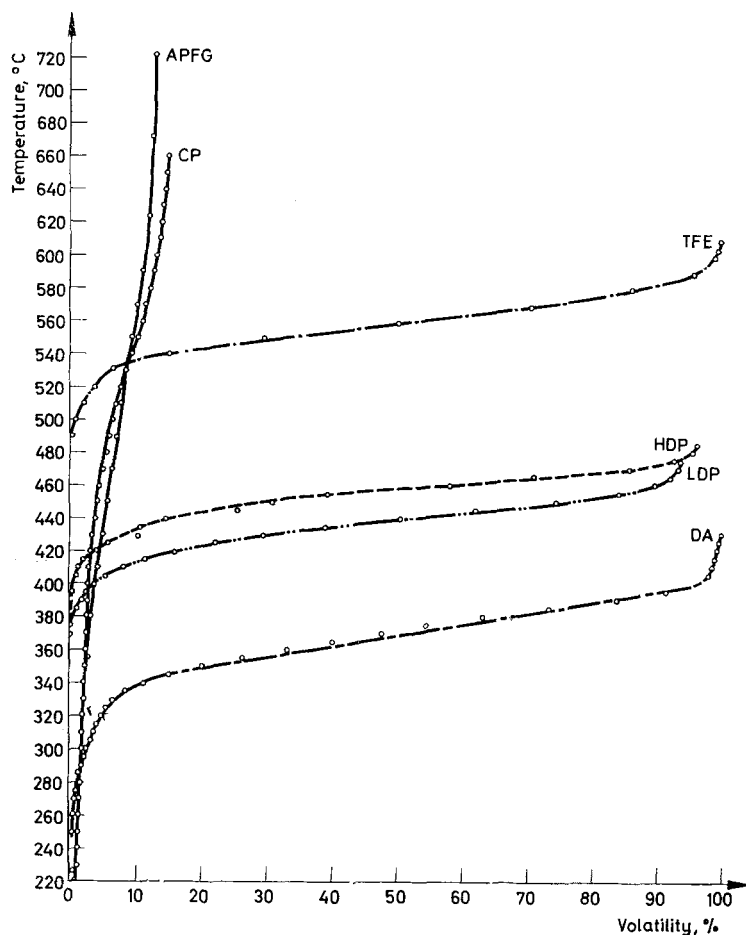

Fig. 2. The total average conversion (volatilization) of the polymers as a function of temperature

Values of the temperature, T, the weight remaining, W, and the change in weight as a function of time, in g/min, (dW/dt), were obtained from Fig. 1. The weight fraction was used to calculate the specific rate constant, k, by means of Eqs (1) and (2) as described previously. Plots of the logarithm of the specific rates vs. the reciprocal of the absolute temperature for the polymers studied are shown in Figs 3 and 4. The slopes of these lines were calculated by the method of least squares and the resulting activation energies and the Arrhenius frequency factors

for the first-order reactions were determined and are given in Table 1. Deviations from first-order reaction kinetics as well as detailed descriptions of the thermal behavior are discussed for the polymers.

