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Kinetics of the Decomposition of Polyoxypropylene Glycols by Differential Scanning Calorimetry and Thermogravimetric Analysis

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ABSTRACT

The thermal decomposition of polyoxypropylene glycols under a nitrogen atmosphere has been studied in the temperature range 320 to 700°K under dynamic operating conditions with a differential scanning calorimeter and a thermogravimetric scanning system. In the DSC studies, Ellerstein's suggestion to use stainless steel mesh was followed to minimize differential energy losses. Differential scanning calorimetry yields zero-order kinetics while the data obtained with the thermogravimetric system fits first-order kinetics. Various ways of decomposition, satisfying both zero- and first-order kinetics, are discussed. The heat of decomposition is found to change with temperature, and activation energies obtained by DTG increase with rate of heating. Differential enthalpic analyses

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provide activation energies applicable to chain ruptures as well as volatile product evaporation, whereas thermogravimetric analyses furnish activation energies only for the second stage.

INTRODUCTION

Advances in technology have been taking place with such rapidity during the past few decades that it is now possible to study degradation reactions, for instance, by several techniques and thus evaluate in detail many of the factors affecting such reactions. Sometimes, however, in the absence of a complete understanding of all of the implications involved in the techniques being used, the final results arising out of the studies undertaken with each of these may be somewhat different. This does not, however, necessarily reflect unfavorably on the technology or techniques used, but rather it would suggest that certain modifications may be necessary in the practical or even theoretical approach to the problem being investigated.

Earlier in this laboratory a study of the thermal decomposition of polyoxypropylene glycols [1] was undertaken with a Perkin-Elmer DSC-1B differential scanning calorimeter. Interpretation of the results obtained, based on the Borchardt and Daniels expression [2] developed for differential thermal analysis, was made in the light of a limited number of assumptions and the corresponding corrections. Recently, Ellerstein [3] has suggested using 100-mesh stainless steel screening, rather than working with uncovered pans, so as to avoid or at least minimize the energy losses caused by heat transfer between these pans and the surrounding gaseous atmosphere. Ellerstein's suggestion has been tried out here on work carried out earlier in order to appreciate the effects of this new mode of operation.

This decomposition reaction has also been studied with a thermogravimetric balance operating under isothermal as well as dynamic conditions. The results of the present study are compared with the work reported earlier.

EXPERIMENTAL

Apparatus

A Perkin-Elmer DSC-1B differential scanning calorimeter was used in this work and was operated at a heating rate of 20°K/min with an inert nitrogen atmosphere and samples weighing from 2 to 3 mg. Each sample was placed between two layers of 100-mesh stainless steel screening as suggested by Ellerstein. During the course of the

degradation the nitrogen gas was made to flow continuously through the cell to remove volatile products. Analysis of the thermograms was based on the theory of Borchardt and Daniels.

A Perkin-Elmer TGS-1 thermobalance was also used in this work. It was likewise operated at a heating rate of 20°K/min in an inert nitrogen atmosphere with samples weighing from 2 to 5 mg. The nitrogen was made to flow continuously throughout the apparatus to flush out the degradation products which otherwise might have proven harmful to the delicate electrobalance [4].

Polymer Samples

Polyoxypropylene glycol (POPG) samples with molecular weights from 425 to 4025 were generously provided by the Union Carbide Company of Canada. These colorless transparent liquid polymers were used as such without further purification after preliminary tests with purified (by precipitation) and nonpurified samples yielded the same results.

RESULTS AND DISCUSSION

In the earlier study [1] with the DSC-1B instrument, values of m , the mass of polymer at each temperature (T), were calculated with the assumption that the heat of decomposition (ΔH) remained constant during the reaction. With the thermogravimetric technique (TGS), the values of m were recorded directly as a function of temperature and no assumptions were needed. Figure 1 illustrates, for comparison purposes, the decomposition of a 4025 POPG sample as recorded by the TGS and the DSC-1B instruments, m/m_0 being the decreasing element as the temperature is increased. On the TGS curve, it can be seen that the mass begins to decrease slowly at 420°K and on up until 520°K, beyond which the decrease in mass accelerates until the end of the reaction at 670°K. It is clear that the mass recorded by TGS is higher than that calculated through the DSC-method [1].

