HYDROLYTIC THERMAL DEGRADATION OF POLYAMIDOBENZIMIDAZOLE IN CONCENTRATED SULPHURIC ACID

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Thermal analysis has been carried out on the process of degradation of polyamido-benzimidazole in solution in 97.8% sulphuric acid for 0.2 to 200 hr at 20 to 110°. Hydrodynamic and optical methods were used to establish that the degraded macro-molecules exhibit the same equilibrium rigidity and optical anisotropy of unit length as the undegraded molecules of polyamidobenzimidazole of various molecular weights. Thermal degradation proceeds according to the law of probability. The activation energy of degradation, 134 kJ/mol, coincides with that for low molecular weight amides. Hence, the main degradation mechanism is the breaking of the macromolecules at the amide bonds. This phenomenon can be used for analytical purposes to achieve a controlled decrease in the length of the macromolecules. In 112.5% oleum, thermal degradation proceeds much faster and the activation energy is lower by a factor of two-three.

The investigation of the resistance of high-strength polyamide materials to the action of aggressive media, determined by the activation energy of the chemical degradation of the macromolecules, is of great practical interest [1]. The rate of degradation of polyamide molecules in solutions of sulphuric acid depends on the temperature, the concentration of the acid and the chemical structure of the macromolecules [2]. The phenomenon of acid hydrolysis can be used to obtain samples of lower molecular weight M, with the analytical purpose of establishing the relationship between hydrodynamic, optical and other properties of the macro-molecules of polyamides and their M, if a decrease in their length during hydrolysis not accompanied by a change in chemical structure. In the course of hydrolysis, the amide bond in the macromolecule is broken first but, as has already been shown [2], acid hydrolysis of a heterochain polymer can also be accompanied by the breaking of other bonds of the macromolecule.

In order to establish the mechanism of hydrolytical thermal degradation of polyamidobenzimidazole (PABI) in concentrated H_2SO_4, the hydrodynamic and optical properties of the products of hydrolysis of this polyamide were investigated in this work.

If chemical bonds responsible for the high equilibrium rigidity of the PABI molecules [3] were broken during hydrolysis, this would lead to a change in the conformation of the macromolecule (its coiling), and hence to a change in the hydrodynamic properties of the products of hydrolysis, whereas the degradation

of optically anisotropic groups (e.g. the opening of imidazole rings) would lead to a decrease in the optical anisotropy of the monomer unit. Both factors should cause a sharp decrease in the flow birefringence of the solution. Hence, the conformational (hydrodynamic and optical) characteristics of the macromolecules of hydrolysis products were compared over a wide range of molecular weights with the characteristics of PABI samples and fractions (investigated previously by the same methods [3, 4]). Different values of M of these samples and fractions were obtained by varying the conditions of the synthesis and by fractionation. The kinetics of the hydrolysis of PABI in concentrated H_2SO_4 were also characterized and the activation energy of this process was calculated.

Experimental

Polyamidobenzimidazole (PABI) exhibits the following structure:
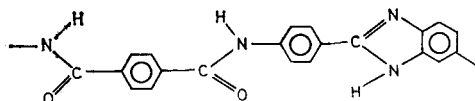
A PABI sample of molecular weight $M = 52\,000*$ was used as the initial sample. The concentration of sulphuric acid (97.8%) was established by titration with an aqueous alkali solution, and its density and viscosity at 26° were $\rho_0 = 1.8306$ g/cm³ and $\eta_0 = 0.191$ poise. PABI was dissolved in sulphuric acid at room temperature for three days with stirring. The hydrolysis of PABI in this sulphuric

Table 1

Hydrodynamic characteristics, measured in 97.8% H_2SO_4 at 26°, of the products of hydrolytic thermal degradation of polyamidobenzimidazole at 110° in 97.8% H_2SO_4 (series A)

Sample number	Time of thermal degradation	$[\eta] \cdot 10^{-3}$, cm³/g	$D \cdot 10^7$, cm²/s	$M_{D\eta} \cdot 10^{-3}$, g/mol
I	0	4.7	0.09	52.0
II	10	3.9	0.10	47.0
III	20	3.2	0.11	41.4
IV	40	2.3	0.13	36.1
V	80	1.7	0.15	31.2
VI	160	0.95	0.21	20.3
VII	300	0.54	0.29	13.6
VIII	600	0.30	0.43	7.5
IX	6130	0.03	2.00	0.8

acid was carried out in two ways. In the first (series A), solutions of PABI in H_2SO_4 at a concentration $c = 0.55$ g/dl in sealed glass ampoules were placed in a thermostat and heated at $110 \pm 0.2°$ for varius periods of time from 10 min to 100 hr (Table 1). In series B, solutions of PABI in H_2SO_4 at $c = 1.00$ g/dl in sealed ampoules were thermostated for 200 hr at various temperatures from 50 to 90° (Table 2). The use of different concentrations of the initial solution is not essential, because it has been shown previously [2] that the rate of hydrolysis of PABI in solution in sulphuric acid at moderate polymer concentrations is virtually independent of the solution concentration (for poly-p-phenyleneterephthalamide, PPPT, this conclusion has been established in ref. [5]).

