

Kinetic Study of the Thermal Decomposition of Poly(oxypropylene) Glycols by Differential Scanning Calorimetry

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Synopsis

The thermal decomposition of poly(oxypropylene) glycols was studied under nitrogen and dynamic operating conditions over the temperature range of 320° to 700°K by means of a differential scanning calorimeter. The differential energy losses due to changes in emissivity of the reference and sample pans were computed by modifying the baseline of the thermograms. Kinetic parameters obtained with the help of the Borchardt and Daniels theory indicate that the reaction is zero order and that the activation energy increases with molecular weight of the polymer. The rate of heating of the sample, the rate of flow of nitrogen, and the initial mass of the sample do not have significant effects on the kinetics of the decomposition.

INTRODUCTION

In recent years, the degradation of polymers has been the subject of considerable interest; however, most of the work published^{1,2,3} is limited to solid polymers of high molecular weight (polystyrenes, polyethylenes, polyurethanes, poly(vinyl chlorides), and some copolymers). Little is known about the decomposition of polymers of low molecular weight (liquid oligomers where $M < 5.0 \times 10^3$) such as poly(oxypropylene) glycols. Taking into consideration the important role played by poly(oxypropylene) glycols in the production of polyurethane foams, for instance, it is of utmost interest to study the thermal stability of the glycols as such to better understand that of the polyurethanes prepared with them. A kinetic study of this decomposition was therefore carried out⁴ using the differential scanning calorimetry technique. Due to practical difficulties arising out of the liquid nature of the polymers, it was necessary to modify the techniques usually used. This demanded changes in the practical as well as theoretical approach to the problem. In order to relate these in detail, it was essential that the problem be tackled from a fundamental point of view at first and then correlated with the improvisations and modifications that were adopted afterward. In keeping with the continuity of the text,

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it has been necessary to derive some of the equations which otherwise could be considered as standard expressions. The results obtained are interpreted in the light of equations formulated by Borchardt and Daniels⁵ and presented here in eqs. (18) to (33).

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 1-B differential scanning calorimeter was used throughout this work. It was usually operated at a heating rate of 20°K/min with polymer samples weighing approximately 4 mg each. Dry nitrogen at atmospheric pressure was used as the carrier gas at a flow rate of 27 ml/min in order to eliminate possible oxidation reactions.

Polymer Samples

Colorless transparent poly(oxypropylene) glycols of various molecular weights were graciously provided by the Union Carbide Company of Canada and used as such directly without further purification when preliminary tests with purified (by precipitation) and nonpurified material gave the same results.

Analysis of the Thermograms

Determination of T_0 and T_f

A typical thermogram obtained during the decomposition of a standard sample of 4025 POPG is shown in Figure 1. On examining the curve, one observes that the value for the temperature of fusion, T_f , is clearly defined, whereas the initial temperature of decomposition, T_0 , is difficult to locate, particularly because of the presence of volatile products whose temperatures

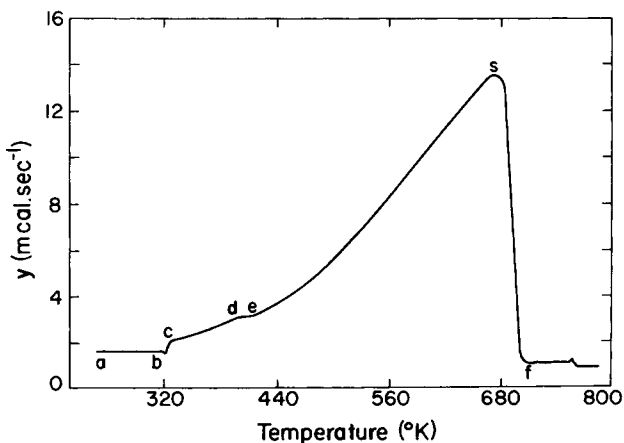


Fig. 1. Typical thermogram obtained by the decomposition of POPG 4025.

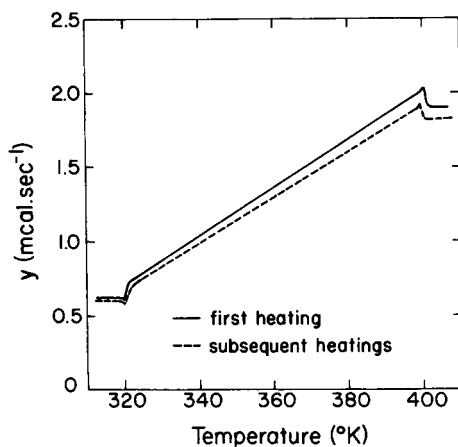


Fig. 2. Thermogram obtained by the partial heating of POPG 4025.

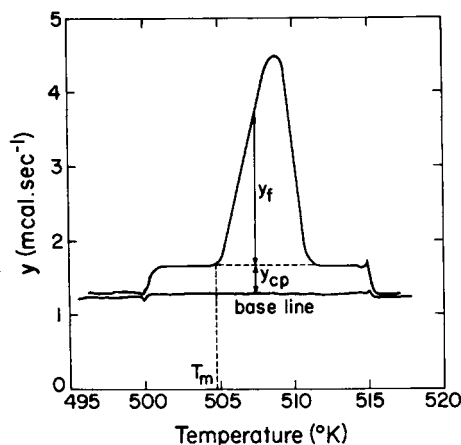


Fig. 3. Thermogram obtained by the fusion of tin.

of volatilization are similar to the initial temperatures of decomposition. The plateau, d-e, in the figure thus represents the ending of one type of "decomposition" and the beginning of another.

The presence of this so-called first decomposition is of no particular interest and was eliminated from the curves by the use of a preliminary heating technique wherein a definite amount of polymer is heated from 320° to 400°K at a rate of 20°K/min (Fig. 2). On reaching 400°K, the sample is rapidly cooled to 320°K and its weight is rechecked. The process of heating and cooling is repeated (two or three times) until no further volatile products are left. The sample is then ready for heating up to 700°K in the DSC. The preheating technique gives T_0 values which fall within $\pm 10^\circ\text{K}$ of one another.