With the isothermal gravimetric method, the rate law can be written in the form:

$$d\alpha/d\theta = k(1 - \alpha)^n \quad (1)$$

where α is the fraction decomposed, n is the order of the reaction and k is the rate constant. For a first-order reaction one can write:

$$d\alpha/d\theta = k(1 - \alpha) \quad (2)$$

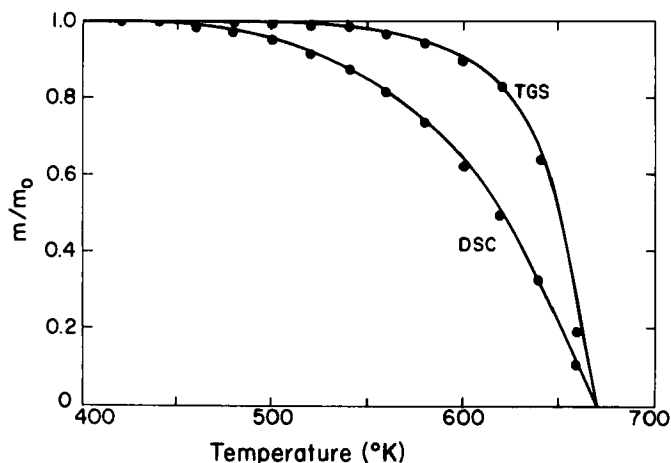


FIG. 1. A comparison of POPG 4025 decomposition by TGS and DSC analyses.

Integrating Eq. (2),

$$-\ln(1 - \alpha) = k\theta \quad (3)$$

On the hypothesis that the rate constant k varies with temperature according to the Arrhenius law, then

$$k = Z \exp(-E/RT) \quad (4)$$

where Z is the frequency factor and E is the overall energy of activation. In logarithmic form, Eq. (4) becomes

$$\ln k = \ln Z - E/RT \quad (5)$$

With the help of this equation, the overall activation energy of the reaction can be calculated by making use of the values of k from the isotherms obtained at different temperatures.

In the case of POPG 1025, isothermal decompositions were carried out at 493, 513, 538, and 553°K. The results obtained are presented in Fig. 2. It is apparent from the curves that $d\alpha/d\theta$, the rate of decomposition, decreases with time, thus indicating that the order of the reaction is not zero. From the isothermal decomposition reaction data, $-\ln(1 - \alpha)$ was calculated as a function time. The results are shown in Fig. 3. The straight lines passing through the origin, for all four temperatures studied, verify indeed that the reaction is first

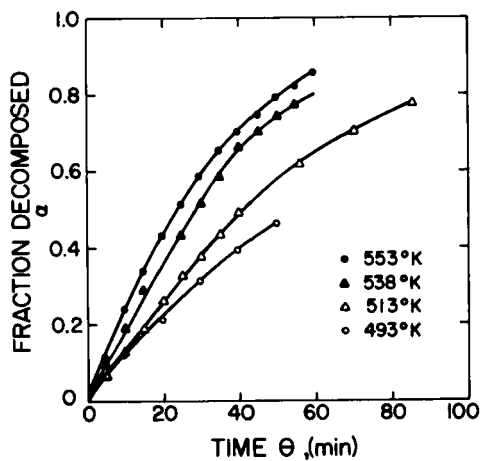


FIG. 2. Variation of α with θ in ITG analyses at different temperatures.