The products of hydrolysis in solution were investigated by the methods of molecular hydrodynamics (translational diffusion and intrinsic viscosity) and optics (flow birefringence). The procedures for the determination of the diffusion coefficient D, the intrinsic viscosity $[\eta]$ and the flow birefringence $[n]$ of PABI in sulphuric acid have been described previously [3, 4]. The experimental values of $[\eta]$, D and $M_{D\eta}$ for series A are given in Table 1. The dependence $\eta_{sp}/c = [\eta]_+^2 k'c$, according to which the values of $[\eta]$ for the products of series B were determined, is shown in Fig. 1. The average value of the Huggins' constant k' was 0.6. Diffusion coefficients D were calculated from the slopes of the dependence of the displacement dispersion of the diffusion boundary on time $\langle \Delta^2 \rangle = \Delta_0^2 + 2\,Dt$ (Fig. 2). The molecular weights of the products of hydrolysis were calculated via the equation $M_{D\eta} = (A_0 T/\eta_0)^3/D^3[\eta]$ by using the value of Tsvetkov — Klenin's hydrodynamic constant, $A_0 = 3.6 \cdot 10^{-10}$ erg/degr. $mol^{1/3}$ [3]. The values of $[\eta]$, D and $M_{D\eta}$ are listed in Table 2.

The flow birefringence (FB) of the hydrolysis products of series B was investigated in a teflon dynamooptimeter, with a rotor height of 6 cm and a width of the gap between the rotor and the stator of 0.055 cm. The dependence of the flow

Table 2

Hydrodynamic characteristics, measured in 97.8 % H_2SO_4 at 26°, of the products of hydrolytic thermal degradation of polyamidobenzimidazole in 97.8 % H_2SO_4 for 200 hr at different temperatures (series B)

Sample number	Temperature, °C	$[\eta] \cdot 10^{-2}$, cm³/g	$D \cdot 10^7$, cm²/s	$\Delta n/\Delta c$, cm³/g	$M_{D\eta} \cdot 10^{-3}$, g/mol	$k \cdot 10^7$, min⁻¹
1	—	4.7	0.09	0.24	52	—
2	50.0	4.4	0.095	0.29	47.5	0.55
3	60.0	3.7	0.10	0.26	41.7	1.3
4	65.0	3.15	0.11	0.30	39.4	1.8
5	70.0	2.4	0.135	0.31	30.3	4.1
6	75.0	1.5	0.175	0.28	22.3	7.5
7	80.0	0.90	0.25	0.31	12.1	18.7
8	85.0	0.49	0.36	0.27	8	31.2
9	90.0	0.26	0.57	0.25	3.8	72

birefringence Δn of solutions in sulphuric acid on the flow rate gradient g was measured for all products (Fig. 3). The linear character of these dependences and the low values of g ($10 \leq g \leq 80$ s^{-1}) permitted a reliable extrapolation to $g \to 0$. These measurements were carried out for each product of the hydrolysis of PABI at several concentrations c ($c \leq 0.2 \cdot 10^{-2}$ g/cm^3) (Fig. 4). Characteristic values of

$$FB\ [n] = \lim_{c \to 0} \lim_{g \to 0} \left(\frac{\Delta n}{gc\eta_0} \right)\ \text{in H}_2\text{SO}_4\ \text{are given in Table 3.}$$
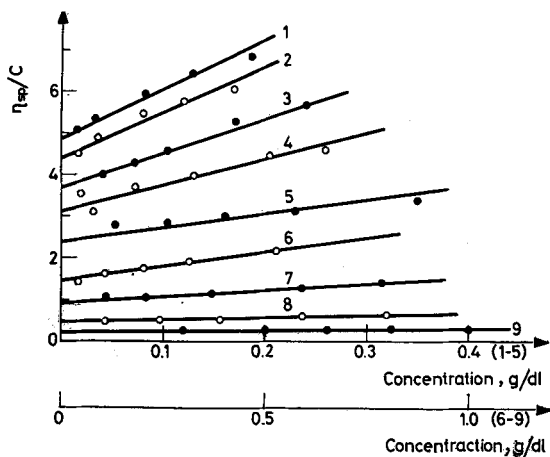