Baseline Determination

With Covered Sample Pans. Under closed conditions, the tracing of a baseline does not present any particular problem, as is shown for the fusion of tin in Figure 3. The thermogram can be divided into two parts:

(a) *Before fusion*, when the energy supplied serves only to raise the temperature of the sample at some given rate $dT/d\theta$. Under these conditions,

$$y = y_{cp} = m \cdot cp \cdot \frac{dT}{d\theta} \quad (1)$$

where y (in mcal/sec) is the vertical distance separating the baseline from the trace of the thermogram at any given temperature T ; m (in mg) is the mass of the sample in the pan; cp (in mcal/mg·°K) is the specific heat of the sample; and $dT/d\theta$ (in °K/sec) is the heating rate.

(b) *During fusion*, when the sample absorbs energy $(dH/d\theta)_f$ in excess of y_{cp} for the fusion of tin. Under these conditions:

$$y = y_{cp} + y_f = m \cdot cp \cdot \frac{dT}{d\theta} + \left(\frac{dH}{d\theta} \right)_f \quad (2)$$

With Uncovered Sample Pans. During the decomposition of poly(oxypropylene)glycol samples, gasses are evolved, and it is therefore essential to use uncovered sample pans. This leads to the addition of another term, y_p , to account for the additional energy lost when operating without covers. Before decomposition,

$$y = m \cdot cp \cdot \frac{dT}{d\theta} + y_p \quad (3)$$

Under isothermal conditions, when $dT/d\theta = 0$,

$$y = y_p \quad (4)$$

During decomposition,

$$y = y_{cp} + y_H + y_p \quad (5)$$

where y_H is the energy absorbed by the decomposition reaction. Also,

$$y = m \cdot cp \cdot \frac{dT}{d\theta} + \frac{dH}{d\theta} + y_p \quad (6)$$

Under isothermal conditions, eq. (5) becomes

$$y = y_{Hi} + y_p \quad (7)$$

where y_{Hi} (in mcal/sec) is the energy absorbed by the decomposition reaction at a given temperature T .

In eq. (2), only the values of y are known; therefore, in order to compute the values of $dH/d\theta$, it is necessary to obtain the values of y_p and y_{cp} .

Calculation of y_p . The value of y_p can be computed from Figure 3 at any temperature below T_0 , the initial decomposition temperature under isothermal conditions. Beyond T_0 , it is not possible to evaluate y_p directly because of the presence of another unknown, y_{Hi} , in eq. (7). The only

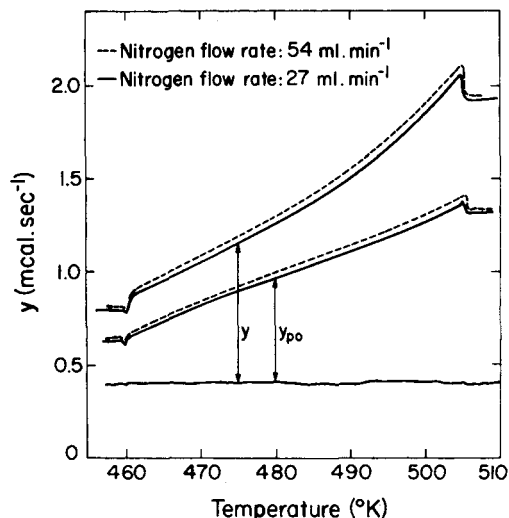


Fig. 4. Influence of the nitrogen flow rate on the decomposition of POPG.

means of solving eq. (7) beyond T_0 is to evaluate y_p below this temperature and use extrapolation values in keeping with the various factors that may influence its value.

The physical conditions of the atmosphere surrounding the sample suggest two possible modes of energy loss: (1) by convection currents produced by the circulation of nitrogen in the analysis chamber; and (2) by radiation due to temperature differences between the sample itself and the inner surface of the analyzer chamber.

Energy losses due to convection currents produced by the flow of nitrogen were determined at three different nitrogen flow rates between 13 and 54 ml/min. The thermograms obtained were practically identical (Fig. 4) at a sensitivity of 16 on the apparatus. However, at a higher sensitivity ($x = 4$, i.e., four times greater than $x = 16$), y , the ordinate of the thermogram, and y_{p0} , the energy loss as measured with aluminum, both increase when the flow rate of nitrogen passes from 27 to 54 ml/min, but the energy absorbed by the decomposition, as obtained from the difference between y and y_{p0} , becomes such that the total increase in y_H becomes negligible. It can safely be assumed from the results obtained that the losses in energy from the two sample pans (unknown and reference) are equal.

Energy losses by radiation depend in general on (a) the surface (S) involved in the transfer of heat, (b) the emissivity (ϵ) of the sample, (c) the temperature (T) of the sample, and (d) the temperature (T_c) of the inner surface of the analyzer, such that

$$y_p = f(S, \epsilon, T, T_c \dots). \quad (8)$$

(a) *Variation of S with temperature.* The aluminum sample pans provided by the supplier, Perkin-Elmer (Canada) Limited, are cylindrical in shape. With the POPG samples, the free surface has a concave shape due

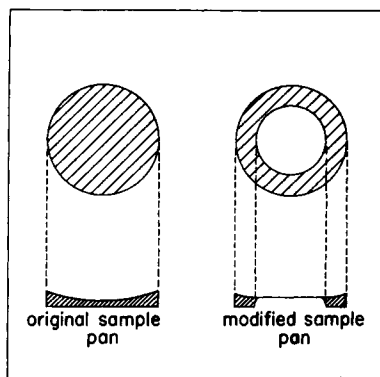


Fig. 5. Schematic view of original and modified crucible pans.

to the surface tension of the liquids. Because of the nonuniform thickness of the samples in the pan, that part situated in the middle decomposed sooner than the part near the edge. In the studies carried out where samples were not completely decomposed, it was found that all of the material in the center of the pan decomposed, whereas along the wall there was always some left. This suggests that the free surface S of the sample diminishes as the decomposition proceeds.