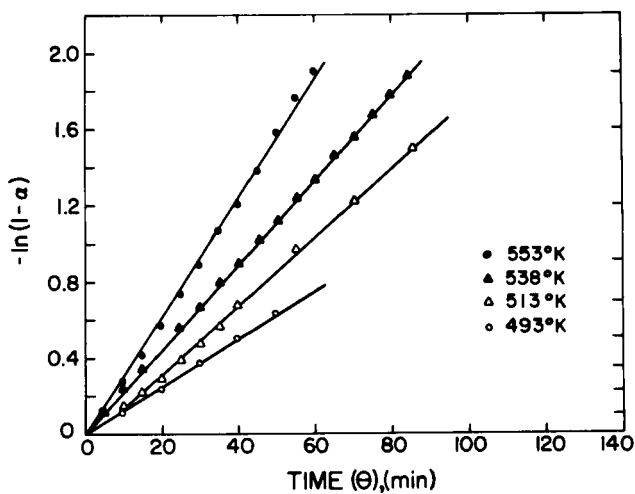


FIG. 3. First-order plots, $-\ln(1 - \alpha)$ vs θ , at different temperatures.

TABLE 1. Variation of the Rate Constant k as a Function of Temperature

T (°K)	$10^3/T$ (°K ⁻¹)	k (min ⁻¹) × 10 ²
493	2.03	1.2
513	1.95	1.7
538	1.86	2.6
553	1.81	3.1

order. From the slopes of the straight lines given in Fig. 3, the rate constants were calculated for the four different temperatures used and are presented in Table 1.

Evaluation of the Overall Activation Energy by Isothermal Gravimetry (ITG)

Figure 4 shows the Arrhenius plot of the 1025 POPG sample traced with the help of the k values in Table 1. From the slope of the line, the calculated overall energy of activation is 8.7 ± 3 kcal/g-mole. The relative error assigned to the value of E was calculated on the basis of the temperature error in the sample, which was found to be of the order of $\pm 5\%$.

In dynamic thermogravimetry (DTG), the temperature of decomposition is constantly increased at a fixed rate while the mass of the sample is recorded continuously. With a heating rate q where

$$q = dT/d\theta \quad (6)$$

one can write from Eq. (1):

$$\frac{d\alpha}{d\theta} = \frac{k}{q} (1 - \alpha)^n \quad (7)$$

Replacing the value of k by the Arrhenius expression one obtains

$$\frac{d\alpha}{d\theta} = \frac{Z}{q} \exp(-E/RT)(1 - \alpha)^n \quad (8)$$

To calculate the overall energy of activation from a single thermogram, where α , the fraction of the sample decomposed, is recorded as

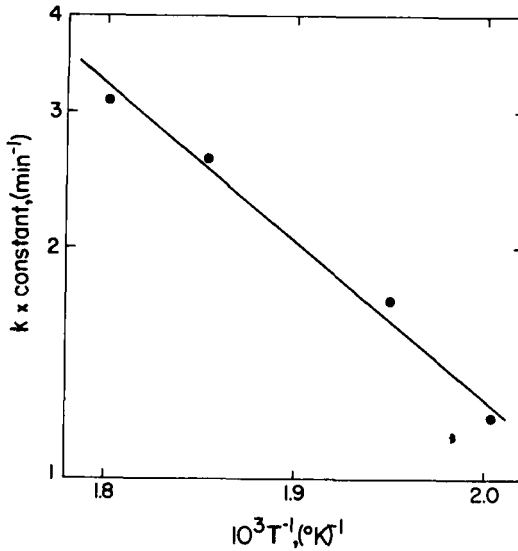


FIG. 4. Arrhenius plot from ITG data based on first-order kinetics for the decomposition of POPG 1025.

a function of T, Coats and Redfern [5] have proposed the integration of Eq. (8) between the limits: initial temperature of decomposition T_0 and a higher temperature T. Thus

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{q} \int_{T_0}^T \exp(-E/RT) dt \tag{9}$$

Making use of approximations in the integration, Eq. (9) becomes

$$\frac{F(\alpha)}{T^2} = \frac{A}{q} \frac{R}{E} \exp(-E/RT) \tag{10}$$

which in the logarithmic form yields:

$$\ln \frac{F(\alpha)}{T^2} = \ln \left(\frac{AR}{qE} \right) - E/RT \tag{11}$$

where

$$F(\alpha) = \alpha \quad \text{for } n = 0$$

and

$$F(\alpha) = -\ln(1 - \alpha) \quad \text{for } n = 1$$

The overall energy of activation can now be computed from the slope of a single $\ln[F(\alpha)/T^2]$ vs $1/T$ plot.

