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## Polyanthranilides. I. Synthesis and Characterization of Polyamides from Isatoic Anhydrides

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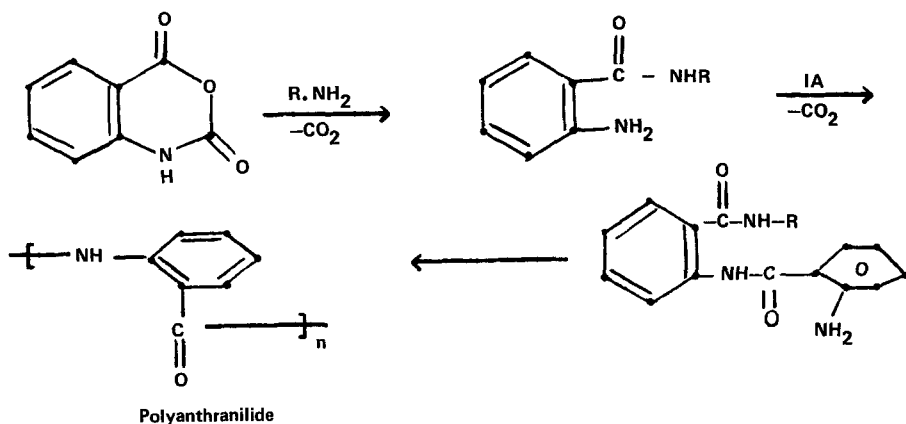
### ABSTRACT

Ring-scission polymerization of simple and bz-nitro and bz-chlorosubstituted isatoic anhydrides is studied in the presence of reagents like aqueous HCl, anthranilamide, N-methyl aniline, o-chloroaniline, and acid amides under various reaction conditions. Only simple isatoic anhydride is found to undergo ring-scission polymerization affording polyanthranilides in the presence of the first four reagents under appropriate conditions. These samples are insoluble in all organic solvents including formic acid. They are characterized by IR spectral study and thermogravimetric and differential thermal analysis.

### INTRODUCTION

The N-carboxy- $\alpha$ -amino-acid anhydrides (NCAs)—also known as Leuch's anhydrides—are reported to undergo lucid ring-scission polymerization on treatment with proper reagents affording corresponding polyamides [1-3]. The reaction system of Leuch's system of Leuch's anhydride is present in isatoic anhydride. Clark and Wagner reported formation of an abnormal product when isatoic anhydride was allowed to react with a much lower proportion of ammonia or a weakly reactive aniline derivative [4]. This work has been critically surveyed

by Elderfield [5]. There are also reports about the formation of the so-called abnormal product in the reactions of both simple and substituted isatoic anhydrides with amines. These products are reported to be abnormal because they are insoluble in ethanol, unlike the normal products, and melt over a wide temperature range [6-9].



In fact, no systematic work has been carried out to investigate these so-called abnormal products. Most of these reports about the properties of the so-called abnormal products suggest that they are mixtures of normal products [6-9]. Elderfield [5] suggested that anthranilamide formed in the reaction of isatoic anhydride, affording a dimeric product and carbon dioxide. The latter would then react in a similar manner with another molecule of isatoic anhydride affording a trimer. In this manner a higher polyanthranilide can be built up by successive repetitions [5]. The literature reports about the nature of the products of reaction of isatoic anhydride with reactants such as *o*-bromoaniline [6], *N*-methylaniline [7], and anthranilamide [6] do not furnish any information about whether the product formed or one of the constituents of the product is a polymer or not. In the absence of any definite information about the isolation and characterization of polymer from the so-called abnormal product of isatoic anhydride, it was thought that investigation of the ring-scission polymerization of isatoic anhydride, both simple and substituted, may reveal interesting information on the subject. The present communication reports the results of the study of the ring-scission polymerization of isatoic anhydrides and its 6- and 7-nitro- and chloro-substituted derivatives. 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 suggested in earlier reports. The monomers were prepared by reported methods. It is found that out of the six isatoic anhydrides, only the simple isatoic

anhydride mentioned above afforded the corresponding poly(anthranilide) under favorable reaction conditions. The nitro- and chloro-substituted isatoic anhydrides and benzo[6,7]isatoic anhydride did not participate in ring-scission polymerization but afforded the expected normal product or products of reaction.

## EXPERIMENTAL

Isatoic anhydride and its benz-substituted derivatives were prepared from the corresponding anthranilic acids by treating them with ethyl chloroformate in the presence of an excess of acetyl chloride following the details described in the literature [8]. The ring-scission polymerization reaction of the monomers was investigated under following conditions.

### Using Water as Initiator

A suspension of finely powdered isatoic anhydride (1.0 g) in diphenyl ether (20 mL) containing water (1.0 mL) was heated to 100° and held at that temperature for an hour. The temperature was then raised to 150° and the reaction mixture was held at that temperature for an hour. The solid product obtained on cooling the reaction mixture was unchanged isatoic anhydride.

