

Cyclo Dehydration Reaction of Polyhydrazides. II. Kinetic Parameters Obtained from Isothermal Thermogravimetry

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Synopsis

The kinetics of 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 have been studied with isothermal thermogravimetry in continuation of a study with nonisothermal thermogravimetry described in a previous paper. Although the isothermal measurements are much more time-consuming, they provide some new information and insight about the cyclo dehydration reaction of the polyhydrazide. The physical state of the sample, rubbery or glassy, seems to influence the kinetics considerably. The kinetic parameters determined with the isothermal method for the polymer in its glassy state agree well with the parameters derived from the previously reported nonisothermal measurements, while the kinetic parameters for the expected rubbery state differ considerably. The morphological state or the history of the polymer has also a considerable influence on the kinetics of the isothermal conversion process. The powder form of the polymer has a much lower isothermal conversion rate than the film form.

INTRODUCTION

In a previous paper¹ by the same authors the kinetics of the cyclization reaction of polyhydrazides to polyoxadiazoles was studied with nonisothermal thermogravimetry. Subject to the study was terephthaloyl-isophthaloyl-polyhydrazide (TIPH) consisting of alternating *m*- and *p*-substituted benzene rings in the polymer backbone between the hydrazide groups.

The kinetic parameters obtained did not agree with results Frazer² obtained with some isothermal measurements. One of the possible reasons for these deviations is that the difference is caused by the method of evaluation. MacCallum started a discussion about this point³ and stated that isothermal measurements were necessary for obtaining the real kinetic parameters. In general it should be advisable to use more than one method for evaluating the kinetic parameters⁴ especially for the more complex reactions. A disadvantage of isothermal measurements is that they are very time consuming because it takes long periods of time to obtain a full set of isotherms. Especially for the thermal conversion of the polyhydrazide used this takes a long time.^{5,6} Frazer did perform some isothermal thermogravimetric measurements to determine the order of the reaction but he did not use the data any further for a kinetic evaluation.⁷

In the previously reported nonisothermal measurements¹ a slight difference was observed between the polymer in powder form and the polymer in film form. The energy of activation was in the same order of magnitude, 164

kJ/mol for the powder and 181 kJ/mol for the film sample but the pre-exponential factor differed by a factor of 100. The polymer in film form had a much higher pre-exponential factor resulting in thermogravimetric curves positioned at lower temperatures compared with the corresponding polymer in powder form.

In this paper isothermal thermogravimetry experiments will be discussed employing the same polymer that was used during the nonisothermal experiments, the above mentioned polyhydrazide TIPH. Two morphologies of the polymer will be considered, the powder form, this is the washed and dried polymerization product, and a homogeneous film obtained from a TIPH solution in DMSO by evaporating the solvent.

EXPERIMENTAL

Materials and Sample Preparation

Materials and sample preparation were described in the previous paper (Part I).¹ For both the isothermal and nonisothermal experiments the samples were taken from the same batch to be sure that the samples had the same history. Before the measurements the samples were dried at 200°C overnight.

Thermogravimetric Analysis

A Perkin-Elmer TGS-2 Thermogravimetric analyzer in combination with a system 4 Microprocessor Controller and a Kipp recorder was used for the isothermal thermogravimetry. During all experiments a nitrogen atmosphere was provided by a continuous flow of nitrogen gas of 85 mL/min. All the samples were held isothermally at 200°C for 20 min to remove adsorbed water. Then the sample was heated with a heating rate of 200°C/min to the desired temperature. The point $t = 0$ was taken at the moment where the first weight loss was observed. From measurements of the exact temperature value near the samples a time interval of about 2 min was observed after $t = 0$ before the temperature reached its final constant value.

For calculation of the degree of conversion from the thermogravimetric data the theoretical value for the maximum weight loss was used, being 11.0% of the initial dry weight.

Differential Scanning Calorimetry

A Perkin-Elmer DSC Differential Scanning Calorimeter in combination with a System 4 Microprocessor Controller and a Thermal Analyses Data Station Model 3700 was used for DSC measurements. A nitrogen purge gas and a heating rate of 20°C/min was used.