Figure 5 represents the dynamic thermogravimetric decomposition of POPG 1025 at a heating rate of $10^\circ\text{K}/\text{min}$. The transformation of this thermogram into a $\ln[F(\alpha)/T^2]$ vs $1/T$ plot is shown in Fig. 6. The overall energy of activation as calculated from the slope of this line is 25 ± 1 kcal/g-mole.

Influence of the Rate of Heating on the Activation Energy as Computed from Dynamic Thermogravimetry

The activation energy for the decomposition of POPG 1025 as computed from dynamic thermogravimetry is considerably higher than the value obtained from the isothermal experiments. This observation has led the authors to study the influence of the heating rate on the energy of activation of the decomposition reaction. Values obtained at different

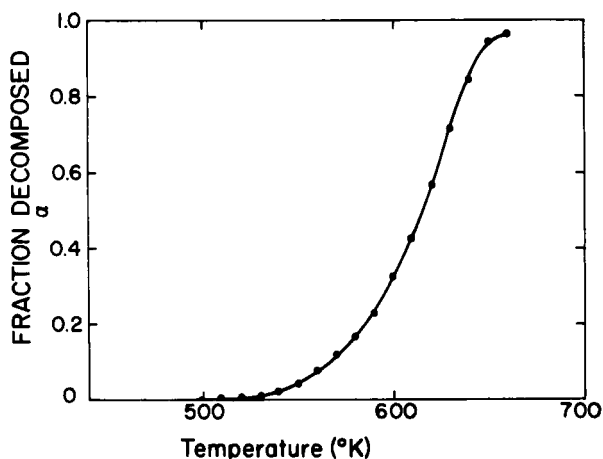


FIG. 5. Dynamic thermogravimetric decomposition of POPG 1025 at a heating rate of $10^\circ\text{K}/\text{min}$.

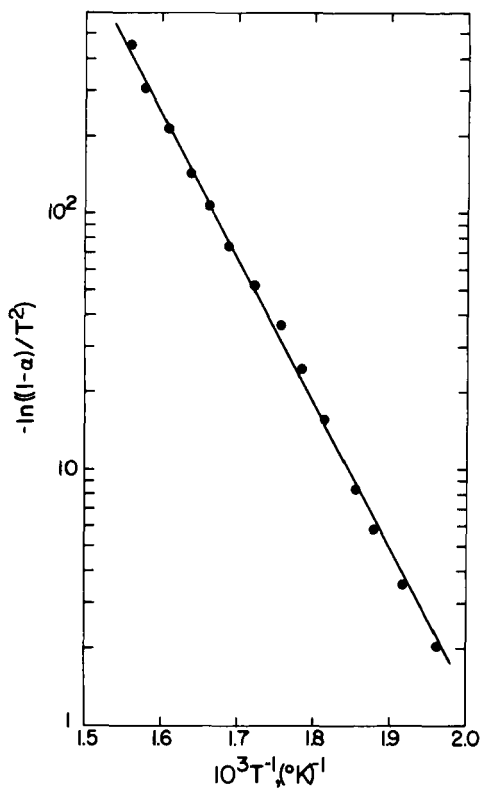


FIG. 6. Variation of $\ln\left(\frac{-\ln(1 - a)}{T^2}\right)$ as a function of $1/T$.

heating rates have been extrapolated to zero heating rate and are presented in Table 2 and Fig. 7. The extrapolated value obtained by this method compares very well with that calculated by isothermal gravimetry.

