

# Hydrolytic Thermal Degradation of Poly(Naphthoyleneimide Benzimidazole) in Concentrated Sulfuric Acid

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## SYNOPSIS

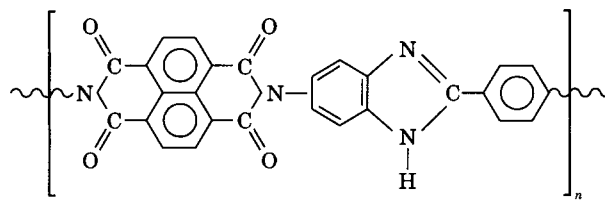
Translational diffusion in 96% H<sub>2</sub>SO<sub>4</sub> and intrinsic viscosity of poly(naphthoyleneimide benzimidazole) (PNIB) have been investigated in different stages of its degradation in solution in the temperature range from 65 to 120°C. The degradation rate constant *k* has been determined from the change in molecular weight *M* of degraded products with time at the fixed temperature of solution. The activation energy of the process *E* was calculated from the temperature dependence of *k*. The difference in *E* values at low and high temperatures was found. At degradation temperatures above 90°C, the activation energy of hydrolysis was obtained as *E* = 133 kJ/mol, which coincides with that of aromatic polyamides in sulfuric acid. The data obtained are compared with the results of the investigations of optical properties of products of PNIB degradation in solution and PNIB stability in the solid state. An explanation of anomalies observed during PNIB degradation at low temperatures is suggested. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The degradation of the macromolecules in solution in concentrated sulfuric acid at abnormally high temperatures is common for many aromatic polyamides and heterocyclic polymers.<sup>1</sup> It was shown, for example, that hydrolytic thermal degradation of poly(amide benzimidazole) (PABI) molecules in 97.8% H<sub>2</sub>SO<sub>4</sub> proceeds<sup>2</sup> according to the probability law and consists in the breaking of the chains at the amide bonds with the retention of the chemical structure elements responsible for short-range interaction in the PABI molecule and for the optical anisotropy of unit length. For this reason, it was concluded that degradation products (obtained in different stages of hydrolysis) represent a polymer-homological series, and this phenomenon can be used for analytical purposes to achieve a controlled decrease in the length of the macromolecules.

This work deals with an analogous investigation of hydrolytic thermal degradation of poly(naphthoyleneimide benzimidazole) (PNIB) in

sulfuric acid solution. This polymer is a new polyheteroarylene with unique mechanical, thermal, and thermooxydative characteristics.<sup>3,4</sup> The chemical structure of the monomer unit is shown below.



PNIB thermal degradation products were investigated by hydrodynamic methods, and the results obtained were used for the quantitative description of the process.

## EXPERIMENTAL

The PNIB sample was synthesized by a published method.<sup>5</sup> The intrinsic viscosity of the sample was  $[\eta] = 10.9$  dL/g. The one initial PNIB solution used for all investigations in 96% H<sub>2</sub>SO<sub>4</sub> at a concentration 0.987 g/dL was prepared at room temperature for 10 days with stirring. The solution was placed

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in sealed glass ampoules. Degradation was carried out by thermostating the ampoule for 100 h at a fixed temperature  $T$  in the range from 65 to 120°C.

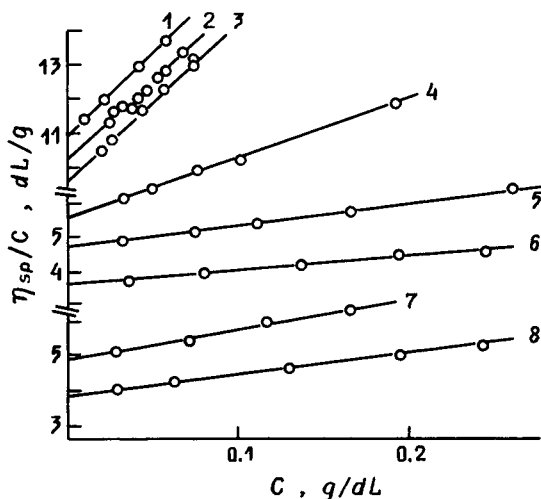
The solvent used was 96%  $H_2SO_4$  with the following characteristics at 30°C: density 1.8255 g/mL, viscosity 0.1649 g/cm s, and refractive index  $n_D = 1.4373$ .

