

# Cyclo Dehydration Reaction of Polyhydrazides.

## I. Kinetic Parameters Obtained with Nonisothermal Thermogravimetry

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### Synopsis

The thermal conversion reaction of poly-(1,3-phenyl-1,4-phenyl)-hydrazide into poly-(1,3-phenyl-1,4-phenyl)-1,3,4-oxadiazole has been studied using thermogravimetry (TG). For the evaluation of the energy of activation and other kinetic parameters of this cyclo dehydration reaction a method developed by Ozawa was used, where polymer samples are heated with different constant heating rates. With this method the energy of activation can be determined accurately as a function of the degree of conversion. In this way a parallel reaction could be observed starting at the end of the nonisothermal conversion process. The polymer was used in two different morphological states, a powder and a film. A slightly higher energy of activation and a considerably higher pre-exponential factor were observed for the film indicating a dependency of the kinetics on the morphological state or on the history of the polymer sample.

### INTRODUCTION

Aromatic polyhydrazides can be used as precursor polymers for the preparation of thermally stable and chemically resistant polyoxadiazoles.<sup>1,2</sup> When a polyhydrazide is heated, a cyclo dehydration reaction of the hydrazide groups in the polymer backbone results in a polymer with oxadiazole five-rings in the backbone. The reaction scheme is shown in Figure 1 for poly-(1,3-phenyl-1,4-phenyl)-hydrazide (TIPH) consisting of alternating *m*- and *p*-substituted benzene rings in the polymer backbone between the hydrazide groups.

Little attention has been paid in the literature to the kinetics of this conversion reaction. Only Frazer<sup>3,4</sup> did some kinetic experiments and calculated the kinetic parameters. He performed isothermal treatments with his polymer samples at different temperatures and used oxygen analyses to follow the conversion reaction.<sup>3</sup> To obtain a degree of conversion of 100% it takes prolonged heating times at elevated temperatures, e.g., 48 h at 280°C.<sup>4</sup> It is therefore very time consuming to obtain a full set of isotherms.

In this paper dynamical thermogravimetry (TG) is used to follow the conversion of the polyhydrazide TIPH into the corresponding polyoxadiazole. During TG a specimen is heated with a constant heating rate and weighed continuously. Besides the fact that these measurements are less time consuming than the conventional isothermal procedures they have a further advantage over measurements at constant temperature because in the latter procedure a part of the sample may already start converting while the sample

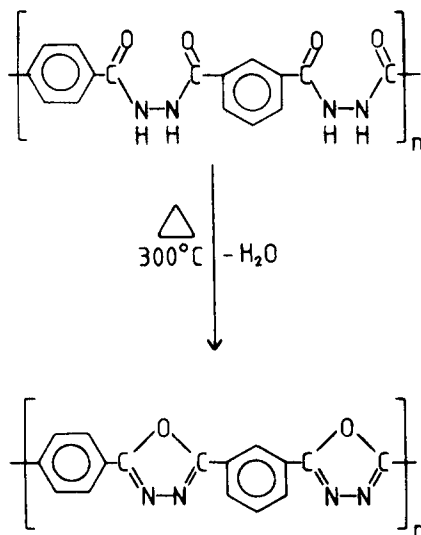


Fig. 1. Reaction scheme for the thermal conversion of poly-(1,3-phenyl-1,4-phenyl)-hydrazide (TIPH) to poly-(1,3-phenyl-1,4-phenyl)-1,3,4-oxadiazole.

is being heated to the desired temperature. The kinetic parameters are calculated from the thermogravimetric data according to a method developed by Ozawa,<sup>5</sup> in which nonisothermal TG experiments are conducted at a series of constant heating rates.

Also a different method, developed by Flynn<sup>13,14</sup> for the calculation of the initial stage energy of activation from a nonisothermal TG experiment, is applied for comparison. Both methods have the advantage over other data evaluation methods in the fact that they do not require an assumption for the rate dependency on the composition of the sample. For heterogeneous reactions like the one treated here a simple model function for this dependency is mostly inadequate in describing the process and can lead to erroneous results.<sup>6</sup>

### THEORY OF CONVERSION KINETICS UNDER NONISOTHERMAL CONDITIONS

The general mathematical model to describe the kinetics of a system undergoing chemical change is

$$d\alpha/dt = f(\alpha)k(T) \quad (1)$$

where  $\alpha$  is the degree of conversion and  $t$  is the time.