It was found that the use of ethanol and also of o-cresol as initiator in place of water did not bring about ring-scission polymerization.

### Using 0.1 M HCl as Initiator

The reaction was carried out in the manner described above in diphenyl ether using aqueous hydrochloric acid (1 mL, 0.1 M) in place of water. The hot reaction mixture was filtered and the solid left behind was washed with hot diphenyl ether followed by boiling ethanol (20 mL). The solid which remained behind was collected, powdered, and washed twice with boiling ethanol (20 mL). The solid product thus obtained weighed 0.05 g. It did not melt up to 300°. This polyanthranilide sample is designated as PA-1. Unchanged monomer (0.8 g) and a small amount of anthranilic acid were recovered from the alcohol extract and diphenyl ether washings.

### Using Lower Molar Proportion of Ammonia

The reaction between isatoic anhydride (1.0 g) and dilute ammonia solution (1%, 0.5 mL) was carried out and worked up in the manner described above. The product obtained was a mixture of unchanged

monomer, anthranilamide, and anthranilic acid. It did not contain any polymeric material.

#### Using Anthranilamide (AnA) as Initiator

A uniform mixture of isatoic anhydride (1.0 g) and anthranilamide (0.1 g) was heated at 180° for 3 h under a nitrogen atmosphere. The cooled reaction mixture was powdered and treated successively with cold 5% aqueous carbonate solution (50 mL) and cold ethanol. The solid material was Soxhleted in ethanol for 2 h. The polymer thus obtained is designated as PA-2. Anthranilic acid (0.5 g) was isolated from the carbonate extract.

When this reaction was carried out at 120° under similar experimental conditions, no polymeric product was formed. The product of the reaction was unchanged monomer and anthranilamide.

The above reaction was also carried out at 225° under exactly similar conditions. The polymer obtained is designated as PA-3.

The above reaction was also carried out using isatoic anhydride and anthranilamide in the ratio of 1:2 by weight at 180° for 3 h under a nitrogen atmosphere. The polymer is designated as PA-4.

#### Using N-Methylaniline (N-MeAn) as Initiator

The reaction was carried out using isatoic anhydride (1 g) and N-methylaniline (0.1 g) at 180° for 3 h under a nitrogen atmosphere. The reaction mixture was worked up as described above. The polyanthranilide thus obtained is designated as PA-5.

This reaction was also carried out in a similar manner at 225°. The polymer obtained is designated as PA-6.

#### Using o-Chloroaniline(O-ClAn) as Initiator

The reaction was carried out and worked up in the manner described above under two different conditions using o-chloroaniline (0.1 g) in place of N-methylaniline. The polyanthranilamide sample formed at 180° is labeled as PA-7 while that formed at 225° is labeled as PA-8. Anthranilic acid (0.1 g) and unchanged monomer (0.2 g) were recovered, respectively, from bicarbonate and mixed ethanol extracts.

#### Using Acid Amides as Initiators

A mixture of isatoic anhydride (1.0 g) and formamide (0.1 g) was heated up to 200° for an hour. The product was found to be a mixture of unchanged isatoic anhydride and 2H-4-oxoquinazoline.

A similar reaction using benzamide afforded 2-phenyl-4-oxoquinazoline along with unchanged isatoic anhydride.

### Hydrolysis of Polymeric Product

The polymer sample (0.1 g) was stirred in aqueous sulfuric acid (50%, 20 mL) and refluxed for an hour. The suspension dissolved in about 20 min after heating. The clear solution was very carefully neutralized and cooled. Anthranilic acid separated out in crystalline form.

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

## MEASUREMENTS

### Estimation of $\overline{DP}$

The method comprised hydrolysis of a known weight of polymer following the method described above. Anthranilic acid was estimated in the reaction mixture by bromometric titration. It is known that a mole of anthranilic acid consumes 4 moles of bromine atoms. Hence the average degree of polymerization ( $\overline{DP}$ ) of the polymer would be given by

$$\frac{\overline{DP} - 1}{\overline{DP}} = \frac{1}{17} (136 - 137/f) \quad (1)$$

where  $f$  is the ratio of the weight of anthranilic acid to the weight of the polymer used for estimation. The average of three independent estimations was made. The values are reported in Table 1.

### Thermal Analysis

Differential thermal analysis (DTA) was carried out on a Linseis Thermobalance and thermogravimetric analysis (TGA) was made on a Perkin-Elmer-951 Thermoanalyzer. DTA and TGA of the polyanthranilide samples were carried out in a  $\text{CO}_2$  atmosphere at a heating rate of  $10^\circ/\text{min}$ .