Fig. 1. Plots of η_{sp}/c vs. c for the products of hydrolysis of polyamidobenzimidazole in 97.8 % H$_2$SO$_4$ (series B). Here and in subsequent Figures the numbers on the curves are the sample numbers in Table 2
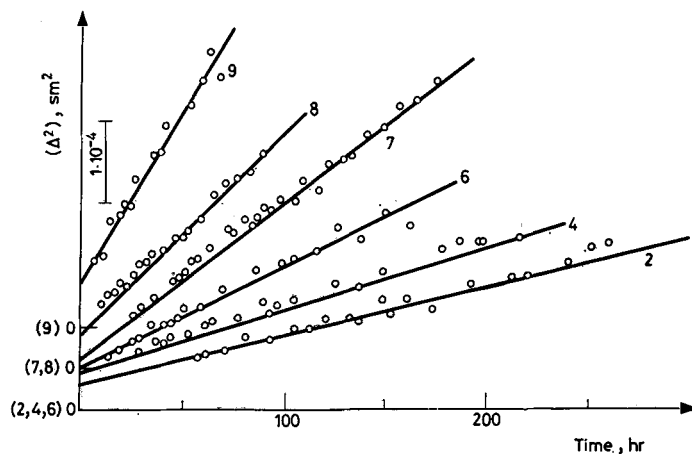

Fig. 2. Displacement dispersion of diffusion boundaries $\langle \Delta^2 \rangle$ vs. time t in 97.8 % H$_2$SO$_4$ for the same samples as in Fig. 1
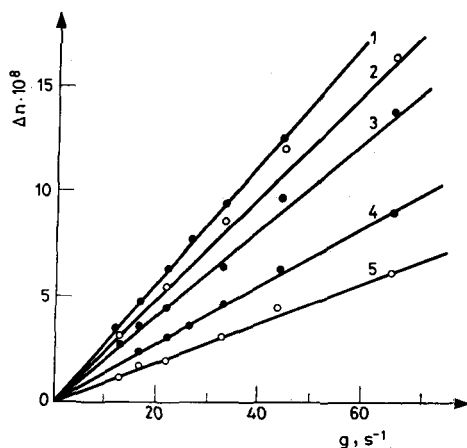
Fig. 3. Flow birefringence Δn of solutions of sample 4 of polyamidobenzimidazole in 97.8 % H_2SO_4 vs. flow rate gradient g; solution concentrations $c = 0.11$ (1), $c = 0.07$ (2), $c = 0.054$ (3), $c = 0.037$ (4) and $c = 0.016$ (5) g/dl
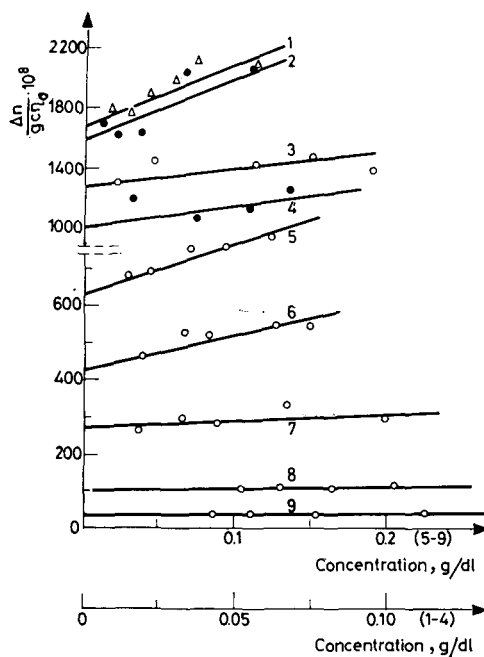

Fig. 4. Concentration dependence of reduced birefringence $\Delta n/gc\eta_0$ for products 1—9 of the hydrolysis of polyamidobenzimidazole in 97.8 % H_2SO_4

Table 3

Dynamooptical properties, measured in 97.8 % H_2SO_4 at 21°, of products of hydrolytic thermal degradation of polyamidobenzimidazole (series B)