From eq. (1) it can be seen that the rate of conversion is both a function of the degree of conversion, given by  $f(\alpha)$ , and a function of temperature, given by  $k(T)$ . When a constant heating rate is used,  $\beta = dT/dt$ , eq. (1) becomes

$$d\alpha/dT = f(\alpha)k(T)/\beta \quad (2)$$

The conversion function  $f(\alpha)$  is in general extremely complicated for heterogeneous reactions and specific assumptions for  $f(\alpha)$  often lead to erroneous

predictions.<sup>6</sup> The two methods discussed below are methods which do not require a specific expression for  $f(\alpha)$ .

Like in most kinetic studies the Arrhenius equation is used for expressing the temperature dependence of  $k(T)$ . Equation (2) now becomes

$$d\alpha/dT = f(\alpha)(A/\beta)\exp(-E/RT) \quad (3)$$

where  $A$  is the pre-exponential factor,  $E$  is the energy of activation,  $R$  is the gas constant and  $T$  is the absolute temperature. Equation (3) can be written in the following integrated form

$$\int_0^\alpha d\alpha/f(\alpha) = (A/\beta) \int_{T_0}^T \exp(-E/RT) dT \quad (4)$$

The left-hand side of eq. (4) is the conversion integral  $F(\alpha)$ , which cannot be solved because of the unknown conversion function  $f(\alpha)$ . The right hand side of eq. (4) contains a temperature integral which cannot be expressed in a closed form.<sup>7</sup> The value of the temperature integral is expressed and tabulated by Doyle<sup>7-9</sup> as the following function  $p$ :

$$\int_0^T \exp(-E/RT) dT = (E/R) \times p(E/RT) \quad (5)$$

If the value  $(E/RT)$  is larger than 20,  $p(E/RT)$  can be approximated by the following formula<sup>10</sup>

$$\log p(E/RT) = -2.315 - 0.457E/RT \quad (6)$$

Both Ozawa<sup>5</sup> and Flynn and Wall<sup>12</sup> independently used Doyle's solution [eq. (6)] for their method of data processing, which runs as follows. Using eq. (6) the solution of eq. (4) becomes

$$\log F(\alpha) = \log(AE/R) - \log \beta - 2.315 - 0.457E/RT \quad (7)$$

Equation (7) generates straight lines of slope  $-0.457E/R$  by plotting  $\log \beta$  against  $1/T$  for iso-fractional conversions and considering  $A$  and  $E$  to be independent of the applied heating rate. Equation (7) can be written as

$$\Delta \log \beta / \Delta(T)^{-1} = -0.457E/R \quad [\alpha = \text{constant}] \quad (8)$$

Thus it is possible to calculate from the slopes of such an Ozawa plot an energy of activation and to follow this energy during conversion.

As  $\log[(AE/\beta R)p(E/RT)]$  is equal to  $\log F(\alpha)$ , according to eq. (7), both  $A$  and  $n$ , the order of reaction, can be determined by comparing both values for any degree of conversion. This can be done graphically by comparing the experimental master curve with the theoretical master curves for different orders of reaction. The experimental master curve can be obtained by plotting  $\log[(E/\beta R)p(E/RT)]$ , using the determined  $E$ , against  $\alpha$ . The experimental master curve has to be shifted along the abscissa with a factor  $\log A$  to be superposed upon one of the theoretical curves. By comparing the shape of the

curves the order  $n$  can be determined. The theoretical master curves can be obtained by plotting  $\log F(\alpha)$  against  $\alpha$ . For the calculation of  $\log F(\alpha)$  an expression for the conversion function is absolutely required. The most simple and most applied expression for the conversion function is<sup>7</sup>

$$f(\alpha) = (1 - \alpha)^n \quad (9)$$

where  $n$  is the exponential factor, also called the order of reaction.  $\log F(\alpha)$  then becomes respectively