PNIB degradation products were investigated by translational diffusion and viscometry. The methods of investigations and procedures for the determination of  $[\eta]$ , diffusion coefficient  $D$ , and refractive index increment  $dn/dc$  were the same as used previously.<sup>6</sup>

## RESULTS AND DISCUSSION

### Stability of PNIB Solution in 96% $H_2SO_4$ at Room Temperature

PNIB samples in sulfuric acid solution are highly stable for a long period of time when stored (in sealed ampoules) at room temperature. Figure 1 (curves 1–3) demonstrates the dependencies of reduced viscosity  $\eta_{sp}/c$  on concentration  $c$  obtained for the same initial PNIB sample in 96%  $H_2SO_4$  at 30°C after different time intervals from solution preparation. Figure 1 shows that these dependencies are linear,



**Figure 1** Reduced viscosity  $\eta_{sp}/c$  vs. concentration of PNIB solution in 96%  $H_2SO_4$  at 30°C: (1–3) initial sample after storage in a sulfuric acid solution at room temperature for (1) 50, (2) 1200, and (3) 2000 days; (4–6) initial sample after (4) one, (5) two, and (6) three precipitations into ice water; (7–8) the same for a PABI sample in 96%  $H_2SO_4$  before (7) and after (8) one precipitation from sulfuric acid solution into ice water.

and the intercepts with the ordinate give intrinsic viscosity values which are listed below together with Huggin's constants  $k_H$ .

Storage time, days	50	300	1200	2000
$[\eta]$ , dL/g	10.9	10.9	10.2	9.6
$k_H$	0.42	0.43	0.45	0.51

One can see that after 5.5 years of storage under the conditions described above,  $[\eta]$  decreases only by 13%, which corresponds to a decrease in the molecular weight  $M$  of the polymer approximately by a quarter, the  $k_H$  values remaining reasonable.

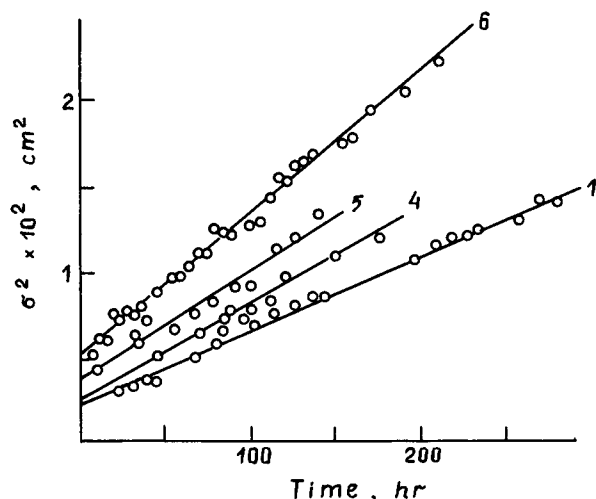
The degradation process of PNIB accelerates noticeably with increasing  $T$ , and at 110°C in 97.8%  $H_2SO_4$  as shown previously,<sup>6</sup> the reduced viscosity of the PNIB solution decreases with time at a rate comparable with that of PABI, i.e., PNIB degrades similarly to PABI under these conditions. The measurements of  $[\eta]$  and  $D$  for degraded products were carried out for the quantitative description of PNIB degradation in solution in 96%  $H_2SO_4$  without extracting the products from sulfuric acid solution because extraction involved the following difficulties.

### Precipitation of the PNIB Sample

It is known that the extraction of the polymer from sulfuric acid solution is accompanied by an additional (and hardly controlled) decrease in  $M$ . This procedure for PNIB was carried out quantitatively as follows.

