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### Polyanthranilides. III. Synthesis and Characterization of Polyamides from 6,6'-Bis[3,1-benzoxazin-2,4-dione]

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## **Polyanthranilides. III. Synthesis and Characterization of Polyamides from 6,6'-Bis[3,1-benzoxazin-2,4-dione]**

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### **A B S T R A C T**

Ring-scission polymerization of 6,6'-bis[3,1-benzoxazin-2,4-dione] was studied in presence of such catalysts as aqueous HCl, benzidine-3,3'-dicarboxamide, N-methyl aniline, o-chloroaniline, benzidine-3,3'-dicarboxylic acid, and acid amides under various experimental conditions. It was found that 6,6'-bis[3,1-benzoxazin-2,4-dione] undergoes ring-scission polymerization, affording polyanthranilides in the presence of the first five catalysts under appropriate experimental conditions. The samples are insoluble in all organic solvents including formic acid. They are soluble in sulfuric acid with degradation. They are characterized by IR spectral and thermogravimetric analysis.

### **I N T R O D U C T I O N**

It has been reported [1, 2] that no systematic work has been carried out to investigate the ring-scission polymerization of isatoic anhydrides [3-5]. In our search for thermally stable polymers [6] we prepared bisisatoic anhydride, systematically named 6,6'-bis[3,1-benzoxazin-2,4-dione], from benzidine-3,3'-dicarboxylic acid (BDC).

The present communication reports the results of the study of the ring-scission polymerization of 6,6'-bis[3,1-benzoxazin-2,4-dione]. The conditions employed for the study of ring-scission polymerization are described in the experimental part. Some of these are based on the reaction conditions employed in earlier reports [7, 8].

## EXPERIMENTAL

Benzidine-3,3'-dicarboxylic acid (BDC) was prepared according to the literature [9].

### Synthesis of 6,6'-Bis[3,1-benzoxazin-2,4-dione]

BDC (1.36 g, 0.005 mol) was refluxed with ethyl chloroformate (20 mL) at 105°C until the solution became clear. This required nearly 4 h. An excess amount of acetyl chloride (12 mL) was added to the cold reaction mixture. The reaction mixture was refluxed for 4 h at 110°C until evolution of hydrogen chloride gas ceased. Acetyl chloride was removed by distillation, and the solid which separated out on cooling the reaction was filtered, washed with petroleum ether (60 mL), and dried. The yield was 80%, mp 360°C, mixed mp 240-250°C (decomp.). It was soluble in N,N-dimethylformamide.

Analysis: Found: N, 8.60%;  $C_{16}H_8N_2O_6$  requires 8.64% N.

### Ammonolysis of 6,6'-Bis[3,1-benzoxazin-2,4-dione]

#### Formation of Benzidine-3,3'-dicarboxamide

A suspension of 6,6'-bis[3,1-benzoxazin-2,4-dione] (1 g) and liquor ammonia (10 mL) were shaken occasionally and kept at a boiling water bath temperature for 2 h. The reaction mixture was cooled and the solid was filtered, washed with cold water, and dried. It was soluble in DMF and DMAC.

Analysis: Found: N, 20.8%;  $C_{14}H_{14}N_4O_2$  requires 20.74% N.

Ring-scission polymerization of 6,6'-bis[3,1-benzoxazin-2,4-dione] was investigated under the following conditions.

#### Using 0.1 M HCl as Catalyst

A suspension of finely powdered 6,6'-bis[3,1-benzoxazin-2,4-dione] (1.08 g) in diphenyl ether (20 mL) and aqueous hydrochloric acid (0.1 M, 1 mL) was heated up to 100°C and held at this temperature for 1 h. The temperature was then raised to 180°C and the reaction mixture was held at this temperature for 1 h. The solid mass obtained was filtered and washed with boiling ethanol (20 mL). The solid product was dried, powdered, and washed twice with boiling ethanol

(2 × 20 mL). The solid product thus obtained weighed 0.2 g. It did not melt up to 360°C and was insoluble in DMF, alkali, and aqueous acids. This polyanthranilide was labeled PBA1.

#### Using Lower Proportion of Ammonia

The reaction of 6,6'-bis[3,1-benzoxazin-2,4-dione] (0.5 g) with ammonia solution (1%, 0.5 mL) was carried out and worked up in the manner described earlier. The product obtained was a mixture of unchanged benzidine-3,3'-dicarboxamide and BDC. It was fairly soluble in DMF.

#### Using Benzidine-3,3'-dicarboxamide as Catalyst

A mixture of 6,6'-bis[3,1-benzoxazin-2,4-dione] (1.08 g) and benzidine-3,3'-dicarboxamide (0.1 g) was heated at 225°C for 5 h under nitrogen atmosphere. The cooled reaction mixture was powdered and treated successively with cold 5% aqueous carbonate solution (50 mL) and with cold ethanol. The solid was boiled with ethanol and filtered. The polymer thus obtained was labeled PBA2.

The above reaction was also carried out using 6,6'-bis[3,1-benzoxazin-2,4-dione] and BDC-3,3'-dicarboxamide in a ratio of 1:2 by w/w, respectively, at 225°C for 5 h under nitrogen atmosphere. The polymer was labeled PBA3.