$$\log F(\alpha) = \log[(1 - n)^{-1} \times (1 - (1 - \alpha)^{(1-n)})] \quad \text{for } n \neq 1 \quad (10)$$

$$\log F(\alpha) = \log[-\ln(1 - \alpha)] \quad \text{for } n = 1 \quad (11)$$

Another method of calculating an energy of activation without requiring an expression for  $f(\alpha)$  was developed by Flynn,<sup>13,14</sup> now using the differential form of the kinetic equation. Differentiation of eq. (3) with respect to  $\alpha$  gives<sup>13</sup>

$$d(d\alpha/dT)/d\alpha = E/RT^2 + f'(\alpha)/f(\alpha) d\alpha/dT \quad (12)$$

By applying the mean value theorem, one obtains for  $\alpha \ll 1$

$$(d/d\alpha)(T^2 d\alpha/dT) = E/R + 2T \quad (0 < \alpha \leq 0.05) \quad (13)$$

where  $T$  and  $\alpha$  are values averaged over the intervals  $\Delta T$  and  $\Delta\alpha$ . With this method the energy of activation of the initial stage of the reaction can be obtained from the slope of a plot in which  $T^2 d\alpha/dT$  is plotted against  $\alpha$ .

## EXPERIMENTAL

### Materials

Terephthaloylchloride was supplied by Merck and recrystallized from hexane before use. Isophthaloyldihydrazide was prepared according to Frazer<sup>1</sup> from isophthalic acid dimethyl ester and hydrated hydrazine, both supplied by Merck. The isophthaloyldihydrazide was recrystallized from water. The solvents NMP and DMSO were supplied by Merck and dried with 3 Å molecular sieves.

### Polyhydrazide Syntheses

The polyhydrazide, TIPH, was synthesised according to Frazer<sup>1-5</sup> from isophthaloyldihydrazide and terephthaloylchloride using a low temperature, solution polycondensation reaction in NMP. The reaction temperature was 0°C, the reaction time was 2 h. The reaction medium was poured in excess of water and the precipitated polymer was washed several times with water and methanol and dried in an oven at 80°C. The inherent viscosity measured with an Ubbelohde viscometer using a 0.5 g/100 mL DMSO solution at 30°C was  $\eta_{inh} = 1.3$  dL/g.

### Sample Preparation

The powder samples were taken from the washed and dried polymer and subsequently dried in a N<sub>2</sub>-atmosphere at 200°C overnight. A homogeneous film was cast from a 15 wt% solution of the washed and dried polymer in DMSO and evaporated for 3 h at 80°C in a N<sub>2</sub>-atmosphere. Subsequently the film was dried at 200°C overnight in a N<sub>2</sub>-atmosphere. Samples were cut from the polymer film to fit in the TG sample pans. The initial weight of all samples was about 1.0–1.5 mg.

### Thermal Analyses

A Perkin-Elmer TGS-2 Thermogravimetric Analyser in combination with a System 4 Microprocessor Controller and a model 3600 Thermal Analysis Data Station was used for the TG experiments. During all experiments a N<sub>2</sub>-atmosphere was provided by a continuous gasflow of 85 mL/min. The applied constant heating rates were: 1, 2, 5, 10, 20, and 50°C/min. Before each run every sample was held isothermally at 200°C for 20 min to make sure that the samples were completely freed from adsorbed water. Each run was started from 200°C.

The degree of conversion,  $\alpha$ , can be determined from the thermogravimetric weight loss curves by

$$\alpha = (w_0 - w_t) / \Delta w_{\max} \quad (14)$$

where  $w_0$  and  $w_t$  represent the sample weight at the beginning and at time  $t$ , respectively. The determination of the experimental maximal weight loss from dynamic runs is obstructed by the fact that after 100% conversion no period of constant weight is reached. The maximal weight loss for completion of the reaction,  $\Delta w_{\max}$ , was therefore calculated theoretically from the structural formula of the polymer, being 11.0% of  $w_0$ .

## RESULTS AND DISCUSSION

Figure 2 shows a complete TG curve for the polyhydrazide powder sample recorded at a heating rate of 20°C/min. Three distinct phases of weight loss can be observed. According to Frazer<sup>3</sup> the first one represents the loss of adsorbed water, the second one represents the loss of water caused by the cyclo dehydration reaction of the hydrazide groups and the third phase of weight loss represents the loss of volatiles caused by the degradation of the polyoxadiazole formed *in situ*.

