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APPLICATION OF NEW KINETIC TECHNIQUES TO THE LIFETIME PREDICTIO--ETC(U)
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Prediction of the lifetime of a polymer by extrapolation of weight-loss data is a tenuous procedure and a thorough analysis of the kinetics over a wide temperature range is a requisite. Several experimental methods and kinetic analytical techniques have been developed which are designed to overcome the problems of conventional methods. These include: (1) a factor-jump method in which a fully automated and minicomputer directed system calculates activation energies using one sample and a series of short, isothermal over

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plateaus, this avoids complications from the comparison of samples with diverse properties and thermal histories. (2) a diagnostic test for the consistency of kinetic parameters over a broad region of temperature and conversion. (3) a comparison of experiments performed at constant heating rates from 6 K/min. to 9 K/day; this allows an insight into the mode of kinetic coupling of competing processes and better prediction of the dominant low-temperature process. (4) a detailed analysis of the kinetics of the first several percentages weight-loss at slow heating rates and low temperatures; many polymers lose their useful properties in this region. These methods are being applied to polystyrene and polyurethanes in vacuum, nitrogen, and nitrogen-oxygen mixtures.

APPLICATION OF NEW KINETIC TECHNIQUES TO THE LIFETIME PREDICTION OF POLYMERS FROM WEIGHT-LOSS DATA

Joseph H. Flynn and Brian Dickens

Polymer Science and Standards Division
Center for Materials Science
National Measurement Laboratory
National Bureau of Standards
Washington, DC 20234

As more and more polymeric materials are used both in the replacement of other materials and by the creation of new applications, the study of their expected lifetimes assumes greater and greater importance. It is more economical to plan for replacement of defective parts than to suffer an unexpected failure which may occur under inhospitable, inconvenient or even dangerous conditions. Philosophies of how to assess lifetimes fall into several schools. These include: evaluation of experience with the materials under actual service conditions, acceleration of the aging process by increasing one or more degradation factors above their normal levels and assessing the degradation rate by monitoring the first appearances of degradation under service-like conditions.

We have chosen to examine the applicability to lifetime prediction of four methods of thermogravimetry. Although one can argue that many useful properties of polymers may disappear before weight loss occurs, it is worthwhile to examine the role of thermogravimetry in lifetime prediction because the technique can be applied to any condensed phase sample, soluble or not, in almost any geometric form. Further, thermogravimetry is simple, convenient, and, in some modes of application, fairly fast. The hardware is rugged, reliable and stable. Finally, the process which results in the volatilization of small fragments is often closely related to the process which results in the loss of desired properties.

The four methods of thermogravimetry which we discuss here are complementary. No one method is all-encompassing. All provide relevant information. The methods are:

I. Factor-jump Thermogravimetry
II. Isoconversional Diagnostic Plots
III. Varied Heating Rate Analysis
IV. Analysis at Low Conversion

Method I consists of a series of isothermals; the temperature is increased continuously in Methods II, III and IV.

I. Factor-jump Thermogravimetry

In its usual application, the factor-jump method (1) consists of imposing a series of temperature plateaus on a sample while recording its weight. The rates of weight-loss and the temperatures at adjacent isothermals are extrapolated to halfway between the plateaus in terms of time or in terms of the associated parameter, extent of reaction. The activation energy, E, is then estimated from the Arrhenius equation

$$E = \frac{RT_1T_2}{\Delta T} \ln \frac{r_2}{r_1} \qquad (1)$$

where R is the gas constant, r's and T's are extrapolated rates and temperatures from two adjacent plateaus and $\Delta T = T_2 - T_1$. Because both rates and both temperatures are estimated at the same extent of reaction, the term containing the extent of reaction and other temperature-independent factors cancel out [see ref. (1)]. The factor-jump method, in our implementation, is automated (2, 3, 4, 5, 6) and computer controlled.

The strong points of the method are as follows:

i) Activation energies are determined using only one sample. (In multi-sample techniques, one must assume that thermal histories are unimportant.)

ii) The model, Eq. (1), is simple and contains no complicating extent of reaction terms.

iii) The experiment is conducted over a narrow range of rates of weight-loss. Thus the concentrations of reactants within and products above the sample are roughly constant.

iv) The quantities used to calculate the activation energy are obtained from a small (6-10°C) temperature range. We may assume that the Arrhenius equation is valid and the pre-exponential factor is independent of temperature over this small interval.

The weakest points of the method are:

i) The initial activation energy cannot be determined because the first determination is made between the first and second isothermal plateaus. This is usually at 5-10% weight-loss.

ii) The method is not computationally robust. It requires that the weight-time trend be fitted to a polynomial which is then differentiated and extrapolated ∿ 15% beyond the range of data. The loss of weight during the degradation of many polymers results from bursting of bubbles. In a derivative-calculating method such as this one, only slight perturbations in the sample weight are needed to mitigate the successful calculation of the derivative. This is because "wild" values can have enormous effects (proportional to the square of their wildness) on the least squares curve fitting which tries to minimize the sum of squared deviations.

II. Isoconversional Diagnostic Plots

This method, together with methods III and IV, is a treatment of weight-loss/temperature data obtained in constant heating rate thermogravimetric experiments. Provided we assume that the Arrhenius equation is valid and that the same form, $F(\alpha)$, of the dependence of rate on extent of reaction, α, maintains throughout all the runs at a constant heating rate, β, we can formulate (7, 8), for a given extent of reaction, the equation

$$\Delta \log \beta = - 0.457(E/R)\ \Delta(1/T). \qquad (2)$$
$$(\alpha = \text{constant})$$

E can be estimated from the slope of a plot of log β vs. 1/T at a given extent of reaction from runs at several different heating rates. This can be extended to give E for several extents of reaction, typically every 10%.

The advantages of this method are:

i) The form of the dependence of rate on extent of reaction need not be known or guessed at.

ii) A wide temperature range can be covered.

iii) The method is computationally robust--weight-loss curves are utilized directly.

iv) The change in conditions (usually only the temperature) is constant and can be automated with little need for sophistication.

v) Parallel lines on the plot show in an obvious fashion the consistency of activation energy throughout the range of reaction and throughout a wide temperature range.

The method is not without its disadvantages:

i) As with all integral methods, the effects of errors are cumulative--early errors are passed on to later results.

ii) One must use more than one sample and must assume that the weight-loss kinetics are independent of the differing physical character and thermal histories of the samples. This means that, regardless of the thermal history of the sample, regardless of the temperature and regardless of the effects of degradation, the dependence of rate of weight-loss on the extent of reaction is the same in all samples for a given extent of reaction.

iii) As is the case with all dynamic heating experiments, the temperature may not be able to "equilibrate" at the faster heating rates.

III. Varied Heating Rate Analysis

This method is based on examining the shift with heating rate of peaks in the plots of $d\alpha/dT$ vs. T. Theoretical considerations (9) show that peaks corresponding to independent reactions with widely differing activation energies can be resolved at some attainable heating rate. For competitive reactions, one peak or the other will dominate as the heating rate is changed.

The advantages of the method are:

i) One can resolve whether the weight-loss process is simple or complex in favorable cases.

ii) Likewise, one can resolve whether any complication arises from competing or independent reactions.

iii) As in II, the conditions may include a wide range of temperatures and heating rates and the complete range of the degradation reaction is examined.

iv) From experiments at very slow heating rates, one can better predict which reaction will dominate at service conditions.

The disadvantages are:

i) The difference in activation energies must be rather large ($\sim$ 20 kcal/mole) to obtain good resolution since one can obtain only a factor of $\sim 10^4$ in heating rates. It is probably rather rare that such large differences in activation energy are found in reactions occurring at the same temperature range and as alternatives to one another.

ii) The method requires very slow heating rates with the result that the duration of the experiment may become excessive.

iii) It may be that very fast heating rates are required where the transfer of heat to the specimen becomes a limiting factor.

IV. Analysis at Low Conversion

The heart of this method (10, 11) is to plot $T^2 d\alpha/dT$ against α to obtain a slope of $E/R + 2T$ at low extent of reaction ($\alpha \leq .05$). This can be done simply from a single thermogravimetric trace of weight against time or temperature.