The initial PNIB solution was poured slowly into ice water with stirring to avoid the overheating of the mixture. The precipitated polymer in a gel form was washed with water controlling the pH of the media, then with alcohol, and vacuum-dried at room temperature to constant weight. Precipitation was carried out one, two, and three times. The resulting dry polymer was dissolved in 96%  $H_2SO_4$  and investigated. Figure 1 shows the results of viscometric measurements of the initial sample (curve 1) and of the samples precipitated one, two, and three times (curves 4–6). The dependencies of  $\eta_{sp}/c$  on  $c$  in Figure 1 are linear, and the ordinate intercept (the value of  $[\eta]$ ) decreases with the numbers of precipitations, the  $k_H$  values remaining reasonable.

The data obtained coincide with the diffusion investigations of the same PNIB solutions (Fig. 2). The slope of the time dependency of the dispersion  $\sigma^2$  of the diffusion curve increases with the number of precipitations. This means that the diffusion coefficient  $D$  related to  $\sigma^2$  by the equation  $\sigma^2 = 2Dt$  in-



**Figure 2** Time dependence of dispersion of diffusion boundary in 96%  $\text{H}_2\text{SO}_4$  at  $30^\circ\text{C}$  for the initial PNIB sample (1) before and after (4) one, (5) two, and (6) three precipitations from sulfuric acid solution into ice water.

creases. This increase in  $D$  agrees with decrease in  $[\eta]$ , thus indicating that  $M$  decreases during precipitation. The  $M$  value was calculated from the equation

$$M_{D\eta} = (A_0 T / D \eta_0)^3 / [\eta]$$

using the value of  $A_0 = 3.55 \times 10^{-10}$  erg  $\text{K}^{-1}$   $\text{mol}^{-1/3}$ .<sup>7</sup> The values of  $M_{D\eta}$  are listed in Table I. It can also be seen from Table I that the value of refractive index increment  $dn/dc$  does not change, i.e., the refractive index of the polymer remains the same during precipitation.

The well-known fact of a decrease in  $M$  during polymer precipitation from sulfuric acid solution is attributed to the hydrolysis of the macromolecules with local overheating. However, the quantitative characteristics of this effect are absent in the literature. Therefore, the observed effect for PNIB was compared with that of PABI.

The PABI sample No. 6 (Ref. 7) was dissolved in 96%  $\text{H}_2\text{SO}_4$  and precipitated from a solution at a concentration  $c = 0.5$  g/dL by the procedure described above for PNIB. After the first precipitation, the  $[\eta]$  value of PABI dropped from 4.83 to 3.75 dL/g (curves 7 and 8 in Fig. 1), i.e., this effect was close to that for PNIB after the third precipitation.

The data on the change in  $[\eta]$  during precipitation may be of interest not only from the analytical point of view but also for determining the change in  $M$  during fiber spinning from the sulfuric acid solution in the precipitation bath. It is clear from Table I that each precipitation of PNIB from 96%  $\text{H}_2\text{SO}_4$  into water is accompanied by a 10–30% decrease in  $M$ . However, when the initial molecular weight is high, this effect does not influence noticeably the physico-mechanical properties of the fibers. Moreover, the process of fiber spinning is carried out under milder conditions (60–65%  $\text{H}_2\text{SO}_4$ ).

Nevertheless, it is clear from the above data and considerations that the procedure of hydrolysis products precipitation is undesirable for the quantitative description of molecular degradation, and its dependence on the treatment temperature and, therefore, was not used in this work.

#### Thermal Degradation of PNIB in 96% $\text{H}_2\text{SO}_4$

Degradation was investigated at heating temperatures from 65 to  $120^\circ\text{C}$ . The results of viscometric and diffusion investigations of the degraded PNIB products are shown in Figures 3 and 4 and are listed in Table II. The degradation of the PNIB macromolecules in 96%  $\text{H}_2\text{SO}_4$  was described by the equation<sup>8</sup>

$$1/P_w = (1/P_w^0) + (\frac{1}{2})kt \quad (1)$$

where  $P_w^0$  and  $P_w$  are the weight-average degrees of polymerization of the initial sample and the degraded product,  $t$  is the degradation time, and  $k$  is the degradation rate constant. It is assumed in this

**Table I** Change in Hydrodynamic Properties and Molecular Weight during Precipitation of PNIB to Ice Water from Solution in 96%  $\text{H}_2\text{SO}_4$