The results of the thermogravimetry at various heating rates as they are recorded are shown in Figures 3 and 4 for powder and film sample, respectively. The TG curves shift to higher temperatures with increasing heating rate. Both the shape and the position of the curves in the thermograms are different for both kinds of samples. The curves of the film samples are shifted to less higher temperatures compared to the powder samples and seem to be more steep. Both samples show a slight decrease in weight after the cyclization weight loss, which makes it difficult to distinguish both the end of the cyclization and the beginning of the degradation process.

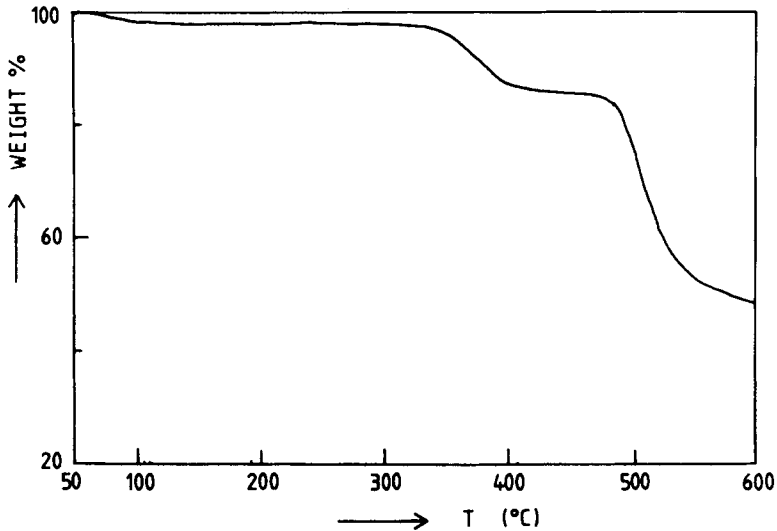


Fig. 2. Thermogravimetric weight loss curve for TIPH recorded at a heating rate of 20°C/min in a nitrogen atmosphere.

The Ozawa plots, according to eq. (7) are given in Figures 5 and 6 where the logarithms of the heating rates are plotted against the reciprocal of the absolute temperatures for iso-fractional conversions. Through the iso-conversional points straight lines can be drawn by the method of least squares. Straight lines are obtained except for the top left hand corner of the film plot. A possible explanation for this deviation may be the fact that at high heating rates the heat flow to the samples can become rate determining. This was already pointed out by Flynn<sup>12</sup> who indicated that the upper limit of

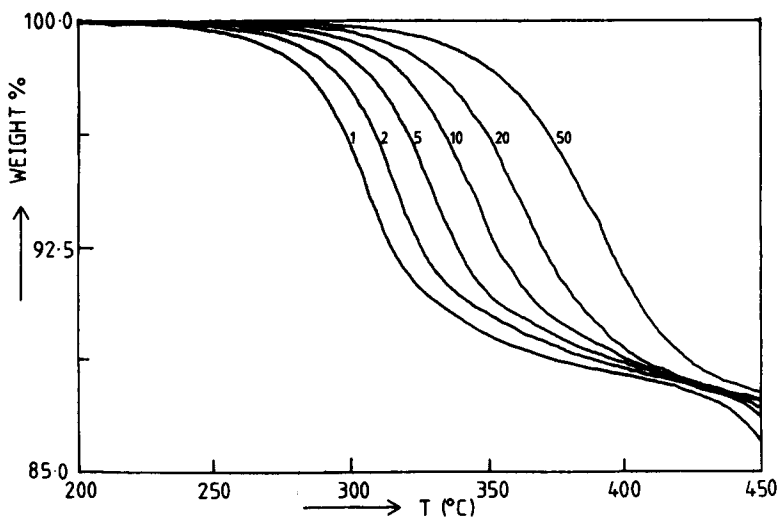


Fig. 3. Thermogravimetric weight loss curves for a TIPH polymer powder recorded at six different heating rates  $\beta$ .

