Determination of the Kinetic Parameters for the Polymerization of a Polyurethane Using an Improved Method of Differential Scanning Calorimetry

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SYNOPSIS

The kinetic parameters for the polymerization reactions of two polyurethane systems were determined by using an improved method of differential scanning calorymetry (DSC). The calculated activation energy, reaction order, and Arrhenius prefactor show good correlation with the experimental results. The method used here shows several improvements as respects to other DSC methods: the three kinetic parameters can be calculated directly; it is more accurate than other DSC methods; and it requires only one heating rate, during the calorimetric experiments, to determine the activation energy.

INTRODUCTION

In recent years differential scanning calorimetry (DSC) has been widely used to study the kinetics of chemical reactions, particularly during polymerization processes.[1-3] Several DSC methods—isothermal, semiadiabatic, and adiabatic—have been developed to calculate the activation energy, the reaction order, and the rate constant of polymerization. In most of them it is necessary to assume certain values of one of the parameters in order to calculate the others.[1,4] In other methods only one parameter can be calculated.[2,5,6]

Fundamentally, the method used by Hager et al.[1] gives the three kinetic parameters directly. However, it is necessary to assume different reaction order values until the correct one is found. The method used by Barton[2] directly gives the activation energy, making it unnecessary to know the reaction order; apparently this is a good method, but it will be seen that it is not accurate, at least in the present case.

The objective of this work is the application of an improved method of DSC, recently reported,[3] to determine the kinetic parameters, including the activation energy, during the polimerization reaction of a glycol and a diisiocyanate, by using the equalization process of the conversion rate for the Arrhenius model. Within this method it is not necessary to assume one of the parameters in order to calculate the others. To determine the activation energy, while using this method, it is necessary to calculate first the reaction order, which is done as shown below. Eventually, the Arrhenius prefactor can also be determined.

THEORY

The method of Hager et al.[1] works only with one heating rate (during the DSC measurements) by directly using the following form of the Arrhenius equation:

$$\ln \frac{\dot{\alpha}}{(1-\alpha)^n} = -\frac{E}{R}\frac{1}{T} + \ln(K_0) \qquad (1)$$

where α is the conversion, $\dot{\alpha}$ is the conversion rate ($d\alpha/dt$), t is the time, R is the universal constant of gases, T is the temperature, E is the activation energy, K_0 is the Arrhenius prefactor, and n is the reaction order. Equation (1) corresponds to a

straight line where the slope is $-E/R$, and K_0 is the Y intercept.

Barton[2] used the Arrhenius model by experimenting with two heating rates, $\dot{T}_1 = (dT_1/dt)$, and $\dot{T}_2 = (dT_2/dt)$, giving a set of two equations similar to Eq. (1):

$$\ln\frac{\dot{\alpha}_1}{(1-\alpha_1)^n} = -\frac{E}{RT_1} + \ln(K_0) \qquad (2)$$

$$\ln\frac{\dot{\alpha}_2}{(1-\alpha_2)^n} = -\frac{E}{RT_2} + \ln(K_0) \qquad (3)$$

by taking both equations and equalizing the conversions; in other words, $\alpha_1 = \alpha_2$, so

$$\ln\frac{\dot{\alpha}_2}{\dot{\alpha}_1} = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

In this way the activation energy can be evaluated, although neither the reaction order nor the Arrhenius prefactor can be determined.

In the method used here,[3] Eqs. (2) and (3) are combined after equalizing the conversion rates; $\dot{\alpha}_1$ and $\dot{\alpha}_2$, so

$$\ln\frac{1-\alpha_1}{1-\alpha_2} = -\frac{E}{nR}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (5)$$

It will be shown that Eq. (5) can be used for one or two heating rates.

Out of Eq. (5) it is possible to determine the activation energy, E, if the reaction order, n, is previously known.

In order to calculate the reaction order, Eqs. (2) and (3) are now combined after equalizing the temperatures, T_1 and T_2, resulting in the following expression of a straight line:

$$\ln\frac{\dot{\alpha}_1}{\dot{\alpha}_2} = n \ln\frac{1-\alpha_1}{1-\alpha_2} \qquad (6)$$

where the slope is the reaction order n. The value obtained for n is substituted in Eq. (5) to determine the activation energy.

EXPERIMENTAL

Materials

For the studied reactions the following substances were used: 97% purity 2,6-tolylene diisocyanate (2,6-TDI); a mixture of 80% 2,4-tolylen diisocyanate

with 20% 2,6-TDI (refered to as 2,4-TDI); and 1,4-butandiol, all supplied from Aldrich Chemical Co., 99% purity 2-hydroxyethytl ether (DEG) supplied by Merck; and two glycols, 496 and 497, supplied by Polioles S.A.