Evaluation of the Kinetic Data

For the evaluation of the kinetic data, the following rate equation is used

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

where the reaction rate r is described by $k(T)$, the rate constant which is a

function of temperature only, and $f(\alpha)$, which is a function of the degree of conversion α only. Upon integration eq. (1) yields

$$\int_0^\alpha d\alpha/f(\alpha) = g(\alpha) = k(T)t \quad (2)$$

The linear dependence of $g(\alpha)$ on time t makes it possible to find by way of trial and error the function which best fits the experimental data and to determine the rate constant $k(T)$.

For investigation of the mechanism of conversion we use a model relation for the conversion function $f(\alpha)$ in the most simple form:

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where n is the exponential factor, sometimes called the order of reaction. Although this is a very simplified model relation it may serve well as preliminary information to the reaction kinetics and furthermore it is suitable for observing changes in the kinetic process.⁴ The following functions $g(\alpha)$ are obtained for n being respectively 0, 1, 2 and 3:

$$g(\alpha) = \alpha \quad [n = 0] \quad (4)$$

$$g(\alpha) = -\ln(1 - \alpha) \quad [n = 1] \quad (5)$$

$$g(\alpha) = 1/(1 - \alpha) - 1 \quad [n = 2] \quad (6)$$

$$g(\alpha) = 0.5(1 - \alpha)^{-2} - 0.5 \quad [n = 3] \quad (7)$$

For $k(T)$ the Arrhenius relation is used:

$$k(T) = A \exp(-E/RT) \quad (8)$$

Both the pre-exponential factor A and the energy of activation E can be determined by plotting $\ln k(T)$ against the reciprocal temperature ($1/T$).

RESULTS AND DISCUSSION

Figure 1 shows some isotherms in a zero order plot for both the polymer powder and the film. The plot indicates the prolonged heating times needed to obtain completion of the conversion and a striking difference can be observed between both morphologies of the polymer samples. The conversion rate of the homogeneous films is much higher than that of the powder and also the shape of the isotherms is different. Especially the shape of the powder isotherms is remarkable in its dependency on the temperature. After a high initial rate of conversion it drops suddenly to a much lower rate at a moment that seems to be depending on the temperature. The film isotherms show a more gradual decrease in the conversion rate.

First and second order plots of the data for the polymer in the powdered form are presented in Figures 2 and 3 to test the different functions $g(\alpha)$ for linearity with time. Only the first 130 min of the conversion process are

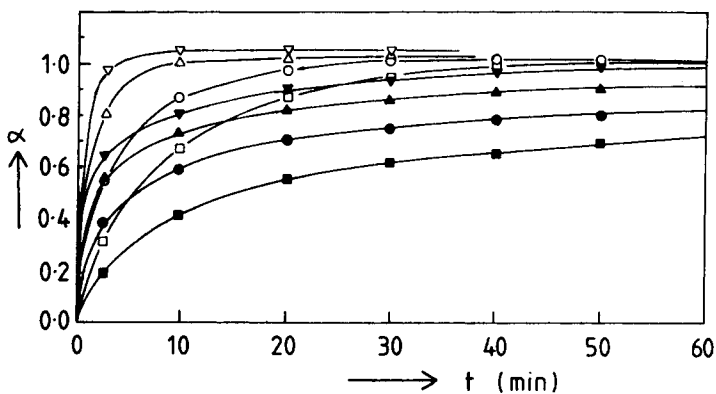


Fig. 1. Zero order plot for the thermal conversion reaction of the polyhydrazide TIPH in powder form with the following isotherms: 268.8°C (■), 278.5°C (●), 282.8°C (▲), 290.0°C (▼), and in film form with the following isotherms 259.5°C (□), 274.3°C (○), 282.6°C (△), and 290.2°C (▽).