The advantages are:

i) Only one sample is required, thus circumventing all problems arising from differing sample histories.

ii) Because the extent of reaction is always small, the form of the dependence of rate of reaction on extent of reaction may be safely ignored.

iii) One can estimate other aspects of the kinetics from the change in slope as α increases. If the slope increases with increasing α, then the dependence on weight-loss has an autocatalytic character as in the random degradation of polymers. When the slope decreases with increasing α, the kinetics behave as a positive order reaction. A slope independent of α implies zero order kinetics.

The disadvantages are:

i) The extent of conversion enters into both quantities plotted, therefore, one must be more than usually consistent in picking the beginning of the polymer degradation.

ii) The initial rates of weight-loss are especially sensitive to volatile contaminants including monomer, solvent, plasticizer, etc. Their effects often must be minimized by pretreatment.

iii) Chemical effects from residual catalysts, antioxidants, stabilizers, etc. and labile linkages introduced during synthesis and storage may affect the initial kinetics.

Important Parameters in Lifetime Prediction

The four methods just described determine the apparent activation energy, E, rather than the dependence of rate of reaction on extent of reaction, $f(\alpha)$. In fact, they specifically avoid having to estimate the latter term. This is especially appropriate in lifetime prediction where temperature is the only accelerating factor between test and service conditions. The functional form of $f(\alpha)$ affects only the shape of the kinetic curve and not its time-temperature positioning. In any event, for these complex condensed phase reactions, $f(\alpha)$ cannot be separated from the pre-exponential factor of the Arrhenius equation and other factors related to the physical properties of the sample without composing a detailed kinetic model. Such models are often simplistic in their construction and their use can introduce gross errors in the determination of E (1, 12). The omission of any temperature dependence of the pre-exponential factor will be partially compensated for in the calculation of apparent activation energy. These errors should have considerably less effect than errors in E itself which are promulgated exponentially.

Because activation energy represents the temperature dependence of a process, it is important to estimate the precision in the activation energy needed to provide useful estimates of service life after extrapolation of the rates to service temperatures. We may estimate the effects of error, σ, in the activation energy, E, from the Arrhenius equation written in the form

$$\frac{r(T_2)}{r(T_1)} = e^{(E + \sigma)\Delta T/RT_1T_2} = e^{E\Delta T/RT_1T_2}\, e^{\sigma\Delta T/RT_1T_2} \qquad (3)$$

This gives the relationship between rates at temperatures T_1 and T_2 where $T_2 - T_1 = \Delta T$. The temperature scaling factor for the reaction rate is $\exp(E\Delta T/RT_1T_2)$. The term $\exp(\sigma\Delta T/RT_1T_2)$ transmits the error in the activation energy into the ratio of rates. It should be noted that this is a multiplicative exponential effect; in other words, a small amount of error has a large effect. Note that the effect of the error is independent of the activation energy, which is often determined to a percentage of error. Thus at first sight it may appear that processes with large activation energies may, because of the larger error in the value assigned to the activation energy, have greater uncertainty in their extrapolated rates. However, the size of ΔT necessary to accelerate the process is inversely proportional to the activation energy so that for high activation energy reactions the ΔT will be relatively small. If the error in activation energy determinations is anywhere near constant, processes with large activation energies may give more reliable extrapolations than those with low activation energies.

It is illuminating to consider the effects of errors in activation energy on scaled tests. As an illustration, we draw on recent results for the oxidation of polystyrene (13). Table I shows the error in activation energy (σ) at test temperatures of 100, 200, 300, 400 and 500°C which will result in errors in rates of 1, 5, 10, 25, 50, 100 and 250% at service conditions of 25°C.

Table I

Effect of Error in Activation Energy on Accelerated Rate Tests

Service Temp = 25°C

% Error in Rate*	Error($\pm\sigma$) in Activation Energy in kcal/mole				
	Test Temp °C = 100	200	300	400	500
1	0.03	0.02	0.01	0.01	0.01
5	0.15	0.08	0.06	0.05	0.05
10	0.28	0.15	0.12	0.10	0.09
25	0.66	0.36	0.28	0.24	0.22
50	1.20	0.65	0.50	0.43	0.39
100	2.05	1.11	0.86	0.74	0.67
250	3.71	2.01	1.56	1.34	1.22

*Calculated at service temperature from rate observed at test temperature by means of Equation (3).

The greater the temperature difference between service life and accelerated test, the smaller the error in activation energy must be for a given error in scaled rate. In the oxidation of polystyrene between 225°C and 275°C, the final averaged activation energy is 21.5 ± 0.2 kcal/mole. Using an error value of $2\sigma = 0.4$ kcal/mole for a 95% confidence level, we estimate by interpolation in Table I that an error of 31% would be introduced into the calculated rate if the rates observed at ∿ 225°C were scaled to room temperature.

The above analysis suggests that extrapolation to lower temperatures of results obtained in accelerated tests at higher temperatures requires activation energies which are known to great accuracy, i.e., to within 0.1 kcal/mole in some cases. Such high precision will be rarely attained even using an average of a large number, N, values from many runs to give a factor of $\sqrt{N}$ in the denominator of the estimated standard deviation. Uncertainties in the continuity of the processes themselves over the extrapolated range further cloud the issue. In cases where such precision is required, the accelerated test will have to be conducted under extremely modest temperature acceleration. However, such a procedure limits the number of values for determining an average activation energy and may require experiments of impracticably long duration. If the rates of weight-loss processes are not sufficiently fast under those conditions, one must look to the analysis of rates of production of minute amounts of products or changes in physical properties of the material as alternate methods of lifetime prediction.

The extrapolation of typical rates of degradation from the temperature at which E is determined to service conditions will change the rates by a factor of 10^{-7} to 10^{-20} due to the large ΔT involved. Therefore, extrapolated rates using $E + 2\sigma$ and $E - 2\sigma$ will probably differ by at least 50%. This all reinforces the conclusion that the temperatures at which ordinary thermogravimetric methods determine E are too high to permit meaningful aging prediction. For example, in Ref. (13), the activation energy for polystyrene oxidation was determined to be 21.5 ± .2 kcal/mole above 280°C. For extrapolation to 25°C, a unit rate at 280°C is transformed to a rate of 0.54×10^{-7}, i.e., a process occurring in 30 minutes at 280°C takes 1057 years at 25°C. If we proprogate the $\pm 2\sigma$ errors in the activation energy, the reaction would take between 770 and 1427 years at service conditions.

Thus, the philosophy of lifetime prediction using temperature-accelerated tests is as follows:

1) Determine the activation energy of the degradation process at the lowest possible temperature to the best possible precision ($\sim$ 0.2 kcal/mole in thermogravimetry).

2) Consider the accuracy of this measurement and compare it with other estimates of the activation energy made using other techniques and the measurements of other experimental factors.

3) Assess the desired lengths of time for the accelerated test and service life. Assuming E from 1) is applicable, compute ΔT between service and test conditions and try to prove that the same kinetic processes are going on at the test and service temperatures. Some of the latter techniques in this paper are useful in this connection.

4) Compute, using the error in E, the maximum change in temperature between service and use conditions which will still give the extrapolated rates within the desired bounds and compute the error in these rates using these temperatures. Then attempt

to devise a test which uses this highest permissible temperature and still gives changes in the sample which are well characterized and measurable to considerable precision. It may be necessary to accelerate other factors such as oxygen concentration, pressure, etc., to lower the test temperature. Unfortunately, an increase in the intensity of these other factors may introduce errors in their extrapolation to use conditions similar to those resulting from temperature extrapolation.

We will now illustrate these points very briefly using our results (13) for the oxidation of polystyrene:

1) The activation energy for the oxidation of polystyrene is 21.5 ±.2 kcal/mole.

2) This value, obtained by the factor-jump method of thermogravimetry, appears to be realistically precise, i.e., different runs agree well. There seem to be no other studies of comparable precision from which to assess accuracy. For the moment, we will assume the reported value is accurate as well as precise.