Two reactions systems were studied: (A) 2,4-TDI with the following mixture; glycol 496, 1,4-butanodiol and glycol 497, in a proportion of 80, 15, and 5%, respectively, and (B) 2,6-TDI with DEG. The amounts of reactants injected in both systems to keep an stoichometric relation 1 : 1 were carefuly measured. Both systems were treated under two heating rates: 5 and 10 K/min.

Measurements

The reactants for each DSC experiment were placed into aluminum liquid-sample pans (Perkin-Elmer, Co.) inside of a glove box purged with dry nitrogen, under a procedure described below to ensure homogeniety of the mixture.[3] After pouring 3.0 μL of diisocyanate into an aluminum liquid-sample pan already placed in the oven cell of the DSC, it was cooled down to 263 K. The diol was then added to the frozen diisocyanate. After equilibration at 263 K three DSC consecutive runs were performed on each specimen by triplicate at different heating rates. After each one ended the system was cooled down to 263 K before the next run was performed.

Homogeneity tests on each reactive mixture (systems A and B) were made by measuring the refractive index as a function of time.[3] These tests were made in the same type of aluminum liquid-sample pans used for the DSC experiments in order to reproduce similar mixing conditions. Mixing of reactants were also monitored by optical microscopy in a reflexion microscope (Photomakroskop WILD M400).
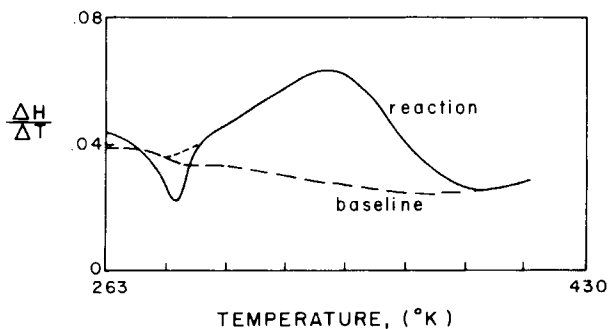
Figure 1 Thermogram of the system A chemical reaction. Baseline is the thermogram of the obtained polyurethane.
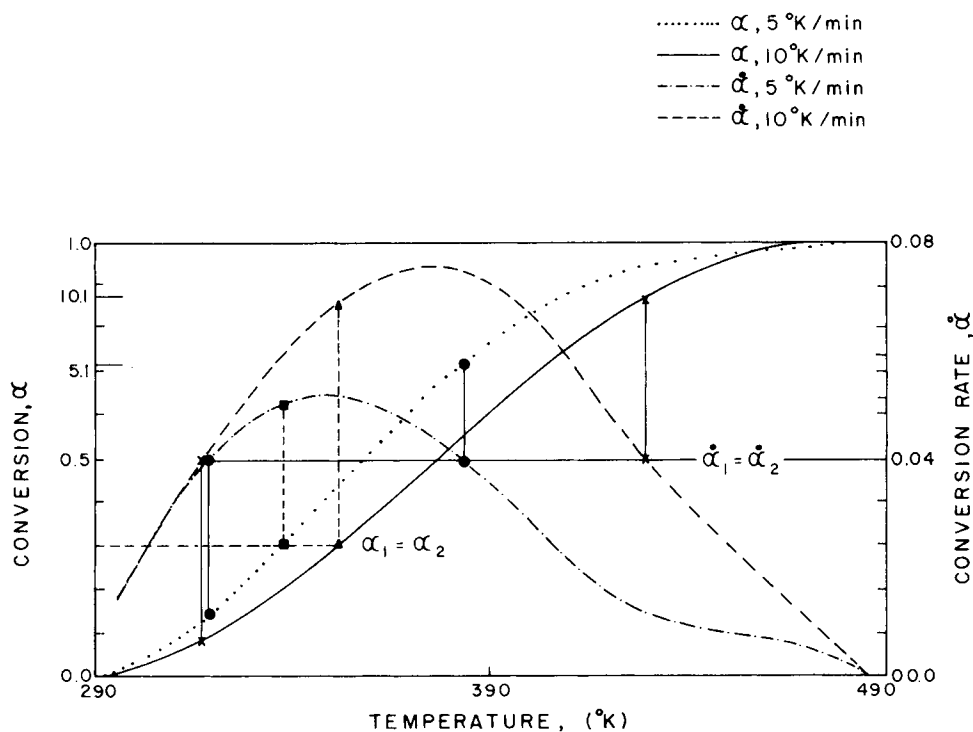
Figure 2   Plots of conversion rates (bell-shaped lines) and conversions, for system A reaction at two heating rates; 5 and 10 K/min.

A Perkin-Elmer 2C differential scanning calorimeter was used, connected to a Perkin-Elmer 3600 data station. The DSC was periodically calibrated with two model samples: indium and tin. The experiments were carried out in a dry nitrogen atmosphere, with a 20 mL/min flux.