considered in these figures since this period represents the most interesting part of the isotherms. Although it is difficult to discriminate between both orders the best linearity is obtained for second order plots, except for the break in the slopes of the isotherms. Frazer⁷ also found the best fit for the second order function but he did not observe a break in his isotherms. Frazer plotted his isotherms for a much more expanded time scale so that a possible breakpoint or curvature may have disappeared in the inaccuracy of the plot. Very accurate measurements and precise plotting of the data in our case shows a breakpoint in the isotherms from high slopes/high reaction rates to smaller slopes/lower reaction rates. The position of the points of intersection of the slopes composing each isotherm is represented in Figure 4 where the

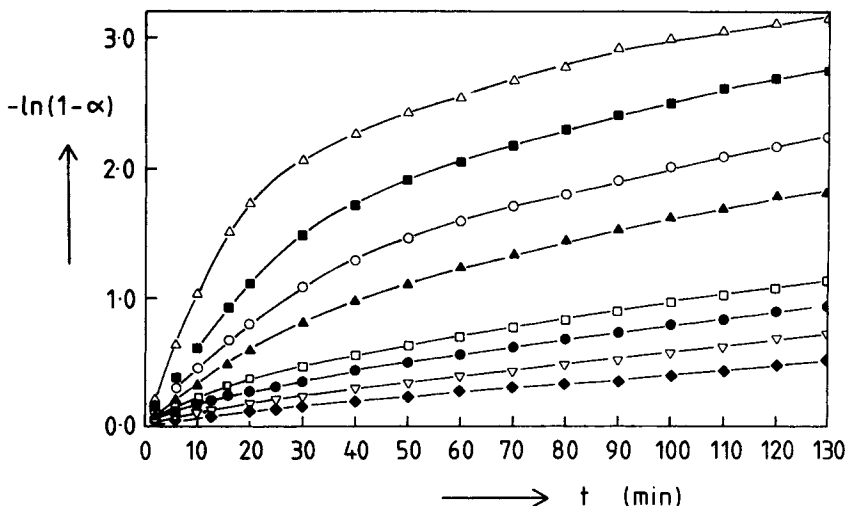


Fig. 2. First order plot for the polyhydrazide in powder form with the following isotherms: 306.7°C (△), 299.8°C (■), 290.0°C (○), 282.8°C (▲), 278.5°C (□), 272.7°C (●), 268.8°C (▽), 265.0°C (◆).

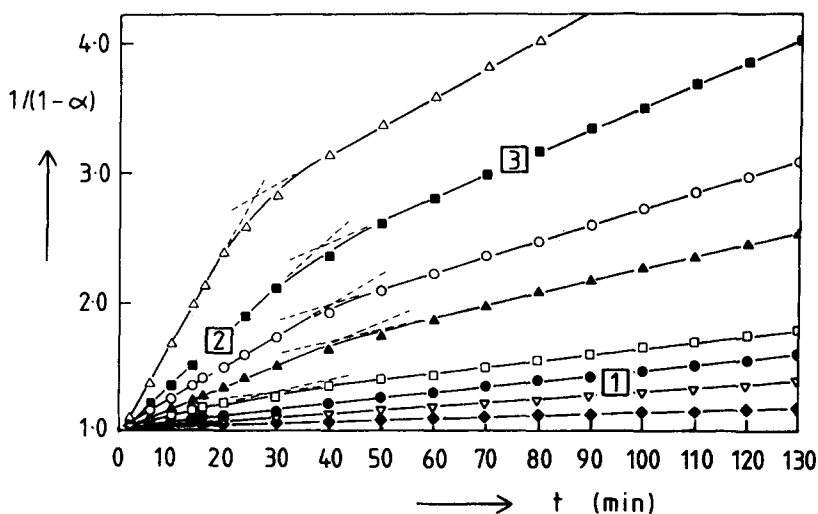


Fig. 3. Second order plot for the polyhydrazide in powder form with the following isotherms: 306.7°C (Δ), 299.8°C (\blacksquare), 290.0°C (\circ), 282.8°C (\blacktriangle), 278.5°C (\square), 272.7°C (\bullet), 268.8°C (∇), 265.0°C (\blacklozenge).

degree of conversion at the breakpoint is plotted against the temperature. This figure shows that the higher the conversion temperature the higher the degree of conversion where the breakpoint occurs.