Polytetrafluoroethylene (TFE-Teflon). The dynamic thermogravimetric curve for Teflon (Fig. 1) illustrates the great thermal stability of this polymer. In the
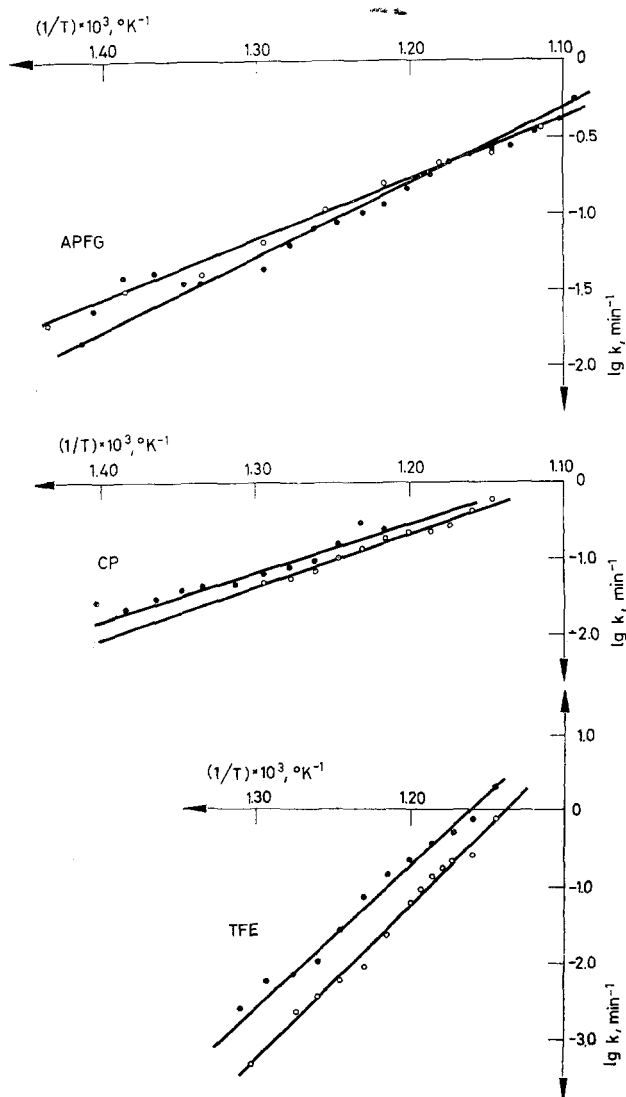

Fig. 3. Arrhenius plots for the degradation of AVCO Phenolic Fiberglass (APFG), carbon phenolic (CP), and tetrafluoroethylene (TFE), ● in vacuo (10^{-4} torr); ○ in nitrogen (flow rate 28 l/hr)

nitrogen atmosphere the TG curve showed little or no weight loss until approximately 490° where it dropped rapidly to 610° at which time volatilization was complete. Under vacuum the maximum degradation rate occurred from approximately 480° to 600° with a small amount of decomposition beginning at 485°. A dW/dt
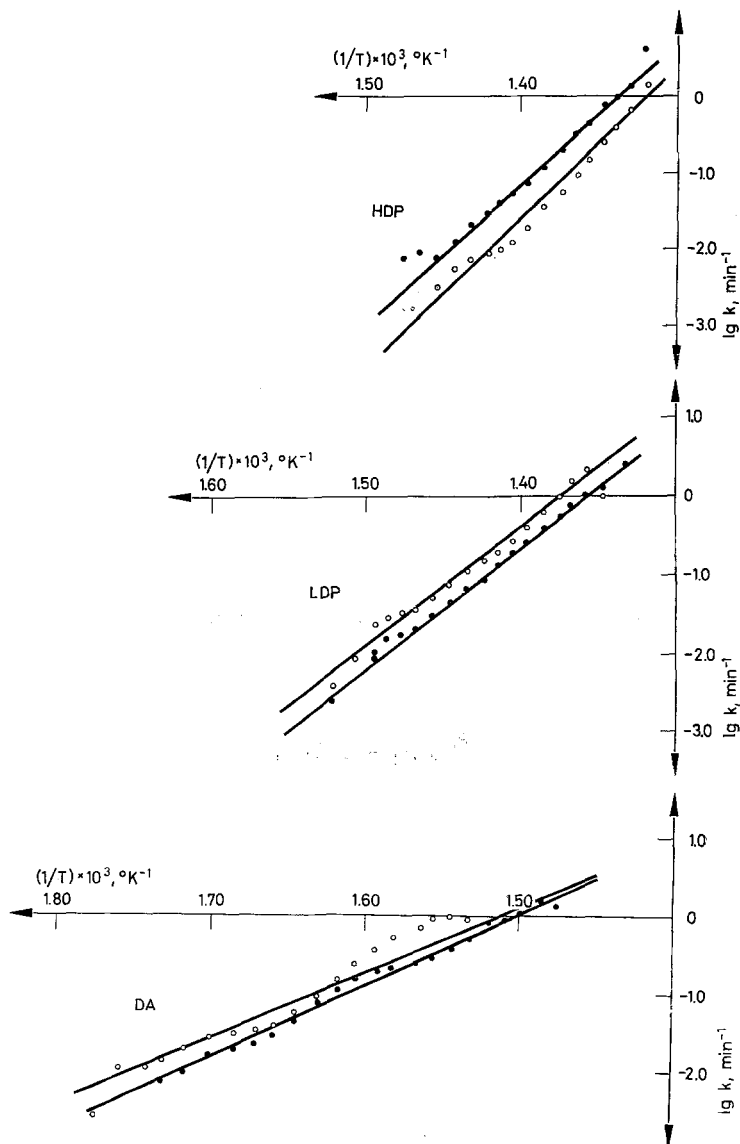