In the result obtained earlier for the thermal decomposition of POPG samples [1] studied by DSC, it had been observed that the values of the rate constants, k_0 and k_1 , when plotted on semilog paper as a function of $1/T$, yielded straight lines in both cases; however, the linearity of the first-order line was limited to the low temperature region. Further studies have been made on the POPG samples with the DSC, but under different operating conditions. Figure 8 shows a typical thermogram obtained during the decomposition of POPG 1025 using the modifications suggested by Ellerstein [3]. Compared to the

TABLE 2. Influence of the Heating Rate on the Energy of Activation (Basis: First-Order Kinetics and Data Obtained on the Decomposition of POPG 1025 by Dynamic Thermogravimetry)

Heating rate (°K/min)	Activation energy (kcal/g-mole)
0.00 (Extrapolated value)	8
0.625	9
1.25	16
2.50	19
5.00	21
10.00	25

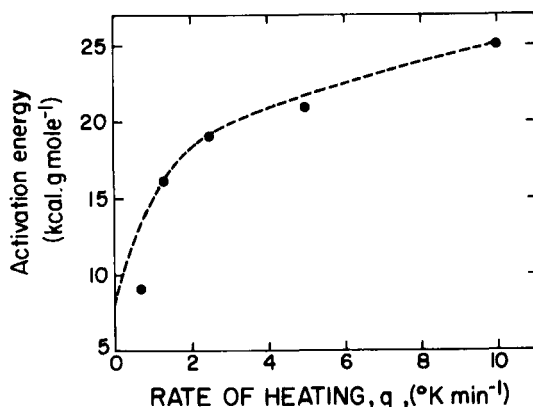


FIG. 7. Influence of heating rate on the activation energy of decomposition.

earlier work [1], where the tracing of a base line with the open pan system was a very complex process, the base line in this work is much more clearly defined.

Figure 9 shows an Arrhenius plot for the decomposition of the POPG 1025 sample as computed from the data in Fig. 8 for first-order kinetics. Here, $\ln(dH/d\theta)/(A - a)$ is plotted as a function of $1/T$. The curve obtained exhibits two slopes depending on the temperature region

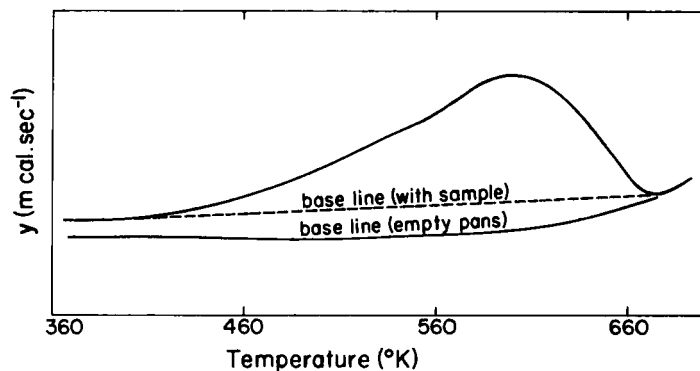


FIG. 8. Dynamic differential enthalpic decomposition of POPG 1025 using Ellerstein's modification.

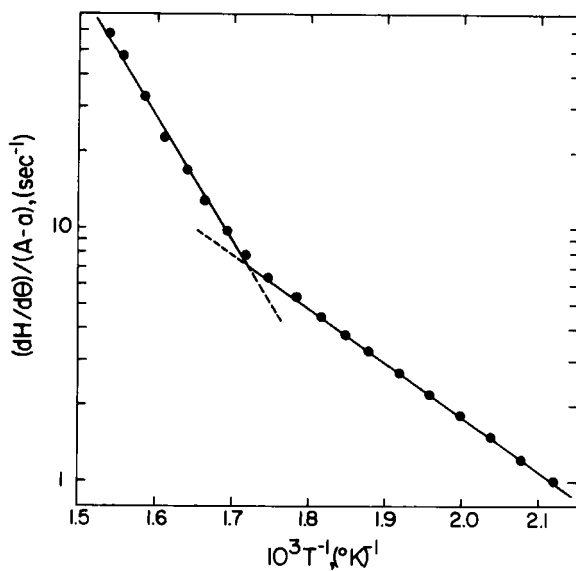


FIG. 9. Arrhenius plot from DSC data based on first-order kinetics for the decomposition of POPG 1025.

examined. One can therefore compute two activation energy values:

$E_1 = 10 \pm 0.4$ kcal/g-mole (for the low temperature region) and

$E_2 = 23 \pm 1.0$ kcal/g-mole (for the high temperature region).