Both facts, change of slope from high to low values and breakpoint dependent on the conversion temperature, lead to the assumption that the break-

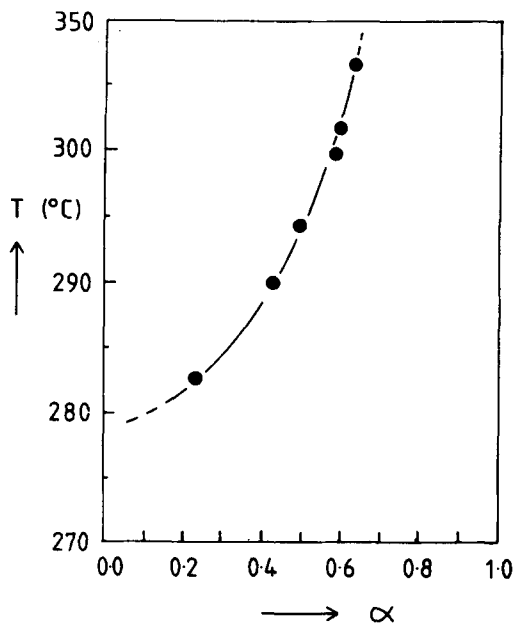


Fig. 4. Temperature plotted against the degree of conversion belonging to the points of intersection of the second order isotherms belonging to the powder.

point represents a kind of transition in the polymer sample, possibly the rubber-glass transition. The conversion starts at a temperature above the T_g of the initial polyhydrazide, in the rubbery state, with a high conversion rate. Then due to the conversion of the flexible hydrazide groups into the more rigid oxadiazole rings the T_g increases and at a given moment it becomes higher than the applied isothermal temperature. The polymer sample thus undergoes a rubber-glass transition and attains its glassy state, where the conversion rate is slowed down. If this assumption is correct, Figure 4 can be considered as the glass transition temperature as a function of the degree of conversion of the initial polyhydrazide.

Extrapolation of this curve to $\alpha = 0$ gives a value of about 278°C for the T_g of the initial polyhydrazide, extrapolation to $\alpha = 1$ gives the T_g of the corresponding polyoxadiazole being higher than 400°C.

Figure 5 shows the DSC thermograms for the polyhydrazide powder and film and for their corresponding polyoxadiazoles recorded at a heating rate of 20°C/min. In the powder thermogram two endothermic peaks can be observed: the first one at about 100°C most likely represents the loss of absorbed water; the second one from about 300°C to 400°C represents the conversion process. There seems to be a shoulder on the left-hand branch of this conversion peak which might represent a glass transition but a glass transition is not clearly observed possibly because it coincides with the broad endothermic peak or it is not there at all. Also a shoulder or a peak at the right-hand branch of the conversion peak is observed, which possibly represents the

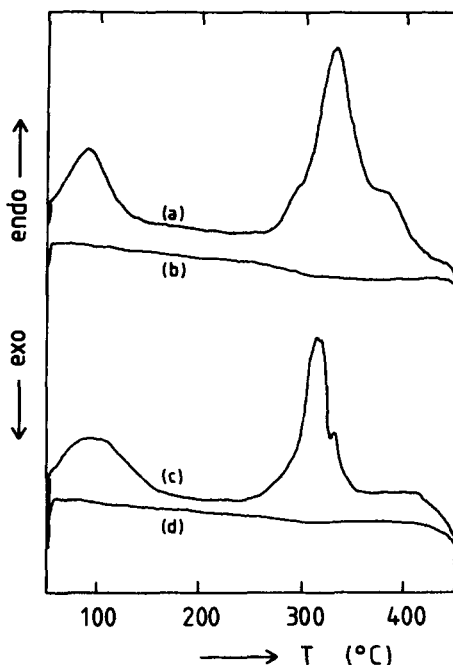


Fig. 5. DSC thermograms for the polyhydrazide, TIPH, as a powder (a) and its corresponding polyoxadiazole (b) and for the polymer as a homogeneous film (c) and its corresponding polyoxadiazole film (d).