Fig. 4. Arrhenius plots for the degradation of high and low density polyethylene (HDP and LDP respectively), and Delrin Acetal (DA). ● in vacuo (10^{-4} torr); ○ in nitrogen (flow rate 28 l/hr)

peak maximum observed at 565° was the peak decomposition temperature of the polymer. This temperature agrees well with the temperature noted on the differential thermal analysis (DTA) curve [10].

The Arrhenius plot for Teflon is shown in Fig. 2. All the data fit the first-order Arrhenius line very closely throughout the entire temperature range. The least squares fit gives $k = 8.3 \times 10^{19} \, e^{-79.226/RT}$ min^{-1} which is in good agreement with results presented by Siegle and Muus [11], and Madorsky et al. [12]. The value for the rate constant in an atmosphere of nitrogen was $k = 4.3 \times 10^{19} \, e^{-79.511/RT}$ min^{-1}.
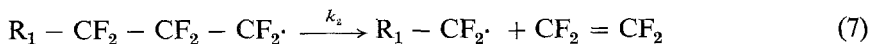
The thermal stability of Teflon is shown by the graph of the per cent conversion versus temperature (Fig. 2). The rate of decomposition in vacuo and in an atmosphere of nitrogen is constant and therefore characteristic of a diffusion controlled reaction.

Mass spectrophotometric studies by Madorsky et al. [12] showed that the gaseous products of pyrolysis were 95.1 per cent tetrafluoroethylene (C_2F_4), and 3.7 per cent hexafluoropropylene (C_3F_6). Since the composition of the volatile products remained constant and the rates of degradation were shown to be independent of molecular weight, the polymer was said to degrade by a first-order rate law at temperatures above 510°. The mechanism of degradation may be represented by

Initiation

$$R_1 - (CF_2)_4 - R_2 \xrightarrow{k_1} R_1 - CF_2 - CF_2 - CF_2 \cdot \; + R_2 - CF_2. \tag{6}$$

Propagation

$$R_1 - CF_2 - CF_2 - CF_2 \cdot \xrightarrow{k_2} R_1 - CF_2 \cdot \; + CF_2 = CF_2 \tag{7}$$

Termination

$$2 \; R_2 - CF_2 \cdot \xrightarrow{k_3} \text{Polymer} \tag{8}$$

and/or

$$R_m \, CF_2 \cdot \xrightarrow{k_4} \text{Evaporation} \tag{9}$$

where the R's represent $(CF_2)_n$ chains of any length n but with a non-reactive end, R_m is a chain of about 70 carbon atoms, and the k's are the specific rate constants.

The proposed mechanism could account for the first-order kinetics and the high frequency factor for the observed overall rate constant reported in this study as well as by other investigators [13—17].

The reported activation energies (79.2 and 79.5 kcal/mole in vacuo and in nitrogen, respectively) are not far above the carbon–carbon bond energy of 74 kcal//mole reported by Patrick [16] and thus verify the above mechanism in which the polymer breaks up at free-radical ends of the chain by an unzipping process to yield mostly monomer. This unzipping process, once started, proceeds until the whole chain is consumed. It is likely that in the nitrogen atmosphere at high temperatures some of the shorter free-radical chains evaporate before they have a chance to decompose into monomer, thus producing larger fractions of volatile components which affect the value of the Arrhenius frequency factor and the activation energy (Table 1).
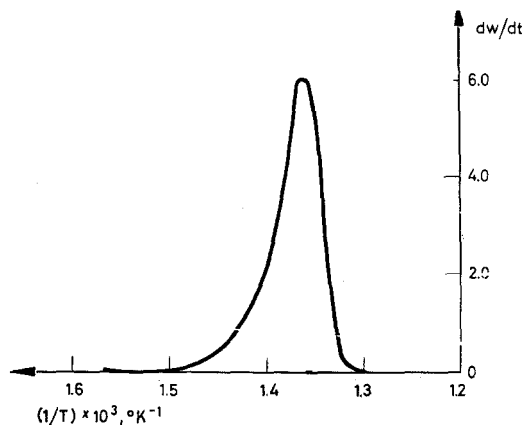