RESULTS AND DISCUSSION

Results

The refractive index of each reactive mixture (systems A and B) were similar to the values expected
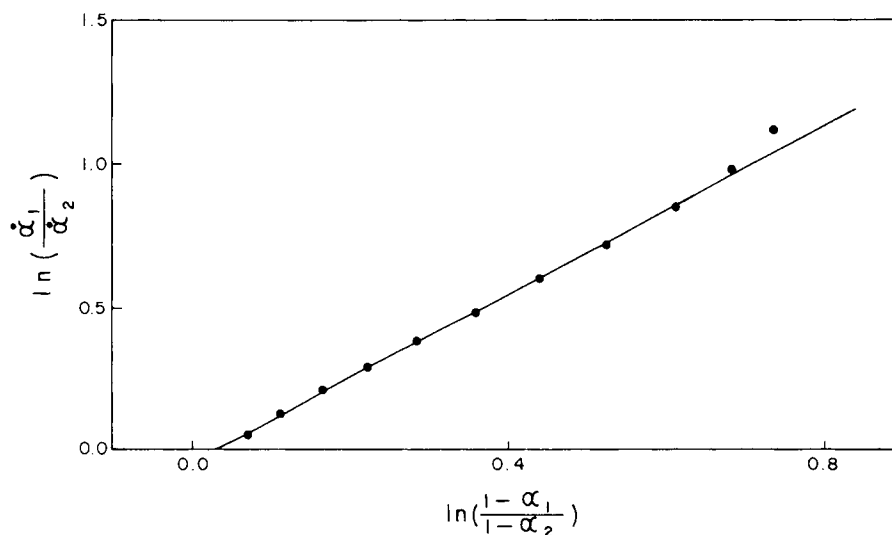
Figure 3   Plot of $\ln(\dot{\alpha}_1/\dot{\alpha}_2)$ vs. $\ln[(1-\alpha_1)/(1-\alpha_2)]$, for system A, obtained by equalizing T_1 with T_2, at two heating rates; 5 and 10 K/min.

Table I   Kinetic Parameters of Systems A and B, as Determined from Ref. 3

System	$\dot{\alpha}_1 = \dot{\alpha}_2$ $(E/(nR))$ K	$T_1 = T_2$ n	E cal/g mol	K_0 1/min
A: 2,4-TDI with mixture of glycols	2,222.2	1.63	7,197.3	3,875
B: 2,6-TDI, with DEG (1:1)	6,470	2.5	32,141	1.8×10^{19}

by considering that the refractive indexes of the components follow the rule of additivity in their mixtures. These results may be on account of the ratio of the high initial interfacial area between reactants and the small volume (10 μL) of the reactive mixture in the conditions used. Observations in the optical microscope showed that just after placing the glycol over the frozen diisocyanate the interface between the reactants is clearly distinguished. However, as the diisocyanate melts the liquids get mixed, and after 5 min no signals of phase segregation were observed. These tests suggest that each reactive mixture used in the DSC experiments was homogeneous as well.
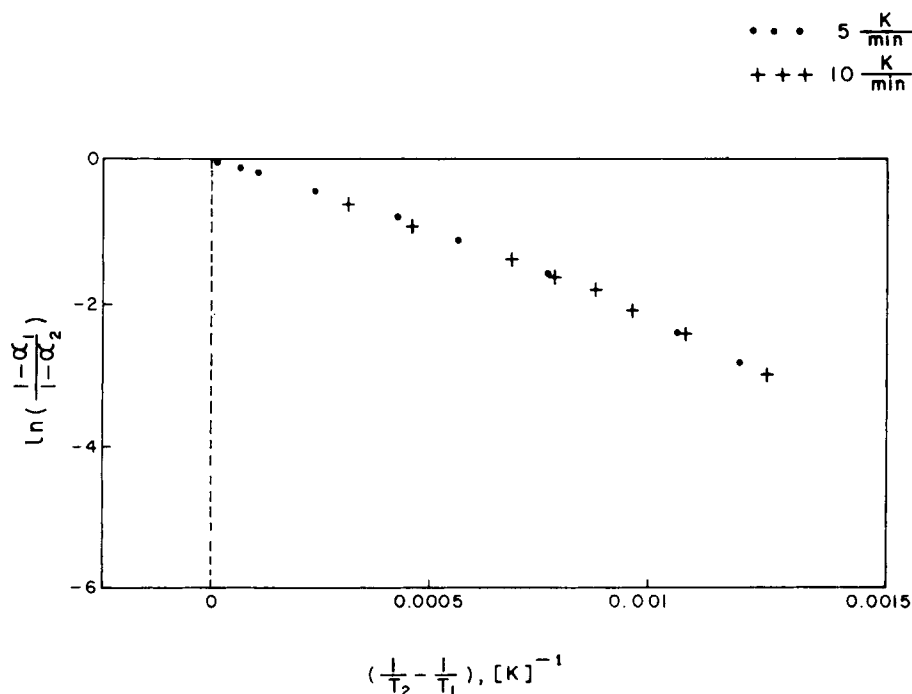
System A

The thermogram of this system is shown in Figure 1. The baseline was obtained by making a run of the polyurethane got out of the reaction (dotted line in Fig. 1). The conversions, α, are obtained as described elsewhere.[3] The height measured from the baseline to the corresponding reaction signal is proportional to the conversion rate, $\dot{\alpha}$. By following this procedure α_i and $\dot{}_i$ were obtained as a function of temperature.