It is difficult, to say the least, to find an appropriate mathematical function relating the free surface with the temperature of decomposition, because the thickness of the liquid polymer cannot be measured with precision at the beginning of the experiment.

This difficulty can be solved by modifying the shape of the sample pans so that the thickness of the sample remains more uniform and nearly constant during the entire period of decomposition. With this notion in mind, a groove was made in the form of a ring at the bottom of the aluminum pans (Fig. 5). The sample pans were then filled only to the brim of the groove. This modification yields two advantages: (1) the surface S is more constant. (2) The energy loss due to radiation is diminished because of the reduction in the free surface of the sample from 34 to 22 mm²; the decrease in surface, however, carries with it a disadvantage, namely, a less extensive contact between the modified pan and its support when compared to that of an original sample pan, but this disadvantage is not believed to be critical because of the high thermal conductivity of aluminum and the reduced thickness of the sample.

(b) *Variation of ϵ with temperature.* During the course of a dynamic test involving decomposition, the temperature of a sample increases with time while its mass decreases. These two factors influence differently variations of the emissivity of the sample.

The influence of mass: Poly(oxypropylene) glycol is a transparent material, and, as a consequence, its emissivity ϵ is a function of its thickness d . This in turn is related as follows to the mass of the sample:

$$d = m/S\rho \quad (9)$$

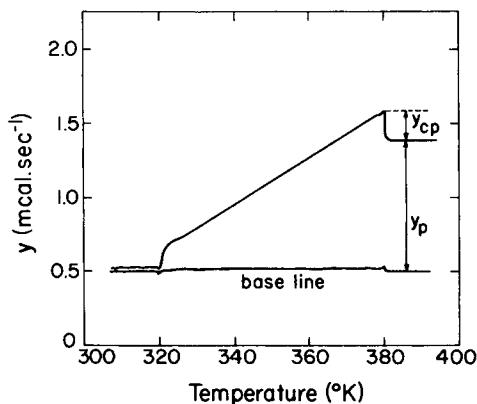


Fig. 6. Measurement of heat loss by the isothermal technique.

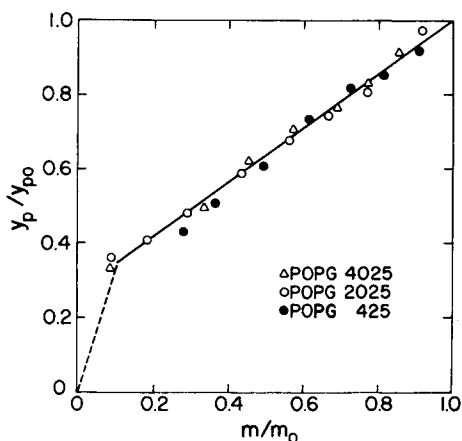


Fig. 7. Variation of y_p with mass of the sample.

where d is the thickness, m is the mass, ρ is the density, and, S is the free surface of the sample.

With modified pans, the free surface of the sample remains almost constant during the period of decomposition. If the density of the sample changes but slightly during the decomposition, it can safely be assumed that d will be directly proportional to the mass.

To establish a relationship between y_p , the differential loss of energy, and m , the mass of the sample, a series of experiments were carried out in which a finite amount of polymer was preheated under nitrogen to 400°K, then degraded at 500°K for different periods of time. The pan was weighed after each degradation. With the knowledge of y_p , the vertical distance between the baseline and the isotherm line (Fig. 6), and m at different stages it was possible to trace y_p/y_{p0} versus m/m_0 (Fig. 7). Between 0.1 and 1.0, all of the points fall on a straight line. At values of m/m_0 below 0.1 however, it was not possible to measure y_p because, as the degradation progressed

to more than 90%, the residue was too little and sometimes completely decomposed before it could be cooled to 320°K for weighing.

For $m/m_0 = 0$, the value of y_p/y_{p_0} is also equal to zero. The graph can therefore be completed, to a first approximation, by simply joining with a straight line the point at $m/m_0 = 0.1$ to zero at the origin. This approximation should have but little effect on the overall results since it represents only the final 10% of the decomposition. The results with polymers of different molecular weights all fall around one and the same curve. The influence of mass on the differential loss of energy can therefore be written in the following forms:

For $0 \leq m/m_0 < 0.1$:

$$y_p/y_{p_0} = 3.49 (m/m_0). \quad (10)$$

For $0.1 \leq m/m_0 < 1.0$:

$$y_p/y_{p_0} = [0.723 (m/m_0) + 0.277].$$

The influence of temperature: For most substances, emissivity increases with temperature. However, for poly(oxypropylene) glycol, the influence of temperature on its emissivity is much less important than that of its mass in the sample pan. This can be explained as follows:

1. The term y_p takes into account differences in energy losses between the sample and the reference pans. An increase in temperature of one of the pans is always accompanied by a corresponding increase of the other. As the temperature is always the same on each of the pans, the net gain of emissivity as a function of temperature can be expected to be negligibly low on the sample pan.

2. The difference in emissivity from one pan to the other is believed to decrease as the temperature increases, because the more the reaction advances, the lesser becomes the thickness of the liquid polymer in the sample pan. The emissivity of the sample pan thus approaches that of the reference pan, and the net difference in emissivity tends toward zero as the temperature is increased.

(c) and (d) *Influence of T and T_c on y_p :* It was mentioned earlier that y_p , the differential loss of energy, depends on T , the temperature of the sample, and on T_c , the temperature of the inner walls of the analyzer cover. During a decomposition run, the temperature T is indicated on the thermogram, while T_c is unknown. T_c nevertheless is known to increase with T because a part of the energy lost by radiation is absorbed by the analyzer cover. It is difficult, however, to measure this temperature with any degree of precision. Therefore, the simplest way to study the effect of the two on y_p is to use an inert material which allows the measurement of y_p to be made between temperatures of 320° and 700°K. Calcinated aluminum oxide (Al_2O_3) which undergoes no physical or chemical changes in this temperature interval was found to be a most suitable substance for this purpose.