Fig. 5. The temperature dependency plot of the thermal degradation of high density polyethylene in vacuo

High density polyethylene (HDP). Fig. 1 shows the continuous weight loss curve for the thermal degradation of high density polyethylene (0.967 g/cm^3) under vacuum conditions. A similar curve (approximately 10° higher than that obtained in vacuo) was obtained in the nitrogen atmosphere.

Decomposition of the sample in vacuo was observed to begin at approximately 375° and was essentially complete at 485°. Examination of the data calculated by the least-squares fit for a first-order reaction Eqs. (1 − 4) showed deviations at the upper and lower temperature limits indicating deviations in kinetic reaction order.

The temperature dependency plot of the thermal degradation in vacuum $(dW/dt$ versus $1/T$; Fig. 5) suggested a zero-order reaction mechanism at the onset of degradation since the weight appears to be independent of the percentage weight loss. The graph of the specific rate data (Fig. 4) verified the zero-order mechanism for the temperature range 375 to 400°. For temperatures above 400° (Fig. 4) linearity was approached so that a first-order reaction mechanism was assumed for this region. The graph showing the per cent volatility versus temperature is shown in Fig. 2 for the high density sample measured in vacuo from 375 to 490°.

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The per cent volatility remained essentially constant for the initial temperature rise from 370 to approximately 410°. Beyond this temperature the graph curved slightly to approximately 15 per cent conversion and approached linearity from 15 to 95 per cent conversion. The deviation from linearity beyond 95 per cent conversion is probably associated with an increased number of volatile products which could cause additional reaction mechanisms in this high temperature region.
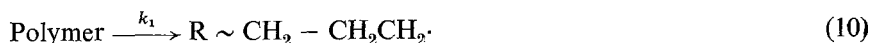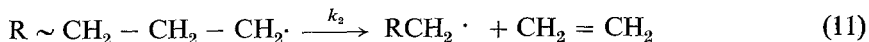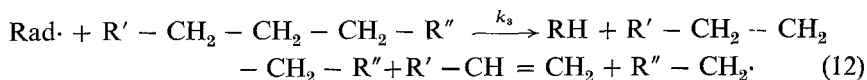
Activation energies for this material reported by various investigators [18−21] varied from approximately 45 to 70 kcal/mole. Oakes and Richards [18] obtained values between 60 and 70 kcal/mole for the activation energy as calculated from the initial drop in molecular weight. From the initial rates of volatilization, Jellinek [19] derived E values of 45 to 66 kcal/mole depending on the molecular weight of the polyethylene sample. Madorsky [20] obtained an E value of 45 kcal/mole by extrapolating the initial part of the rate curve to zero conversion and 68± ±3 kcal/mole for the first-order reaction range. Wall et al. [21] analyzed the discrepancies in the reported activation energies. The values of 60 to 70 kcal/mole found by Oakes and Richards [18] should correspond to the value of 68± 3 kcal/mole reported by Madorsky [20] which is based on high conversion rates. Jellinek's values (45 to 66 kcal/mole) [19] were obtained from initial rates and hence correspond to Madorsky's value of 45 kcal/mole for the zero-order reaction mechanism.