The plots of α and $\dot{\alpha}$ versus temperature are shown in Figure 2 for the two heating rates. Because the $\dot{\alpha}$ plots in Figure 2 resemble a bell-shaped Gaussian function, for almost each conversion rate value (except at the maximum) two corresponding temperatures and conversions can be obtained.

The obtained data can now be used to calculate the reaction order by applying Eq. (6). The results of system A are shown in Figure 3, the slope is the reaction order, n, and its value is shown in Table I.

Now the activation energy can be determined out of Eq. (5). Because of the bell-shaped Gaussian form of the $\dot{\alpha}$ plots, this equation can be used indepen-

Figure 4   Plots of $\ln[(1 - \alpha_1)/(1 - \alpha_2)]$ vs. $[(1/T_2) - (1/T_1)]$, for system A, obtained by equalizing the heating rates.

dently for each heating rate. For system A it results in the straight lines shown in Figure 4, one for each heating rate. The slope, $-E/(nR)$, is shown in Table I.

Eventually, the Arrhenius prefactor is calculated out of Eq. (1) as the slope of the straight line that is obtained by plotting $\dot{\alpha}/(1-\alpha)^n$ versus $\exp(-E/RT)$ as shown in Figure 5(a).

The Arrhenius prefactor can also be evaluated if $\dot{\alpha}$ is not known.[3] In this case it is necessary to plot $\int d\alpha/(1-\alpha)^n$ versus $\int \exp(-E/RT)\,dt$ as shown in Figure 5(b).

To corroborate these results, the α's can be predicted by introducing the values of K_0, n, and E into

the Arrhenius equation. For system A this results in the following expression:

$$\frac{d\alpha}{dt} = 3875\,\frac{1}{\min}\,(1-\alpha)^{1.63}$$

$$\times \exp\frac{-7197.3\,\text{cal/g mol}}{RT} \quad (7)$$

In Figure 6 the predicted $\dot{\alpha}$'s from Eq. (7) are compared with the experimental data for the two heating rates of 5 and 10 K/min, respectively. A good correlation can be observed.
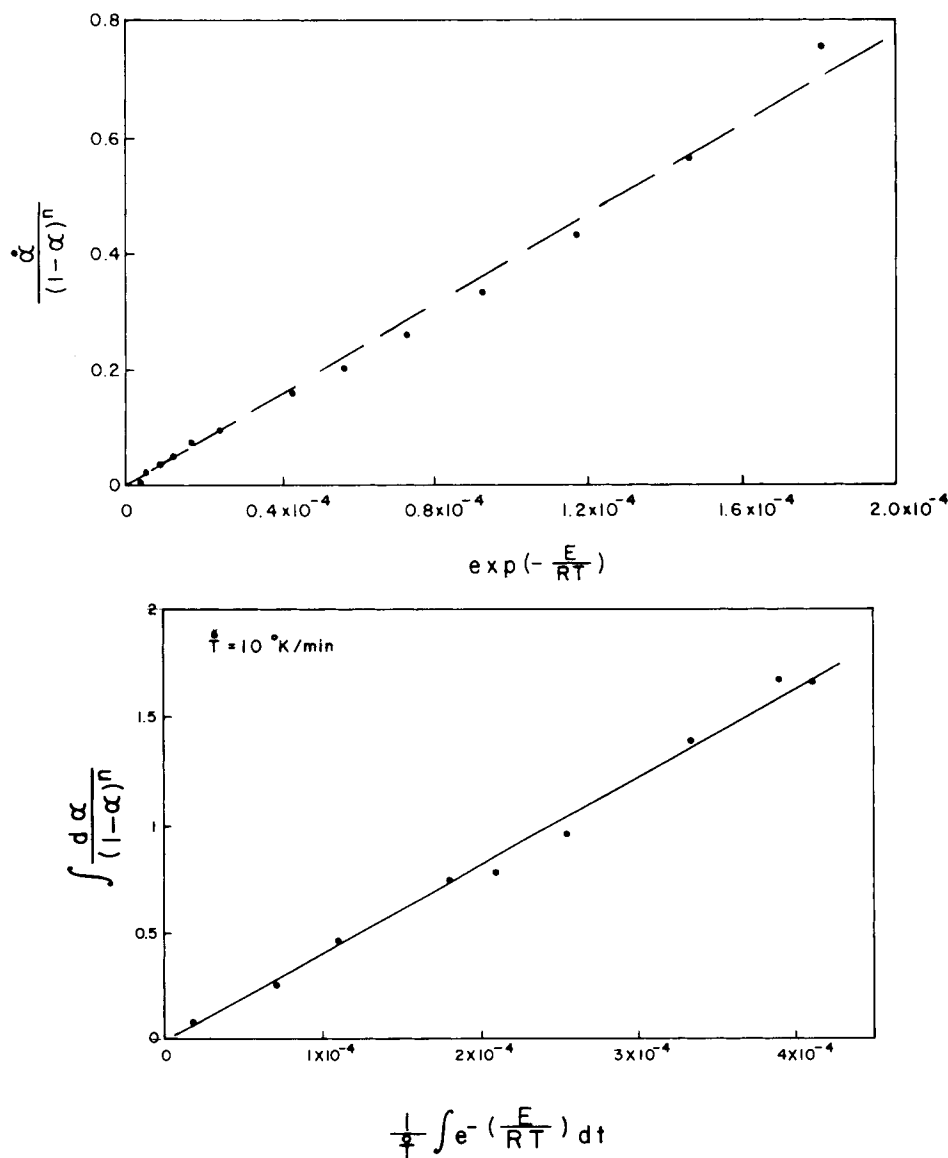
Figure 5 Plots used to calculate the Arrhenius prefactor for system A. (a) Plot of $\dot{\alpha}/(1-\alpha)$ vs. $\exp(-E/RT)$. (b) Plot of $\int d\alpha/[(1-\alpha)^n]$ vs. $1/\dot{T}\int \exp(-E/RT)\,dt$.
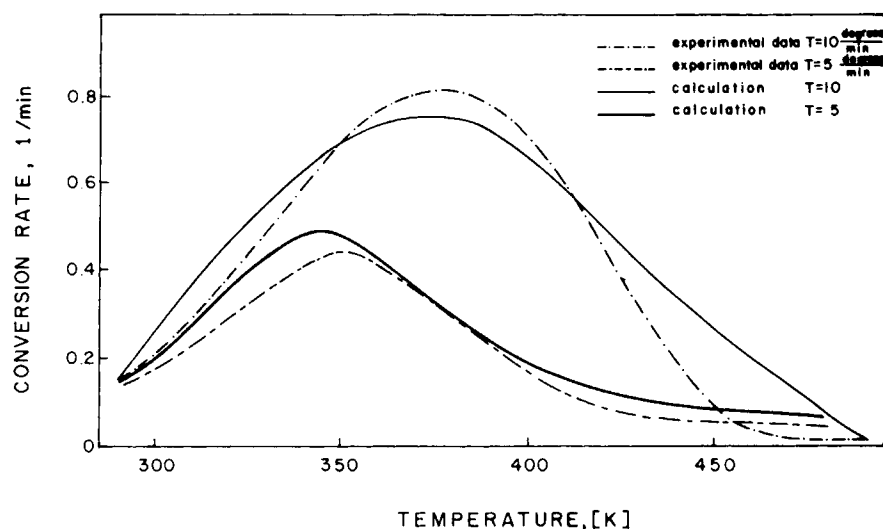
Figure 6   Plots of $\dot{\alpha}$ vs. T, obtained from experimental data and theoretical calculations for system A at two heating rates; 5 and 10 degrees/min.

Discussion

System B

The procedure to determine the parameters of this system is the same as that for the preceding system A. The plots to get the activation energy, the reaction order, and the Arrhenius prefactor are shown in Figures 7, 8, and 9, respectively. The obtained values are stated in Table I. The Arrhenius equation is