Influence of Molecular Weight on the Energy of Activation

The ways to compute the activation energies from differential enthalpic and dynamic thermogravimetric data have been mentioned earlier. These methods have been used to compute the activation energies for four samples of different molecular weights. The results are presented in Table 3.

It is quite clear that if the reaction is first order, as is suggested by the TGS data and on the basis of which all computations were made for both the DTG and the DSC methods, then the activation energies obtained by the DTG method must be overall values only yielding no information as to the nature of the decomposition process. However, the two activation energy values obtained by the DSC method suggest that the process of decomposition proceeds via two separate steps depending upon the temperature at which the process is examined. This question will be discussed in more detail further on.

The data obtained by the DTG method and treated earlier has been found to fit first-order kinetics; however, this data can also be interpreted with the help of another expression based on the simple reaction

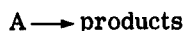


TABLE 3. Influence of Molecular Weight on the Energy of Activation (Basis: First-Order Kinetics and DSC and DTG Data Obtained at a Heating Rate of $10^\circ\text{K}/\text{min}$)

Molecular weight	Energy of activation (kcal/g-mole)		
	By DTG	By DSC	
		Low temp region	High temp region
425	23	6	11
1025	25	10	23
2025	31	19	23
4025	28	17	22

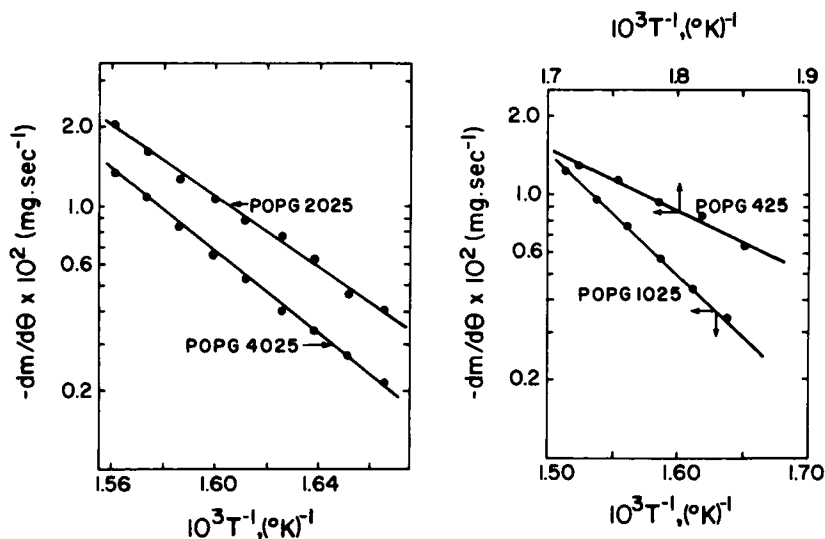


FIG. 10. Variation of $\ln(-dm/d\theta)$ with $1/T$ based on DTG data obeying zero-order kinetics.

from which it follows that:

$$-dm/d\theta = km^x \tag{12}$$

where m is the mass of the polymer intact at temperature T , k is the rate constant at that temperature, and x is the order of the reaction.

For a zero-order reaction,

$$-dm/d\theta = k_0 \tag{13}$$

Values of $-dm/d\theta$ can be computed from the DTG curves obtained with different POPG samples. The data in the form of $\ln(-dm/d\theta)$ can then be plotted as a function of $1/T$. The four straight lines obtained with the samples are shown in Fig. 10. They indicate that the order of the reaction for the decomposition of POPG is zero.

The contradicting results obtained by the two interpretations of the DTG data indicate that one of the two expressions used here, Eq. (11) or (12), needs to be modified. Recently, Thomas et al. [6] have pointed out that Eq. (12) is not applicable for solid-state and/or heterogeneous decompositions of the type



This equation, in fact, has been modified by MacCallum and Tanner [7] who have pointed out and made corrections for its dimensional inadequacy. It is not known whether Eq. (12) is valid or not for liquids, but based on the results obtained in this work it can safely be said that there certainly is some doubt.