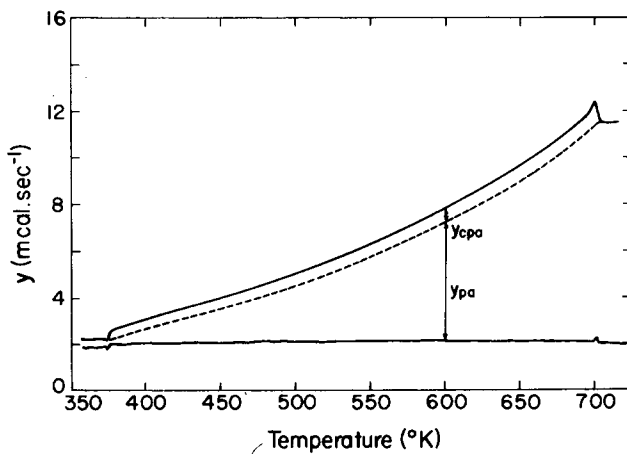


Fig. 8. Measurement of y_{pa} with aluminum oxide.

Only a thin layer of aluminum oxide was used for the measurement of the energy losses because these do not depend on m_a but only on the surface S_a . In the measurement of y_{pa} as a function of T , S_a was adjusted in such a way that the differential energy loss at 380°K was equal to y_{po} measured with m_0 (mg) of polymer:

$$(y_{pa})_{\text{aluminum}} = (y_{po})_{\text{polymer}} \quad (11)$$

at 380°K at 380°K

As mentioned earlier, y_p depends on ϵ , S , T , and T_c . In the measurement of y_{pa} and y_{po} , the temperatures are the same so that eq. (11) may be written in the following form:

$$(\epsilon_a S_a)_{\text{aluminum}} = (\epsilon_p S_p)_{\text{polymer}}. \quad (12)$$

Furthermore, it has been shown that ϵ and S do not change much, if at all, with temperature. Therefore, it can be said that y_{pa} is equal to y_{po} at 380°K. This relationship also holds at other temperatures, and

$$(y_{pa})_{\text{aluminum}} = (y_{po})_{\text{polymer}}. \quad (13)$$

With the polymer samples, however, an increase in temperature brings about a decrease in weight of the sample because of decomposition. Therefore, the differential energy loss no longer corresponds to y_{po} but rather to y_p , which can be computed from (1) the value of y_{po} obtained via y_{pa} of aluminum; and (2) the value of the mass of the sample at different temperatures.

The calculation of y_{pa} at 10° intervals between 380° and 700°K by isothermal methods requires much time. However, it can be done much more quickly by dynamic means, as the ordinate y_a at each temperature is equal to the sum of y_{pa} and y_{cpa} . With the values of y_{cpa} at 380° and 700°K (Fig. 8) and the assumption that these vary linearly with temperature, one can obtain y_{cpa} at any intermediate temperature by interpolation. Knowing m

at any given temperature, the differential energy loss y_p at that temperature can be calculated with the help of Figure 6.

Calculation of the Variation of m with T

It is known that $m = m_0$ at the initial temperature T_0 and that $m = 0$ at the final temperature T_f . At intermediate temperatures, estimated values of m are retained and corrected thereafter by the following procedure.

1. The mass of the sample was assumed to diminish linearly with time. Thus, between T_0 and T_f , the values of m , at 10° intervals, were calculated from the following expression:

$$m = m_0 \frac{T_f - T}{T_f - T_0} \quad (14)$$

2. The y_{cp} was calculated from eq. (1),

$$y_{cp} = m \cdot cp \cdot \frac{dT}{d\theta} \quad (1)$$

on making the assumption that cp , measured at 380°K , remained essentially constant over the rest of the temperature range.

3. The energy absorbed, $dH/d\theta$, during the decomposition reaction was calculated from eq (5):

$$y = y_{cp} + \frac{dH}{d\theta} + y_p \quad (5)$$

4. With the values of $dH/d\theta$ at all temperature intervals between T_0 and T_f , the following integrals were evaluated:

$$\int_{T_0}^T \frac{dH}{d\theta} \cdot \frac{d\theta}{dT} \cdot dT = a \quad (15)$$

A representing the surface under the curve from T_0 to T' ; and

$$\int_{T_0}^{T'} \frac{dH}{d\theta} \cdot \frac{d\theta}{dT} \cdot dT = A \quad (16)$$

A representing the total surface under the curve from T_f to T_0 .

Based on the hypothesis that the mass of polymer decomposed was directly proportional to the energy absorbed by the sample, the following relationship (17) was retained:

$$\frac{a}{A} = \frac{m_0 - m}{m_0} \quad (17)$$

This is another form of eq. (27) derived later on in the text. The values of m computed from eq. (17) were compared with those computed from eq. (14) at each temperature interval. If a difference showed up between the two values, the value computed from eq. (17) was fed to eq. (1), $y_{cp} = m \cdot cp \cdot dT/d\theta$, and the calculations repeated again until the values of m were constant to better than 2% at any given temperature (Fig. 9). The curve