$$\frac{d\alpha}{dt} = 1.8 \times 10^{19} \frac{1}{\min} (1 - \alpha)^{2.5}$$

$$\times \exp \frac{-32,141 \text{ cal/g mol}}{RT} \quad (8)$$

It is worth noting that the temperature range used here to determine the kinetic parameters corresponds to points where the beginning and the end of the reaction are excluded. Otherwise a relevant unfitness of points is observed in the plots $(1/T_2 - 1/T_1)$ versus $\ln(1 - \alpha_1)/(1 - \alpha_2)$. The reliable temperature ranges where the beginning and the end of the reaction were excluded are: for system A 320–430 K and for system B 350–400 K. It is observed that in the pure components reaction (system B) the temperature range used for the analysis is lower
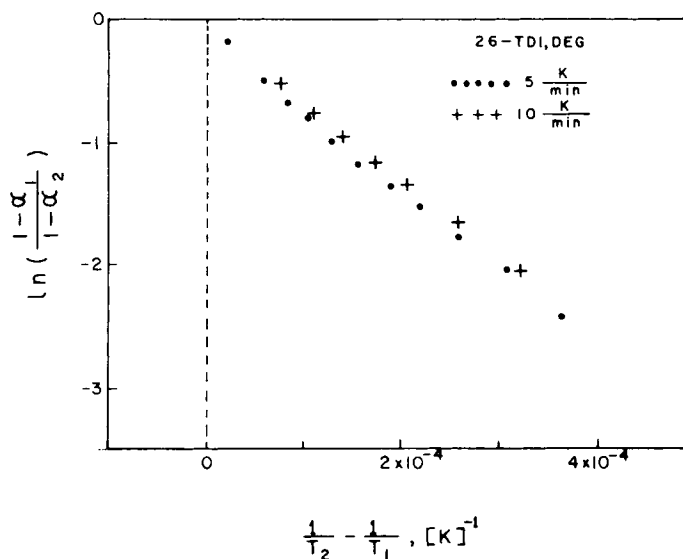
Figure 7   Plots of $\ln[(1 - \alpha_1)/(1 - \alpha_2)]$ vs. $[(1/T_2) - (1/T_1)]$, for system B, obtained by equalizing the heating rates.
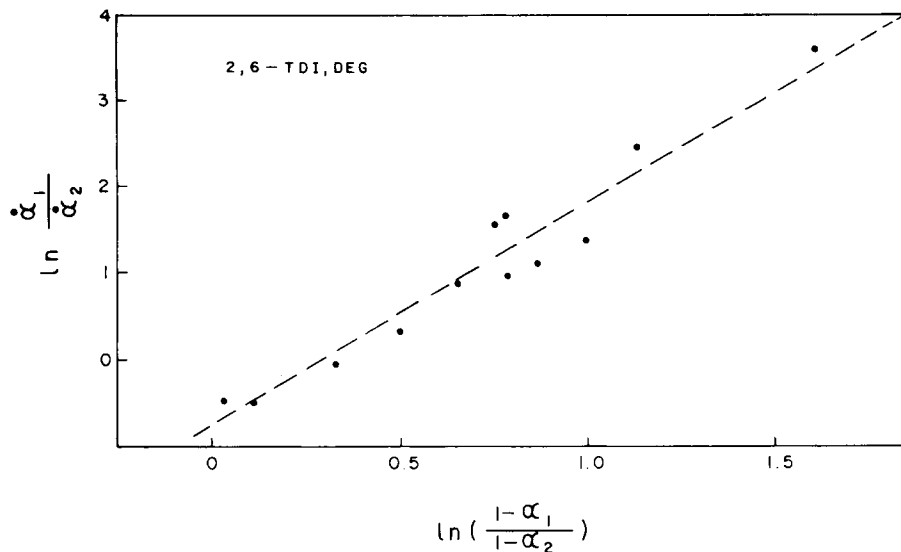
Figure 8   Plots of $\ln(\dot{\alpha}_1/\dot{\alpha}_2)$ vs. $\ln[(1-\alpha_1)/(1-\alpha_2)]$, for system B, obtained by equalizing T_1 with T_2 at two heating rates; 5 and 10 K/min.

than for system A. However, it is large enough to get reliable results.

Out of the method used by Hager et al.,[1] it is possible to determine the three kinetic parameters of the reaction by using only one heating rate. Both the activation energy and the Arrhenius prefactor are calculated graphically, but the reaction order has to be supposed until the correct value is found, since, as Eq. (1) shows, the lineal relation is fulfilled for only one n value. By using this method, there is a range of values for the Arrhenius prefactor in which

it is difficult to appreciate a significant difference in the linarity of Eq. (1); this results in a noticeable error in the slope, which may be reflected as an important error in the calculation of the activation energy, particularly in polymerization reactions, Table II. Besides, since both the Arrhenius prefactor is the Y intercept and extrapolation occurs at a great distance, it means that a small variation in the slope may represent an error up to 70% in the calculation of the Arrhenius prefactor (Fig. 10).

Barton[2] directly solves out of Eq. (4) for the ac-
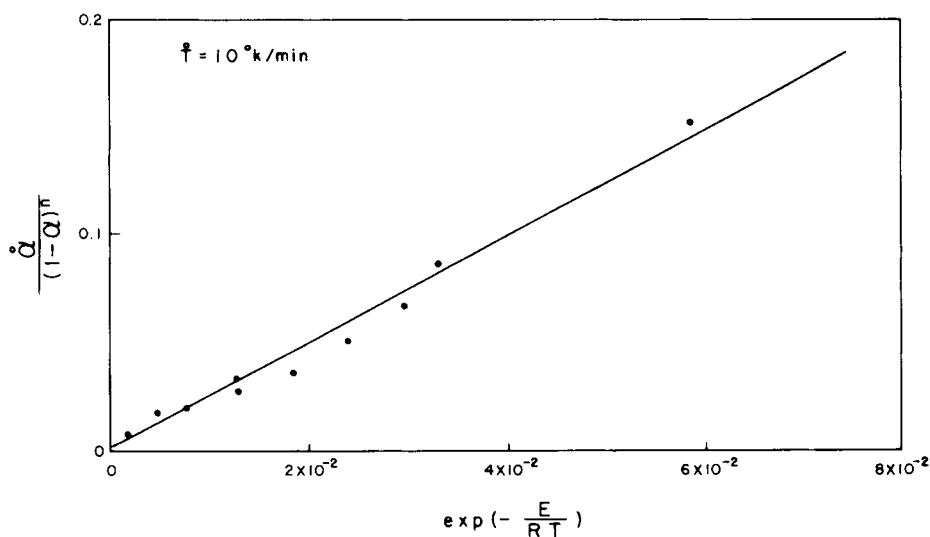
Figure 9   Plots of $\dot{\alpha}/(1-\alpha)$ vs. $\exp(-E/RT)$, for system B, used to calculate the Arrhenius prefactor.

