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STUDIES IN HETEROCYCLIC POLYMERS. PART VI. A WEIGHT-LOSS STUDY OF THE FORMATION OF A POLYBENZOXAZOLE

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ABSTRACT

The cyclisation of an aromatic poly(*o*-hydroxyamide) to form polybenzoxazole has been studied by combining isothermal weight-loss and thermogravimetric analyses. The thermogravimetric data were analysed by the method of Gyulai and Greenhow [4] to derive values for the apparent activation energy of the cyclisation process which was found to double at about 50% conversion (74—155 kJ mole^{-1}). A similar result was observed when the process was studied in the presence of low concentrations of *p*-toluene sulphonic acid, which appears to have a moderate catalytic effect upon the cyclisation process. The apparent order of reaction of the process has been found to be close to 2, contrary to previous studies which have assumed it to be unimolecular.

INTRODUCTION

Thermogravimetry has been widely applied to the study of polymer degradation, for, as Doyle [1] has pointed out, the thermogravimetric data record of residual weight vs. time and temperature is richly comprehensive, encompassing a full range of weight change in a single trace. In this respect, one thermogram is equivalent to a very large family of isothermal weight-change curves and avoids sample to sample error.

However, thermogravimetric data are only narrowly definitive and routine kinetic analysis may lead to trivial kinetic parameters unless much additional evidence relating to the process being observed is available. With many studies of polymer degradation, owing to the complexity or obscurity of the molecular structure of the polymers and of their decomposition reactions, in many instances not nearly enough pertinent information is available to warrant undertaking meaningful kinetic analysis. For this reason, weight-change data for polymers are commonly subjected to empirical kinetic treatment.

One group of polymer reactions which may be studied by thermogravimetry for which both the precursor and the product are well defined is the dehydration step involved in the formation of aromatic heterocyclic polymers, of which the polybenzoxazoles are an example.

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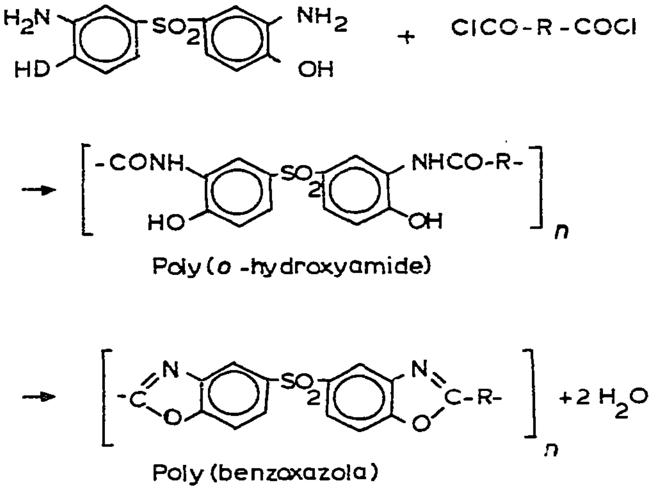

Fig. 1. Conversion of poly(*o*-hydroxyamide) to poly(benzoxazole).

The polybenzoxazoles constitute a species of heterocyclic polymer which has been relatively little studied, although in aromatic forms it has a good technical profile and a range of potential applications in plastics and in fibre form.

Figure 1 identifies the characteristic two-step synthesis of a polybenzoxazole. The second step, the intramolecular cyclodehydration in the poly(*o*-hydroxyamide), is completed by heating this precursor for a long period at a temperature above 523 K. This phase of the formation of polybenzoxazoles has been followed by Kardesh et al. [2] and Hodd [3] using isothermal weight-loss studies. The interpretation of the data obtained from isothermal weight-loss studies presents some problems, for the cyclodehydration is advanced before the isothermal temperature is attained and this introduces an element of uncertainty into the kinetic analysis. This uncertainty arises from the polymeric nature of the material being studied, for the glass transition temperature of the product, which at any instant during conversion is a random benzoxazole-co-(*o*-hydroxyamide) polymer, is increasing throughout the reaction period.