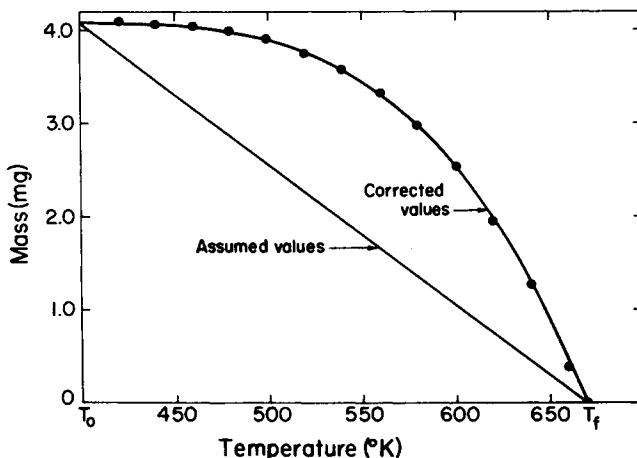
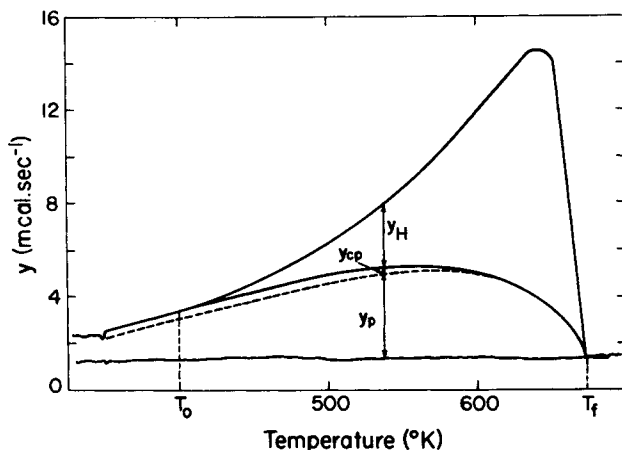
Fig. 9. Variation of polymer mass with T .

Fig. 10. Component parts of a thermogram obtained by the decomposition of POPG 4025.

obtained on the basis of the final values of m (Fig. 10) represents the variation of y_p , y_{cp} , and y_H as a function of T , from T_0 to T_f .

The Theory of Borchardt and Daniels and the DSC-1B

In the theory of Borchardt and Daniels,⁵ the total surface S under the DTA curve is directly proportional to the heat of decomposition ΔH_{tot} . The relationship between the two terms can be written as follows:

$$\Delta H_{tot} = K_S \cdot S \quad (18)$$

where K_S is a proportionality constant.

In DSC, the rate of energy supplied to each of the sample and reference pans to heat these through a given temperature range is continuously adjusted in order to eliminate any temperature differential between the two.

The increments of rate involved are continuously recorded such that the area under the curve becomes directly proportional to the net heats of any reactions taking place in the sample pan. Using the definition of eq. (16), eq. (18) can be redefined as follows for DSC:

$$\Delta H_{\text{tot}} = \int_{T_0}^{T_f} \frac{dH}{d\theta} \cdot \frac{d\theta}{dT} \cdot dT = A. \quad (18a)$$

Dividing ΔH_{tot} by the initial mass of the polymer, eq. (18a) yields

$$\Delta H' = \frac{\Delta H_{\text{tot}}}{m_0} = \frac{A}{m_0}. \quad (19)$$

If the energy absorbed by the sample is directly proportional to the mass that is decomposed,

$$- \frac{dH}{d\theta} = \Delta H' \cdot \frac{dm}{d\theta} \quad (20)$$

or

$$- \frac{dm}{d\theta} = \frac{1}{\Delta H'} \cdot \frac{dH}{d\theta}. \quad (21)$$

The mass of unreacted polymer intact at any time, θ , may be calculated by the expression

$$m = m_0 - \int_0^\theta - \frac{dm}{d\theta} \cdot d\theta. \quad (22)$$

Combining eqs. (21) and (22), one obtains

$$m = m_0 - \int_0^\theta \frac{1}{\Delta H'} \cdot \frac{dH}{d\theta} \cdot d\theta \quad (23)$$

or

$$m = m_0 - \int_{T_0}^T \frac{1}{\Delta H'} \cdot \frac{dH}{d\theta} \cdot \frac{d\theta}{dT} \cdot dT. \quad (24)$$

If the heat of decomposition $\Delta H'$ remains constant during the reaction, eq. (24) takes the form

$$m = m_0 - \frac{1}{\Delta H'} \int_{T_0}^T \frac{dH}{d\theta} \cdot \frac{d\theta}{dT} \cdot dT. \quad (25)$$

Combining eqs. (19) and (25) gives

$$m = m_0 - \frac{m_0}{A} \int_{T_0}^T \frac{dH}{d\theta} \cdot \frac{d\theta}{dT} \cdot dT \quad (26)$$

where, as in eq. (15), the integral $\int_{T_0}^T (dH/d\theta) \cdot (d\theta/dT) \cdot dT$ represents the surface, located under the curve between T_0 and T , and eq. (26) now becomes

$$m = m_0 \left(1 - \frac{a}{A} \right). \quad (27)$$

When decomposing a polymer, the rate of reaction may be defined as

$$-\frac{dm}{d\theta} = km^x \quad (28)$$

where m is the mass of the sample at a temperature T , k is the rate constant, and x is the order of the reaction. Substituting $-dm/d\theta$ and m with the expressions from eqs. (19), (21), and (27), one obtains

$$\frac{m_0}{A} \cdot \frac{dH}{d\theta} = k \left[\frac{m_0}{A} (A - a) \right]^x \quad (29)$$

from which

$$k = \frac{A^{x-1}}{m_0} \cdot \frac{dH/d\theta}{(A - a)^x} \quad (30)$$

For zero-order reactions,

$$k_0 = \frac{m_0}{A} \cdot \frac{dH}{d\theta} \quad (31)$$

while for first-order reactions,

$$k_1 = \frac{dH/d\theta}{A - a} \quad (32)$$

RESULTS AND DISCUSSION

Table I shows the rate constants for zero- and first-order reactions as computed from eqs. (31) and (32). These have been plotted on semilog paper as a function of $1/T$ (Fig. 11). For $x = 0$, the variations of $\ln k$ versus $1/T$ is linear from 440° to 620°K, while for $x = 1$ the linearity exist only from 440° to 560°K, beyond which curvature appears on the line. Because of the inherent limitations in computing the values of the partial area represented by a , which progressively increase to that represented by A , as the temperature is varied from T to T_f , one cannot reject outrightly the value of 1 for x . However, based exclusively on the theory of Borchardt and Daniels, one would be lead to choose zero rather than 1 as the order of the reaction.