Sample number	$M_{D\eta} \cdot 10^{-3}$, g/mol	$[\eta] \cdot 10^3$, $g^{-2}cm^4 s^2$	$[\eta]/[\eta] \cdot 10^{10}$, cm s²/g	$\dfrac{[\eta]}{[\eta]} \Big/ \Big(\dfrac{[\eta]}{[\eta]}\Big)_\infty$	$[\chi/g] \cdot 10^5$, s.	G
1	52	1700	360	1.06	10	0.425
2	47.5	1570	350	1.03	7	0.34
3	41.7	1280	345	1.01	4.4	0.296
4	39	1000	340	1.0	2.85	0.258
5	34	630	315	0.926	1.5	0.229
6	22.3	425	303	0.891	—	—
7	12	270	285	0.838	—	—
8	8	103	206	0.606	—	—
9	3.8	32.7	148	0.435	—	—

For the products of the PABI hydrolysis with intrinsic viscosities $[\eta] \geq 2 \cdot 10^2$ (i.e. at $M_{D\eta} \geq 3.4 \cdot 10^4$), the dependence of the orientation angle α with respect to the flow direction on the rate gradient g was measured (Fig. 5). Figure 6 shows the dependence of the value of $(\chi/g)_{g \to 0} = \left(\dfrac{45° - \alpha}{g}\right)_{g \to 0}$ on the solution concentration for the PABI investigated. The extrapolation of these dependences to zero solution concentration gives the values of the characteristic orientation angle $[\chi/g] = \lim\limits_{c \to 0} \lim\limits_{g \to 0} \left(\dfrac{45° - \alpha}{g}\right)$, also listed in Table 3. It should be noted that the solu-
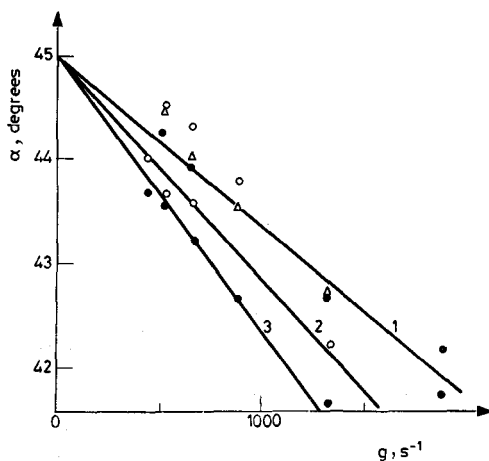

Fig. 5. Orientation angle α *vs.* rate gradient for solutions of degraded sample 4 in 97.8 % H_2SO_4; $c = 0.016$, 0.030 and 0.037 (1), $c = 0.054$ (2) and $c = 0.07$ (3) g/dl
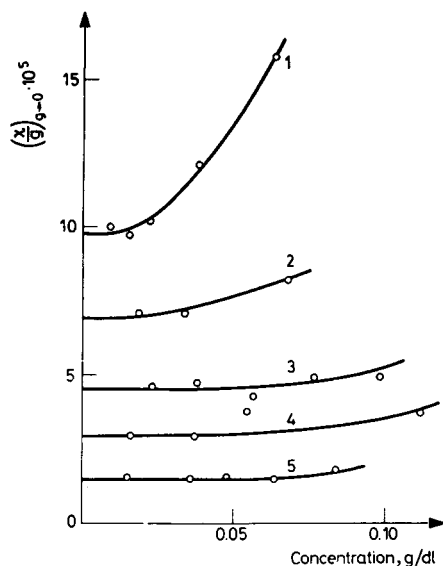
Fig. 6. Reduced orientation angle $(\chi/g)_{g \to 0}$ vs. solution concentration for degraded samples 1—5 of polyamidobenzimidazole

tions of the products of PABI hydrolysis in sulphuric acid are more coloured than those of undegraded PABI samples of the same M at the same concentration. Hence, it was possible to determine their $[\chi/g]$ values over a narrower range of $M_{D\eta}$ (for undegraded PABI fractions the orientation angles could be measured at the same parameters of the instrument used up to $M_{D\eta} \approx 10 \cdot 10^3$ [4]).

Discussion of results

Hydrodynamic properties

The molecular weight of the products of hydrolytic thermal degradation of PABI in sulphuric acid at 110° (series A) decreases very rapidly with time (Table 1). Although the refractive indices of the hydrolysis products in this series are close to that for the initial sample [2], their hydrodynamic properties differ somewhat from those of the undegraded fractions. This can be caused by the fact that, owing to the high rate of thermal degradation under these conditions, the duration of hydrolysis was low and comparable to the time required for the heating of the whole volume of the solution. Heterogeneous heating, in turn, should lead to an increase in the molecular inhomogeneity of the products of series A as compared to that of the initial sample.