To avoid this problem and also to take advantage of the rapidity and comprehensive nature of TGA, this method of analysis has been used to study the cyclodehydration of the poly(*o*-hydroxyamide) (Fig. 1). The resulting thermograms were analysed using the method of Gyulai and Greenhow [4] and, together with data gained from isothermal weight-loss studies, the kinetic parameters of the cyclodehydration determined. Finally, the effectiveness of *p*-toluene sulphonic acid previously reported as a catalyst for the cyclodehydration [3] was re-evaluated.

OUTLINE OF THE METHOD OF GYULAI AND GREENHOW [4]

To obtain kinetic data, activation energy, pre-exponential factor and reaction order from the recorded weight-loss curves the following general rate expression serves as a basis for calculation

$$-\frac{\mathrm{d}h}{\mathrm{d}t} = k\mathrm{f}(h) \tag{1}$$

where h is the residual active weight fraction, k is the apparent specific rate constant, and $\mathrm{f}(h)$ is a function of the weight loss, the form of which is dependent upon the process being studied.

Equation (1) may be re-written (upon incorporating the Arrhenius equation)

$$-\frac{\mathrm{d}h}{\mathrm{d}t} = (A/q)\,\mathrm{e}^{-E/RT}\,\mathrm{f}(h) \tag{2}$$

where A is the preexponential factor, E is the activation energy, T is the absolute temperature, q is the heating rate, and R is the gas constant.

Kinetic parameters may then be derived by introducing TGA data into a suitably revised form of eqn. (2). This may involve either (a) obtaining the data in a differential form and setting the values of $-\mathrm{d}h/\mathrm{d}t$, h, and T into eqn. (2) or a revised form of the same, or (b) by integral analysis, which considers expressions (1) and (2) as differential equations and obtains the kinetic parameters from their integrated forms.

Approach (a) requires either a derivative thermogravimetric apparatus or the differentiation of the thermogram, a lengthy and not too accurate procedure when conducted graphically. For approach (b) the thermograms as obtained are sufficient. However, difficulties do arise in the integration of eqn. (2) and its derivatives such as eqn. (3)

$$-\frac{\mathrm{d}h}{\mathrm{f}(h)} = \left(\frac{A}{q}\right)\mathrm{e}^{-E/RT}\,\mathrm{d}t \tag{3}$$

for neither the analytical form of $\mathrm{f}(h)$ is known, nor can the right-hand side of the expression be integrated in finite form. The problem then becomes the solution of eqn. (4)

$$\mathrm{g}(h) = \int_0^h \frac{\mathrm{d}h}{\mathrm{f}(h)} = \frac{A}{q}\int_{T_0}^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{4}$$

To solve eqn. (4) Gyulai and Greenhow use the notation

$$i = \int_{T_0}^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}t \tag{5}$$

So that eqn. (4) may be re-written

$$\mathrm{g}(h) = (A/q)i \tag{6}$$

From two thermograms of a process obtained at two different heating rates, points of the same extent of reaction, i.e. identical h values, may be identified. The following expressions may then be written

$$i_{11} = \int_{T_0}^{T_{11}} \mathrm{e}^{-E/RT}\,\mathrm{d}T\,; \qquad i_{21} = \int_{T_0}^{T_{21}} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{7}$$

and

$$g(h)_{11} = (A/q_1)\, i_{11}\,; \qquad g(h)_{21} = (A/q_2)\, i_{21} \tag{8}$$

$$g(h)_{11} = g(h)_{21} \tag{9}$$

where the first subscripts 1 and 2 for the heating rate (q) represent the different thermograms and the second subscript 1 refers to the selected conversion value.