3) A typical service life requirement is > 20 years at 25°C. Suppose that the test can be made safely in 3 hours or with marginal confidence in 30 minutes. (Problems arise with short test times in equilibrating the specimen to its test temperature and performing meaningful measurements in the allotted time.) The acceleration factors, A_1, for the two cases are thus 20 yrs./3 hrs. = 58,400 and 20 yrs./30 min. = 350,400. Using $A_1 = \exp(21500\ \Delta T/RT_1T_2)$ we find the test temperature for these accelerations to be respectively, 154°C and 186°C.

4) We will consider the limits imposed by the error, σ, in the activation energy, E. If the percentage error allowed is 100 P_E, then Equation (4)

$$\frac{(1 - P_E)}{1} = \frac{\exp[(E - n\sigma)\ \Delta T/(RT_1T_2)]}{\exp[E\Delta T/RT_1T_2]} \qquad (4)$$

specifies that the test temperature, T_2, be such that the effect of $n\sigma$ in scaling ΔT between T_2 and the service temperature, T_1, is to impart 100 P_E% of error. Thus the rearranged form, $\ln(1 - P_E) = -\, n\sigma\ \Delta T/(RT_1T_2)$, can be used to provide an estimate of T_2. Since E measures the temperature dependence of the process, if we use a value for E which is too high, we obtain inflated values for the estimated service life. If we use an E which is too low, we obtain an underestimate of the service life and will waste effort on needless improvements. Whether both limits apply or whether a one-tailed test (e.g., 95% of all components should exceed 20 years in service) is appropriate depends on the particular application. In either case it is important to use a good estimate of E.

For 2σ = 0.4 kcal/mole, to estimate a rate which is within 5% of the true rate at a service temperature of 25°C, the test temperature would have to be no higher than 50°C. For an allowed error of 10%, the test temperature could be as high as 80°C, and for an error of 25%, it could be as high as 245°C. Therefore, depending on the desired precision and degree of extrapolation it may be necessary to aim for a service life well over the required value to fit within the limits of error.

The above considerations show that although estimate of service life is not straightforward, our methods of thermogravimetry can provide useful information in the form of activation energies and, at least qualitatively, about reaction kinetics.

However, it is obvious that conflicts will often occur between the predictive criteria and the accelerated weight-loss experimental data. The three techniques which we described in Sections II, III and IV are being directed toward two serious problems which remain even for cases in which accelerated weight-loss measurement is a valid criteria for predicting aging at service conditions. These problems are: a) the great length of the temperature range of extrapolation which may render aging predictions too uncertain to be useful, and b) any hidden changes in the rate-limiting step of the degradation in the extrapolated region which will invalidate the use of Arrhenius parameter, E, determined at accelerated conditions, for prediction.

The consequences of these problems may be lessened by a) extending the constant heating rate measurements to as slow a heating rate and, as a result, to as low a temperature as practical, and b) conducting experiments over as wide a range of heating rates (and temperatures) (14) as will give meaningful weight-loss measurements so as to better detect any trends in the degradation kinetics and to interpret these trends to predict which of competing processes may dominate at service conditions.

The heating rates are limited at the fast end of the range by the lags in thermal and mass flow in the sample and time constants of the apparatus and measurement sensors. It is difficult to obtain unperturbed weight-loss measurements at heating rates above 10^{-1} deg/sec(6 deg/min) without specially designed thermogravimetric apparatus. The limit at slow heating rates is entirely up to the experimenter's patience and longevity, as many modern electrobalances exhibit excellent long term base line stability. It requires three and a half days to cover a 300° temperature range at 10^{-3} deg/sec (4 deg/hr), a month at 10^{-4} deg/sec (9 deg/day) and the better part of a year at 10^{-5} deg/sec. If only initial rates are of interest the duration of the experiment can be reduced considerably. Also, non-linear temperature programming, e.g., $dT/dt = aT^2$, will further reduce the length of the experiment.

For E = 40 kcal/mole, a factor of 10^4 in heating rate will result in a 150° shift in temperature at constant extent of reaction (14). This same heating rate factor, 10^4, also brings about a fairly good resolution of two competing independent reactions with respective activation energies of 40 and 60 kcal/mole (14).

Therefore, by examining the weight-loss kinetics over a wide range of heating rates, especially down to very slow rates and low temperatures, one will be able to 1) shorten the temperature extrapolation to service conditions, and 2) infer which of competing reactions will be rate limiting at service conditions. Using techniques in which experiments at different partial pressures of gaseous atmospheres, e.g., water vapor and oxygen, are compared will assist in selecting dominant low temperature processes.

Polyurethanes

The factor-jump method when applied to polyurethane provides information which is interesting for its qualitative trends rather than for the actual numerical quantities estimated for the activation energies. For example, Figure 1 shows the sequence of events during the degradation in vacuum of a methylene diphenyl diisocyanate-polyethylene adipate diol-butanediol polyurethane. The runs produced extensive char of the sample: the best method of sample presentation may be the evaporation of a solution of the polymer directly in the sample pan to produce an extensive thin film. Three methods of sample preparation were used in the experiments summarized in Figure 1a. However, the essential features are common to all three curves. The activation energy data indicate that an early process terminates at between 30 and 40% weight-loss and the residue decomposes further to produce a final char involatile in vacuum below 500°C and amounting to about 30% of the final weight. Comparison of Figures 1a and and 1b indicates that the plateau at 45% to 70% conversion may arise from the decomposition or vaporization of polyester. Thus, the early stages may be inferred to be the weight-loss of methylene diphenyl diisocyanate (MDI) from the sample, apparently with an activation energy of 40-45 kcal/mole. However, this method is not suited to examine the first five percent extent of reaction. The activation energy of the first process falls off with increasing conversion to 24 to 31 kcal/mole, depending on the sample, suggesting that diffusional processes are increasing in importance. A reasonable explanation is that a crust is formed on the samples but cracks as the degradation proceeds.

The activation energies calculated during the in vacuo degradation of three samples of a methylene diphenyl diisocyanate-polytetramethylene oxide-butanediol polyurethane are shown in Figure 2. The gaps indicate regions where the activation energy could not be calculated reliably because the rates of weight-loss become too low. In these regions the temperature was increased by the computer program in several steps to force the rate of weight-loss of the sample above the minimum allowed limits. These results imply that a change in the degradation process occurs at about 50% weight-loss. Comparison of Figure 2a with 2b shows that degradation of the polyether alone is not a dominant process in the in vacuo degradation of the MDI/polyether polyurethanes. MDI-related fragments probably escape from polyether-based polyurethanes during the first part of the weight-loss process just as they do from polyester-based polyurethanes. Figure 2a suggests that there is a complex interplay between the MDI and polyester weight-loss reactions as the activation energy remains at around 35-40 kcal/mole--considerably higher than the 26 kcal/mole, characteristic of the polyether degradation shown in Figure 2b.

In the degradation of polyurethanes, the dominant process changes markedly during the course of the reaction. The activation energy vs. extent of reaction plots provide useful information on the effects of sample geometry (Fig. 1a), the dominant processes (Fig. 1a vs. Fig. 1b) and the extent to which processes are (Fig. 1a), or are not (Fig. 2a) separated. However, as the initial activation energy is not determined by the factor jump method, it provides little information of value for use in extrapolating from test to service conditions.

The second technique for analyzing weight-loss data is illustrated in Figure 3 for an MDI-polytetramethylene oxide-butanediol polymer. The logarithm of the heating rate is plotted against the reciprocal of the temperature necessary to reach 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90 fractional weight-loss at heating rates of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} degrees per second and covers a temperature range from 175 to 400°C.

The nearly parallel straight lines for the first 10% weight-loss yield, by means of Equation 2, activation energies from 35 to 40 kcal/mole. This suggests that a single process may be operative over this early range of weight-loss between temperatures of 175 and 300°C. However, at greater than ten percent conversion, the curves deviate from linearity at temperature below 300°C, indicating complexities in the kinetics. At faster rates and higher temperatures, the activation energies from the slopes increase from 40 to 62 kcal/mole for 30-50% weight-loss. Cumulative effects from competing processes do not allow any reasonable interpretation of data for greater than 50% weight-loss.