Table II   Kinetic Parameters of System A and B, as Determined from Refs. 1 and 2

| System | Hager (Ref. 1) | | Barton (Ref. 2) |
	E, cal/g mol	K_0, 1/min	E, cal/g mol
A: 2,4-TDI with mixture of glycols	6,490	2×10^6	4,000
B: 2,6-TDI with DEG (1:1)	30,000	5×10^{11}	18,000

tivation energy by substituting the experimental values of $\dot{\alpha}_i$ and T_i obtained from two heating rates. By doing so, this method assumes that the origin is an experimental point, but when calculating each set of values $\dot{\alpha}_1$, $\dot{\alpha}_2$ and T_1, T_2, it is estimating the slope of the straight line that joins the experimental point to the origin, thus getting an average for the E's. By using Barton's method and plotting his data (from Ref. 2) as well as our data, it can be seen (Fig. 11) that both actually tend to form straight lines (although in an imperfect manner); but both lines pass far away from the origin.

Within the method used here (equalization of $\dot{\alpha}$'s) the $E/(nR)$ points are very clearly aligned in a straight line (Fig. 4) when the data is obtained from only one heating rate, as outlined in Figure 2. The same happens when the data obtained from two heating rates are used, handling the first side of one of the bell-shaped Gaussian curves of a heating rate and the second side of the other one, as described elsewhere.[3]

However, when the data is obtained from the same side of the bell-shaped Gaussian curves, as in Barton's method, the $E/(nR)$ points cannot be aligned in a straight line. This is due to the fact that, in this case, the difference, $1/T_2 - 1/T_1$, is very small. In other words, when the slopes, in Eqs. (4) and (5) (terms containing the E), are calculated from two points that are very close to each other, significant errors are introduced in the evaluation of the activation energy, particularly in polymerization reactions, because of the overlapping of several reaction steps occurring during the process.

In the method described here the reliable temperature range is large enough to avoid the error of Barton's method (Fig. 12).
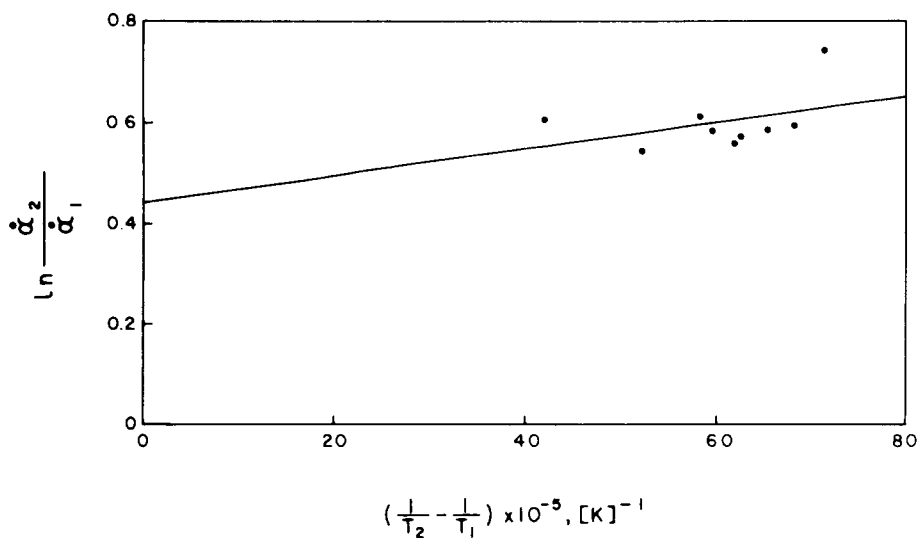
CONCLUDING REMARKS