#### Using N-Methyl Aniline as Catalyst

The reaction was carried out using 6,6'-bis[3,1-benzoxazin-2,4-dione] (1 g) and N-methylaniline (0.1 g) at 225°C for 4 h under nitrogen atmosphere. The reaction mixture was worked up as described above. The polymer sample was labeled PBA4.

#### Using o-Chloroaniline as Catalyst

The reaction was carried out and worked up in the manner described above using o-chloroaniline (0.1 g) in place of N-methylaniline. The sample was labeled PBA5. The unreacted material from the bicarbonate extract, upon acidification, was benzidine-3,3'-dicarboxylic acid (0.3 g).

#### Using Benzidine-3,3'-dicarboxylic Acid as Catalyst

The reaction was carried out and worked up in the manner described above using benzidine-3,3'-dicarboxylic acid (0.1 g) as catalyst. The sample was labeled PBA6.

#### Using Formamide as Catalyst

A mixture of 6,6'-bis[3,1-benzoxazin-2,4-dione] (1.0 g) and formamide (0.1 g) was heated up to 200°C for 1 h. The product was found to be a mixture of products fairly soluble in DMF. The products were not analyzed.

A similar reaction using acetamide afforded a mixture of products soluble in DMF. The products were not further analyzed.

### Hydrolysis of Polymeric Product

The polymer sample (0.1 g) was stirred in aqueous sulfuric acid (50%, 20 mL) and refluxed for 2 h. The suspension dissolved in about 30 min after heating. The clear solution was diluted with water (100 mL) and cooled. Benzidine-3,3'-dicarboxylic acid separated out as a yellowish green powder.

Details about the yield of the polyanthranilides and the nitrogen analysis are furnished in Table 1.

## MEASUREMENTS

### IR Spectra

IR spectra of all these polyanthranilide samples were scanned in KBr with a Carl Zeiss UR-10 Spectrophotometer.

### Thermogravimetric Analysis

The TG analyses of the polymer samples were carried out using a Du Pont 951 Thermogravimetric Analyzer in air. The heating rate was 10°C/min.

## RESULTS AND DISCUSSION

All the polyanthranilide samples are insoluble in common organic solvents including formic acid. They dissolve only in concentrated sulfuric acid, leading to degradation in the polymer. All the polymer samples are insoluble in aqueous alkali and do not show any sign of fusion below 300°C. The polymer samples were analyzed for N by a Coleman Nitrogen Analyzer. The values of %N in the samples are shown in Table 1. They are somewhat lower than expected, possibly because of incomplete decomposition due to the high thermal stability of polymers.

Examination of the IR spectra of the polymer samples from 6,6'-bis[3,1-benzoxazin-2,4-dione] reveals that the spectra of all the polyanthranilide samples described in this paper are identical. They comprised all the bands characteristic of the secondary amide of an aromatic acid. However, the IR spectra of the polymer samples prepared from 6,6'-bis[3,1-benzoxazin-2,4-dione] in the presence of different catalysts are similar in their essential details but are not superposable. This is due to the fact that one of the endgroups in

TABLE 1. Preparation and Characterization of Polyanthranilides

Sample	Polymerization			Polymers		
	Catalyst <sup>a</sup>	Experimental condition	Yield <sup>b</sup>	% N <sup>c</sup>	IR frequency (cm <sup>-1</sup> )	
PBA1	0.1 M HCl	Ph <sub>2</sub> O, aq medium, 180°	200	10.4	1640	
PBA2	BDC-A	N <sub>2</sub> atmosphere, 225°	430	10.3	1645	
PBA3	BDC-A <sup>d</sup>	" "	225	10.7	1639	
PBA4	N-Me	" "	510	9.8	1643	
PBA5	o-Cl.An	" "	480	10.8	1635	
PBA6	BDC	" "	220	10.7	1630	

<sup>a</sup>0.1 g of catalyst per 1 g of 6,6'-bis[3,1-benzoxazin-2,4-dione].

<sup>b</sup>From 1 g of 6,6'-bis[3,1-benzoxazin-2,4-dione].

<sup>c</sup>% N expected on the basis of the repeat unit is 11.86%.

<sup>d</sup>BDC-amide: 6,6'-bis[3,1-benzoxazin-2,4-dione] ratio 2:1.