In general, from eqns. (8) and (9) the following expression may be gained

$$q_k/q_1 = i_{k1}/i_{11} = i_{k2}/i_{12} = i_{kn}/i_{1n} \tag{10}$$

Gyulai and Greenhow computed values of log i utilising a 32-point gaussian numerical integration formula and tabulated them for different temperatures and activation energies.

To determine the activation energy (E) of a given process the temperatures (T_{11}, T_{21}) of the same conversion point (i.e. h value) from two TG thermograms obtained at different heating rates (q_1 and q_2) are noted. The values of i corresponding to these temperatures and various values of E can be obtained from the tabulated values. Now if i_1/i_2 is plotted against E the unknown E can be located as the value of E corresponding to

$$\log q_1/q_2 = \log i_1/i_2 \tag{11}$$

Then assuming that

$$g(h) = \left(\frac{1}{n-1}\right)\left(\frac{1}{(1-x)^{n-1}} - 1\right) \tag{12}$$

and knowing the order of the reaction, g(h) can be determined and the pre-exponential factor (A) can be found from the equation

$$\log A = \log q - \log i + \log g(h) \tag{13}$$

for any extent of conversion.

EXPERIMENTAL

Materials

Poly(1-sulphonyl-3-hydroxy-4-phenyleneimino-1-oxo-4-phenyleneoxy-1-oxo-4-phenylene-1-imino-2-hydroxy-4-phenylene) (PHA), where R is 4,4'-diphenylene ether in Fig. 1, was supplied by Yorkshire Chemicals Ltd. Toluene-4-sulphonic acid, m.p. 378 K, b.p. 413 K at 2.666 kN m^{-2}, was obtained from B.D.H.

Weight-change studies

These were made using a Stanton-Redcroft TR-02 thermobalance, adapted to allow an inert atmosphere for the sample, and fitted with a Stanton-Redcroft LPV/CA10 variable rate linear programmer and a Stanton-Redcroft three-clock furnace timer. Approximately 200 mg samples of the poly(*o*-hydroxyamide) were used, of a particle size less than 0.15 mm in diameter. Samples were maintained at the selected isothermal temperatures for up to 12 h under nitrogen with a flow rate of 0.5 min^{-1}. A drying period of 1 h at 400 K was included in the heating programme of each sample before each isothermal run. Samples for thermogravimetry were heated at one of two heating rates, either 0.3 or 10 K min^{-1}.

Characterisation of polymers

The PHA and the products of the cyclodehydration were identified by C, H and N and by UV and IR spectrophotometry.

RESULTS AND DISCUSSION

*The characterisation of polybenzoxazole and its precursory poly(*o*-hydroxyamide) (PHA)*

The elemental analyses of PHA and its fully cyclised form (PBO) were in good agreement with the calculated values. The major features of the IR absorption spectra of PHA and the fully cyclised PBO are compared in Fig. 2, which shows the IR absorption of PHA, PBO, and two samples of partially cyclised PHA prepared by heating for 6 h at 516 K(2) and 536 K(3), respectively. The progressive disappearance of the carbonyl absorption, characteristic of polyamides, at 1660 cm^{-1} and the parallel appearance of an

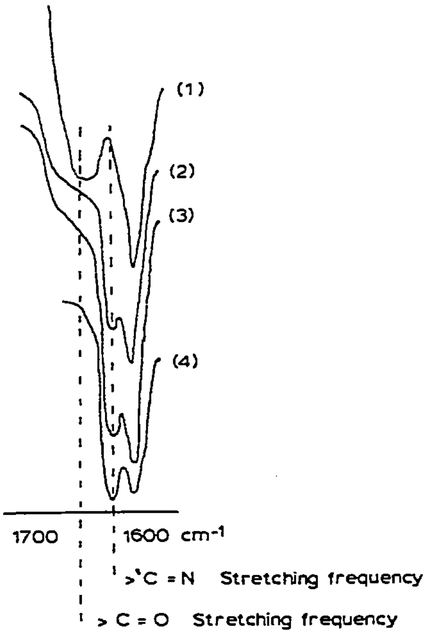

Fig. 2. Comparison of IR traces of (1) poly(*o*-hydroxyamide) (PHA), (2) PHA after 6 h at 516 K, (3) PHA after 6 h at 536 K, and (4) poly(benzoxazole).