Values of the overall activation energy E , as computed from the slope of the k_0 line in Figure 11 or directly from the slope of the y_H line from a similar graph, could differ depending on (a) the initial mass of sample placed in the pans, (b) the heating rate adopted for the test, (c) the molecular weight of the sample, and (d) the starting temperature T_0 .

Each of these factors has been looked at separately.

Influence of Initial Mass of Sample

From the Borchardt and Daniels relationship,

$$\ln \left(\frac{dH}{d\theta} \right) = \ln z' - \frac{E}{R} \cdot \frac{1}{T} \quad (33)$$

where $z' = \ln z - \ln \left(\frac{m_0}{A} \right)$.

TABLE I
Rate Constants for Zero- and First-Order Reactions

$T, ^\circ\text{K}$	$10^3/T, ^\circ\text{K}^{-1}$	$10^4k_0, \text{mg/sec}$	$10^4k_1, \text{sec}^{-1}$
390	2.564	0.42	0.16
400	2.500	0.86	0.32
410	2.439	1.09	0.41
420	2.381	1.75	0.65
430	2.325	2.65	0.99
440	2.273	3.16	1.19
450	2.222	3.71	1.39
460	2.174	4.70	1.78
470	2.128	5.75	2.19
480	2.083	7.10	2.72
490	2.041	9.38	3.63
500	2.000	11.61	4.55
510	1.960	13.38	5.32
520	1.923	16.80	6.80
530	1.887	19.03	7.88
540	1.852	22.45	9.54
550	1.818	27.40	12.03
560	1.785	32.61	14.90
570	1.754	38.76	18.63
580	1.724	43.86	22.42
590	1.695	50.32	27.72
600	1.666	56.45	34.10
610	1.639	61.36	41.51
620	1.613	68.36	53.25
630	1.587	74.59	69.73
640	1.562	83.94	101.00
650	1.538	94.50	167.79
660	1.515	106.20	405.40

TABLE II
Influence of Initial Mass of Sample on Overall Activation Energy of Reactions

m_0, mg	$E, \text{kcal/g-mole}$
4.90	8.6 ± 0.8
3.60	8.4 ± 0.8
2.74	8.5 ± 0.8

One can see that the activation energy of the reaction should not depend on the initial mass of the sample. To verify this fact, three different masses (4.90, 3.60, and 2.74 mg) of a POPG polymer were charged in sample pans. The thermograms obtained are shown in Figures 12 and 13, and the values of E are listed in Table II. These results show clearly that the initial mass of the sample does not affect the value of the activation energy of the reaction.

Influence of Heating Rate

The influence of the heating rate on the kinetics of the decomposition was studied with the same POPG polymer (Fig. 14). The experiments were

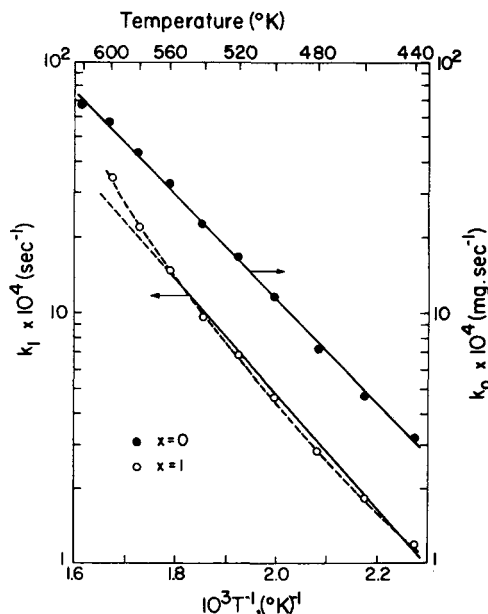


Fig. 11. Arrhenius plot for POPG 4025 with $x = 0$ and $x = 1$.

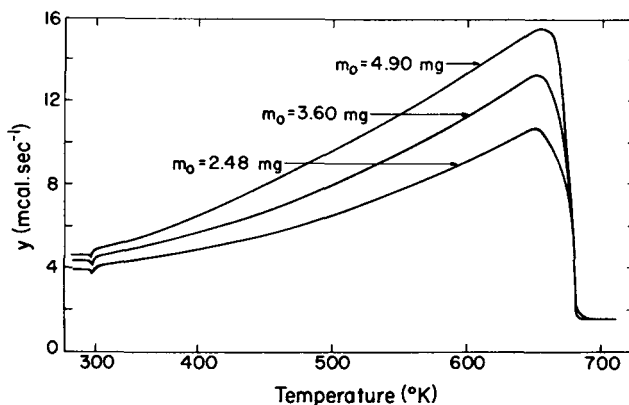


Fig. 12. Thermograms obtained by the decomposition of POPG 2025 with several initial masses.

carried out at heating rates of 10, 20, and 40°K/min with polymer samples weighing initially 4.08, 4.06, and 4.08 mg, respectively. An examination of these curves shows that the final temperature of decomposition varies with the rate of heating. At $\alpha = 40^\circ\text{K}/\text{min}$, the polymer is completely decomposed by 670°K, while at 20 and 10°K/min, respectively, the decompositions are completed only at 680° and 690°K. It appears that doubling the rate of heating displaces the thermogram by 10°K, but does not affect the kinetics of the decomposition.