An entirely different situation is observed after a prolonged exposure of PABI solutions to lower temperatures (series B). The change in the values of $[\eta]$, D and $M_{D\eta}$ for the products of hydrolysis of series B, obtained by a prolonged (200 hr) heating of PABI in sulphuric acid at various temperatures, is given in Table 2. Figure 7 shows a comparison of these hydrodynamic characteristics with those of the PABI samples investigated previously, for which the difference in M was achieved by varying the conditions of synthesis and by fractionation [3]. To within experimental error, the experimental points fall on the plot of the dependence of $\lg[\eta]$ on $\lg D$ obtained previously for undegraded fractions, and the value of the slope of this dependence is characteristic of rigid-chain polymers, with the equilib-
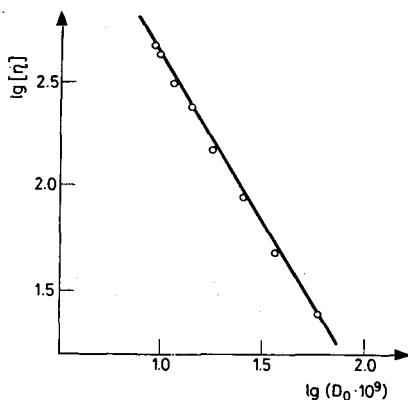

Fig. 7. Value of $\lg[\eta]$ vs. $\lg D_0$ for the products of hydrolysis of polyamidobenzimidazole in 97.8 % H_2SO_4, series B (points) and undegraded fractions [3] (full curve)
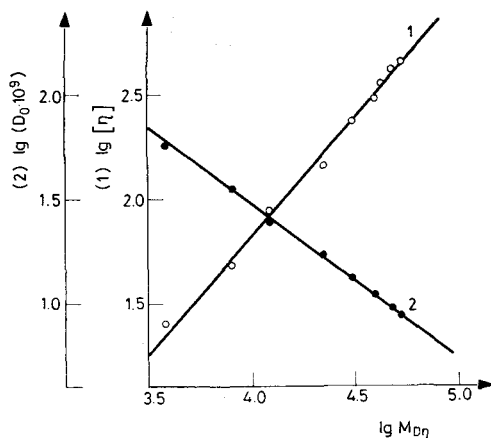

Fig. 8. Values of $\lg[\eta]$ (1) and $\lg D_0$ (2) vs. $\lg M_{D\eta}$ for the products of hydrolysis of poly-amidobenzimidazole in 97.8 % H_2SO_4

rium rigidity corresponding to that of PABI macromolecules (for the PABI molecules the length of the Kuhn segment is $A = 250$ Å according to hydrodynamic data [3], and $A = 500$ Å according to optical data [4]).

The dependences of $[\eta]$ and D on $M_{D\eta}$ are represented on the logarithmic scale (Fig. 8) by straight lines corresponding to the equations:

$$[\eta] = 1.7 \cdot 10^{-3} M_{D\eta}^{1.15}$$

$$D_0 = 2.7 \cdot 10^{-5} M_{D\eta}^{-0.74} .$$

The exponents in these equations are close to those obtained for the undegraded fractions [3] and are also characteristic of rigid-chain polymers. Hence, the comparison of the hydrodynamic properties of the undegraded fractions and the products of hydrolysis indicates that the elements of the chemical structure of PABI responsible for the high equilibrium rigidity of the PABI macromolecules remain invariable during hydrolysis.

Optical properties

The dependence of the reduced birefringence $[n]/[\eta]$ on the molecular weight is a characteristic feature of the solutions of rigid-chain polymers. The values of $[n]/[\eta]$ for the products of PABI hydrolysis in sulphuric acid of series B given in Table 3 also decrease markedly with M. This change in $[n]/[\eta]$ with M can be compared to the dependence obtained previously for the PABI fractions in sulphuric acid [4]. This comparison is made in Fig. 9, which also show the theoretical curve
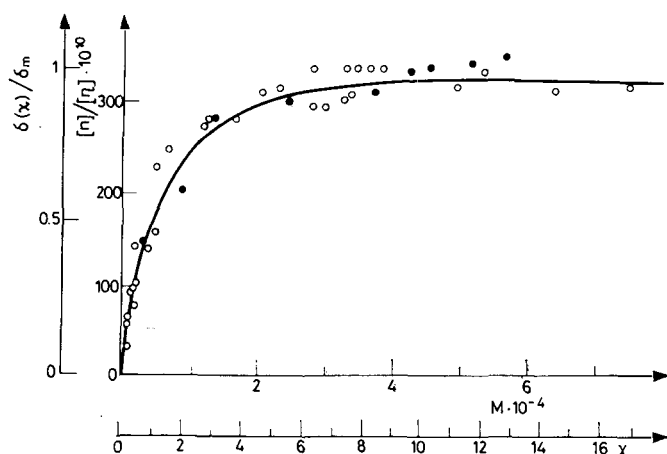

