

DYNAMIC BIREFRINGENCE IN SOLUTIONS OF POLY(NAPHTHOYLENEIMIDE BENZIMIDAZOLE) IN DIFFERENT STAGES OF HYDROLYTIC THERMAL DEGRADATION

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Abstract

Flow birefringence (FB) has been investigated in solutions of products of hydrolytic degradation of poly(naphthoyleneimide benzimidazole) (PNIB) in 96% sulphuric acid PNIB solutions have previously been subjected to heating at various temperatures from 65 to 120°C and then investigated at 22°C by FB and viscometry. A monotonic decrease in intrinsic viscosity and the molecular weight M of thermal degradation products with increasing degradation temperature was detected. At the same time, the shear optical coefficients in a series of products with decreasing M first increases and then, at treatment temperatures exceeding 90°C, decreases with decreasing $[\eta]$ in accordance with decreasing M of the product. Possible reasons for the detected anomaly have been discussed.

Keywords: hydrolytic thermal degradation, poly(naphthoyleneimide benzimidazole)

Introduction

It has been proven previously for poly(amide benzimidazole) (PABI) [1] that for analytical purposes the M of the polymer can be reduced to the desired value by the hydrolytic degradation of the macromolecules in a sulphuric acid solution. Moreover the products of this thermal degradation form a polymer – homologous series. This conclusion was based on the fact that after this degradation, the macromolecule still contains both the structural elements responsible for the optical anisotropy of unit chain length and the equilibrium rigidity of the macromolecule.

In order to check the applicability of this method of M control to other polymers, in the present work flow birefringence (FB) in sulphuric acid solutions of another heterocyclic polymer, poly(naphthoyleneimide benzimidazole) (PNIB) was investigated in different stages of its hydrolytic thermal degradation. The

results were compared with the properties of samples which did not undergo any thermal treatment. A previous investigation of PNIB by FB in sulphuric acid solutions has led to the establishment of its optical characteristics [2]. PNIB samples with different intrinsic viscosities $[\eta]$ from 0.7 to 12.0 dl/g in [2] were obtained by varying the conditions of synthesis. It was not possible to prepare a polymer – homologous PNIB series by fractionation because PNIB is soluble only in concentrated H_2SO_4 . PNIB solutions in this acid are molecularly disperse and stable: their properties do not change for a long time (not less than a year) at room temperature [3].

Experimental

PNIB based on a dianhydrid of 1,4,5,8-naphtalenetetracarboxylic acid and 5-amino-2(*p*-aminophenyl)benzimidazole was obtained by a published method [3], washed, and vacuum – dried to constant weight. After 2 days 96% H_2SO_4 was poured on the high molecular weight PNIB sample. PNIB solution in

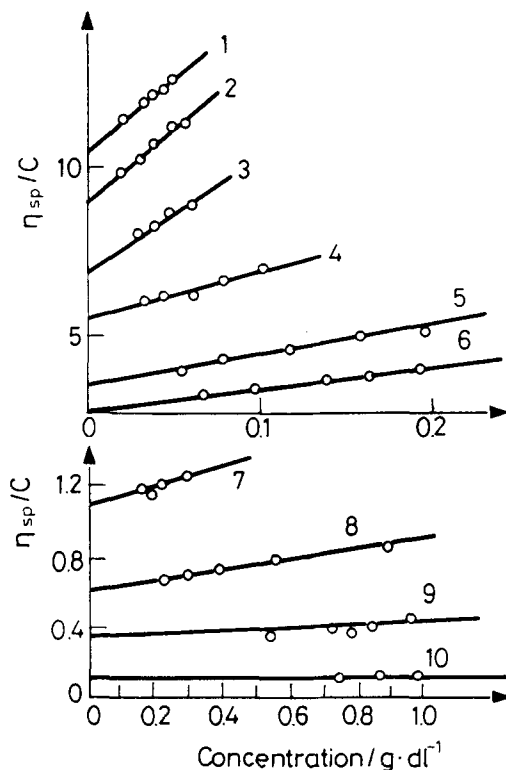


Fig. 1 Dependence of η_{sp}/c on concentration for PNIB solutions in 96% sulphuric acid. Numbers on the curves correspond to product numbers in Table 1