TABLE 1

Data for the cyclisation of poly(hydroxyamide) from isothermal weight-loss studies

Temp. (K)	% Cyclisation ($x \times 10^2$)	$-\log(1-x)$	Rate of reaction (moles s^{-1})($R \times 10^3$)	$-\log R$
488	16	0.076	5.35	2.27
	20	0.097	3.66	2.44
	28	0.143	2.35	2.63
	35	0.187	0.7	3.11
503	20	0.097	8.00	2.1
	25	0.125	6.19	2.21
	30	0.155	4.49	2.35
	36	0.199	4.00	2.4
	40	0.222	3.16	2.5
	50	0.301	1.73	2.76
	60	0.398	1.23	2.91
516	24	0.119	12.0	1.92
	30	0.155	8.35	2.08
	38	0.208	6.40	2.19
	45	0.260	5.46	2.26
	52	0.319	4.00	2.40
	60	0.398	2.22	2.65
	70	0.523	1.10	2.96
527	32	0.167	10.5	1.98
	40	0.222	7.66	2.12
	54	0.337	5.64	2.25
	60	0.398	3.77	2.42
	76	0.620	1.54	2.81
	79	0.678	0.6	3.22

absorption band at 1625 cm^{-1} attributable to the —C=N stretching frequency of the oxazole ring may be noted in Fig. 2 proceeding from PHA, (2), (3) to PBO. These changes were good indicators of development of the cyclic structure in the PHA.

The UV absorption spectrum of PBO in concentrated sulphuric acid solution also has features strongly characteristic of the benzoxazole structure, e.g. a strong absorption at 445 cm^{-1}.

Both UV and IR spectroscopy were employed to check qualitatively the extent of conversion of PHA to PBO during the course of the weight loss studies reported. These examinations also confirmed the absence of other structural developments during the course of heating PHA samples.

Processes which may not have been identifiable spectroscopically were crosslinking and chain scission. That neither of these processes occurred to any significant extent during the conversion of PHA to PBO was confirmed by the complete solubility of the fully and partially cyclised PBOs in concentrated sulphuric acid, and by the inherent viscosities of the solutions of these polymers which remained fairly constant throughout.

Isothermal weight-change studies

The results of the weight-loss studies of the cyclisation process made at fixed temperatures in the range 488 to 536 K, corrected for buoyancy and for weight losses due to cyclisation prior to the attainment of the isothermal temperature, were converted to % cyclisation vs. heating time isotherms and typical examples are shown in Fig. 3. It will be noted that each of the curves in Fig. 3 intersects the ordinate at a point other than zero. The point of intersection indicates the extent of cyclisation prior to the attainment of the isothermal temperature. At 536 K, for example, it was 43%, and in the presence of a catalyst, such as *p*-toluene sulphonic acid, even higher initial cyclisation levels were attained.

Kinetic parameters of the cyclisation

Order of reaction

The slopes of the cyclisation curves were measured at a number of values of % cyclisation and the rates of cyclisation derived from the slopes. The slopes of plots [—log (rate)] against [$-\log(1-x)$] (where x is the fractional conversion) at the temperatures studied were then used to determine the order of the cyclisation reaction (see Fig. 4). Table 2 shows the collected [—log(rate)] vs. [$-\log(1-x)$] plots for the different temperatures. The average order of the reaction was found to be close to 2.

Thermogravimetry

The cyclodehydration of PHA to PBO was also followed by thermogravimetry. As may be seen in Fig. 5, the plateau corresponding to the existence of PBO is well defined and this polymer is stable to about 750 K in nitrogen. Thermogravimetry was conducted at a number of heating rates but for analytical purposes two heating rates were selected, 0.3 and 10 K min^{-1}. Figure 6 shows two thermograms obtained at these heating rates in which the % cyclisation is plotted against temperature.