Fig. 9. Change in reduced birefringence $\dfrac{[n]}{[\eta]}$ with increasing M or length of the macromolecule, expressed as the number of persistent lengths $x = \dfrac{2M\lambda}{M_0 A}$, $\lambda = 17.7$ Å for ($\bullet$) products of hydrolysis and ($\circ$) undegraded fractions: theoretical curve $\delta(\chi)/\delta_m$ was plotted [6] at $\delta_m = 0.57$

of the changes in relative FB $\left(\dfrac{[n]}{[\eta]}\right)\Big/\left(\dfrac{[n]}{[\eta]}\right)_{\infty}$ [6] plotted at the experimental values of $([n]/[\eta])_{\infty} = 340 \cdot 10^{-10}$ $(([n]/[\eta])_{\infty}$, is the limiting FB at $M \to \infty)$, $\Delta a = 300 \cdot 10^{-25}$ and $A = 500$ Å, i.e. for the parameters of the PABI chain determined previously [4] for the PABI fractions by FB over a wide range of M. The fact that the
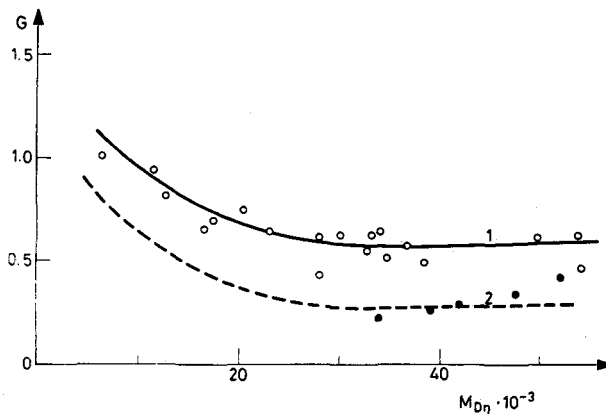

Fig. 10. Parameter G vs. molecular weight M_{D_η} of (1) undegraded fractions and (2) products of hydrolysis of polyamidobenzimidazole in 97.8% H_2SO_4

experimental points for the products of hydrolysis are concentrated near the curve plotted for the PABI fractions means that the conformations of the molecules of these products of hydrolysis and the PABI fractions are identical. Both these products and the PABI fractions are characterized by the same equilibrium rigidity and the same optical anisotropy of the monomer unit Δa. Hence, during the hydrolysis of PABI in sulphuric acid, optically anisotropic groups of the chain are not destroyed.

In the investigations of FB, the value of the characteristic orientation angle $[\chi/g]$ was determined. It is related to the M of the macromolecules by the equation [6 − 8]:

$$[\chi/g] = G\frac{M[\eta]\eta_0}{RT}$$

where G is the coefficient depending on the conformation and the rigidity of the macromolecules. Comparison of the values of $[\chi/g]$ for the products of hydrolysis and the undegraded PABI fractions in sulphuric acid at the same values of $[\eta]$ or M_{D_η} (Fig. 10) shows that for the products of hydrolysis the values of $[\chi/g]$ are lower. This difference may indicate that the polydispersity of these samples is different, since the value of $[\chi/g]$ is strongly dependent on the polydispersity [7, 9] and at low rate gradients is determined mainly by the presence of long macromole-

cules. In this case the lower values of $[\chi/g]$ for the products of hydrolysis would indicate that the longer macromolecules are more broken in the thermal degradation process.

Kinetics of PABI hydrolysis in 97.8% H_2SO_4

In hydrolysis occurring according to the laws of chance, the decrease in the moleclaru weight of the polymer with time is described by the equation [10]:

$$\frac{1}{M_w} = \frac{1}{M_w^0} + \frac{1}{M_0} kt \tag{1}$$

where M_w^0, M_w and M_0 are the molecular weights of the initial sample, the product of hydrolysis and the monomer unit of PABI, including two amide bonds, respectively (for PABI, $M_0 = 354.4\ d$), t is the degradation time and k is the degradation rate constant.