Solution	$[\eta]$ (dL/g)	$k_H$	$D \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$dn/dc$ ( $\text{cm}^3/\text{g}$ )	$M_{D\eta} \times 10^{-3}$
Initial solution	10.9	0.45	0.064	0.27	97
Solution after 1 precipitation	5.5	0.60	0.084	0.23	85
After 2 precipitations	4.6	0.33	0.090	0.20	76
After 3 precipitations	3.55	0.32	0.116	0.19	50

**Table II Hydrodynamic Properties of the Hydrolytic Thermal Destruction PNIB Products in Solutions in 96% H<sub>2</sub>SO<sub>4</sub> at 30°C**

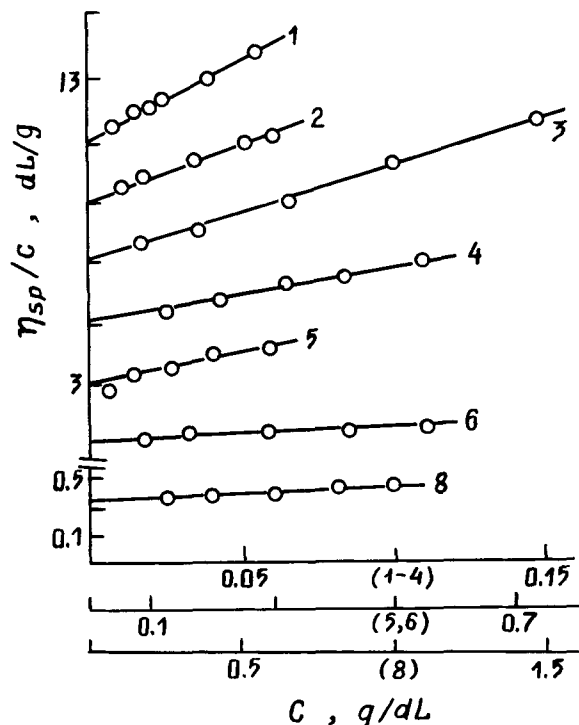
No.	<i>T</i> (°C)	[ $\eta$ ] (dL/g)	<i>k<sub>H</sub></i>	<i>D</i> × 10 <sup>7</sup> (cm <sup>2</sup> /s)	<i>dn/dc</i> (mL/g)	<i>M<sub>D<math>\eta</math></sub></i> × 10 <sup>-3</sup>
1	30	10.9	0.45	0.064	0.27	97
2	65	9.0	0.44	0.079	0.27	62
3	75	7.1	0.59	0.090	0.23	54
4	82	5.2	0.40	0.105	0.25	46
5	90	2.9	0.54	0.147	0.27	30
6	100	1.1	0.50	0.270	0.21	13
7	105	0.63	0.70	0.375	0.31	8.4
8	110	0.32	0.68	0.550	0.24	5.2
9	120	0.10	—	1.310	0.25	1.2

equation that the degradation of the macromolecules proceeding by breaking the bonds of the main chain is of random character. This was achieved by a sufficiently long (*t* = 100 h) heating of the solution in ampoule at a fixed *T*. Taking into account that PNIB was synthesized by polycondensation (just as PABI) and, therefore, was characterized by low polydispersity, it was assumed that its weight-average mo-

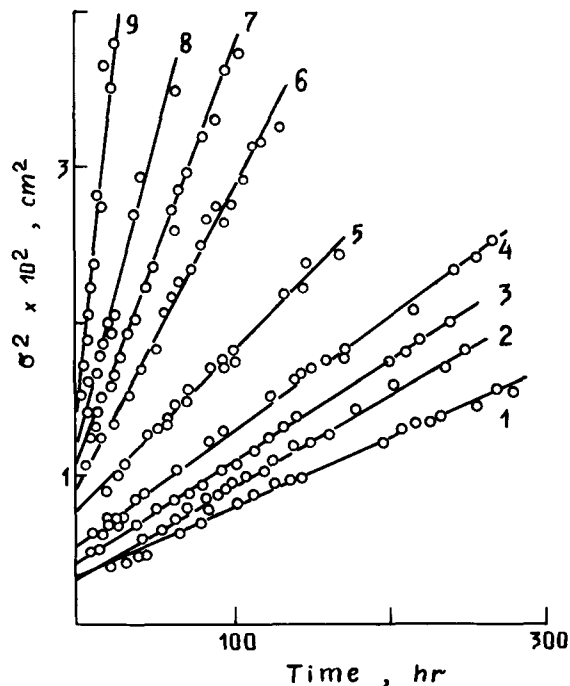
lecular weight *M<sub>w</sub>* is close to *M<sub>D $\eta$</sub>* . Thus, *P<sub>w</sub>* was calculated as the *M<sub>D $\eta$</sub>* /*M<sub>0</sub>* ratio where *M<sub>0</sub>* is the mass of the PNIB monomer unit, *M<sub>0</sub>* = 457.5. Using the *M* values of the initial sample and degraded product obtained at the temperature *T*, the *k* value was calculated according to Eq. (1).