The indication of a single kinetic process in the initial phases of weight-loss from Figure 3 is encouraging. However, the change that occurs at the slowest heating rate at 10% conversion bodes ill for the extrapolation of kinetic parameters for even this initial process to lower temperatures.

A plot of rate of weight-loss ($d\alpha/dT$) vs. temperature for the same experimental data (curves for heating rates of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} deg/sec) is illustrated in Figure 4. If one ignores the minor irregulatities which often occur during polyurethane degradation, there appears to be a sharpening of the higher temperature, higher conversion process and its gradual encroachment upon the lower temperature, initial process as the heating rate is slowed and the curves are shifted to lower temperatures.

Initial rates for a number of polyurethanes which were synthesized in our laboratories are being investigated in detail (11). A plot of $T^2(d\alpha/dT)$ vs. α is shown in Figure 5 for an MDI-polytetramethylene oxide-butanediol polymer. The activation energy calculated from the slope for the first 5% weight-loss is about 35 kcal/mole. This value is typical for initial activation energies for the weight-loss of MDI polyurethanes in nitrogen atmosphere. These experiments yield values in the range 33-37 kcal/mole for 1-3% conversion (12). On the other hand toluene diisocyanate (TDI) polyurethanes gave consistently lower activation energies (28-31 kcal/mole) in the same conversion range. Therefore, it appears that the early kinetics are dominated by the particular diisocyanate group in these polyurethanes.

The TDI polyurethanes begin to decompose at lower temperatures as well as with lower activation energies than MDI polyurethanes do. This difference in stability of the two types of polyurethanes becomes pronounced upon extrapolation to room temperature.

However, factors other than temperature affect the degradation of polyurethanes. Oxygen appears to have little effect upon the degradation process at high temperatures; however, experiments at slow heating rates and low temperatures (9) suggest that degradation at service conditions may be greatly affected by oxidation processes of low activation energy. Also, the presence of water vapor may cause a catastrophic shortening of the service life of polyurethanes (15).

Therefore, more experimentation to determine the effects of water and oxygen upon the initial weight loss kinetics at low temperatures is necessary before we will be able to decide if weight loss thermal analysis is a viable technique to apply to the predicting of the service life of polyurethanes.

Polystyrene

The factor-jump method provides precise results for the degradation of polystyrene because the process of degradation is unchanged during the fulk of the reaction. An extensive study has been reported (13), therefore we summarize the results. The activation energy of polystyrene degrading in vacuum > 350°C was found to be 44.7 ± 0.6 kcal/mole. This result is based on polystyrene from several sources which included both thermally polymerized and anionically prepared monodisperse samples. Measurements in the early part of the degradation have poor precision because bursting bubbles in the sample cause the sample weight to follow an erratic course. Nonetheless, it appears that the same activation energy pertains throughout the degradation (10 to 90% weight-loss). The degradation in flowing 99.995% pure nitrogen has an activation energy of 44.9 ± 0.2 kcal/mole which is not significantly different from and is considerably more precise than the value obtained for degradation in vacuum.

Many reports have been made of the activation energy of polystyrene degradation from measurements of a variety of properties and using different techniques of analysis of the kinetics. The closest to that determined by factor-jump thermogravimetry is 44.7 kcal/mole reported by Jellinek (16). The value, 44.9 kcal/mole is far from a widely accepted value of 55 kcal/mole reported by Madorsky and Wall (17, 18). It falls between the values of ∿ 42 kcal/mole (19, 20) and ∿ 49 kcal/mole (21) viewed favorably by Cameron and MacCallum in their review (22). The degree of ubiquity of 44.9 ± 0.2 kcal/mole as the activation energy of thermally degrading polystyrene is not yet well defined. Thermogravimetric methods including method II (see below), Reference (13) and work reported by Still and Whitehead (23) suggest 43-47 kcal/mole; the high value of 55 reported in Refs. (17) and (18) remains an exception. The work which provided 42 and 49 kcal/mole used quite different measurement techniques.

In the oxidation of polystyrene in flowing 50% O_2/50% N_2, it appears that the rate-determining process is extremely well behaved and the activation energy was easily determined by the factor-jump method to be 21.5 ± 0.2 kcal/mole. The sample degrades to a black char at ∿ 80-90% of reaction. Experiments using a ready access of air also gave a value of 21.5 ± 0.2. When the sample is starved of O_2, the apparent activation energy is between 21 and 30 kcal/mole for oxygen partial pressures greater than 4 mm Hg. The actual values observed depend on the thermal history of the sample and are not completely consistent from run to run. The details are given in Ref. (13).

The second technique for analyzing weight-loss data was applied to the degradation of a thermally polymerized polystyrene (NBS-SRM 706). The results are illustrated in Figure 6 where the logarithm of the heating rate is plotted against the reciprocal of the temperature necessary to reach 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 fractional weight-loss at heating rates of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} deg/sec. The nearly parallel lines which cover a range of temperatures from 280 to 420°C yield activation energies between 47.3 and 47.8 kcal/mole. Therefore it appears that the same rate-limiting kinetics are operative over this broad temperature range and from 10 to 90% conversion. It is worthwhile to point out that the 47.5 kcal/mole activation energy obtained independently here further weakens the case for the more or less accepted "high" value of 55 kcal/mole.

The rate of weight-loss vs. temperature spectra is shown in Figure 7 for the same data and conditions as in Figure 6. The sharpening of the single peak with decrease in heating rate is normal for a single noncompetitive reaction schema. However, at slow heating rates, a peak of low activation energy separates from the main reaction peak at the initial phases of weight-loss. This diffuse peak is barely discernible in the 200-250°C region of the 10^{-4} deg/sec heating rate curve in Figure 7. It amounts to only about 2% of the total weight-loss. Attempts to analyze the initial kinetics in detail have produced erratic results. Further investigation will be necessary to determine if this early peak can be associated with the breaking of "weak links" which has been postulated since 1947 as occurring in the initial phases of polystyrene degradation (24). This initial peak should not be present in the degradation of anionically polymerized polystyrene where "weak links" are reported to be absent (25).

In any event, oxidative reactions which extrapolate to much faster rates at room temperature, are undoubtedly much more relevant to aging prediction for this polymer.

Conclusions

An analysis of error propagation demonstrates that either activation energies must be measured extremely precisely or the temperature extrapolation to service conditions must be over an extremely modest range if life-time prediction from accelerated weight-loss experiments is to be meaningful.

Of the four methods which are described and illustrated by examples from polystyrene and polyurethane degradation, the factor-jump method attacks the problem of attaining high precision. This method determines values for the activation energy which are independent of one another and of sample history. As a result of automation, a large number of values may be calculated and averaged to obtain a small enough standard deviation so that extrapolation to service conditions may give usefully precise results.

The other three methods, when used over a wide range of heating rates and down to very slow heating rates and correspondingly low temperatures, not only have the advantage of reducing the severity of the temperature extrapolation, but also of allowing a detailed kinetic analysis of the important initial phases of the reaction and of permitting, from the kinetic interplay under different atmospheres and at different heating rates, the prediction of which one or combination of thermal, oxidative and hydrolytic reactions will be the primary agent for the deterioration of properties of the polymer at service conditions.