Activation energy values based on zero-order kinetics have been computed and are compared with those obtained earlier in Table 4.

In Tables 3 and 4, activation energy values for the decomposition of POPG samples, as computed by different methods and on the basis of different orders of reaction, have been compared. Unfortunately, these have been computed for only one rate of heating which limits their significance as it is known that the values obtained from DTG are influenced by the rate of heating. As for the values obtained from DSC, they are known to be independent of the rate of heating, but these were computed on the basis that ΔH remains constant throughout the reaction, an assumption which may not be entirely true. One can nevertheless conclude from the results obtained that the increase in the values of E with molecular weight is real and believed to be normal since the longer chains will require more energy to bring about their decomposition.

Variation of ΔH with Temperature

In the studies carried out by differential scanning calorimetry, the assumption was made that ΔH , the heat of decomposition, remains constant throughout the whole process. Using dynamic thermogravimetry together with differential scanning calorimetry, it is possible to study the variation of ΔH with temperature. Figure 11

TABLE 4. Comparison of Activation Energies Obtained with DSC and DTG Data; Computations Are Based on Zero-Order Kinetics. Rate of Heating: 20°K/min

Molecular weights	E from DSC [1] (kcal/g-mole)	E from DTG (kcal/g-mole)
425	6.7 ± 1.0	10 ± 1
1025	7.9 ± 0.6	21 ± 2
2025	8.6 ± 0.8	31 ± 2
4025	9.8 ± 0.6	35 ± 3

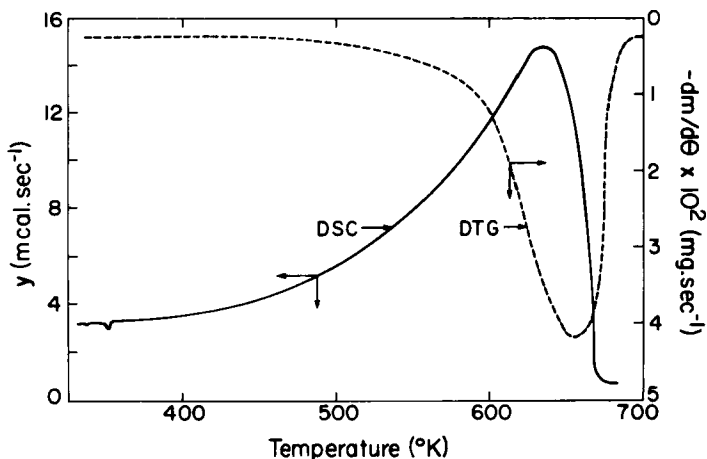


FIG. 11. Dynamic differential scanning calorimetric and thermogravimetric analysis of POPG 4025.

represents DTG and DSC curves for the thermal decomposition of POPG 4025 recorded simultaneously under identical operating conditions at a heating rate of 20°K/min. With the help of

$$- dH/d\theta = \Delta H(dm/d\theta) \tag{14}$$

the heat of decomposition, ΔH , expressed in mcal/mg, can be computed by dividing $dH/d\theta$ by the ordinate of the DTG curve at the same temperature. If one multiplies this value by the molecular weight of the respective sample, one gets ΔH in cal/g-mole. These values have been computed for four different samples of POPG and are presented in Fig. 12 as a function of T. It is obvious that the assumption about ΔH being constant during the whole process for all of the samples is only partially correct. While the argument holds good for low molecular weight POPG samples (425 and 1025), it is no longer valid for the comparatively higher molecular weight samples (POPG 2025 and 4025). Therefore, the activation energy values from DSC may be true only for the lower molecular weight samples.