Figure 15 shows the variation of $\ln y_H$ as a function of $1/T$ for the 2025 polymer sample at the three different heating rates. From these, the over-

TABLE III
Influence of Rate of Heating on Overall Activation Energy of Reactions

α , °K/min	E , kcal/g-mole
10	8.8 ± 0.8
20	8.6 ± 0.8
40	8.5 ± 0.8

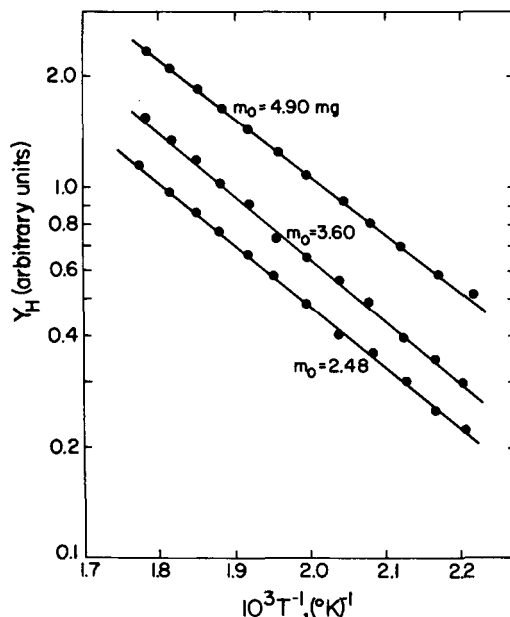


Fig. 13. Arrhenius plots showing effect of initial mass for POPG 2025.

all activation energies have been computed and the values are presented in Table III. It can safely be concluded from the results obtained that the rate of heating of the sample has little effect on the energy of activation.

Influence of Molecular Weight

Thermograms obtained during the decomposition of POPG polymer of different molecular weights (4025, 2025, 1025, and 425) are presented in Figure 16. The results show clearly that for the first three samples (4025, 2025, and 1025), the final temperatures of decomposition are very near one another at 680°K . However, such is not the case for the fourth polymer sample (425) where the final temperature of decomposition is very much lower at 600°K . The y_H value has been plotted on semilog paper versus $1/T$ (Fig. 17), and, from the slopes of the lines, activation energies have been obtained (Table IV).

In Figure 18 is shown the variation of E with the molecular weight of the polymer studied. With increasing molecular weight, there is an increase in

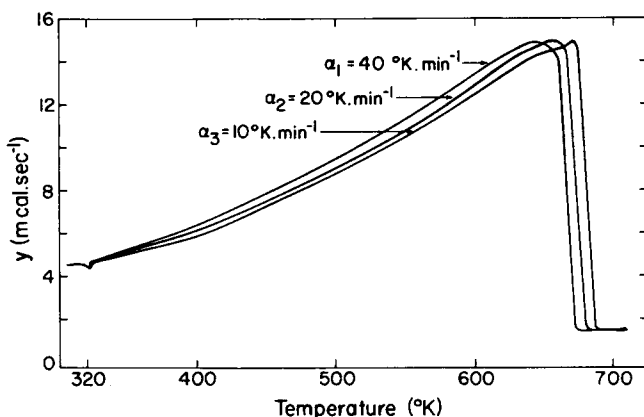


Fig. 14. Thermograms obtained by decomposition of POPG 2025 at several heating rates.

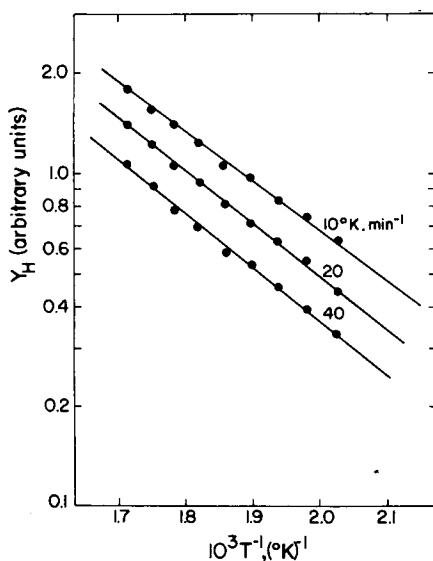


Fig. 15. Arrhenius plots showing effect of heating rate for POPG 2025.

the value of E which, in the light of results obtained in similar studies on other systems,^{6,7} seems normal since, for a long chain molecule, the energy required to dissociate it into volatile components should be higher than that required for small chain molecules because of the higher packing density of the former.

Similar trends have been reported by Madorsky and Strauss⁸ for the decomposition of poly(oxypropylene) of higher molecular weights (2.15×10^5 and 1.6×10^4). For the former, E was found to be 45 kcal/g-mole, while for the latter, E was 20 kcal/g-mole. Table IV and Figure 19 also show the variation of ΔH with molecular weight as calculated by dividing the total heat represented by the surface under the thermogram by the

TABLE IV
Influence of Molecular Weight on Overall Energy of Activation and on Total Heat of Decomposition

Mol wt	E , kcal/g-mole	ΔH , kcal/g-mole
4025	9.8 ± 0.6	4140
2025	8.6 ± 0.8	2400
1025	7.9 ± 0.6	1040
425	6.7 ± 1.0	300

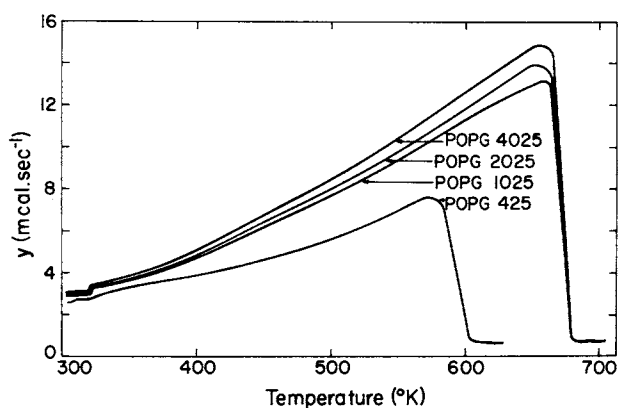


Fig. 16. Thermograms obtained by decomposition of POPG of varying molecular weights (4025, 2025, 1025, and 425).