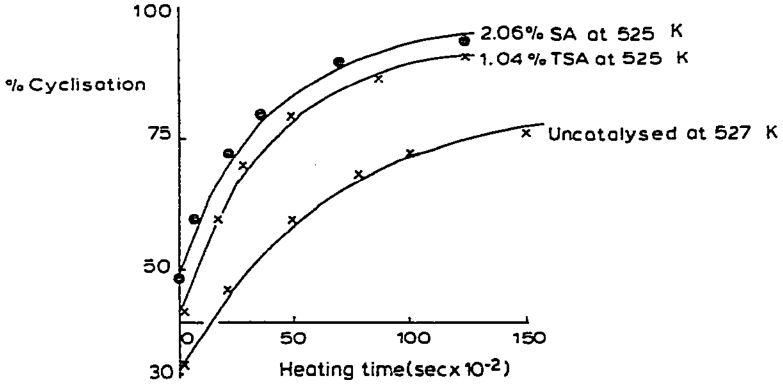

Fig. 3. % Cyclisation curves for poly(*o*-hydroxyamide) in the presence of different concentrations of *p*-toluene sulphonic acid from isothermal weight-loss studies.

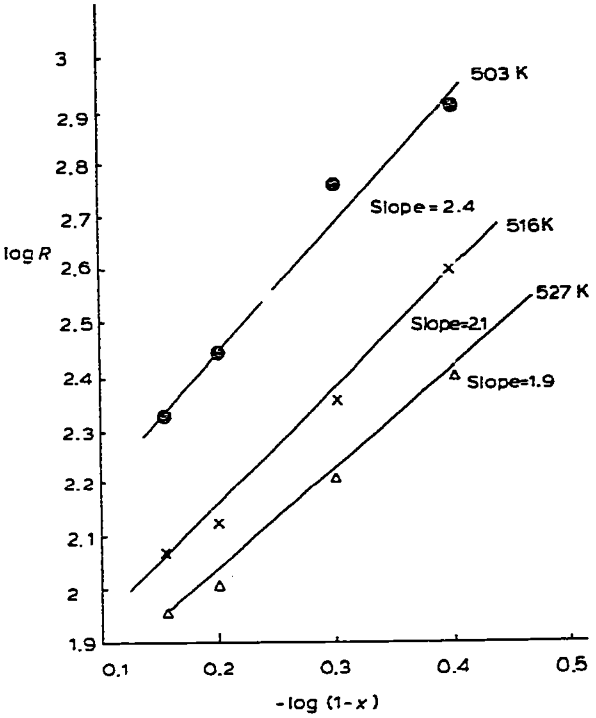

Fig. 4. Plots of —log R vs. —log(1 — x) for isothermal cyclisation reactions.

The apparent pre-exponential factor and the apparent activation energy of cyclisation

Calculation of the apparent activation energy (E) and the apparent pre-exponential factor (A) from the isothermal study requires the rate of cyclisation at zero conversion to be extrapolated, and this value can then be used to solve the Arrhenius equation. However, as has already been pointed out the

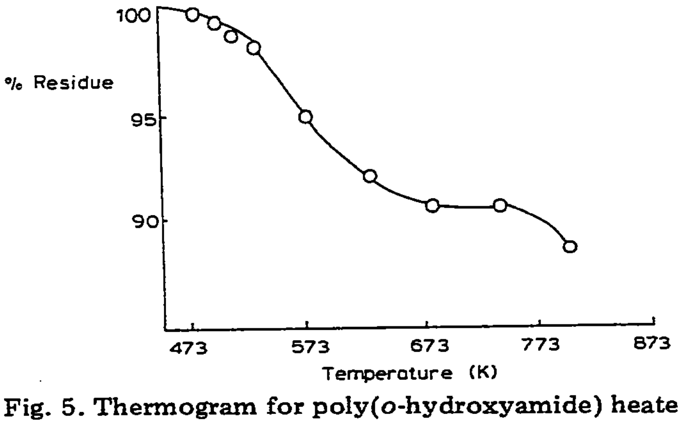

Fig. 5. Thermogram for poly(o-hydroxyamide) heated at 10 K min^{-1} in nitrogen.