In this study, the computer reduced data from initial rates throughout the entire temperature range (375 to 485°, in vacuo) gave rate constant of $k = 1.1 \times \times 10^{12}\, e^{-42,277/RT}$ min^{-1}. Since the log k versus reciprocal of the absolute temperature plot (Fig. 4) indicated pronounced deviations from linearity for the low temperature regions, this suggested the possibility of additional reaction mechanisms. Extrapolation to zero conversion and calculations for zero-order reaction kinetics in vacuo gave an estimated overall activation energy of 41.8 kcal/mole and a corresponding overall rate constant of 1.2×10^{13} min^{-1}. Calculations for the first-order reaction temperature region (410−475°, 15 to 95 per cent conversion; Fig. 2) gave k values of $k = 1.3 \times 10^{21}\, e^{-72,650/RT}$ min^{-1} and $k = 7.1 \times 10^{21}\, e^{-76\,490/RT}$ min^{-1} in vacuo and nitrogen, respectively (Table 1).

Mass spectrophotometric identification of decomposition products [18−22] show that depolymerization produces negligible amounts of the monomer (ethylene) and instead of a predominantly single product a broad spectrum of linear hydrocarbons was observed.

Moiseev [23] reports that the quantity of polyethylene found in the products increased slightly with increase in pyrolysis temperature: 9.1 mole per cent of volatilities at 395° and 11 mole per cent at 425°. These results were in good agreement with the 9.6 mole per cent obtained by Bailey and Liotta [24] but differed from the < 1 mole per cent reported by Grassie [25] and the 4.3 mole per cent obtained by Madorsky and co-workers [26].

Simha et al. [27] have correlated these results on the basis of a free-radical chain reaction involving initiation, propagation, transfer and termination, as follows:

Initiation

$$\text{Polymer} \xrightarrow{k_1} R \sim CH_2 - CH_2CH_2 \cdot \tag{10}$$

Propagation

$$R \sim CH_2 - CH_2 - CH_2 \cdot \xrightarrow{k_2} RCH_2 \cdot + CH_2 = CH_2 \tag{11}$$

Transfer

$$Rad \cdot + R' - CH_2 - CH_2 - CH_2 - R'' \xrightarrow{k_3} RH + R' - CH_2 - CH_2$$
$$- CH_2 - R'' + R' - CH = CH_2 + R'' - CH_2 \cdot \tag{12}$$

Termination

$$Rad \cdot + Rad \cdot \xrightarrow{k_4} \text{Polymer} \tag{13}$$

where the R's are non-radical ends, Rad· is a radical and the k's are the specific rate constants. Because of the small amount of ethylene produced, the propagation step is negligible and the transfer mechanism appears to be the rate determining step; the propagation step must compete with intra- and intermolecular transfer reactions. From these transfer reactions primary and secondary radicals are generated which lead to the formation of *n*-alkenes and *n*-alkanes which are known to make up approximately 80 per cent of the degradation products.

Low density polyethylene (LDP). The per cent volatilization versus temperature plot of LDP (Fig. 2) suggests zero-order kinetics from approximately 0 to 2 per cent conversion for the 360 to 375° temperature range. The first-order kinetic region was varied from approximately 5 to 95 per cent. The initial rapid rise in

Table 1

Kinetic data for polytetrafluoroethylene, high and low density polyethylene, Delrin Acetal, AVCO phenolic fiberglas and carbon phenolic

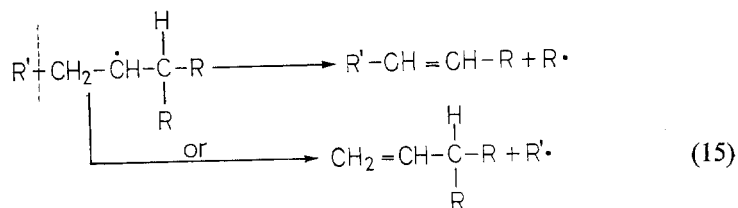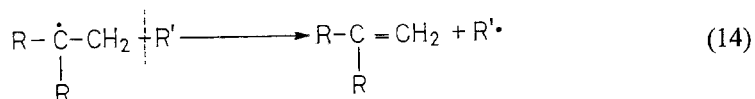| Polymer	Temp. range, °C	Z, min^{-1}	E, kcal/mole
Teflon	480—600*	8.28×10^{19}	79.23
	490—610+	4.27×10^{19}	79.51
Polyethylene (0.967 g/cm³)	400—485*	1.34×10^{21}	72.65
	410—495+	7.11×10^{21}	76.49
Polyethylene (0.922 g/cm³)	375—480*	3.06×10^{20}	69.46
	380—480+	5.78×10^{21}	72.58
Delrin Acetal	290—415*	5.14×10^{13}	41.48
	290—420+	2.71×10^{14}	44.08
APFG	420—650*	1.97×10^{4}	19.49
	425—650+	1.14×10^{4}	18.43
Carbon	430—560*	8.35×10^{5}	24.89
Phenolic	430—630+	5.05×10^{4}	20.55