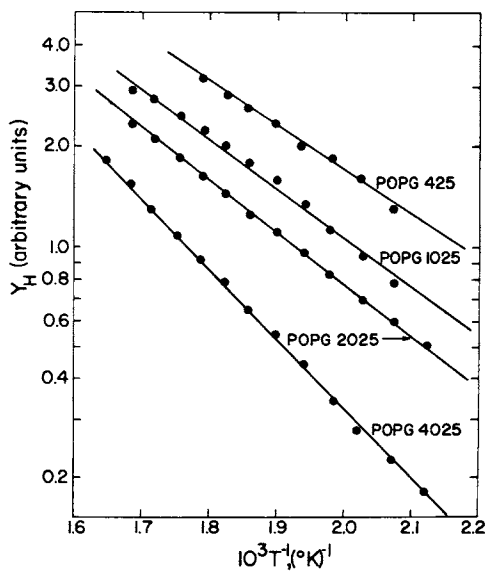


Fig. 17. Arrhenius plots showing effect of different polymer molecular weights.

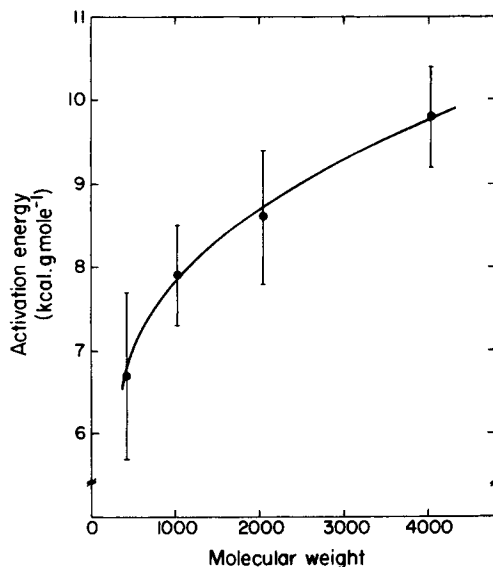


Fig. 18. Variation of activation energy as a function of the molecular weight.

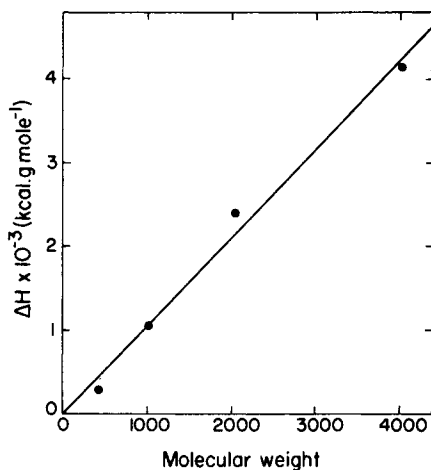


Fig. 19. Variation of heat of decomposition as a function of molecular weight.

initial number of moles of polymer charged into the pan. From the plot of ΔH against the molecular weight of the polymer, one obtains a straight line passing through the origin. The heat of decomposition of POPG is thus directly proportional to the mean average chain length of the molecules.

Influence of Initial Temperature T_0

As was indicated earlier, the partial heating method used to condition the samples provided T_0 values reproducible to within $\pm 10^\circ\text{K}$ of one another. In order to show that this factor does not influence unduly the

TABLE V
Reproducibility of Experimental Results

Expt.	E , kcal/g-mole
A	6.7 ± 1.0
B	6.4 ± 0.8
C	6.6 ± 0.8

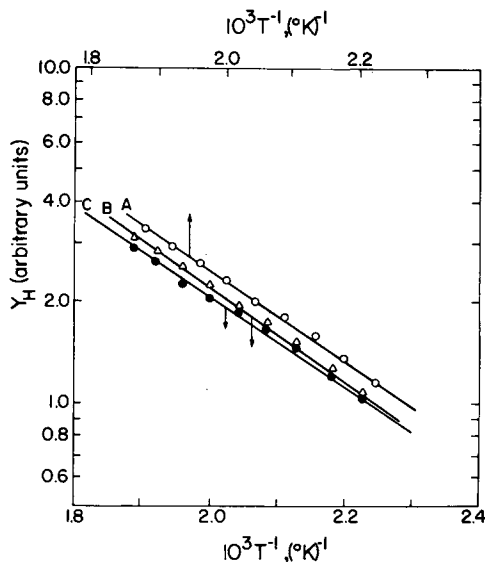


Fig. 20. Arrhenius plots showing the reproducibility of experimental data.

results obtained on the kinetics of the decomposition, values of E were determined for three different values of T_0 . The values of γ_H at a given temperature for three different values of T_0 were found to remain within 2% of one another. Thus, the values of the overall activation energy for the three runs for each of the polymer samples studied lie in the vicinity of 8.6 ± 0.8 kcal/g-mole.

The reproducibility of the results obtained with the DSC-1B has been verified by three separate experiments. The numerical values of the activation energies as computed from the Arrhenius plots (Fig. 20) are given in Table V. The results are reproducible to within $\pm 5\%$.

In concluding, it can be said that (1) the determination of the initial temperature of decomposition T_0 by the partial heating technique gives reproducible values; (2) the modified sample pans provide two advantages over the standard flat-bottomed pans, namely, the surface of the sample exposed is more constant and the energy losses due to radiation are diminished because of the reduction in the free surface of the sample; (3) the order of the reaction for the decomposition of POPG is zero; (4) the overall activation energy for the thermal decomposition of POPG increases with

molecular weight of the sample; however, the rate of flow of nitrogen, the molecular weight of the sample, and the rate of heating of the pans do not seem to have any significant effects on the kinetics of the reaction; and finally, (5) the mean values for the heat of decomposition, ΔH , as measured from DSC-1B thermograms are directly proportional to the average chain length of the polymers.

Further work on this polymer is being pursued with the gravimetric scanning technique. The results will be published at a later date.

The authors gratefully acknowledge the financial assistance of the Defence Research Board of Canada and the National Research Council of Canada. One of the authors (K.V.V.) is grateful to the Colombo Plan for an assistantship during the period of her M.Sc. studies.

The work described in this paper forms part of the research program of the "Groupe de Recherche en Science Macromoléculaire" at Laval University.

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Received November 1, 1973