The change in *k* with *T* was described by the Arrhenius' equation:

$$k = A \exp(-E/k_B T) \tag{2}$$



**Figure 3** Reduced viscosity  $\eta_{sp}/c$  at 30°C vs. concentration for the products of PNIB thermal degradation (numbers at the curves correspond to numbers of products in Table II).



**Figure 4** Change in dispersion  $\sigma^2$  of the diffusion curve with time at 30°C for the products of PNIB thermal degradation in 96% H<sub>2</sub>SO<sub>4</sub> (numbers at the curves correspond to numbers of products in Table II).

where  $E$  is the activation energy,  $k_B$  is the Boltzmann constant. According to Eq. (2), the slope of the dependence of  $-\ln k$  on  $1/T$  is determined by the activation energy  $E$ . However, it is clear from Figure 5 that the experimental points do not fall on a single line. This indicates that PNIB degradation process in 96%  $H_2SO_4$  cannot be described by a single value of  $E$  over the entire range of temperatures investigated.

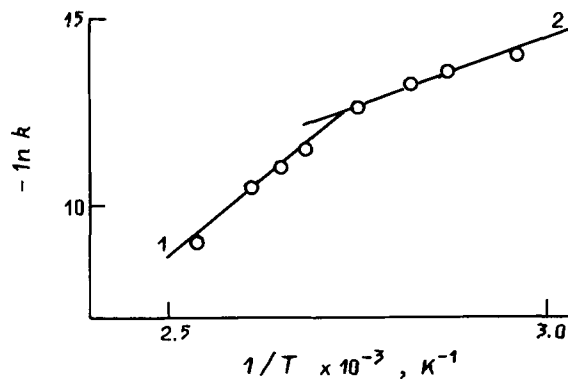
On the other hand, the position of points can be approximated by two straight lines (1 and 2 in Fig. 5) with a larger slope at high  $T$  and a smaller one at low  $T$ . At  $T \geq 90^\circ C$  (straight line 1) the value of  $E = 133$  kJ/mol was obtained. This value coincides with that of PABI (134 kJ/mol) after its hydrolysis in 97.8%  $H_2SO_4$  (Ref. 2) and is close to the value of  $E = 118$  kJ/mol obtained for poly(*p*-phenylene terephthalamide) in 96.5%  $H_2SO_4$  (Ref. 9) and for low-molecular-weight amides.<sup>10</sup> Hence, at high-temperature PNIB hydrolysis is similar to that of the above polymers.

At low  $T$  ( $\leq 90^\circ C$ ) the activation energy of degradation calculated from the slope of curve 2 (in Fig. 5) is about three times lower ( $\sim 50$  kJ/mol). This result can imply that at high and low temperatures the degradation of the macromolecules occurs at different bonds. In this case, the products of PNIB thermal degradation in 96%  $H_2SO_4$  obtained at different  $T$  may differ in chemical structure of the chain and, therefore, are not polymer homologues.

Note that the nonlinear dependency of  $-\ln k$  on  $1/T$  obtained appears to be rather anomalous because for the other polymers mentioned here for which similar investigations were carried out, this dependency was linear.<sup>2,9,10</sup> To understand and explain this fact, additional information on PNIB stability may be useful.