Table 1 Dynamooptical properties of products of PNIB degradation in 96% H₂SO₄

Products	T _{deg} /°C	[η]·10 ⁻² ml·g ⁻¹	k _H	[η]·10 ¹⁰ g ⁻² ·cm ⁴ ·s ²	[η]/[η]·10 ¹⁰ g ⁻¹ ·cm ² ·s ²	[χ/g]·10 ⁵ rad·s	M _w /10 ⁻³ (±20%)
1	initial	10.9±0.1	0.45	4400±300	400	76±10	140
2	65	9.0±0.1	0.50	4100±200	460	51±2	110
3	75	7.1±0.1	0.60	3600±200	500	40±2	110
4	82	5.2±0.1	0.40	2130±60	390	22±5	85
5	85	3.5±0.1	0.70	1890±100	540	6±2	34
6	90	2.9±0.1	0.60	1370±50	490	10±2	69
7	100	1.1±0.1	0.50	450±70	410	—	—
8	105	0.63±0.02	0.70	215±4	340	—	—
9	110	0.32±0.05	0.70	71±3	200	—	—
10	120	0.10±0.05	—	11.8±0.8	110	—	—

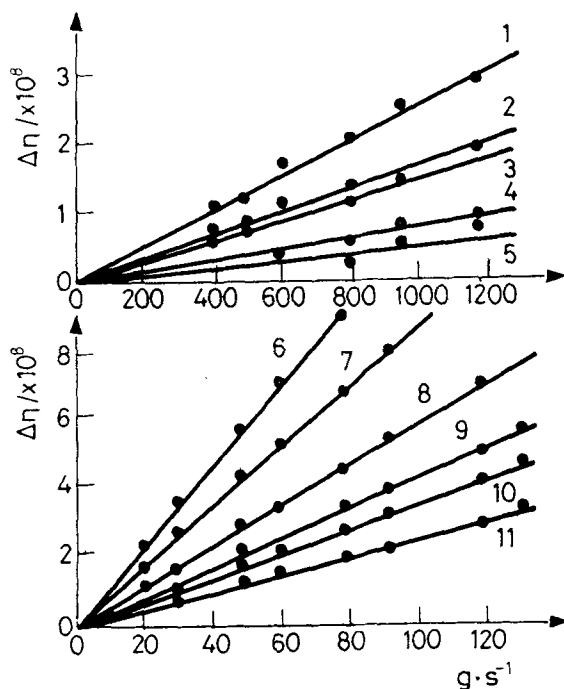


Fig. 2 Dependence of FB on flow rate gradient g for product No. 10 (curve 1–5) and product No. 4 (curve 6–11), solution concentration c (g/dl) are as follows: 0.0924(1); 0.0597(2); 0.0502(3); 0.0352(4); 0.0203(5); 0.0262(6); 0.0201(7); 0.0130(8); 0.0100(9); 0.0078(10); 0.0060(11)

96% H_2SO_4 at a concentration of 0.987 g/dl in sealed glass ampoules was kept in a thermostat at a selected and fixed temperature in the T range from 65 to 120°C. Temperature fluctuations did not exceed $\pm 0.3^\circ\text{C}$. The heating time of 100 h was sufficient to establish the equilibrium state [1].

The solvent used was 96% H_2SO_4 with a density $\rho_0 = 1.838$ g/ml, viscosity $\eta_0 = 0.2026$ g/cm s at 22°C and a refractive index $n_D = 1.4280$. Viscosity was measured in an Ostwald capillary viscometer with solvent flow time of 130 s under the conditions of negligible gradient dependence. The value of intrinsic viscosity $[\eta]$ was obtained by extrapolation of reduced viscosity to $c = 0$. The dependences of η_{sp}/c on c are shown in Fig. 1, and the values of $[\eta]$ and the Huggins constant are given in Table 1.