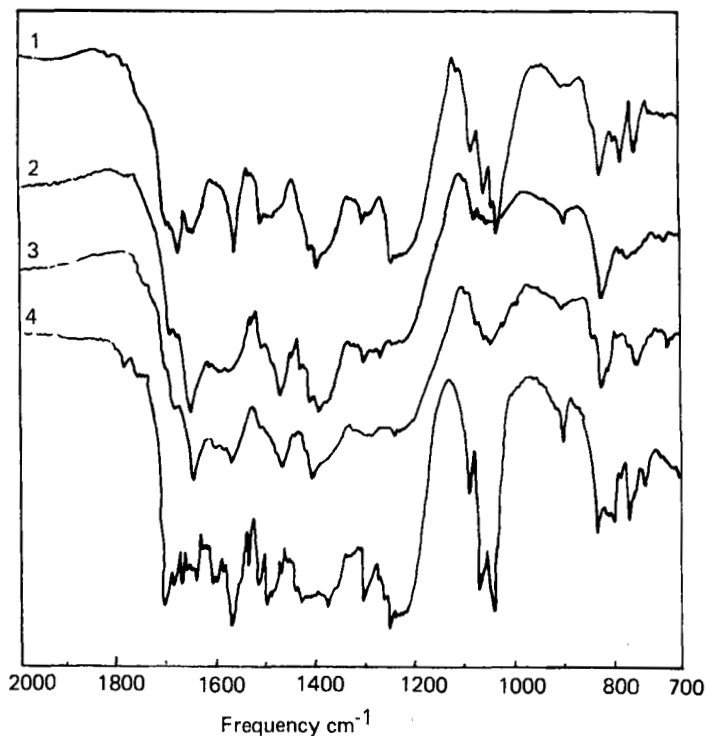


FIG. 1. IR spectra of polyanthranilide samples: (1) PBA1, (2) PBA2, (3) PBA3, (4) PBA5.

the polymer chains of the polymers prepared in the presence of different catalysts is different. The amide C=O band of polyanthranilides appears around  $1640\text{ cm}^{-1}$ , a characteristic aromatic amide frequency.

The spectrum of each polymer sample includes a small inflection at  $1680\text{ cm}^{-1}$  which may be assigned to the C=O of the -COOH forming the endgroup. In the polymer sample formed on using bis-anthranilic acid (benzidine-3,3'-dicarboxylic acid) as catalyst, the band  $1680\text{ cm}^{-1}$  is distinct. This happened because this polymer sample could be on either end of the polymer chain in the -C-OH



group. The IR spectra of some selected samples are presented in Fig. 1.

The thermal stabilities of these polymers were determined by thermogravimetry. Their TGA curves in air follow more or less the same pattern (see Table 2). These polymers showed good thermal stability

TABLE 2. Results of TG Analysis of Polyanthranilides at a Heating Rate of 10°C/min in Air

Polymer	% Weight loss at						Energy of activation, $\Delta E$	Order of reaction, $n$
	300°C	350°C	400°C	500°C	600°C	700°C		
PBA1	12	31	42	52	64	76	28	1.0
PBA2	8	26	38	52	62	72	26	1.0
PBA3	6	26	36	52	65	75	31	1.0
PBA4	9	24	32	44	56	68	34	1.0
PBA5	10	24	36	50	55	65	36	1.0
PBA6	13	24	30	54	54	87	29	1.0



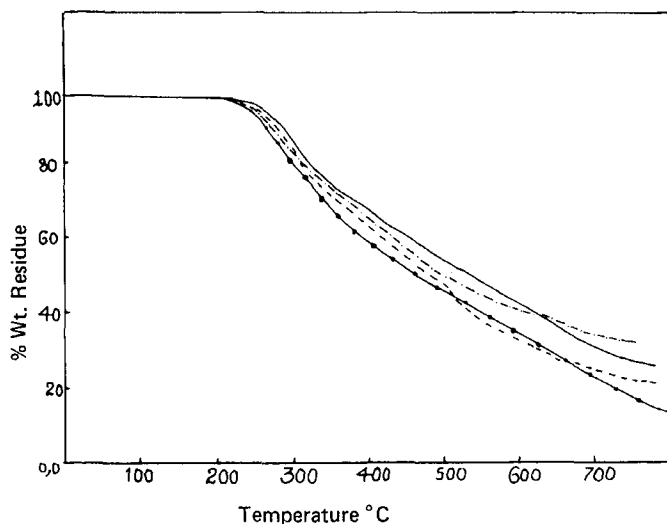


FIG. 2. TG thermograms of polyanthranilide samples: (•) PBA1, (- -) PBA3, (—) PBA4, (- ·) PBA6.

since they lost about 24 to 31% of their weight around 350°C and about 55 to 65% around 600°C. Decomposition occurred above 500°C in all cases, and at 700°C the weight loss was over 65%.

Comparison of the thermal stability of polyanthranilides prepared from 6,6'-bis[3,1-benzoxazin-2,4-dione] with that of poly(6-methyl-anthranilide)s prepared from 6-methyl-3,1-benzoxazin-2,4-dione and of polyanthranilides prepared from simple 3,1-benzoxazin-2,4-dione reveals that the former are less stable than those of the polyanthranilides from 6-methyl-3,1-benzoxazin-2,4-dione [8] and 3,1-benzoxazin-2,4-dione [7]. The thermograms of selected polyanthranilides are shown in Fig. 2. The thermograms of all five polymer samples were analyzed by the method proposed by Broido [10] with a view to estimating the kinetic parameters of the degradation reactions. This analysis revealed that the order of overall degradation reaction of all the polyanthranilide samples is around 1. The energy of activation of the degradation reaction is found to vary between 28 to 36 kcal/mol, depending upon the nature of the polymer sample.

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