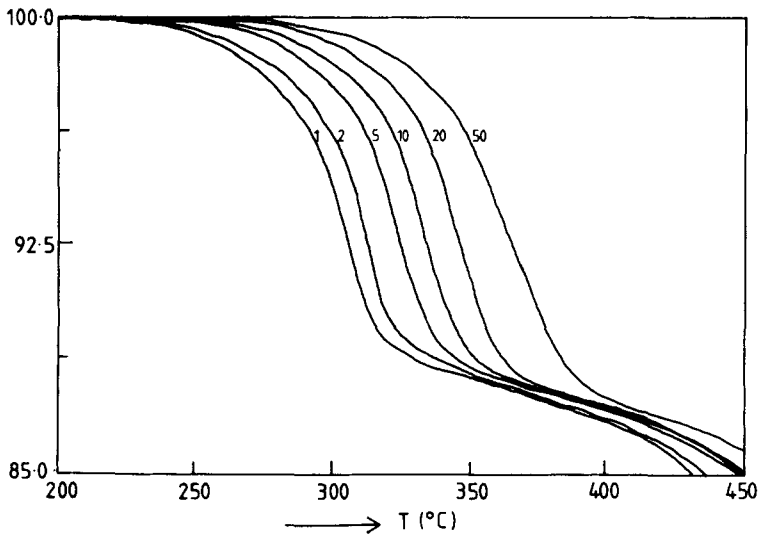


Fig. 4. Thermogravimetric weight loss curves for a TIPH homogeneous film recorded at six different heating rates  $\beta$ .

meaningful kinetic data lies somewhere between 10 and 60°C/min depending on the design of the apparatus and the size of the sample.

From the slopes of the iso-conversional lines energies of activation are calculated using eq. (8) and presented in Table I. The values of both the film and powdered samples do agree well. After a slight increase during the first 10% of conversion a constant value is reached at about 164 kJ/mol for the

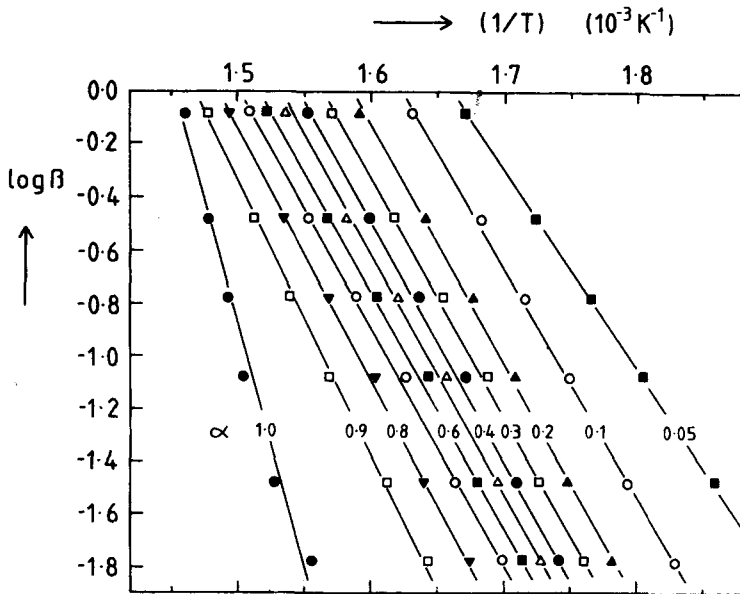


Fig. 5. Ozawa plot for TIPH in powder form ( $\beta$  in °C/min).