TABLE I
Kinetic Parameters for the Conversion of the Polyhydrazide TIPH, in Powder and Film Form, Determined with Isothermal Thermogravimetric Measurements

Area	Conversion temperature (°C)	Expected state	Isothermal Method					
			Powder			Film		
			<i>n</i>	<i>E</i> (kJ/mol)	<i>A</i> (s ⁻¹)	<i>n</i>	<i>E</i> (kJ/mol)	<i>A</i> (s ⁻¹)
1	< 278	glassy	3	160	2 × 10 ¹⁰	3	193	2 × 10 ¹⁷
2	> 278	rubbery	2	244	2 × 10 ¹⁸	2	244	2 × 10 ¹⁹
3	> 278	glassy	2	172	2 × 10 ¹¹	1	294	8 × 10 ²³
Nonisothermal Ozawa method:				165.0	5 × 10 ¹¹		182.3	5 × 10 ¹³

parallel reaction, also observed with the Ozawa method¹ and starting at the end of the nonisothermal conversion process.

Also for the polyoxadiazole one does not observe a glass transition in a DSC thermogram before the polymer starts to decompose at about 450°C. This is in agreement with the literature.^{2,6} Because all the usual techniques used for T_g determination require a temperature program, the measurement will always be disturbed by the conversion reaction. These isothermal measurements could possibly represent a method to determine the glass transition temperature despite the disturbing conversion process.

If the isothermal conversion temperature is programmed below the T_g of the initial polyhydrazide the polymer is bound to stay in the glassy state throughout the process and no glass transition should occur. As can be seen in Figure 3 such a break is not observed in the isotherms below 280°C. Figure 3 can now be divided in three different areas, where area 1 represents the isotherms below the expected initial T_g , areas 2 and 3 the isotherms above the initial T_g before and after the glass transition point, respectively.

Table I represents the kinetic parameters calculated from the isothermal data for the different areas. For the conversion of the powder the energy of activation in area 2, the rubbery state, being 244 kJ/mol is higher than the energy of activation in areas 3 and 1, the expected glassy states, being, respectively, 172 and 160 kJ/mol. The latter values agree well with that obtained from the nonisothermal method, being 165.1 kJ/mol. Also the determined pre-exponential factor in area 3 agrees much better with the previously determined value obtained with the nonisothermal method, although the difference is still a factor in the order of 10.

The question now is raised about the physical state (rubber or glass) of the polymer samples during the nonisothermal measurements presented in Part I.¹ Comparing the energies of activation, if they are reliable, one would assume the polymer to be in the glassy state when performing nonisothermal conversions. At the start of a nonisothermal run at a temperature of 200°C the polymer is almost certainly in its glassy state. At the end of the run at a temperature of 450°C the converted polymer is also in its glassy state. During the nonisothermal conversion process no sudden changes in the energy of activation were observed in the Ozawa plots,¹ using heating rates from 1 till 50°C/min. For these reasons it is reasonable to assume the polymer to be in