Acknowledgements

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Literature Cited

1. Flynn, J. H. and Dickens, B., Thermochim. Acta (1976) 15, 1.
2. Dickens, B., Pummer, W. J. and Flynn, J. H., in "Analytical Pyrolysis," pp. 383-391, C. E. R. Jones and C. A. Cramers, Eds., Elsevier, Amsterdam, 1977.
3. Dickens, B. and Flynn, J. H., in "Proceedings of the First European Symposium on Thermal Analysis," pp. 15-18, D. Dollimore, Ed., Heyden, London, 1976.
4. Dickens, B., Thermochim. Acta, in press (1978).
5. Dickens, B., Thermochim. Acta, in press (1978).
6. Dickens, B., Thermochim. Acta, in press (1978).
7. Ozawa, T., Bull. Chem. Soc. Japan (1965) 38, 7883.
8. Flynn, J. H. and Wall, L. A., Polym. Lett. (1966) 4, 323.
9. Flynn, J. H., unpublished.
10. Flynn, J. H. and Wall, L. A., Polym. Lett. (1967) 5, 192.
11. Flynn, J. H., Pummer, W. J. and Smith, L. E., ACS Polym. Preprints (1977) 18 (1) 757.
12. Flynn, J. H., in "Aspects of Degradation and Stabilization of Polymers," Chapter 12, pp. 573-603, H. H. G. Jellinek, Ed., Elsevier, Amsterdam, 1978.
13. Dickens, B., submitted to J. Poly. Sci. (1978).
14. Flynn, J. H., in "Thermal Methods in Polymer Analysis," pp. 163-186, S. W. Shalaby, Ed., Franklin Institute Press, Philadelphia, 1978.
15. Brown, D. W., Lowry, R. E. and Smith, L. E., ACS Polym. Preprints (1978) 19 (2) 822.
16. Jellinek, H. H. G., J. Polym. Sci. (1949) 4, 13.
17. Madorsky. S. L., "Thermal Degradation of Organic Polymers," p. 61, Interscience, NY, 1964.
18. Wall, L. A., Straus, S., Flynn, J. H., McIntyre, D. and Simha, R., J. Phys. Chem. (1966) 70, 53.
19. Boon, J. and Challa, G., Makromol. Chem. (1965) 84, 25.
20. Nakajima, A., Hamada, F. and Shimizu, T., Makromol. Chem. (1966) 90, 229.
21. Wegner, J. and Patat, F., J. Appl. Polym. Sci. (1970) C31, 121.
22. Cameron, G. G. and MacCallum, J. R., J. Macromol. Sci.-Revs. Macromol. Chem. (1967) C1, 327.
23. Still, R. H. and Whitehead, A., J. Appl. Polym. Sci. (1976) 20, 627.
24. Jellinek, H. H. G., "Degradation of Vinyl Polymers," Academic Press, New York, 1955.
25. Cameron, G. G., private communication.

Legends for Figures

Figure 1. Activation energy vs. extent of reaction of a) MDI/polyester polyurethane; b) polyester

————————	small cubes
- - - - - - - - - -	evap. film on pan
——●——●——	evap. film on gauge

Figure 2. Activation energy vs. extent of reaction for a) MDI/polyether polyurethane; b) polyether

————————	small cubes
- - - - - - - - - -	evap. film on pan
——●——●——	evap. film on gauge

Figure 3. Logarithm of heating rate vs. reciprocal absolute temperature. MDI/polyether polyurethane in vacuum, curves for α = 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90.

Figure 4. $d\alpha/dT$ vs. temperature for an MDI/polyether polyurethane in vacuum;

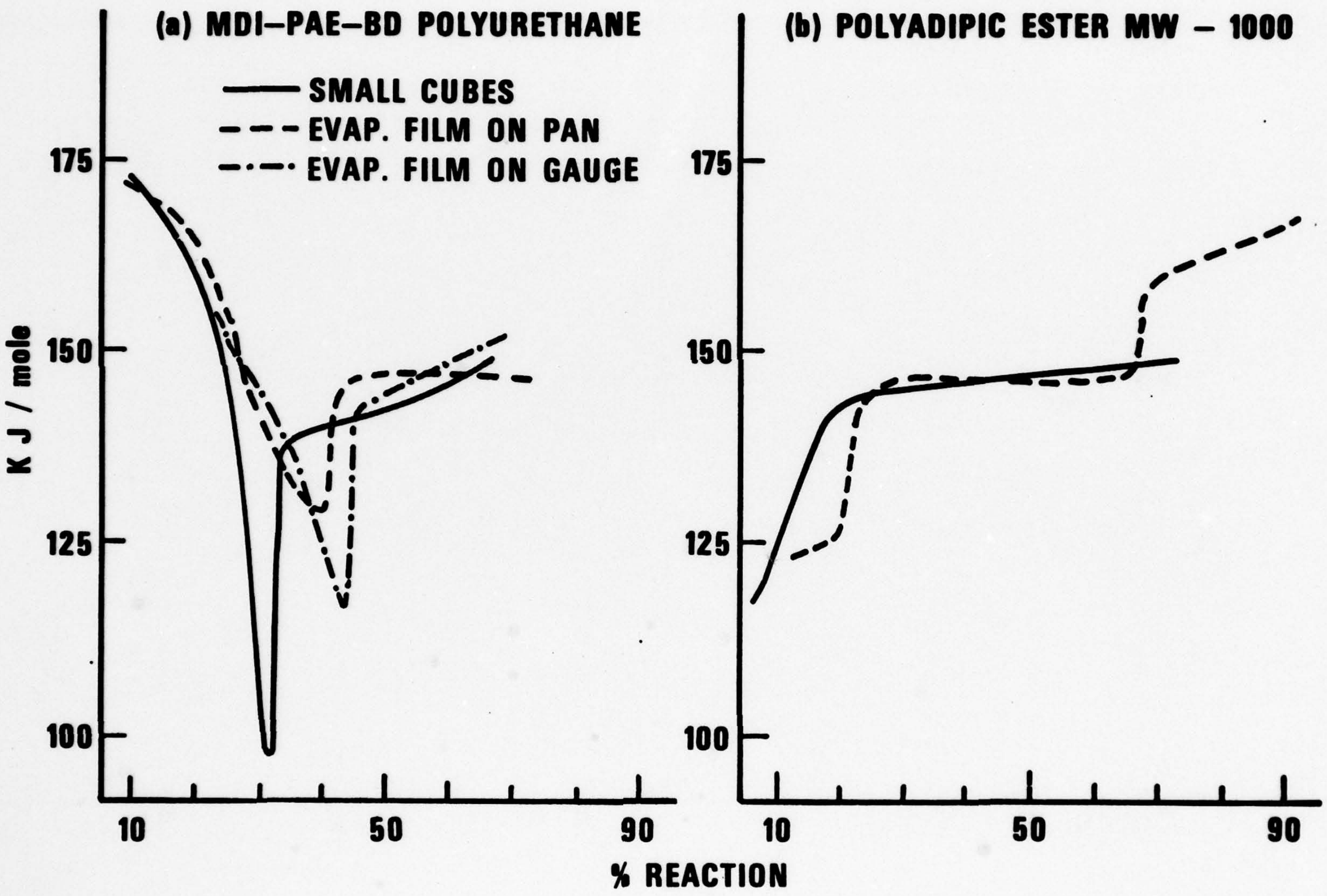
——————————	0.107 deg/sec.
—— —— ——	0.0119 deg/sec.
- - - - - - - - - - - -	0.00119 deg/sec.
●——●——●——	0.000110 deg/sec.