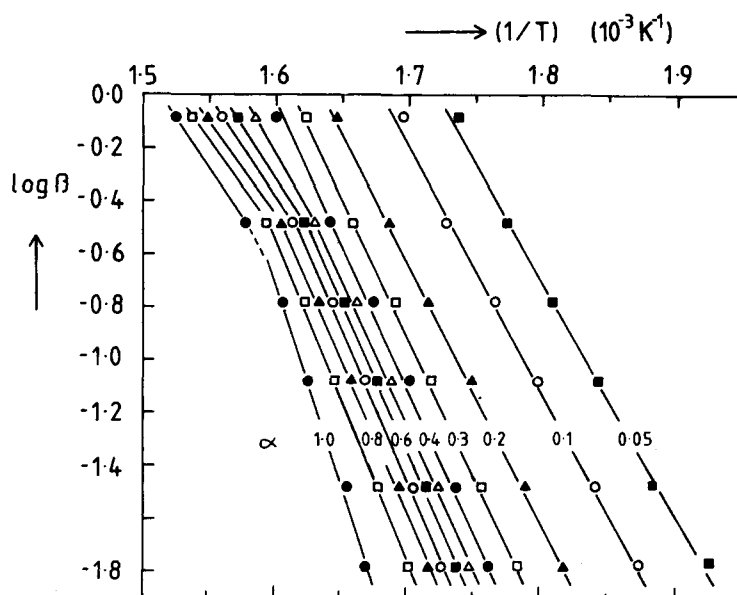


Fig. 6. Ozawa plot for TIPH in film form ( $\beta$  in  $^{\circ}\text{C}/\text{min}$ ).

powder samples. This value does not agree with the value obtained by Frazer<sup>3</sup> who found for the same polymer, in powder form, an energy of activation of 211.3 kcal/mol.

After 70% conversion the energy of activation of the powdered sample slowly increases with increasing degree of conversion until a value of about 302.4 kJ/mol is reached at the theoretical point of complete conversion. A steady increase in the energy of activation can be caused by the occurrence of a parallel competitive or independent reaction with a higher energy of activation as was shown by Ozawa<sup>6,15</sup> and Flynn.<sup>13</sup> In this case we are inclined to think of the beginning of some kind of degradation reaction.

TABLE I  
Energies of Activation for the Conversion of the Polyhydrazide, TIPH,  
in Film and Powdered Form, Calculated with the Ozawa Method

$\alpha$	$E_{\text{akt}}$ (kJ/mol)	
	Film	Powder
0.05	142.4	147.0
0.10	152.5	160.0
0.20	165.9	166.3
0.30	172.2	165.9
0.40	181.4	165.1
0.50	183.5	163.0
0.60	183.1	163.8
0.70	177.7	167.2
0.80	179.8	178.1
0.90	177.7	210.4
1.00	185.6	303.7



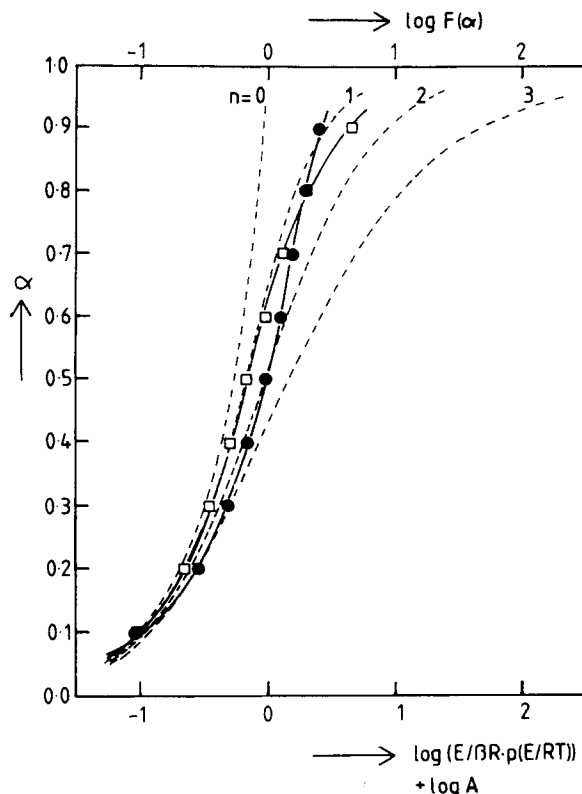


Fig. 7. Theoretical thermogravimetric master curves (dashed lines) for 4 different reaction orders ( $n$ ) compared with the experimental thermogravimetric master curves for TIPH both in film (●) and in powdered (□) form. The experimental master curve for the film has been shifted along the abscissa with a factor 13.7, the curve for the powder has been shifted with a factor 11.7.

The pattern of the film samples is somewhat different. In the beginning a slight increase in the energy of activation from 138 till a mean constant value of 181 kJ/mol is reached at about 40% of conversion which is maintained almost until theoretical completion of the conversion. At this point an increase in the energy of activation appears.