The initial PABI sample is characterized by low polydispersity [3], and therefore its weight-average molecular weight, M_w, is close to $M_{D\eta}$. The same conclusion for PPPT can be drawn from a comparison of the data in refs [11, 12]. This justifies the use of the hydrodynamic molecular weight $M_{D\eta}$ instead of M_w.

The linearity of the dependence of $1/M_{D\eta}$ on t in the hydrolysis of PABI in sulphuric acid (Fig. 11, curve 1) confirms the random character of the degradation of the macromolecule when the probability of breaking of the macromolecule is proportional to its length. This solution is of fundamental importance, since it predicts the decrease in the polydispersity of the products of hydrolysis with increasing degree of thermal degradation. In fact, if we consider simultaneous ther-
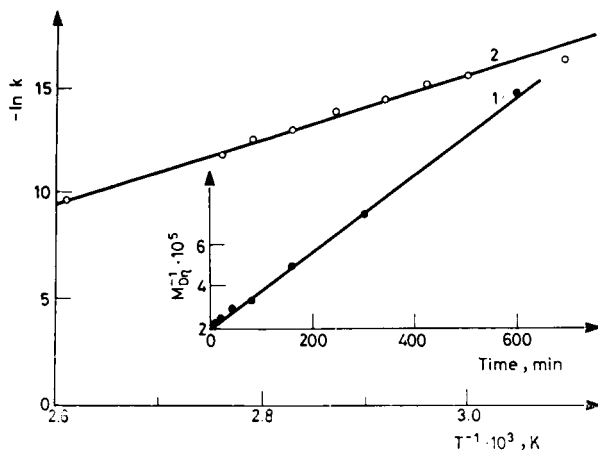

Fig. 11. (1) Decrease in molecular weight $M_{D\eta}$ of the macromolecules of polyamidobenzimidazole with time during hydrolysis in 97.8% H_2SO_4; and (2) degradation rate constant k vs. reciprocal temperature

mal degradation of the macromolecules of different initial molecular weights obeying Eq. (1) with $k \neq k(M)$, it is easy to obtain the equation for the relative dispersion of the weight molecular-weight distribution (MWD) $(\Delta M)^2/M_w^2$:

$$(\Delta M)^2/M_w^2 \simeq \frac{(\Delta M^0)^2}{(M_w^0)^2} \cdot \left(\frac{M_w}{M_w^0}\right)^2$$

where the symbol o refers to the values of the parameters in the initial state. Hence, when the law of probability of thermal degradation is obeyed, the relative dispersion $\left(\text{or, which is the same } \dfrac{M_z}{M_w} - 1\right)$ of the weight MWD approaching Gaussian distribution in type decreases as the square of the change in the molecular weight of the sample. In particular, for samples 2−5 in series B it can be assumed that their polydispersity parameter $\dfrac{M_z}{M_w} - 1$ gradually decreases by a factor of 1.2 to 3 as compared to the initial sample. This may be a reason of some difference in the optical and hydrodynamic characteristics between the products of hydrolysis and the undegraded PABI fractions.

The thermal degradation rate constant of PABI in H_2SO_4 at 110°, determined from the slope of straight line 1 in Fig. 11, is $k = 0.65 \cdot 10^{-4} \text{ min}^{-1}$ and is independent of M. The absence of the dependence of k on M has also been observed for PPPT [13], and the assumption of the probability character of the hydrolysis of polyamides in sulphuric acid was probably first reported in ref. [14].

The values of k at other temperatures were also calculated according to Eq. (1) (Table 2). The dependence of $-\ln k$ on $\dfrac{1}{T}$ (Fig. 11, curve 2) is a straight line. This shows that the chemical mechanism of breaking of the macromolecules along the length is energetically the same over the entire range of temperatures investigated (50−110°). The activation energy of this process, calculated from the slope of the Arrhenius dependence of $-\ln k$ on $\dfrac{1}{T}$, is $E = 134 \pm 4 \text{kJ/mole}$. This value coincides with the energy of breaking of the amide bond in low molecular weight amides in 92−100% H_2SO_4 [15] and is close to the energy ($E = 118 \pm 8 \text{ kJ/mole}$) of activation of the hydrolysis of PPPT in 96.5% H_2SO_4 over the temperature range from 36 to 103° [13]. Hence, the mechanism of thermal degradation of the macromolecules in concentrated sulphuric acid is the same for PABI and PPPT, and evidently consists in the breaking of the macromolecules at the amide bonds. This conclusion supports the suggestion that the phenomenon of hydrolytic degradation can be used to achieve a controlled decrease in the length of the polyamide macromolecules for analytical purposes (with the simultaneous decrease in the polydispersity of the polymer sample). The choice of the experimental conditions for the thermal degradation of PABI in 97.8% H_2SO_4, and in particular for the

decrease of its molecular weight from M_w^0 to M_w, is determined by the equation

$$M_w = M_w^0/[1 + 3.53 \cdot 10^{11} M_w^0 t \exp(-16.1 \cdot 10^3/T)]$$

where t is in min.