* In vacuo — 10^{-4} mm Hg.
+ In nitrogen - flow rate 28 l/hr.

temperature decreases gradually as the reaction proceeds to approximately 95 per cent conversion. The explanation is probably due to segments breaking off from the ends of the highly branched polymer; these branched segments are more volatile than the regular polymer chain.
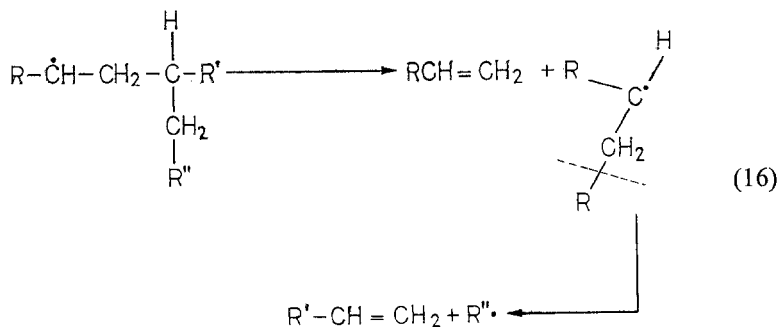
The calculated rate constants obtained for the first-order reaction regions were $k = 3.1 \times 10^{20} \; e^{-69,460/RT} min^{-1}$ and $k = 5.8 \times 10^{21} \; e^{-72,580/RT} min^{-1}$ in vacuo and nitrogen, respectively (Table 1). These values agree well with the activation energy of 68 kcal/mole reported by Madorsky [20] for a highly branched polyethylene sample.

The Arrhenius frequency factors for the postulated kinetic reaction mechanisms are given in Table 1. In agreement with values reported by Jellinek [19, 22] from static pyrolysis studies of polyethylene samples of molecular weights from 11,000 to 23,000, the activation energies and the Arrhenius frequency factors (Table 1) are lower for the low-density polymer. The exact mode of breakdown [19] is not known with certainty, however, the first-order approximation (Fig. 4) plus the loss of weight curve (Fig. 1) suggest a reverse polymerization with a random breaking of the molecular chains.

Wall et al. [21] suggest three possible transfer processes for branched polyethylene wherein the subsequent radicals formed can decompose into molecules with three different types of double bonds as follows:

$$R-\overset{\bullet}{\underset{R}{C}}-CH_2 \;\vert\; R' \longrightarrow R-\underset{R}{C}=CH_2 + R'\bullet \qquad (14)$$

$$R'\;\vert\;CH_2-\overset{\bullet}{C}H-\underset{R}{\overset{H}{C}}-R \longrightarrow R'-CH=CH-R+R\bullet$$

$$\text{or} \longrightarrow CH_2=CH-\underset{R}{\overset{H}{C}}-R+R'\bullet \qquad (15)$$

and

$$R-\overset{\bullet}{C}H-CH_2-\underset{\underset{R''}{\overset{|}{CH_2}}}{\overset{H}{C}}-R' \longrightarrow RCH=CH_2 + R\cdots\overset{H}{\underset{\underset{R}{CH_2}}{C}}\bullet \qquad (16)$$

$$R'-CH=CH_2 + R''\bullet \longleftarrow$$

On this basis, the apparent discrepancies in reported activation energies of poly-ethylene samples seem to be related to the amount of branching present in the polymer. Detailed analyses of the volatile products obtained from the degradation of the branched and unbranched polyethylenes, and accurate molecular weight determinations are necessary before a definite decision as to the exact kinetic mechanism can be postulated.