In order to get information about the pre-exponential factor and the order of reaction a method suggested by Ozawa<sup>5</sup> is applied, in which the experimental master curve is compared with the theoretical master curves calculated with some model functions  $f(\alpha)$ , given by eqs. (10) and (11). The method, however, is not valid in cases of more than one process operating at the same time, therefore only the average energy of activation belonging to the cyclization reaction has been considered. The experimental master curves for a heating rate of 10°C/min, for both the film and the powdered samples, are compared with theoretical master curves for different orders as is shown in Figure 7.

It is very difficult to distinguish between the different orders especially in the first part of the curves. The best fit in this case however seems to be a first order reaction although there is a considerable deviation from this curve for

the film sample. The determination of the order of the process with this method is not unambiguous. This, however, applies to all other methods where a model relation is tested for linearity, because of the small differences between the values of the individual model functions.<sup>7</sup> Furthermore one has to consider that the function  $f(\alpha)$  is a very simple and limited function. For example, it cannot describe in general the kinetics of diffusion or nucleation and nuclei growth. Especially for heterogeneous reactions where, in contrast to homogeneous reactions, several processes can be operating at the same time the factor  $n$  has a purely empirical meaning.

Much more information can be gained from Figure 7 about the pre-exponential factor. The pre-exponential factor  $A$  is of the order of  $10^{12}$  for the powder and  $10^{14}$  for the film sample. A higher value for the pre-exponential factor causes the TG curves to shift to lower temperatures compared to the curves with lower pre-exponential factors as was shown mathematically by Sestak.<sup>16</sup> This explains the position of the film sample curves compared to the powder sample curves at lower temperatures in the thermogram. Frazer<sup>3</sup> determined for the pre-exponential factor a value in the order of  $10^{16} \text{ s}^{-1}$  which is considerably higher than our value. He determined an order of reaction of 1 using the same model function  $f(\alpha)$ .

The pre-exponential factor can be used in calculating the entropy of activation,  $\Delta S^\ddagger$  using the following formula

$$A = (ekT/h)\exp(\Delta S^\ddagger/R) \quad (15)$$

where  $k$  is the Boltzmann constant and  $h$  the Planck constant.

Calculation of this entropy of activation leads to a value of  $-34.4 \text{ J/mol K}$  for the powder, while Frazer finds  $+58.8 \text{ J/mol K}$ . The difference in the sign of these values is very striking. Because of the positive entropy change Frazer suggested a rate controlling process that involves the breaking of some crystalline structure.<sup>3</sup> A negative entropy change does not allow such an explanation, but indicates a process that involves an increase in order or a decrease in flexibility. This is more likely to be the case in a process where a flexible hydrazide group is converted into a more rigid oxadiazole group.

For the polymer in film form however the entropy of activation becomes about  $3.8 \text{ J/mol}$ . Compared with the powder this could indicate a more ordered structure in the beginning of the process, so that less entropy loss occurs during the rate controlling process. As this conversion process is not a simple molecular process however, like for example most gas-phase reactions, care must be taken in the interpretation of the entropies of activation.

The energies of activation of the initial stages of the reaction are also determined with a different method developed by Flynn<sup>12,13</sup> [eq. (13)], using the same data that was used to obtain the Ozawa plots. For determining these energies of activation the first derivatives of  $\alpha$  with respect to the temperature had to be obtained in the first 5% of the conversion process. Because there is much experimental scatter in the thermogravimetric data in this range it is impossible to derive accurate derivatives. Therefore the data (20 points) is used for curve fitting using an exponential function of the form  $y = a + b \exp(cx)$ . The fitted function is then employed to calculate the derivatives. Plots of  $T^2 d\alpha/dT$  against  $\alpha$  are given in Figure 8 for both