Variation of ΔH with temperature for POPG samples of higher molecular weight, viz., 2025 and 4025, may also affect calculations leading to the order of reaction from DSC data. Recalling Eqs. (13) and (14) and rearranging the latter, it can be seen that:

$$- \frac{dm}{d\theta} = \frac{1}{\Delta H} \frac{dH}{d\theta} \tag{15}$$

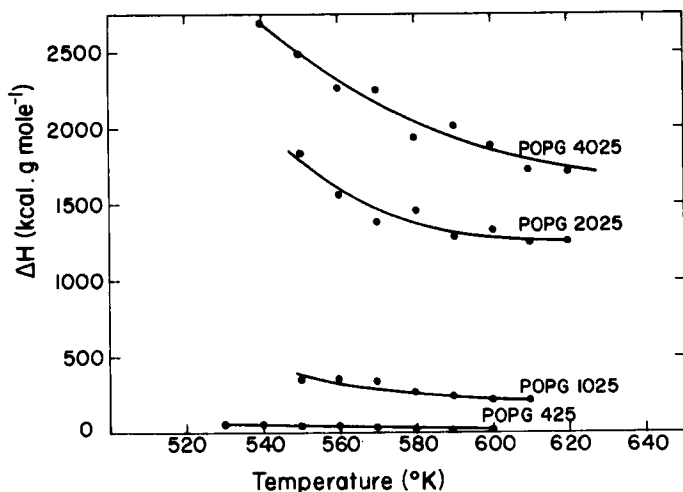


FIG. 12. Variation of heat of decomposition, ΔH , with temperature for four samples of POPG of different molecular weights.

and

$$- dm/d\theta = k_0 \quad (13)$$

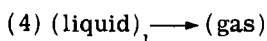
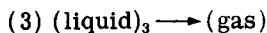
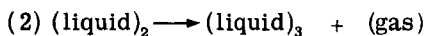
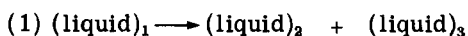
For zero-order kinetics, plots of $\ln(1/\Delta H)(dH/d\theta)$ as a function of $1/T$ should yield straight lines which may be used to obtain correct values of the activation energy. In the earlier studies [1] with the DSC, plots of $\ln(dH/d\theta)$ as a function of $1/T$ for the four different samples of POPG yielded straight lines, indicating that the decomposition of POPG followed zero-order kinetics irrespective of the molecular weight of the sample studied. It appears as a sheer coincidence that the DSC data for the two high molecular weight POPG samples 2025 and 4025 satisfied zero-order kinetics, when one keeps in mind the significant variations in ΔH with temperature as shown in Fig. 12.

The values of ΔH plotted in Fig. 12 were computed from $- dm/d\theta$ values obtained on a single heating rate, $20^\circ\text{K}/\text{min}$. One should preferably carry out experiments at different heating rates and extrapolate the data at different times to zero heating rate in order to compute true values for ΔH , using Eq. (15).

Variation of ΔH during the course of the decomposition process as well as the existence of two activation energy values from DSC data has lead the authors to believe that this process takes place in one of two ways.

A. In two stages: (1) In the first stage a definite amount of heat is utilized to dissociate the molecular chains but no or little volatile products are formed; (2) in the second stage the dissociated fragments decompose further to produce volatile substances. It is at this stage that one observes a rapid loss of weight.

B. By a succession of reactions: In each step the reactants in the liquid state decompose into liquid products of lower molecular weight and some gaseous products, followed in the next stage by still lower molecular weight products and greater quantities of volatile materials until all of the polymer has been volatilized. Schematically the reactions may be written as



In this case, the reaction resembles very much the stepwise depolymerization proposed by Igarashi and Kambe [8] for the decomposition of polyoxymethylene glycol (POMG). It is only in the 4th stage of the decomposition that zero-order kinetics appears valid since then the rate depends only on the gas-liquid interface.

The interface for reactions of Types (2) and (3) is situated either at the level of the bubble or in the liquid itself. The dimensions of the bubble, of course, will change with temperature and likely with the mass of the liquid. In these cases, first-order kinetics is difficult to imagine.

The reactions of Type (1) draw their support from the fact that the values of the initial temperature of decomposition, as determined from TGS data, are higher than the corresponding values obtained by DSC. The latter also yields the value of ΔH for the first type of reaction, whereas the TGS technique records only changes in weight. As there is no change in weight in a process of Type (1), the value of ΔH from TGS can be expected to be higher.

Further work is in progress on the mechanism of these decompositions and will be published as it becomes available.

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