

## **THERMAL DEGRADATION OF THE POLY(*m*-PHENYLENE OXADIAZOLE) MOLECULES IN SULPHURIC ACID**

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### **Abstract**

Translational diffusion of poly-2,5-(1,3-phenylene)-1,3,4-oxadiazole (PMOD) in solution in 96% sulphuric acid was studied, and intrinsic viscosity was measured at different stages of thermal degradation. Polymer solution has previously been subjected to heating at temperature ranging from 75 to 104°C and then investigated at 26°C. A monotonic decrease in intrinsic viscosity and the molecular mass,  $M$ , of degraded products with increasing degradation temperature was detected. The rate constant of the degradation process has been obtained from the change in  $M$  of the degradation products with time at a fixed solution temperature, and the activation energy of the process was calculated by using the temperature dependence of the rate constant. The activation energy ( $E=102\pm 8$  kJ mol<sup>-1</sup>) is close to that obtained previously for the hydrolysis of poly-2,5-(1,4-phenylene)-1,3,4-oxadiazole (PPOD) in sulphuric acid (106 kJ mol<sup>-1</sup>), the rate constant being approximately twice in the value.

**Keywords:** activation energy, hydrolytic thermal degradation, poly(*meta*-phenylene oxadiazole), rate constant

### **Introduction**

It has been proven previously, taking as an example poly(amidobenzimidazole) (PABI) [1], that hydrolytic degradation of the macromolecules in a dilute solution in conc. sulphuric acid may be understood as a random chain scission, and, for analytical purposes, the molecular mass,  $M$ , of the polymer can be reduced to the desired value by this procedure. Moreover, the products of the thermal degradation form a polymer-homologous series. This conclusion was based on the fact that after the degradation, the macromolecule contains without any changes the structural elements responsible for optical anisotropy of unit chain length and equilibrium rigidity of the macromolecule.

Investigations of the hydrodynamic and dynamooptical properties of PABI in solutions at different stages of the hydrolytic thermal degradation showed that the activation energy of this polyamide degradation ( $134 \text{ kJ mol}^{-1}$  [1]) is close to that for the low-molecular-mass amides [2]. The thermal degradation of different aromatic polyamides was found [3] to increase with the number of the amide groups in the backbone repeat chain unit. Therefore, it was concluded that these macromolecules are predominantly broken at the amide bonds.

The other conclusion was made for poly(naphthoyleimide benzimidazole) (PNIB), another heterocyclic polymer whose hydrolytic degradation in the same solvent is characterized by different activation energies, 50 at low and  $103 \text{ kJ mol}^{-1}$  at high temperature, respectively [4].

This work deals with the thermal degradation of the poly-2,5-(1,3-phenylene)-1,3,4-oxadiazole (PMOD) molecules in solution in 96% sulphuric acid. The aim of the present work is to quantitatively characterize the process by the hydrodynamic data in comparison with properties of other polymers, in particular, other polyoxadiazoles (POD).

## Experimental

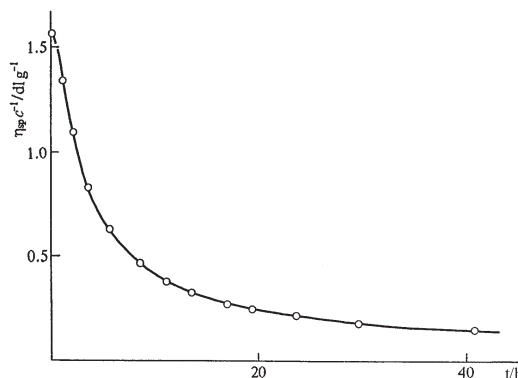
PMOD samples were obtained by a method described earlier [5]. Investigations of hydrodynamic properties and degradation were performed in 96%  $\text{H}_2\text{SO}_4$  as a solvent with a density  $\rho_0 = 1.830 \text{ g ml}^{-1}$ , viscosity  $\eta_0 = 0.184 \text{ g cm}^{-1} \text{ s}^{-1}$  at  $26^\circ\text{C}$  and a refractive index  $n_D = 1.4280$ . The solutions were usually prepared by stirring for 3 days at ambient temperature. The polymer mass concentration  $c$  in each solution was calculated from the mass fraction of the solute with solution density. Degradation was performed as follows. PMOD solution in 96%  $\text{H}_2\text{SO}_4$  at a concentration of  $1.99 \text{ g dl}^{-1}$  in sealed glass ampoules was kept in a thermostat at a selected and fixed temperature  $T$  ranging from  $75$  to  $104^\circ\text{C}$ . Temperature fluctuations did not exceed  $\pm 0.3^\circ\text{C}$ . The heating time of 100 h was sufficient to attain a random-type degradation process [1].