### PNIB Stability and Possible Mechanism of Degradation

PNIB is possibly the only polymer which is more stable in solution in concentrated sulfuric acid than in the dry state. Indeed, the investigation of the molecular properties of PNIB reliably determine the slow decrease in  $M$  of the sample when it is stored in the form of powder or film.<sup>11</sup> Moreover, the rate of decrease in  $M$  increases with the porosity of the material. The unusual behavior of degradation is that the strength characteristics of the PNIB films increase (!) with ageing at early degradation stages (during the first year). Only in further degradation stages (during the second control year) the usual relationships are observed: decrease in  $M$  is accom-



**Figure 5** Rate constant of PNIB degradation in 96%  $H_2SO_4$  vs. inverse temperature at the semilogarithmic scale (points); (1) linear approximation of data at  $T \geq 90^\circ C$ , (2) the same at  $T \leq 90^\circ C$ .

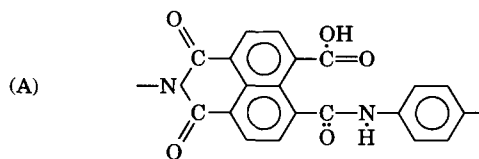
panied by a decrease in the mechanical characteristics of PNIB films.<sup>11</sup>

The similar anomaly at the early stages of PNIB degradation was also noted in the data on flow birefringence (FB) in a PNIB solution in 96%  $H_2SO_4$ .<sup>12</sup> The initial decrease in  $[\eta]$  and  $M$  during the thermal degradation of PNIB is accompanied by an increase (!) in shear optical coefficient which begins to decrease with decreasing  $M$  (usual dependency) only in the more advanced degradation stages.

Therefore, the degradation of PNIB in the early degradation stages is not reduced either to degradation of the macromolecule along the single bonds of the PNIB main chain or to the degradation of cyclic groups retaining high optical anisotropy of the chain.

It can be supposed that the hydrolysis of imide ring in PNIB takes place during the storage of a dry polymer at room temperature. The hydrolysis of the imide ring is provided by (1) the presence of water bound to PNIB chain (hydrophilicity of benzimidazole ring), (2) the basicity of benzimidazole ring, and (3) the high mobility of polymer chain even at room temperature. This assumption coincides with the fact that the rate of PNIB hydrolysis increases with material porosity, and in solution in 96%  $H_2SO_4$  hydrolysis falls sharply because the entire free water in the system is bound by sulfuric acid.

As a result, the gradual formation of groups A proceeds in the PNIB molecule:



These groups are readily hydrolyzed, which explains the low activation energy of thermal degradation of the PNIB molecule in solution at *not high T*.

From the viewpoint of the conformation in solution of the PNIB molecule, group A is a defect which distorts the cyclic structure of the chain and increases, hence, the degree of coiling of the macromolecule. A decrease in the fraction of these defects in the early stages of PNIB degradation in 96% H<sub>2</sub>SO<sub>4</sub> must lead to an increase in the equilibrium rigidity of the macromolecule. This may explain the increase of the shear optical coefficient. The products of this stage of thermal degradation are naturally characterized by different numbers of defects, and, therefore, are not polymer homologues.

At *higher T* the mechanism of PNIB degradation in solution in 96% H<sub>2</sub>SO<sub>4</sub> may consist in simultaneous formation of groups A and their degradation, which would explain the higher activation heat of degradation. On the other hand, this degradation is equivalent to that of the macromolecule along the single bonds of the main chain with the retention of the type of short-range interactions and the optical anisotropy of unit length. The degraded products of PNIB in sulfuric acid solution in these stages of degradation are, probably, polymer homologues.

## CONCLUSIONS

The scheme of PNIB degradation considered here explains qualitatively all experimental data obtained both in solution and in the solid state. However, the chemical mechanism of degradation of the PNIB molecules in the solid state proceeding to such extensive degradation stages which are not typical of other heterocyclic polymers is not completely clear.

It can only be supposed that the slower (in comparison with the decrease in *M*) decrease in mechanical indices of the PNIB films is related to the formation in these films of strong intermolecular (hydrogen and dipole-dipole) bonds which compen-

sate for the breaking of covalent bonds in the PNIB chain. The reliable confirmation of suggested degradation mechanism would show that PNIB is a unique self-degrading polymer in the family of rigid-chain polyheteroarylenes.

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