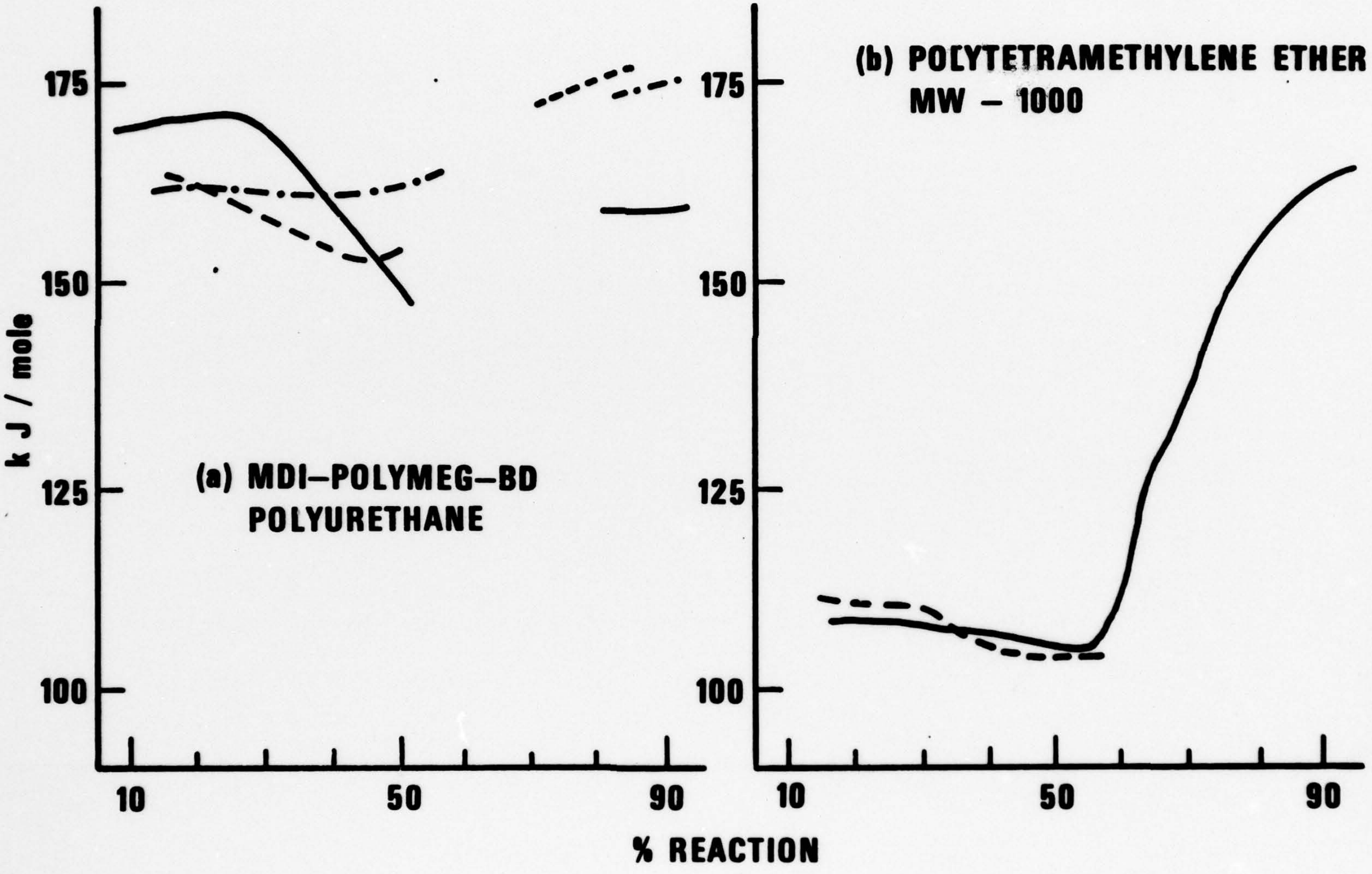
Figure 5. $T^2(d\alpha/dT)$ vs. α for an MDI/polyether polyurethane in nitrogen, heating rate--2.16 deg/min.

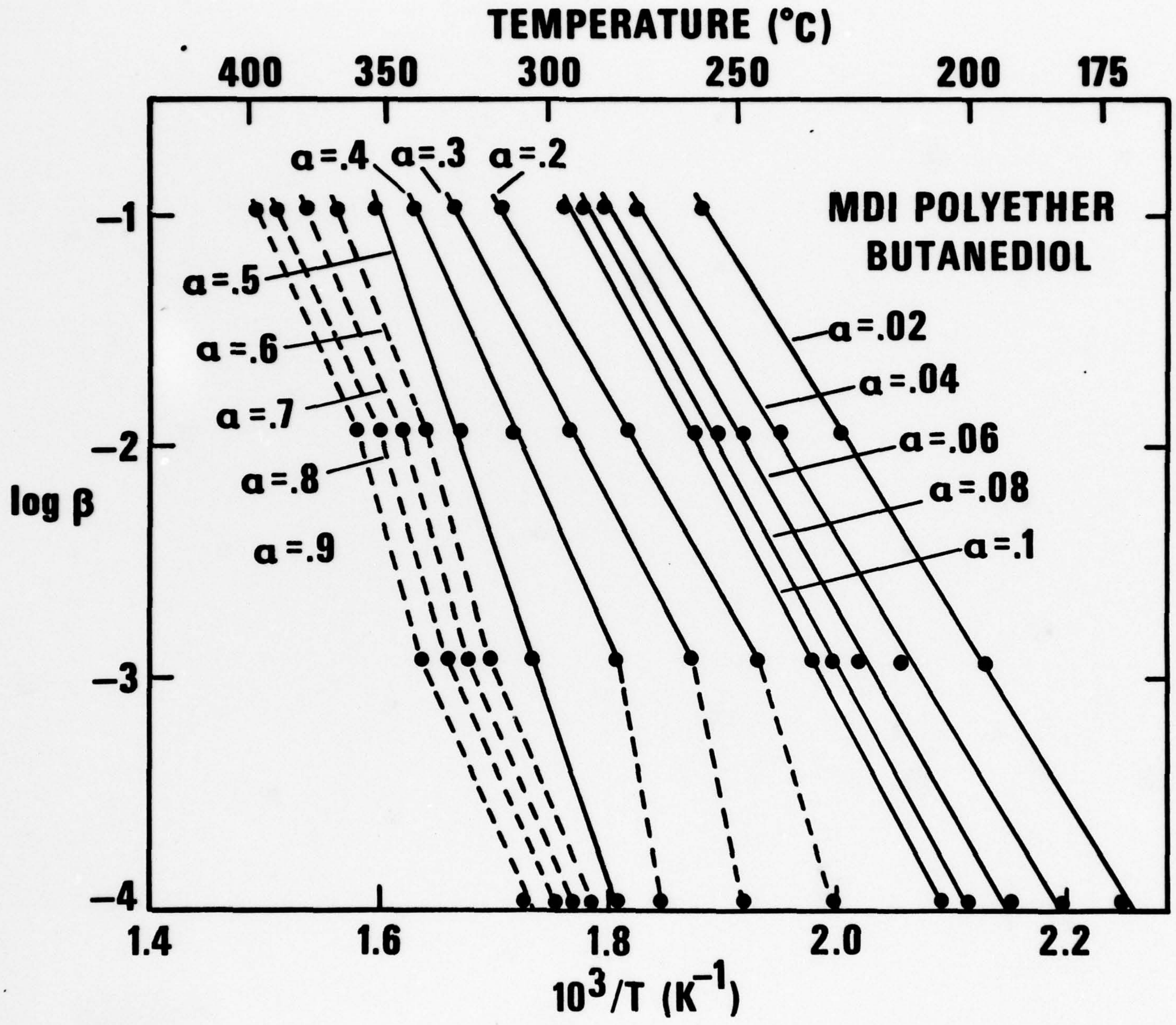
Figure 6. Logarithm of heating rate vs. reciprocal absolute temperature. Polystyrene in vacuum; curves for α = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9.