Viscosity was measured in an Ostwald capillary viscometer with solvent flow time of 58 s under the conditions of negligible kinetic-energy corrections. The intrinsic viscosity  $[\eta]$  was obtained by extrapolating the reduced viscosity  $\eta_{sp} c^{-1}$  to  $c=0$  in accordance with the Huggins equation  $\eta_{sp} c^{-1} = [\eta] + [\eta]^2 k_{HC} c$  where  $k_{HC}$  is the Huggins constant.

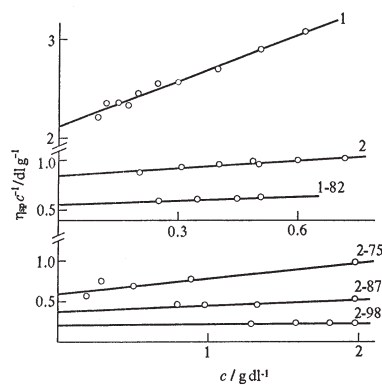
The free translational diffusion of PMOD molecules was investigated by the convection technique as described previously [5]. The dispersion  $\sigma^2$  of the distribution of macromolecules  $\partial c / \partial x$  with respect to the displacements  $x$  was calculated from the area  $Q$  and the maximum ordinate  $H$  of the interference curve using  $H a / Q = \Phi(a/8^{1/2} \sigma)$  where  $\Phi$  is the probability integral and  $a = 0.10 \text{ cm}$  is the spar beam splitting. The specific refractive index increment at  $26^\circ\text{C}$  and  $546 \text{ nm}$  was calculated from the  $Q$  values by the formula  $dn/dc = (\lambda/abh) Q/c$ , where  $\lambda$  is the light wavelength,  $h$  is optical pathlength,  $b$  is the distance between interference bands, and  $c$  is the solute concentration.

## Results and discussion

Figure 1 shows a typical dependence of reduced viscosity of solution  $\eta_{sp} c^{-1}$  on time obtained for PMOD solution in conc. sulphuric acid at high temperature. One can see a monotonous decreasing of  $\eta_{sp} c^{-1}$  with time which might be caused by degradation of the macromolecules. However, this is not a conclusive proof of the degradation phenomenon [6]. To find origins for this experimental observation, more detailed hydrodynamic investigations were performed: intrinsic viscosity  $[\eta]$  and diffusion coefficient  $D$  were measured for the polymer products obtained at different stages of the degradation. Results are presented in Figs 2 and 3.

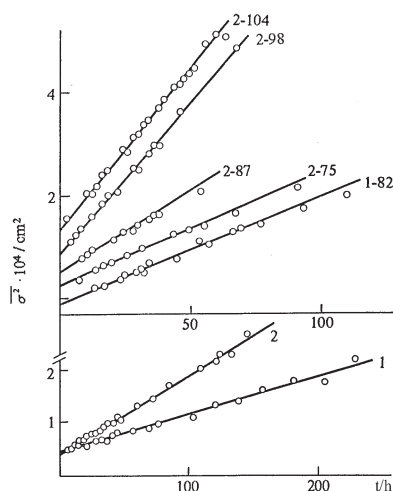


**Fig. 1** Reduced viscosity  $\eta_{sp} c^{-1}$  as measured at 26°C vs. time of the keeping of the PMOD sample No. 2 in solution in 96% sulphuric acid at 110°C. Solute concentration is 2.7 g dl<sup>-1</sup>. Solid curve connects smoothly the data points



**Fig. 2** Reduced viscosity  $\eta_{sp} c^{-1}$  vs. concentration of PMOD solution in 96% sulphuric acid at 26°C. Numbers on the curves correspond to product numbers in Table. Here and in Figs 3 and 4, the solid lines correspond to linear approximations

The dependences of  $\eta_{sp} c^{-1}$  on  $c$  (Fig. 2) were well approximated with straight lines with the intercept equal to  $[\eta]$ . Table 1 presents the  $[\eta]$  and  $k_H$  values calculated



**Fig. 3** Time dependence of dispersion  $\overline{\sigma^2}$  (second central moment) of the  $x$ -spectrum of the macromolecules in the region of the diffusion boundary in a sulphuric acid solution of PMOD at 26°C at solute concentration  $c=0.080 \text{ g dl}^{-1}$ . Numbers on the curves correspond to product numbers in Table

from these data. One can see that the  $[\eta]$  value is lower at higher temperature of the product treatment.