FB was investigated in a teflon dynamometer with an inner rotor, the rotor height was 6.0 cm, and the gap between the stator and rotor was 0.055 cm. A visual optical recording system [4] was used with a compensator $0.0323 \times \lambda$ where λ is the wavelength of the light source $\lambda = 532$ nm.

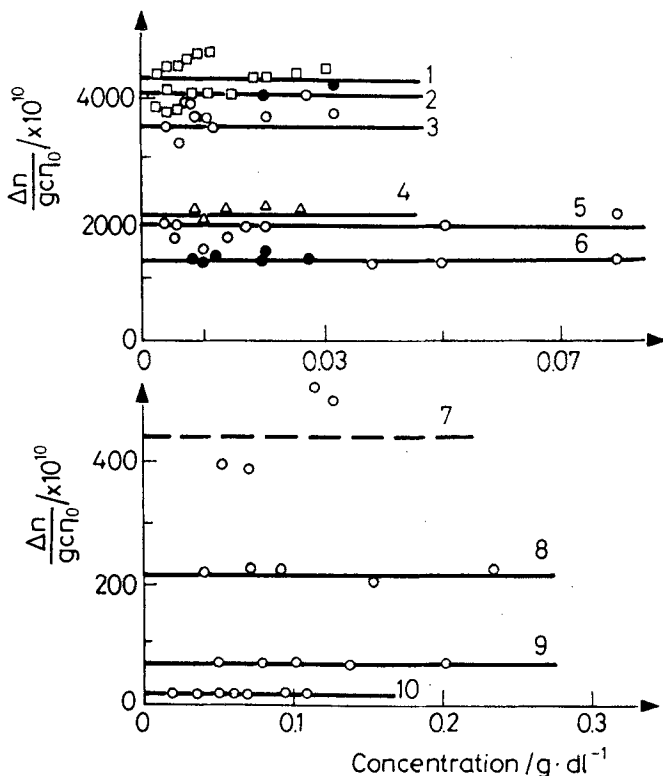


Fig. 3 Dependence of $\Delta n/gc\eta_0$ on solution concentration c . Numbers on the curves correspond to product numbers in Table 1

Results and discussion

FB observed in a PNIB solution in 96% H_2SO_4 is positive in sign, which corresponds to the high polarizability of the PNIB molecule in the direction of its geometrical axis, which is due to the cyclic structure of the main chain. In the investigated gradient range of flow rate g from 20 to 1000 s, the value of FB, increases proportionally to g (Fig. 2). For all degradation products of the initial sample, Fig. 3 shows the dependences of $\Delta n/gc\eta_0$ on solution concentration, which were used to calculate intrinsic birefringence

$$[n] = \lim_{c \rightarrow 0} \lim_{g \rightarrow 0} (\Delta n/gc\eta_0).$$

The values of shear optical coefficient $[n]/[\eta]$ are listed in Table 1.

For PNIB samples with $[\eta] > 2.9$ dl/g, the orientation angles of the optical axis of the solution were measured, and their dependence on g was investigated

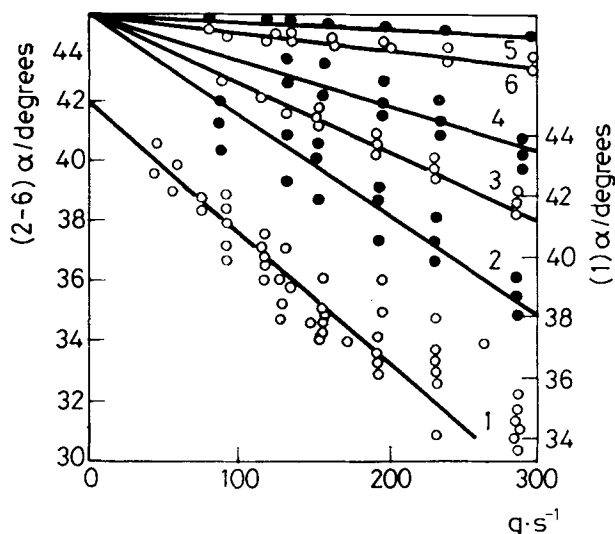


Fig. 4 Orientation angles α as a function of rate gradient g for products obtained by the method of thermal degradation in solutions in 96% sulphuric acid (numbers on the curves correspond to product numbers in Table 1) at the following concentrations c (g/dl): 1 - from 0.004 to 0.03; 2 - from 0.01 to 0.031; 3 - from 0.011 to 0.031; 4 - from 0.013 to 0.026; 5 - from 0.08 to 0.1; 6 - 0.08