TABLE 2

Data used to obtain the apparent activation energy (E) for the poly(hydroxyamide) at different % of conversion from TG thermograms at 0.28 K min^{-1} (q_1) and 10 K min^{-1} (q_2) following Gyulai and Greenhow [4]

% Cyclisation	T_1 (K)	T_2 (K)	Heating rate (K min^{-1})		E (kJ mole^{-1})	— log i_1/i_2
			q_1	q_2		
9	440	524	0.28	10		
					83.6	1.747
					125.4	2.533
					167.2	3.329
					209.0	4.125
					250.8	4.921
20	480	540	0.28	10		
					83.6	1.110
					125.4	1.617
					167.2	2.124
					209.0	2.630
					250.8	3.136
46	520	573	0.28	10		
					83.6	0.871
					125.4	1.266
					167.2	1.661
					100.0	2.056
					250.8	2.451
71	540	596	0.28	10		
					83.6	0.841
					125.4	1.222
					167.2	1.602
					209.0	1.982
					250.8	2.362
93	561	622	0.28	10		
					83.6	0.864
					125.4	1.254
					167.2	1.644
					209.0	2.033
					250.8	2.427

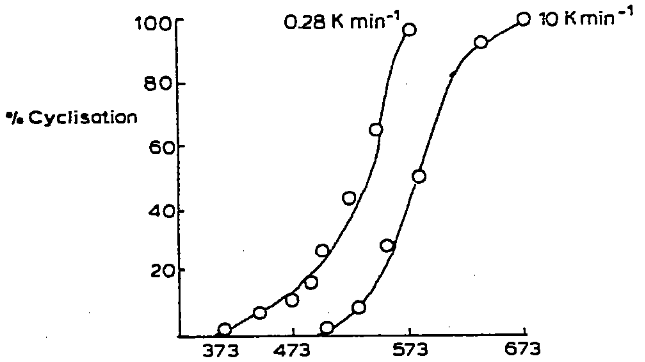

Fig. 6. Thermogravimetric traces for poly(o-hydroxyamide) at different heating rates.

TABLE 3

Cyclisation of the poly(hydroxyamide) in the presence of *p*-toluene sulphonic acid at 525 K

Amount of catalyst (%)	% Cyclisation	Time (s × 10^{-2})	Rate of reaction (moles s^{-1})($R \times 10^2$)	— log *R*
1.04	42.5	0	1.222	1.913
	60	17	0.88	2.056
	70	30	0.695	2.158
	80	50	0.36	2.444
	87	86	0.133	2.876
	90.7	125	0.06	3.222
2.06	48.5	0	1.5	1.824
	60	8	1.048	1.98
	73	22.5	0.74	2.131
	80	35	0.4	2.398
	90	70	0.071	3.149
	95	126	0.023	3.628

cyclisation was far advanced before the isothermal temperature was attained and so the accuracy of an extrapolation to zero conversion is dubious. For this reason, using the order of reaction determined from the isothermal weight-loss study, the values of *E* and *A* were determined following the method of Gyulai and Greenhow [4] referred to above. For this determination, data were derived from TGA thermograms and were used together with published values for *E* and —log *i* [4]. The kinetic parameters determined by this study are collected in Table 2, which also shows the results of a study made of the effect of *p*-toluene sulphonic acid on the cyclisation.