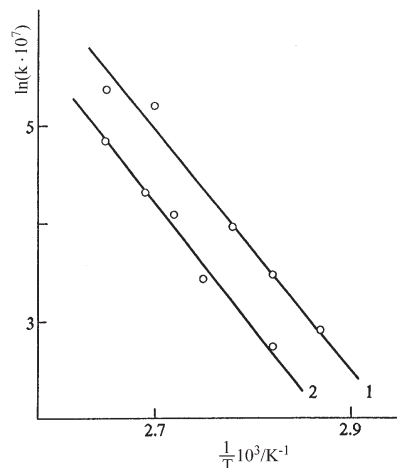
**Table 1** Hydrodynamic properties of undegraded PMOD samples and products of PMOD degradation in 96%  $\text{H}_2\text{SO}_4$

Products	$T_{\text{degr}}/^\circ\text{C}$	$[\eta] \cdot 10^{-2}/\text{ml g}^{-1}$	$k_H$	$D \cdot 10^7/\text{cm}^2 \text{ s}^{-1}$	$dn/dc/\text{ml g}^{-1}$	$M_{D_n} \cdot 10^{-3}/\text{ml mol}^{-1}$	$k \cdot 10^7/\text{min}^{-1}$
1 <sup>a</sup>	—	2.12	0.3	0.10	0.30	87	—
2 <sup>a</sup>	—	0.80	0.5	0.21	0.25	26	—
2-75	75	0.50	0.6	0.31	0.26	13	18
1-82	82	0.55	0.4	0.30	0.28	13	33
2-87	87	0.32	0.5	0.44	0.24	6.8	52
2-98	98	0.16	0.4	0.79	0.22	2.3	187
2-104	104	0.13	—	0.87	0.27	2.2	203

<sup>a</sup> Non-degraded initial PMOD samples

Simultaneously, the slope of the  $\overline{\sigma^2}$  vs. time plotted in Fig. 3 (proportional to the  $D$  value) grows with increasing the treatment temperature. The diffusion coefficient  $D$  was determined by  $D=(1/2)\partial\overline{\sigma^2}/\partial t$ . Results are collected in Table. Also given in Table are the increments of the refractive index, which have proven to be the same for the degradation products and for non-degraded PMOD samples.

The  $[\eta]$  and  $D$  values thus obtained were used to evaluate molecular mass of the product by  $M_{D_n}=100(A_0T/\eta_0)^3/[\eta]D^3$  where  $A_0$  is hydrodynamic parameter invariant



**Fig. 4** Rate constant of degradation vs. inverse temperature at the semilogarithmic scale for (points 1) PMOD and (points 2) PPOD in 96% sulphuric acid

to change in  $M$  [7]. The value  $A_0 = 3.5 \cdot 10^{-10} \text{ erg} \cdot \text{K}^{-1} \text{ mol}^{-1/3}$  was used [5]. The  $M$ -values are listed in Table. Molecular mass of the product is obviously decreasing from  $M_{in}$  to  $M$  in the course of thermal degradation. This effect was described in terms of degradation rate constant  $k$  calculated by the formula

$$P^{-1} - P_{in}^{-1} = (k/2)t$$

where  $P$  and  $P_{in}$  is the degree of polymerization of degradation product and initial PMOD sample, respectively, and  $t$  (in min) is the time of degradation. The above formula is derived assuming a random character of the degradation process, and a single site of potential chain breaking in a monomer unit of the chain.

The  $k$  value thus obtained was found to depend on the degradation temperature  $T$ . This was approximated by the Arrhenius relationship  $k = A \exp(-E/k_B T)$ , where  $A$  is a constant factor,  $k_B$  is the Boltzmann constant, and  $E$  is an activation energy of the macromolecule degradation. The experimental data showed a linear dependence of  $\ln k$  on the inverse temperature (Fig. 4). The slope of the dependence yields  $E = 102 \pm 8 \text{ kJ mol}^{-1}$  which is close to the  $106 \text{ kJ mol}^{-1}$  value obtained earlier for poly(*para*-phenylene oxadiazole) (PPOD) [6]. The obvious coincidence may indicate a common chemical mechanism of the hydrolytic thermal degradation of the macromolecules of both *para*- and *meta*-derivatives of POD in sulphuric acid solution observed at high temperatures.

On the other hand, curve 1 in Fig. 4 is situated higher than curve 2. Hence, the numerical value of  $k$  is found to be higher (approximately two times) for PMOD, i.e., rate of hydrolytic thermal degradation of the PMOD molecules in solution in 96%  $\text{H}_2\text{SO}_4$  is twice the PPOD molecules at the same value of the activation energy. Additional investigations are required to find possible origins for the effect.

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