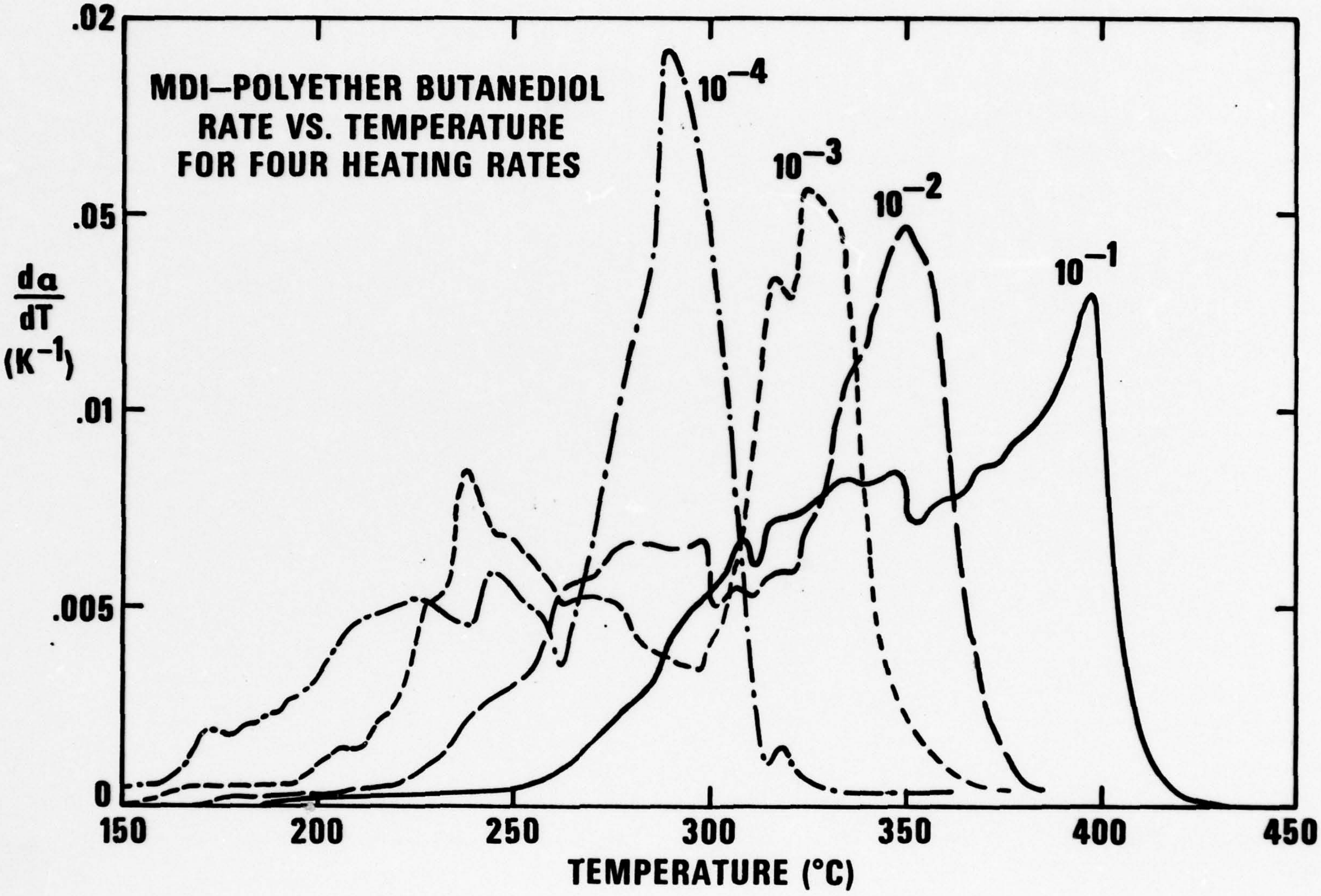
Figure 7. $d\alpha/dT$ vs. temperature for polystyrene in vacuum;

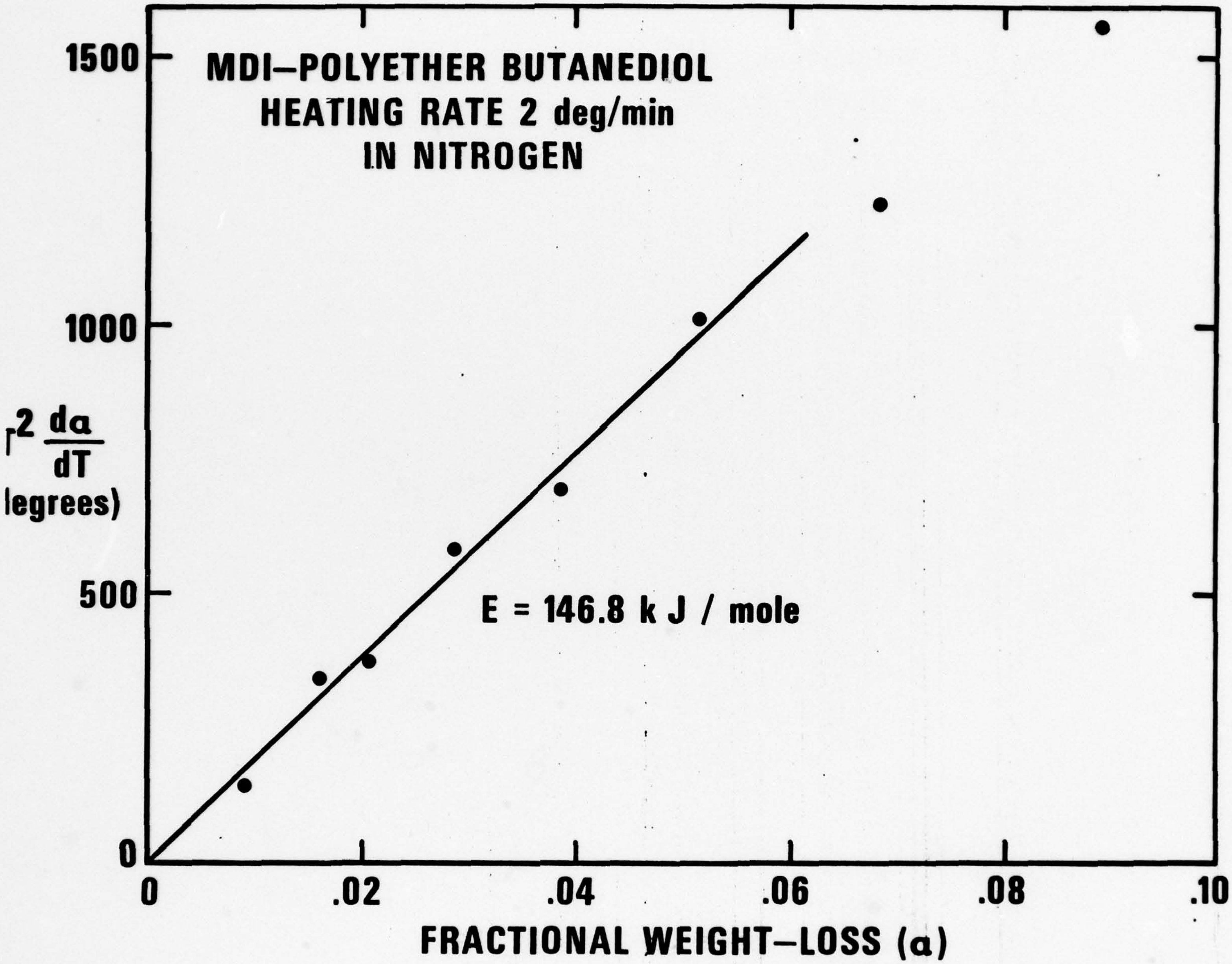
——————————	0.105 deg/sec.
—— —— —— ——	0.0106 deg/sec.
- - - - - - - - - - - - -	0.00116 deg/sec.
——●——●——●——●	0.000107 deg/sec.