The effect of p-*toluene sulphonic acid upon the conversion of PHA to PBO*

To examine the effect which the inclusion of *p*-toluene sulphonic acid (TSA) has upon the cyclisation, isothermal and dynamic weight-loss studies of PHA were conducted in the presence of low concentrations, up to 2% w/w, of this former compound. The experimental procedure and data handling for this study were as described above, and Tables 3 and 4 report the data used for the determination of *n*, *E* and *A*.

Comparison of the kinetic parameters

It will be observed that the apparent activation energies reported in Table 5 approximately double during the course of conversion of PHA to PBO for both the uncatalysed and the catalysed process, so for the former the value of *E* at 9% conversion is 74 kJ $mole^{-1}$ and at 50% it is 157 kJ $mole^{-1}$. This is a feature of the process which has been observed in other unreported

TABLE 4

Data used to obtain the apparent activation energy (E) for the conversion of poly(hydroxyamide) to poly(benzoxazole) in the presence of 2% w/w of *p*-toluene sulphonic acid, from TG thermograms at 0.3 K min^{-1} (q_1) and 10 K min^{-1} (q_2) following Greenhow and Gyulai [4]

% Conversion	T_1 (K)	T_2 (K)	Heating rate (K min^{-1})		E (kJ mole^{-1})	$-\log i_1/i_2$
			q_1	q_2		
10	423	490	0.3	10		
					83.6	1.535
					125.0	2.242
					167.2	2.949
					209.0	3.656
					250.8	4.362
					292.6	5.068
51	490	526	0.3	10		
					83.6	0.671
					125.4	0.977
					167.2	1.284
					209.0	1.590
					250.8	1.896
					292.6	2.202
91	526	562	0.3	10		
					83.6	0.589
					125.4	0.857
					167.2	1.124
					209.0	1.391
					250.8	1.658
					292.6	1.926

TABLE 5

Values of the apparent order of reaction (n), the apparent activation energy (E) and the apparent pre-exponential factor (A) for the catalysed and uncatalysed cyclisation of poly-(*o*-hydroxyamide)

Catalyst — % cyclisation	n	E (kJ mole^{-1})	$\log A$
Uncatalysed	1.8 ± 0.3		
9%		74	5.9
50%		157	13.86
90%		155	13.55
p-Toluene sulphonic acid	1.8 ± 0.3		
10%		84	7.63
51%		199	19.06
91%		230	22.20

studies [5]. With regard to the further increase in E observed at higher % conversions, for the TSA study the rapid changes in temperature for small changes in extent of reaction must be considered. This will affect the precision with which the temperature at which a specific % conversion occurs may be identified and the accuracy of the estimation of E will suffer accordingly. The higher order of the reaction indicates that the cyclisation process may not be a simple unimolecular one, contrary to previous assumptions [2,3]. The observed increase in E has not been previously reported but may originate from the progressive reduction in rotational freedom of the PHA backbone which occurs upon cyclisation. The mechanism of the cyclisation of PHA to PBO has been compared to the well-studied formation of a benzimidazole ring [6], and this hypothesis implies the formation of an hydroxybenzoxazoline intermediate [3]. Cyclisation is completed by the dehydration of this intermediate, a process facilitated by its protonation. This may explain the observed catalytic function of *p*-toluene sulphonic acid and other acidic substances [5]. In the absence of free acid the phenolic hydroxyl may catalyse the process.

CONCLUSIONS

The catalysed and uncatalysed cyclisation of a poly(*o*-hydroxyamide) has been followed by combining isothermal weight-loss and thermogravimetric analyses. The order of reaction has been found to be close to 2 and the reaction is not unimolecular, as has been previously assumed. The apparent activation energy of cyclisation doubles at about 50% conversion. This is attributed to the increasing restriction upon the rotational freedom of the main chain which the formation of benzoxazole structures imposes. *p*-Toluene sulphonic acid has been demonstrated to be a moderately effective catalyst for the cyclisation process.

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