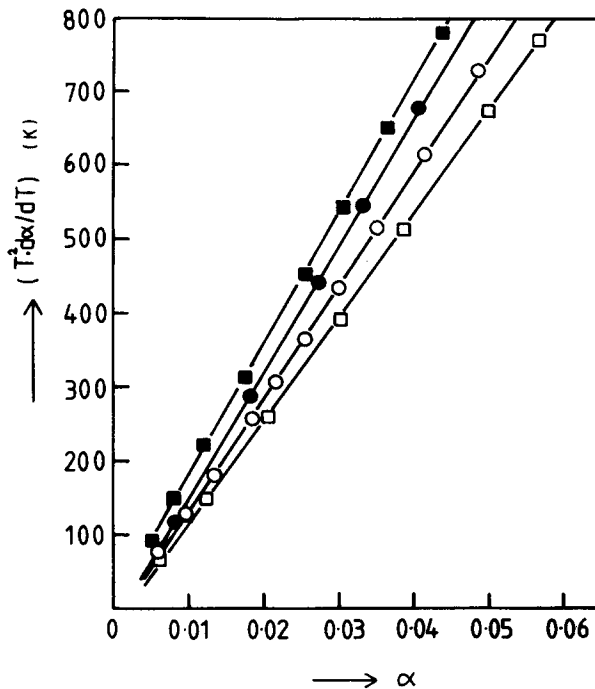


Fig. 8.  $T^2 d\alpha/dT$  plotted against  $\alpha$  for the first 6% of conversion according to eq. (13) for the powder sample at a heating rate of 1 ( $\circ$ ) and 10°C/min ( $\square$ ) and for the film sample at a heating rate of 1 ( $\bullet$ ) and 10°C/min ( $\blacksquare$ ).

powder and film samples and for some different heating rates showing straight lines in all cases. The calculated energies of activation are given in Table II.

Although the accuracy of this method is less than for the Ozawa method, because of the determination of the reaction rates, the determined energies of about 113–143 kJ/mol in the first 5% of conversion agree much better with those obtained by the Ozawa method at  $\alpha = 0.05$ , being about 143–147 kJ/mol, than with those obtained by Frazer. The fact that two different mathematical methods for obtaining the energy of activation, one based on the integral form and the other based on the differential form of the rate equation, give comparable results indicates the correctness and reliability of these methods.<sup>14</sup>

For the apparent differences between our results and Frazer's there are some possible explanations. First there is the difference in analytical technique

TABLE II  
Initial Stage Energies of Activation Determined by the Method of Flynn for  $\alpha < 0.05$

$\beta$ (°/min)	$E_{akt}$ (kJ/mol)	
	Film	Powder
1.0	139.9	118.9
10.0	142.0	112.1

used to follow the degree of conversion. Frazer used oxygen analyses while we used a gravimetric technique of which the latter is in our opinion the more accurate one. A second explanation may be the question of the correctness of the mathematical treatment of the data derived from an isothermal or a dynamical process. MacCallum<sup>16</sup> raised the question whether kinetic parameters obtained in nonisothermal procedures are the same as those obtained by conventional isothermal methods and considers isothermal measurements absolutely necessary in evaluating the true kinetic parameters. At least both methods have to be compared. A last explanation may be that the rate controlling process in the conversion of the polyhydrazide is different whether the process is performed isothermally or dynamically.

In a following paper we will describe and discuss isothermal gravimetric analysis with the same polymer. The results will be compared with the results derived with the nonisothermal measurements given here. Attention will also be focused on both types of morphology of the polymer sample, film and powder, to investigate whether there is an essential difference in kinetics or not. From these results a mechanism for the conversion reaction will be deduced.

## CONCLUSIONS

The Ozawa method for calculating the energy of activation from nonisothermal TG runs at different heating rates proves to be an accurate method for obtaining the energy of activation of the thermal conversion process of polyhydrazide into a polyoxadiazole. The energy of activation in the initial part of the conversion process agrees well when determined with two different evaluation methods.

With the Ozawa method it is possible to follow the energy of activation during the entire conversion process. In this way the appearance of a parallel independent reaction starting at the end of the conversion process was indicated. The determination of the pre-exponential factor and the order of reaction is less reliable as it needs a model describing the dependency of the reaction rate upon the composition of the sample.

Although the determined energies of activation for the polyhydrazide in powder form and in film form do agree the latter does have a considerable higher pre-exponential factor indicating a dependency of the kinetics on the morphological form or the history of the polymer sample.

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