This method is of practical importance if it is born in mind that the fractionation of these polymers is difficult.

The rate of thermal degradation of PABI in concentrated sulphuric acid is strongly dependent on its concentration. Thus, in oleum at a H_2SO_4 concentration of 112.5%, PABI is noticeably degraded even at room temperature, the degradation rate constant k exceeding k in 97.8% H_2SO_4 by two-three orders of magnitude. At the same time, the activation energy of the thermal degradation of PABI in 112.5% oleum, calculated by the method described above, is approximately two-three times lower than in 97.8% H_2SO_4.

The foregoing description of the kinetics of the acid hydrolysis of polyamide at various temperatures, i.e. the determination of k and the activation energy of this process, is based on the possibility for the determination of the molecular weight of the products of hydrolysis. In this sense, the method for the determination of M from the intrinsic viscosities and diffusion coefficients of polyamides in sulphuric acid (which became possible after the development of the method of diffusion analysis [16]) permitted quantitative treatment of the thermal degradation data.

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Résumé — On a effectué l'analyse thermique de la dégradation du polyamidobenzimidazole en solutions 97.8% d'acide sulfurique pendant 0.2 à 200 h, à 20−110°. On s'est servi de méthodes hydrodynamiques et optiques et établi que les macromolécules dégradées montrent la même rigidité à l'équilibre et la même anisotropie optique par unité de longueur que les molécules non dégradées du polyamidobenzimidazole de divers poids moléculaires. La dégradation thermique procède selon une loi de probabilité. L'énergie d'activation de la dégradation, 134 kJ/mole, coïncide avec celle des amides à faibles poids moléculaires. Par conséquent, le mécanisme principal de la dégradation consiste en la rupture des macromolécules aux liaisons amides. Ce phénomène peut être appliqué en analyse, afin de réaliser une diminution contrôlée de la longueur des macromolécules. Dans de l'oléum à 112.5%, la dégradation s'effectue bien plus vite et l'énergie d'activation est plus faible d'un facteur 2 à 3.

Zusammenfassung — Die Thermoanalyse der Zersetzung von Polyamidobenzimidazol wurde in Lösungen von 97.8% Schwefelsäure während 0.2 bis 200 h bei 20 bis 110° durchgeführt. Hydrodynamische und optische Methoden wurden eingesetzt um festzustellen, daß die abgebauten Makromoleküle dieselbe Gleichgewichtsrigidität und optische Anisotropie der Längeneinheit aufweisen wie die nicht abgebauten Moleküle von Polyamidobenzimidazol verschiedenen Molekulargewichts. Die thermische Zersetzung verläuft nach dem Gesetz der Wahrscheinlichkeit. Die Aktivierungsenergie der Zersetzung, 134 kJ/mol, stimmt mit den der Amide niedrigen Molekulargewichts überein. Folglich besteht der Hauptmechanismus der Zersetzung in der Spaltung der Makromoleküle in den Amidbindungen. Dieses Phänomen kann für analytische Zwecke verwendet werden um eine gesteuerte Abnahme der Länge der Makromoleküle zu erzielen. In 112.5%igem Oleum verläuft die Zersetzung viel schneller und die Aktivierungsenergie ist um einen Faktor von 2 bis 3 niedriger.

Резюме — Выполнен термический анализ деструкции молекул полиамидбензимидазола в растворах в 97.8% серной кислоте в течение 0.2—200 часов при температурах 20—110°. Гидродинамическими и оптическими методами установлено, что деструктированные макромолекулы характеризуются той же равновесной жесткостью и оптической анизотропией единицы длины, что и недеструктированные молекулы полиамидбензимидазола различной молекулярной массы. Термодеструкция протекает по вероятностному закону. Энергия активации деструкции 134 кдж/моль совпадает со значением для низкомолекулярных амидов. Следовательно, основным механизмом деструкции является разрыв макромолекул по амидными связям. Явление это может быть использовано в аналитических целях для контролируемого уменьшения длины макромолекул. В 112.5% олеуме термодеструкция протекает много быстрее, а энергия активации примерно в два — три раза ниже.