Delrin Acetal (DA 500). This polymer is a highly crystalline stable form of polymerized formaldehyde sometimes referred to as an acetal resin because of the repeating oxymethylene unit $(-OCH_2-)_n$ in the polymer structure. Hammer et al. [28] define the polymer as linear rather than branched due to the high degree of crystallinity. The measured density of the sample of 1.43 g/cm^3 closely approaches the density of 1.51 g/cm^3 for the pure crystalline material.

The DTA curve [10] indicated an exotherm degradation onset at approximately 230°. In the present study (TG), a degradation onset temperature of approxima-tely 225° was observed both in nitrogen and in vacuo (Fig. 1), whereas, the tem-perature region of maximum degradation occurred at approximately 280 to 415°.

Table 2

Weight loss as a function of time and temperature for Delrin Acetal

Temp. °C	Time, min	Total weight, mg (in nitrogen)*	Total weight, mg (in vacuo)
275	0.0	8.04	5.65
295	2.0	7.95	5.60
315	4.0	7.73	5.47
325	5.0	7.51	5.41
335	6.0	7.20	5.24
345	7.0	6.57	4.83
355	8.0	5.29	4.20
365	9.0	3.29	3.44
375	10.0	1.59	2.55
385	11.0	0.90	1.50
395	12.0	0.66	0.51
405	13.0	0.43	0.09
415	14.0	0.26	0.08
425	15.0	0.14	0.03
435	16.0	0.06	0.01
445	17.0	0.02	

* Flow rate 28 l/hr.

The weight loss versus temperature data (Table 2) indicates deviations from linearity at the upper and lower temperature extremes. Since linearity was approxi-mated from 290 to 410°, the kinetic data of Table 1 (Fig. 4) was obtained for this temperature region. Irregularities occurring at the onset and the conclusion of the

degradation process suggest deviation from first-order reaction kinetics. Again, mass spectrophotometrical analyses of the volatile degradation products are necessary before exact kinetic mechanisms can be defined. Excluding the extreme ends of the temperature range, the calculated E values in nitrogen and in vacuo were 41.4 and 41.8 kcal/mole, respectively.

Phenolic polymers. The two phenolic polymers studied were carbon phenolic (CP — density 1.48 g/cm^3) and AVCO Phenolic Fiberglas (APFG — density 1.71 g/cm^3). The carbon phenolic polymer was 34 weight per cent resin while the APFG sample was 35 per cent resin.

Previous DTA studies on APFG [10] suggested no significant transitions from — 100 to 125° except that the curve exhibited a steady rise in baseline and increase in specific heat. Partial decomposition began at approximately 400° with a decomposition peak at approximately 440°. These results are in agreement with the present TG study which gives the temperature range of 410 to 600° as the region of maximum degradation. DTA studies performed on carbon phenolic [10] showed an exothermic onset at approximately 105° with a continuous rise to a peak temperature of 225°. The latter led into a decomposition valley with a minimum at approximately 475°. Examination of the per cent volatility versus tem-

Table 3

Weight loss as a function of time and temperature for carbon phenolic and AVCO phenolic fiberglas

Temp. °C	Time, min	CP total weight, mg (in vacuo)	APFG total weight, mg (in vacuo)
420	0.0	4.50	4.98
430	2.0	4.49	4.97
440	4.0	4.47	4.95
450	6.0	4.45	4.94
460	8.0	4.43	4.93
470	10.0	4.41	4.91
480	12.0	4.39	4.90
490	14.0	4.36	4.88
500	16.0	4.33	4.86
510	18.0	4.31	4.83
520	20.0	4.27	4.81
530	22.0	4.24	4.78
540	24.0	4.20	4.76
550	26.0	4.16	4.73
560	28.0	4.13	4.70
570	30.0	4.10	4.68
580	32.0	4.07	4.67
590	34.0	4.04	4.65
600	36.0	4.03	4.64

perature curve for carbon phenolic (Fig. 2) indicates that degradation was evident from 110° and reached its maximum value between 360 and 600°. The thermogravimetric weight-loss curves for the polymers are shown in Fig. 2. A summary of the pyrolysis data is given in Table 3 for the carbon and glass phenolics, respectively. The temperature range of maximum degradation for CP was 420 to 620° in a nitrogen atmosphere and 420 to 600° in vacuo. The corresponding nitrogen and vacuo temperature degradation regions for APFG were 425 to 700° and 420 to 650°, respectively. The per cent carbonaceous residue at 460° in vacuo was 85.7 and 92.1 for CP and APFG, respectively.