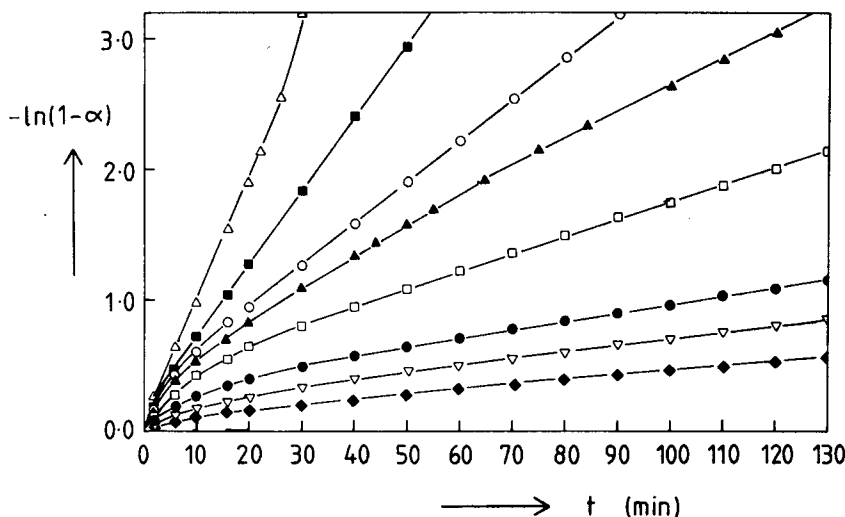


Fig. 6. First order plot for the polyhydrazide in film form with the following isotherms: 305.2°C (Δ), 300.1°C (\blacksquare), 290.2°C (\circ), 282.6°C (\blacktriangle), 278.6°C (\square), 270.0°C (\bullet), 260.2°C (∇), 255.2°C (\blacklozenge).

the glassy state throughout the whole nonisothermal conversion process. This also means that during heating rates up to 50°C/min, the rate of increase in T_g is the same or higher than the heating rate. It is likely that the sample is continuously just below its glass transition temperature in a transition state, where the movements of the polymer chain segments do not contribute to a glass-rubber transition but result in a conversion of a hydrazide group.

Applying a heating rate of 200°C/min however, which is done in the present paper to reach the isothermal temperatures as fast as possible, it is assumed that the polymer undergoes a glass-rubber transition so that the polymer is in its rubbery state when the isothermal process starts. According to this point of view somewhere between heating rates of 50 and 200°C/min a glass-rubber transition should be present during nonisothermal methods.

Now changing to the other morphological state of the polymer, the film, first and second order reaction plots of the film samples are represented in Figures 6 and 7 respectively. Both the orders and the shapes of the isotherms are quite different. Instead of a break point in the second order isotherms the curves show a better linearity in a first order plot from a certain point. Although the second order plot here differs from the plot for the powder the same subdivision into three areas has been made analogous to the powder case.

The calculated kinetic parameters are given in Table I. For the areas 1 and 2 there is a more or less good agreement with the powder, except for the pre-exponential factor of the film in area 1. The kinetic parameters in area 3 however deviate strongly from the parameters determined for the powder and also from the nonisothermal measurements. Both the energy of activation and the pre-exponential factor for area 3 are considerably higher than the previously obtained values. Although these parameter calculations from the isothermal data are not so accurate as compared to those from the nonisothermal

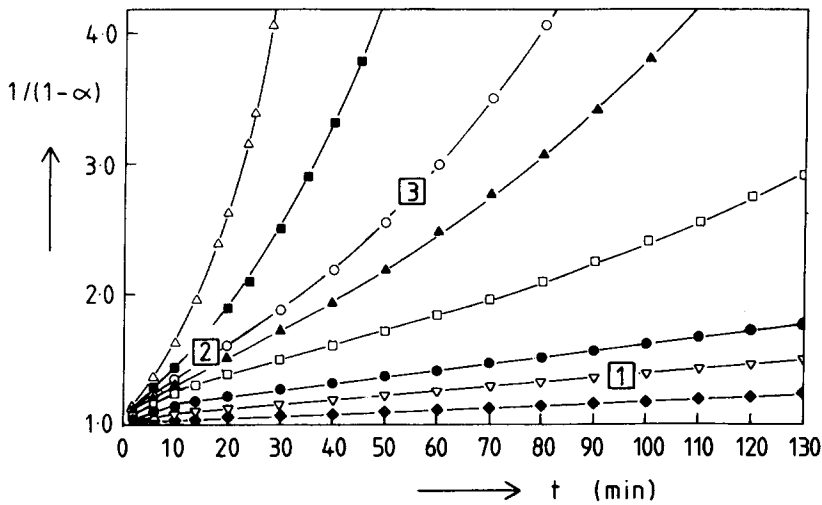


Fig. 7. Second order plot for the polyhydrazide in film form with the following isotherms: 305.2°C (Δ), 300.1°C (\blacksquare), 290.2°C (\circ), 282.6°C (\blacktriangle), 278.6°C (\square), 270.0°C (\bullet), 260.2°C (∇), 255.2°C (\blacklozenge).

method, it looks as if some totally different process is controlling the conversion rate in the polyhydrazide film sample during an isothermal conversion after the glass transition has occurred. This implies that the history and/or the morphological state of the polymer sample determines the kinetics of the conversion process.