The kinetic parameters for the polymerization reactions of two polyurethane systems were deter-
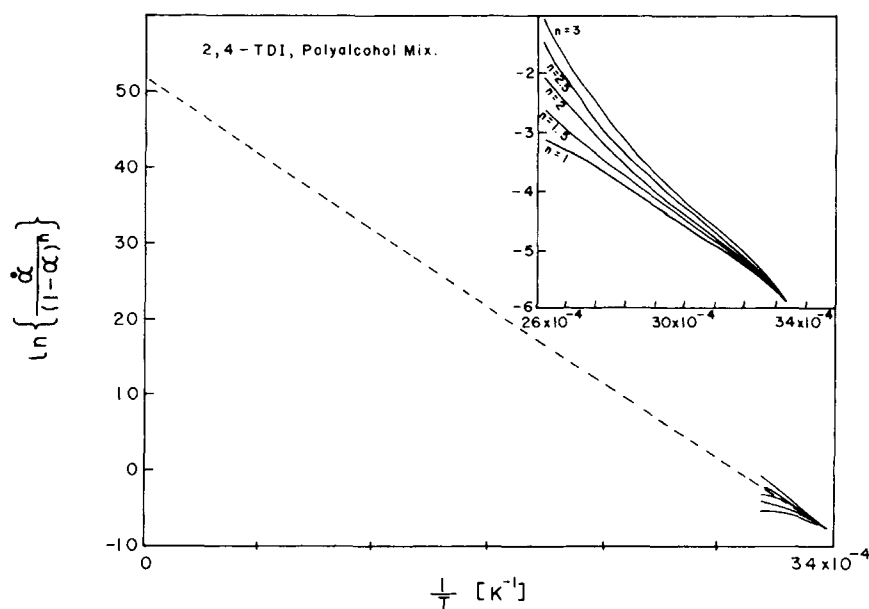
Figure 10   Plots of $\ln[\dot{\alpha}/(1 - \alpha)^n]$ vs. $(1/T)$, for system A, obtained by the Hager et al. method. The lower right corner of the plots are amplified at the upper right corner.

Figure 11   Plot of $\ln(\alpha_2/\alpha_1)$ vs. $[(1/T_2) - (1/T_1)]$ for the reaction system [BAD, 4,4' − DM], according to Barton's method. Data were taken from Ref. 2.

mined by using an improved method of DSC. The results show a reasonable good correlation to the model used in this case.

The application of the DSC method used here to determine the kinetic parameters of polymerization shows several improvements in relation to other DSC methods, in particular, as respects to those reported by Hager and Barton: It is not necessary to assume one of the parameters in order to calculate the others; it is more accurate than the other methods; and it requires only one heating rate during the DSC experiments in order to determine the activation energy.

Applying the Hager[1] method to our data results in an important error in the calculation of the activation energy. In our opinion this method is not
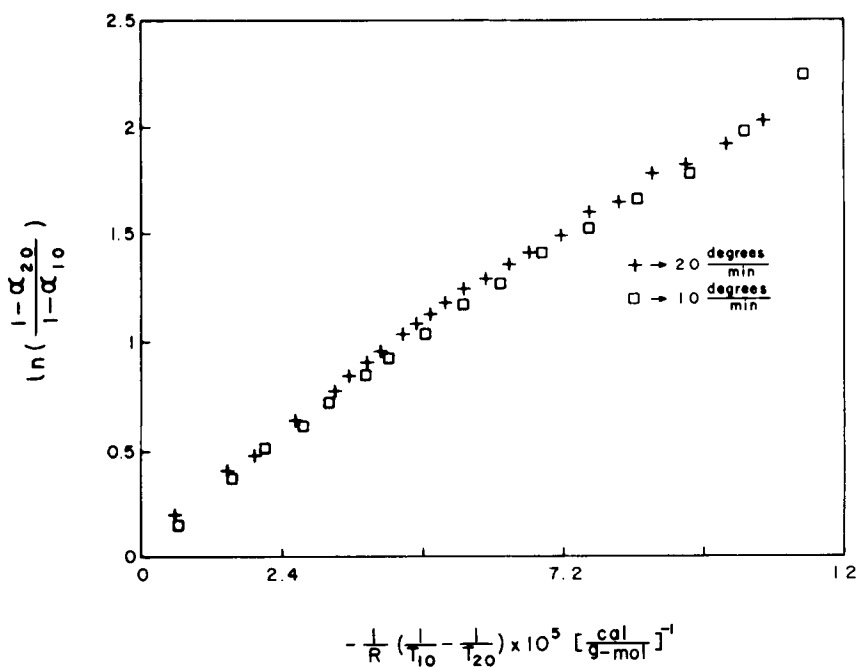
Figure 12   Plot of $\ln[(1 - \alpha_{20})/(1 - \alpha_{10})]$ vs. $(-1/R)\ [(1/T_{10}) - (1/T_{20})]$, for the reaction system [BAD, 4,4' − DM], according to the present method. Data were taken from Ref. 2.

reliable when it is applied to polymerization reactions. Besides, within this method the reaction order must be assumed to determine the activation energy.

The main drawback in the Barton method is that it calculates the activation energy from the same side of the $\dot{\alpha}$ plots; in this way the difference $(1/T_2 - 1/T_1)$ in Eq. (4) is very small, resulting in significant errors for the evaluation of the activation energy, particularly in polymerization reactions. Besides, this method cannot be used to determine the other kinetic parameters.

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