## RESULTS AND DISCUSSION

All the polyanthranilide samples are insoluble in common organic solvents including formic acid. They dissolve only in concentrated

TABLE 1. Polyanthranilides: Experimental Conditions and Some Characteristics

Samples	Initiator <sup>a</sup>	Experimental conditions	Yield <sup>c</sup> (mg)	% N <sup>d</sup>	$\overline{DP} \pm 0.2$	DTA exotherm		
						Commencing at (°C)	Maximum at (°C)	Termination at (°C)
PA-1	0.1 M HCl	Ph <sub>2</sub> O, aq. medium, 180°C	50	10.2	3.1	320	500	600
PA-2	AnA	180°C	100	10.1	3.4	290	530	595
PA-3	AnA	220°C	250	10.3	4.7	325	520	610
PA-4	AnA <sup>b</sup>	180°C	180	10.4	4.3	340	530	620
PA-5	N-MeAn	180°C	200	10.6	5.7	300	510	605
PA-6	N-MeAn	220°C	225	10.0	10.7	305	510	600
PA-7	O-ClAn	180°C	180	10.0	4.8	320	510	570
PA-8	O-ClAn	220°C	210	10.1	5.7	325	505	600

<sup>a</sup>0.1 g of initiator per 1 g of isatoic anhydride.

<sup>b</sup>Anthranilamide:isatoic anhydride ratio 2:1.

<sup>c</sup>From 1 g of IA.

<sup>d</sup>%N expected on the basis of the repeat unit is 11.6%.

TABLE 2. Results of TGA of Polyanthranilides at a Heating Rate of 10°C/min in CO<sub>2</sub> Atmosphere

Sample	% Weight loss at (°C)						
	250	300	350	400	450	500	600
PA-1	5	12	25	38	60	78	80
PA-2	5	12	22	35	57	75	77
PA-3	5	8	22	45	70	78	80
PA-4	3	8	17	40	70	75	80
PA-5	4	6	15	30	45	52	60
PA-6	3	8	13	30	45	50	60
PA-7	4	10	28	55	75	88	90
PA-8	4	5	18	35	65	70	72

sulfuric acid. All the polymer samples are insoluble in aqueous alkali and did not show any sign of fusion below 300°. The polymer samples are analyzed for N by Dumas method. The values of % of N in the samples are shown in Table 1. They are somewhat lower than expected, possibly because of the high thermal stability of polymers. Even on prolonged combustion of the material in the Dumas method, a small amount of material remained uncombusted on the boat.

Examination of the molecular weights of the polymer samples reveals that the average degree of polyanthranilides varies from 3 to 10. The low molecular weight of the polyanthranilide is attributed to the low reactivity of the monomer. The lower reactivity of isatoic anhydride as compared to that of Leuch's anhydride is due to the fact that in the isatoic anhydride molecule the ring undergoing scission is six-membered and has a double bond forming a part of the ring. The double bond is in conjugation with the reaction center, i.e., the carbonyl carbon-4, and the latter is a sterically hindered position. Lower reactivity may also be due to low nucleophilicity and the bulk of the nucleophile i.e., anthranilamide derivative. The fact that 6- and 7-chloro isatoic anhydrides and the corresponding nitro derivatives do not undergo ring-scission polymerization is most probably due to the fact that the intermediate nitro- or chloro-substituted anthranilamide would be much weaker nucleophiles due to the presence of an electronegative group.

Examination of the IR spectra of the polymer samples from the simple isatoic anhydride reveals that the spectra of all the polyanthranilide samples described in this paper are identical. They comprise all the bands characteristic of a secondary amide of an



aromatic acid. These spectra also compare characteristically with that of anthranilide.

Examination of the results of DTA of polyanthranilide samples 1 to 8 reveals that degradation comprises only one step. This exotherm commences at a temperature lying in the range from 300 to 325°C; it passes through a maximum around 500°C and appears to terminate above 570°C. The actual temperature at all the above-mentioned three stages in the exotherm depends upon the nature of the polyanthranilide sample. The analysis of DTA thermograms of all the polymer samples by the Reich method [9] revealed that the order of degradation reaction of polyanthranilide samples ranged from 0.9 to 1.1 and the energy of activation ranged from 28 to 34 kcal/mol depending upon the nature of the polymer sample. It is reported that TGA is a more sensitive method than DTA for degradation studies. The results of TGA (Table 2) show that polyanthranilide loses around 5 to 12% of its weight when heated to 300°C and around 60 to 80% of its weight when heated to 600°C, depending upon the nature of the polymer sample. The rate of weight loss beyond 600° becomes very slow. Comparison of results of TGA of polyanthranilide samples prepared in the presence of the same reagent reveals that thermal stability increases with an increase in the degree of polymerization.

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