Looking more closely at the isotherms of area 1, for both powder and film, it seems that the best linearity is even obtained with a third order. Figures 8 and 9 represent the third order plots for the isotherms below the expected glass transition temperature. It can be seen from these plots that during the first 10–20 min (area 1a) the slopes are somewhat higher than after this period

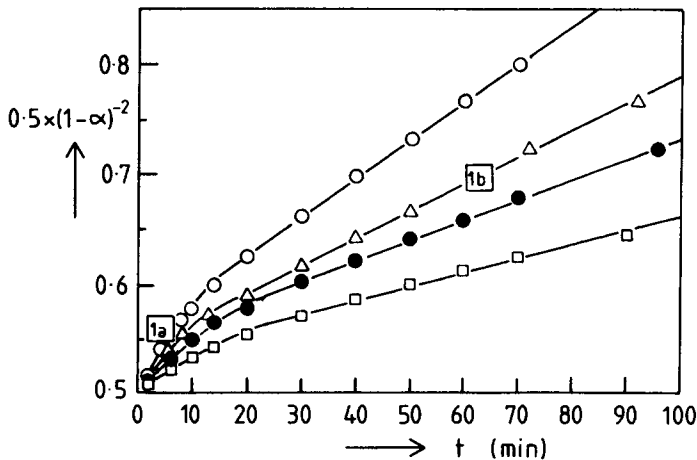


Fig. 8. Third order plot for the polyhydrazide in powder form with the following isotherms: 260.4°C (\square), 264.7°C (\bullet), 269.9°C (Δ), 274.5°C (\circ).

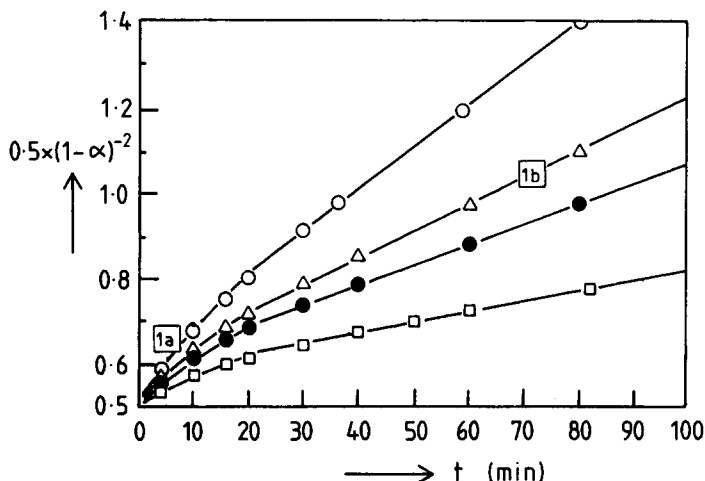


Fig. 9. Third order plot for the polyhydrazide in film form with the following isotherms: 254.6°C (□), 259.5°C (●), 264.6°C (Δ), 269.7°C (○).