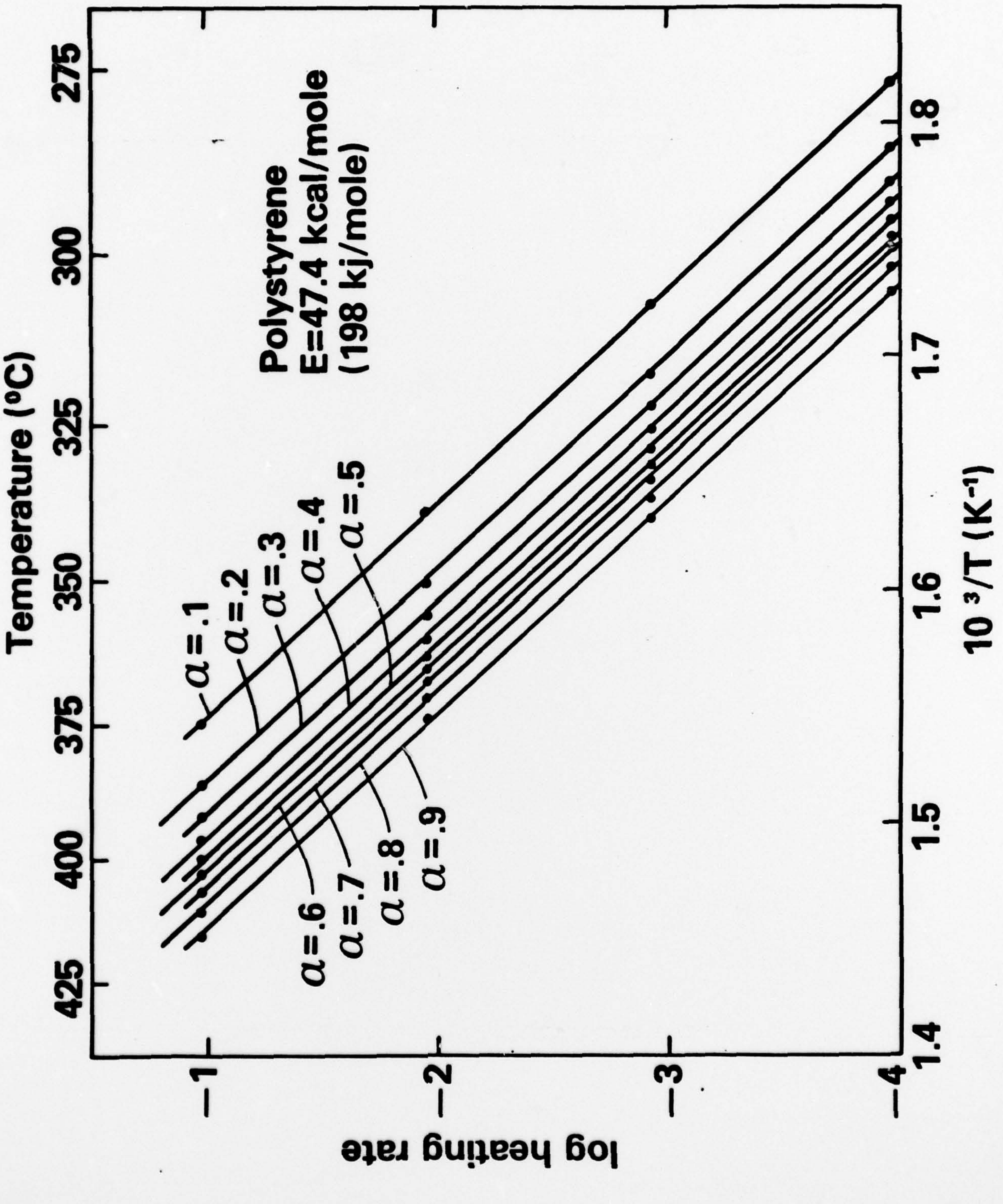

(a) MDI–PAE–BD POLYURETHANE
SMALL CUBES
EVAP. FILM ON PAN
EVAP. FILM ON GAUGE
(b) POLYADIPIC ESTER MW – 1000
K J / mole
175
150
125
100
10
50
90
% REACTION

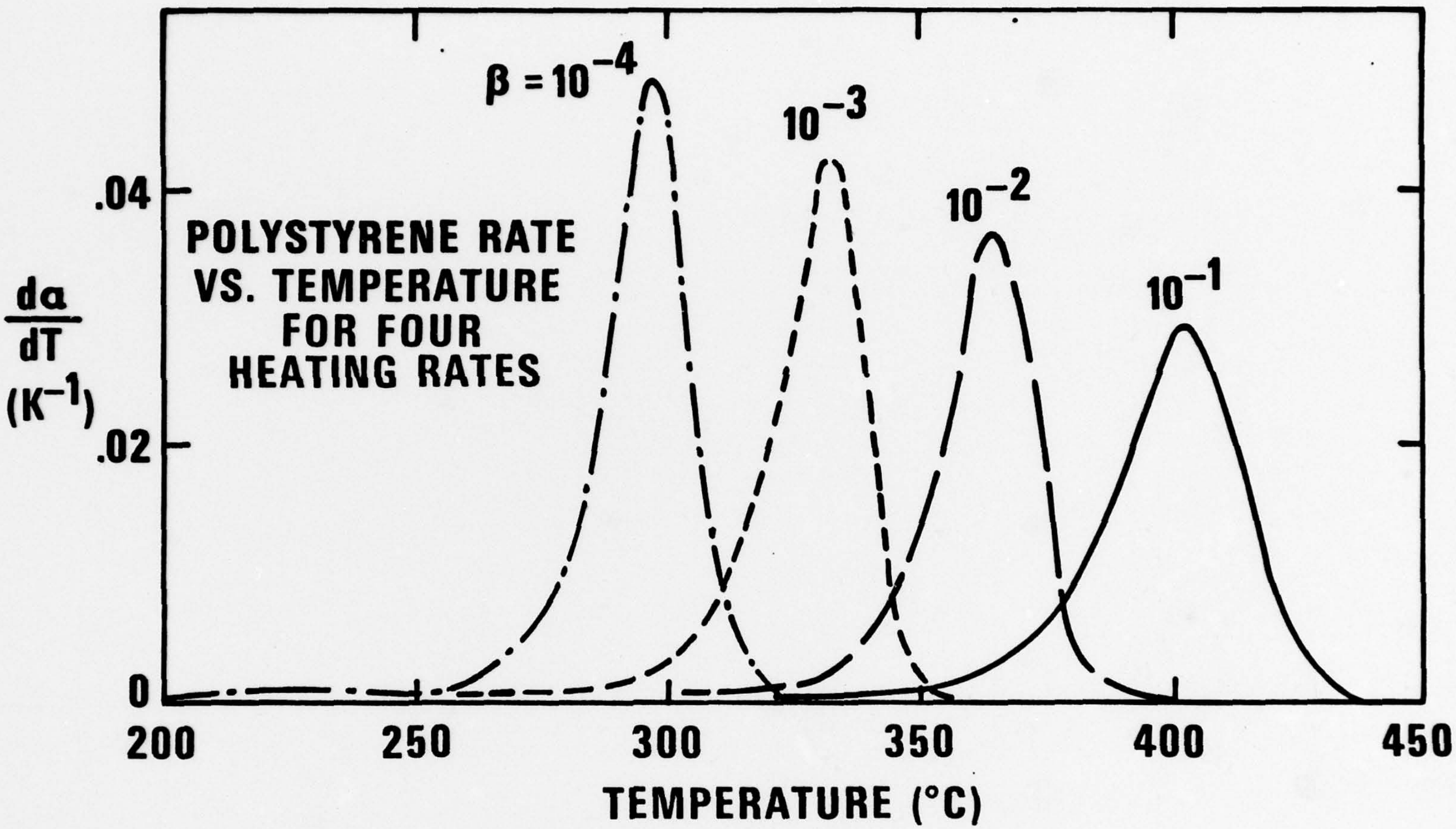

k J / mole
175
150
125
100
(a) MDI–POLYMEG–BD
POLYURETHANE
(b) POLYTETRAMETHYLENE ETHER
MW – 1000
10
50
90
10
50
90
% REACTION


TEMPERATURE (°C)
400
350
300
250
200
175
MDI POLYETHER
BUTANEDIOL
a=.4
a=.3
a=.2
a=.5
a=.6
a=.7
a=.8
a=.9
a=.02
a=.04
a=.06
a=.08
a=.1
log β
−1
−2
−3
−4
1.4
1.6
1.8
2.0
2.2
10^3/T (K^-1)


MDI–POLYETHER BUTANEDIOL
RATE VS. TEMPERATURE
FOR FOUR HEATING RATES
$\frac{d\alpha}{dT}$
(K^{-1})
.02
.05
.01
.005
0
150
200
250
300
350
400
450
TEMPERATURE (°C)
10^{-4}
10^{-3}
10^{-2}
10^{-1}


MDI—POLYETHER BUTANEDIOL
HEATING RATE 2 deg/min
IN NITROGEN
E = 146.8 k J / mole
1500
1000
500
0
$T^2 \frac{d\alpha}{dT}$
legrees)
0
.02
.04
.06
.08
.10
FRACTIONAL WEIGHT—LOSS (α)


Temperature (°C)
275
300
325
350
375
400
425
Polystyrene
E=47.4 kcal/mole
(198 kj/mole)
α = .1
α = .2
α = .3
α = .4
α = .5
α = .6
α = .7
α = .8
α = .9
log heating rate
−1
−2
−3
−4
1.4
1.5
1.6
1.7
1.8
10^3/T (K^{-1})


POLYSTYRENE RATE
VS. TEMPERATURE
FOR FOUR
HEATING RATES
$\beta = 10^{-4}$
10^{-3}
10^{-2}
10^{-1}
$\frac{d\alpha}{dT}$
(K^{-1})
.04
.02
0
200
250
300
350
400
450
TEMPERATURE (°C)