Specific rates plotted as a function of temperature are given in Fig. 3 for the carbon and glass reinforced polymers in nitrogen and in vacuo. An unusually slow rate was observed for the early weight loss occurring below 200°, which accounted for less than 10 per cent of the total weight-loss and which appeared to be associated with a different process than that discussed previously. This initial weight loss was eliminated from the kinetic calculations of Table 1, which presupposes first-order reaction mechanisms. Although it was likely that the main degradation process started at somewhat lower temperatures, and that the early degassing process continued to higher temperatures, it was felt that the errors associated with rate maesurements would be far more serious than errors caused by a qualified estimate of the original weight.

Conclusions

This work shows that kinetic data for polymers may be calculated from a thermogravimetric computer program [5, 29] which utilizes raw thermogravimetric time, weight and temperature values as input data. The method of least squares defined the proper polynomial which gave the best fit to time–weight values by choosing the value which minimized the sum of the squares of the deviations of these measurements. The resulting activation energies and Arrhenius frequency factors agreed well with kinetic data obtained under static conditions. Decompositional temperature regions for the polymers agree well with previously obtained DTA studies [10, 29 – 32].

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Credit

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RÉSUMÉ — Etude de la décomposition thermique du polytétrafluoroéthylène (Téflon), du polyéthylène haute et basse densité, de l'acétal Delrin, de la fibre de verre phénolique AVCO et du carbone phénolique par TG à vitesse d'échauffement constante. Enregistrement de la perte de poids en fonction du temps ou de la température, depuis la température ambiante jusqu'à 700°C environ. Détermination de l'ordre des réactions en portant le logarithme de la vitesse en fonction de la température. Détermination des facteurs de fréquence et des énergies d'activation moyennes par intégration numérique des équations de vitesse appropriées en traitant les résultats sur la base de mécanismes réactionnels du 1er ordre dans les domaines de température correspondants. Emploi des méthodes graphiques habituelles dans le cas des réactions d'ordre zéro.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Polytetrafluoräthylen (TFE, Teflon), von Polyäthylen niedriger und hoher Dichte (HDP und LDP), von Delrin Acetal (DA), von AVCO Phenolglaswolle (APFG) und von Phenolkohle (CP) wurde thermogravimetrisch mit konstanter Aufheizgeschwindigkeit untersucht. Der Gewichtsverlust wurde als Funktion der Zeit und der Temperatur von Zimmertemperatur bis zu 700° registriert. Aus der Darstellung der Logarithmen der Reaktionsgeschwindigkeit gegen die Temperatur wurde die Reaktionsordnung ermittelt. Die Arrheniusschen Frequenzfaktoren und die Werte der durchschnittlichen Aktivierungsenergien wurden durch komputierte Integrierung der geeigneten Geschwindigkeitsgleichungen bestimmt. In den entsprechenden Geschwindigkeitsgleichungen wurden für spezielle Temperaturgebiete die Ergebnisse aufgrund des Reaktionsmechanismus von erster Ordnung behandelt. Reaktionen nullter Ordnung wurden nach den üblichen graphischen Methoden ausgewertet.

Р е з ю м е — Термораспад политетрафторэтилена (ТФЭ, ТЭФЛОН), полиэтилена с высокой и низкой плотностью (ХДП, ЛДП), Делрин Ацеталя (ДА), АВЦО фенольного фиберглаза (АПФГ) и карбон фенолика (ЦП) изучен методом термогравиметрии с использованием постоянной скорости нагрева. Потеря веса образца фиксирована как функция времени или температуры (от комнатной до, приблизительно, 700°). Порядок реакции определен по зависимости логарифма скорости от температуры. Фактор частоты Аррениуса и общая энергия активации расчитаны интегрированием на вычислительной машине уравнений подходящей скорости. Результаты обработаны на основании механизма реакции первого порядка для определенной области температуры. Механизм нулевого порядка оценен известным графическим методом.