(area 1b) when a good linear behavior is obtained. This break point however represents a different transition than the transition from area 2 to 3 in Figure 3 because the energies of activation before this break point are in the order of 118 kJ/mol, which is much lower than the energy of activation found for area 2, the rubber area. The value of 118 kJ/mol, however, agrees well with the energy of activation determined during the first 5% of the nonisothermal conversion. This slightly lower energy of activation in the very beginning of the conversion process is possibly caused by a simultaneous loss of traces of solvent which were still present in the polymer matrix as was already pointed out in Part I.¹

It seems that the determined order of the reaction decreases during the conversion process. In the beginning the order is high, being 3 or 2, and then it decreases until it has become almost zero at the end of the conversion process as can be seen from Figure 1. One has to be careful not to give too much significance to the determined orders of reaction because for complicated heterogeneous reactions, like the one we are dealing with here, in contrast with most homogeneous reactions a simplified model relation like eq. (3) is mostly inadequate to describe the process. In literature for example even negative orders have been observed.⁴ Frazer⁷ tried to explain the second order by some kind of interaction between two reacting hydrazide groups. He suggested hydrogen bonding. This suggestion fitted well with his earlier assumption that the rate controlling process was the breaking out of some crystalline order.²

In contrast to Frazer's approach we would like to propose an alternative mechanism. Another explanation for an order higher than 1 can be the fact that the hydrazide groups have a mutual interaction because they are part of the same main chain. Looking at the polymer structure more closely it can be seen that the conformation of the hydrazide group does not have to be in the "folded" conformation which is mostly presented in literature^{5,6} (see Part I, Fig. 1¹). In fact there are many different conformations possible. One of them

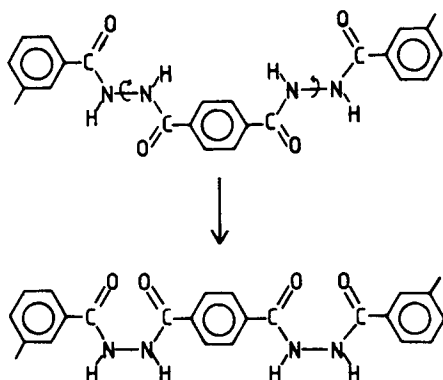


Fig. 10. Schematic representation of a part from the main chain of the polyhydrazide TIPH. The arrows represent a coupled rotation around the N-N axis.

is illustrated in Figure 10, which is called the "extended" conformation,⁶ where the carbonyl oxygen groups of the hydrazide group are turned away from each other. For a ring closure reaction the folded conformation seems favourable and can be attained from the extended conformation by a rotation of the chain round the N-N-axis of the hydrazide group. Such a rotation implies the rest of the chain to translate or rotate as well, sometimes to a great extent. As Figure 10 illustrates such a rotation can bring two hydrazide groups, because of their interaction, in the favourable conformation for ring closure with a kind of crank-shaft movement.

The proposed rate controlling mechanism for the conversion process derived from this is the rotation or movement of polyhydrazide chain segments. With this mechanism the differences between the reaction rates in the rubbery and glassy state can be explained. Also the differences between the two morphological states can, to some extent, be explained with a difference in polymer conformation. This difference is probably caused by the history of the polymer sample. It is not unreasonable to assume that the different preparation processes of the samples induce different conformations of the polymer chains with respect to the required conversion. Further research is necessary to explain these differences. This will be discussed in more detail in a forthcoming paper.

CONCLUSION

In addition to the nonisothermal measurements, given in Part 1, the isothermal measurements described in this paper provide some new information and insight about the reaction kinetics of the thermal cyclisation reaction of a polyhydrazide. For example, the physical state of the polymer, rubbery or glassy, seems to be relevant. A considerable difference in the determined kinetic parameters is observed between both expected physical states, with a distinct transition at the expected glass transition temperature of the polymer. The kinetic parameters determined with the isothermal method for the polymer in its glassy state agree well with the parameters derived from the nonisothermal measurements.

The difference in the observed kinetics between the polymer in powder and in film form is much more pronounced with these isothermal conversions as it was with the previously reported nonisothermal conversions. The powder form of the polymer has a much lower isothermal conversion rate than a homogeneous film of the same polymer, showing a dependency of the kinetics on the morphological state or the history of the polymer sample.

As a mechanism for the rate controlling process in the cyclo dehydration process of the polyhydrazide a rotation of segments in the polyhydrazide chain is proposed.

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