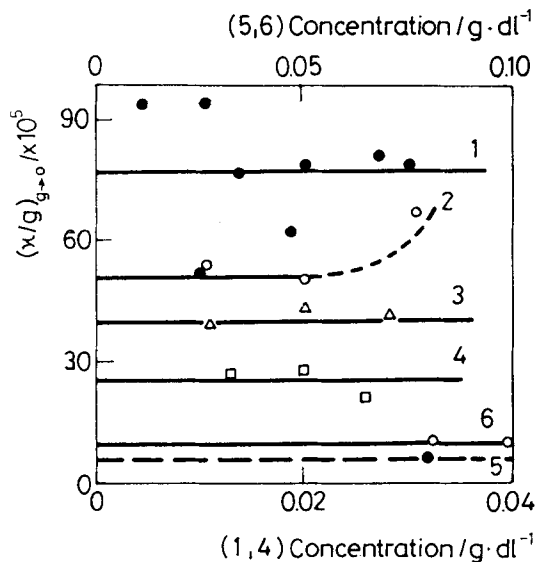


Fig. 5 Dependence of χ/g at $g \rightarrow 0$ on concentration for various PNIB degradation products in sulphuric acid. Numbers on near the curves correspond to product numbers in Table 1

(Fig. 4). The experimental points virtually fall on the straight lines having the ordinate intercept 45° , which shows that the solutions are of the molecular type and made it possible to determine the initial slopes of χ/g at $g \rightarrow 0$ for the curves of the dependence of χ on g . In this case, concentrations were attained at which the angle was virtually independent of solution concentration (Fig. 5). Hence, it was possible to determine the intrinsic orientation of FB

$$[\chi/g] = \lim_{c \rightarrow 0} \lim_{g \rightarrow 0} (\chi/g).$$

Its values are also given in Table 1.

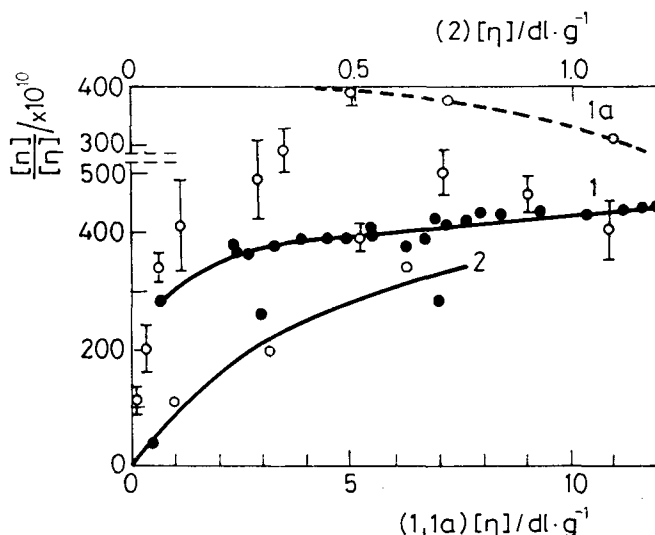


Fig. 6 Shear optical coefficient $[\eta]/[\eta]$ vs. intrinsic viscosity for solutions of the PNIB degradation products in 96% sulphuric acid (open circles the 'whiskers' at which correspond to experimental error). Filled circles represent the data of Pogodina *et al.* [2] for undegraded PNIB products. Curve 2 is the singled out range of low M

The character of experimental dependences shown in Figs 1–5 does not differ qualitatively from that observed previously [2] for undegraded PNIB samples. Therefore, it is possible to pass to quantitative data processing.

The data in Table 1 show that with increasing degradation temperature the $[\eta]$ value of the product decreases. Is it due to decreasing M of the product? To answer this question, the relationship between intrinsic orientation $[\chi/g]$ and M [4] was used:

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

Using the value of the coefficient $G=0.6$ [5] M were calculated for products 1–6 for which $[\chi/g]$ could be evaluated (Table I). It is clear that a decrease in the $[\eta]$ value of the product from 10.9 to 2.9 dl/g is accompanied by a monotonic decrease in M_{ν_g} from $140 \cdot 10^3$ to about $50 \cdot 10^3$. This relationship is similar to that which has been observed for PABI [1].

However, it follows from Table 1 that in the same series of products, the shear optical coefficient $[n]/[\eta]$ does not decrease but exhibits a tendency to increase. In Fig. 6 $[n]/[\eta]$ is shown as a function of $[\eta]$ for products of hydrolytic thermal degradation (circles) and undergraded PNIB samples investigated previously [2] (full curves 1 and 2). It is clear that with decreasing $[\eta]$ (approximately to the value of 4 dl/g), the shear optical coefficient of the product exhibits an anomalous tendency to increase, which is higher than the experimental error (deviation of points upwards from curve 1 in Fig. 6). To check the tendency, one more series of experiments was performed using experimental technique (data 1a in Fig. 6). It is clear that discussed tendency is confirmed by these data. Only in the further stages of thermal degradation, a characteristic decrease in $[n]/[\eta]$ is observed with decreasing $[\eta]$ (coincidence of filled circles with curve 2 in Fig. 6).

This nonmonotonic change in the shear optical coefficient with a change in $[\eta]$ differs profoundly from the properties of PABI for which the FB data coincided for the undergraded samples and the products of hydrolytic degradation [1]. This should be explained and this explanation will provide an answer to the question what decrease in M may be accompanied by an increase in $[n]/[\eta]$. It may be assumed that this anomaly indicates that this series of products of PNIB thermal degradation in a sulphuric acid solution is not a polymer-homologous series, and PNIB hydrolysis in sulphuric acid is accompanied by a change in the structural inhomogeneity of the sample.

In the gaussian range of lengths of the macromolecules, the $[n]/[\eta]$ ratio is determined by the optical anisotropy of the segment [4]. Hence, the increase in $[n]/[\eta]$ in this M range (for solutions of the molecular type) implies an increase in either the segment length or the optical anisotropy of unit length of the macromolecule. The above suggestion is equivalent, therefore, it leads to the conclusion that at low temperature degradation in H_2SO_4 (monitored from a decrease in $[\eta]$), the decrease in M is accompanied by the formation (or an increase in the fraction of) optically more anisotropic structures. At higher degradation temperatures, the decrease in $[n]$ and $[n]/[\eta]$ reflects a decrease in M as a result of the degradation of the backbone of the macromolecule. To obtain more definite conclusions, additional investigations are required.

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Zusammenfassung — In Lösungen der Produkte des hydrolytischen Abbaus von Poly(naphthoylenimid-benzimidazol) (PNIB) in 96%-igen Schwefelsäurelösungen, die zuvor auf verschiedene Temperaturen zwischen 65 und 120°C erhitzt wurden, wurde anschließend die Strömungsdoppelbrechung (FB) und die Viskosität untersucht. Mit zunehmender Abbautemperatur konnte ein monotoner Rückgang der Grenzviskosität und des Molekulgewichtes M der thermischen Abbauprodukte beobachtet werden. Gleichzeitig nehmen jedoch die optischen Scheidungskoeffizienten in einer Reihe von Produkten mit steigendem M zuerst zu und sinken dann bei Behandlungstemperaturen über 90°C mit abnehmender $[\eta]$ in Übereinstimmung mit sinkendem M des Produktes wieder ab. Mögliche Gründe für diese Anomalie wurden ebenfalls diskutiert.