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SYNTHESIS AND PROPERTIES OF NEW POLYAZINES—III

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Abstract—Polycondensations of 1,2- and 1,4-naphthoquinones with hydrazine hydrate and disulphinylhydrazine under various conditions were carried out. The optimum parameters for the disulphinylhydrazine synthesis were established. The thermal stabilities and electrical conductivities of the polynaphthoquinoneazines were determined.

INTRODUCTION

In previous papers [1, 2] the polycondensations of acenaphthenequinone, 9,10-anthraquinone and 9,10-phenanthrenequinone, as well as of their chlorinated and nitro derivatives, with hydrazine and disulphinylhydrazine were described. The present paper refers to the syntheses and properties of poly-α- and poly-β-naphthoquinoneazines. The polyazines show semiconducting properties [1–5], may be used for preparing poroplasts [1, 3, 6–9] and as catalysts for polymer halogenations [10–12].

EXPERIMENTAL

Materials

α- and β-Naphthoquinone were Schuchard products; hydrazine hydrate was a LOBA-Chemie-Wien-Fischamend product 100% p.a. and disulphinylhydrazine was synthesized by us.

The i.r. spectra were recorded on Specord i.r. UR 20 apparatus. The thermograms were recorded by means of apparatus due to J. Paulik, F. Paulik and L. Erdey, MOM Budapest.

Polycondensation procedure

Polycondensation with hydrazine hydrate was carried out in both protic and aprotic solvents (acetic acid, dimethylformamide, xylene), both in the presence and in the absence of catalysts (H_2SO_4, $ZnCl_2$), at quinone–hydrazine mole ratios of 1:1 and 1:2, at 110–115° (bath temperature) and otpimum reaction time of 10 hr [1, 2]. The polycondensations in acetic acid resulted in both soluble and insoluble products. In xylene, only an insoluble fraction was obtained in a rather good yield; the soluble fraction could not be separated. The polynaphthoquinoneazines obtained in DMF were soluble in the reaction medium and were separated by precipitation in water.

Most of the polynaphthoquinoneazines were obtained as powders of various brown and black shades; they were purified by repeated washings with either $CHCl_3$ or benzene for removal of unconverted quinone. The products synthesized in the presence of $ZnCl_2$ were first treated with NH_4OH solution for removing the catalyst. These polyazines formed as complexes. The poly-1,4-naphthoquinoneazines were separated from the complexes by dissolving in hot formic acid, followed by filtration and precipitation in water. The poly-1,2-naphthoquinoneazine obtained in xylene was washed with hot acetic acid while the product synthesized in DMF was dissolved in hot acetic acid, filtered and precipitated in water. For removal of quinone, the products were finally washed with $CHCl_3$.

Polycondensation with disulphinylhydrazine was carried out in pyridine acting both as a solvent and as a catalyst [2, 13]. Polynaphthoquinoneazine, which is soluble in the reaction medium, was separated from disulphinylhydrazine by filtration and then precipitated in water. Poly-α-naphthoquinoneazine was purified by washing with hot ethanol for removal of quinone and disulphinylhydrazine. When poly-β-naphthoquinoneazine was precipitated in water, a sticky paste separated; it was converted to a brown powder by treating with diethyl ether; it was then washed with $CHCl_3$ and C_2H_5OH.

Synthesis of disulphinylhydrazine

The disulphinylhydrazine was obtained by the condensation of hydrazine hydrate with thionyl chloride according to a method applied for diamines [14, 15]. Thionyl chloride (0.35 mol) was added dropwise for an hour at room temperature to a solution of hydrazine hydrate (0.15 mol) in benzene (45 ml). The disulphinylhydrazine thus formed separated from the reaction medium. The mixture was stirred for another half an hour for completion of the reaction, then filtered and washed with ether. Yield 70%, m.p. 139°.

RESULTS AND DISCUSSION

Synthesis and molecular structure of the polymers

Polycondensation with hydrazine hydrate. Unlike the anthraquinone [2], the naphthoquinones react with hydrazine hydrate in acetic acid medium, in higher yield with H_2SO_4 as a catalyst. Some of the polymer characteristics and the yields obtained under various conditions are given in Tables 1 and 2. As in the case of diamines [16], excess of hydrazine hydrate leads to higher yield. The optimum reaction time is 10 hr; shorter periods result in a significant decrease in the yield of insoluble product. Generally, the polycondensations of α-naphthoquinone led to higher yields, probably because the β-isomer is less stable.

Polycondensation with disulphinylhydrazine. The condensation of hydrazine hydrate with thionyl chloride was carried out under various conditions. By

Table 1. Characteristics of poly-1,4-naphthoquinoneazines

No.	Hydrazine	Solvent	Catalyst	Quinone hydrazine mole ratio	Time (hr)	Product insoluble in the reaction medium: Yield (%)	Product insoluble in the reaction medium: m.p. (°C)	Product soluble in the reaction medium: Yield (%)	Product soluble in the reaction medium: m.p. (°C)
1.	$H_2N—NH_2 \cdot H_2O$	CH_3COOH	H_2SO_4	1:1	10	53.09	>300	27.75	174–180
2.	$H_2N—NH_2 \cdot H_2O$	CH_3COOH	H_2SO_4	1:1	7	39.10	>300	35.80	161–168
3.	$H_2N—NH_2 \cdot H_2O$	CH_3COOH	H_2SO_4	1:2	10	52.46	>300	31.58	140 decomp.
4.	$H_2N \cdot NH_2 \cdot H_2O$	CH_3COOH	—	1:2	10	52.63	>300	15.17	142–147
5.	$H_2N—NH_2 \cdot H_2O$	*o*-Xylene	$ZnCl_2$	1:1	10	69.02	280–300	—	—
6.	$H_2N—NH_2 \cdot H_2O$	DMF	$ZnCl_2$	1:1	10	—	—	75.60	>300
7.*	$H_2N—NH_2 \cdot H_2O$	DMF	$ZnCl_2$	1:1	10	—	—	81.22	>300
8.	O=S=N—N=S=O	Pyridine	Pyridine	1:2	20	—	—	88.80	>300

*DMF was first treated with $ZnCl_2$ and hydrazine hydrate. An additional product of hydrazine to DMF was obtained which is complexed with $ZnCl_2$ and then quinone is added [2].

performing the reaction at the boiling temperature of thionyl chloride, as in the case of diamines [14, 15], most of the disulphinylhydrazine dissolved in the reaction medium and did not separate after non-solvent addition.

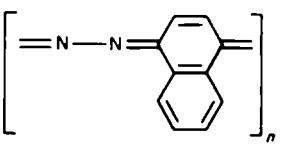
$$2SOCl_2 + H_2N—NH_2 \xrightarrow{4HCl} O=S=N—N=S=O$$

The structure was confirmed by analyses for nitrogen, as well as by the i.r. measurements. The i.r. spectra show the absorptions characteristic of the O=S and S=N bonds (1100 and 1495 cm^{-1}, respectively) and a sharp peak indicating the cumulative double bond system (O=S=N) at 2090 cm^{-1}.

Since the disulphinyl hydrazine is insoluble in common solvents, the polycondensations were carried out in pyridine. The polycondensation with α-naphthoquinone gave a much higher yield than that with β-quinone, the products being less soluble in the common solvents.

The molecular weights of the polynaphthoquinoneazines could not be estimated since they are not soluble in common solvents. For the fractions soluble in DMF, the intrinsic viscosities were measured; they had values in the range 0.0367–0.049 dl/g. The values are comparable to those given in the literature for polybenzylazines [4] and the polyquinoneazines synthesized by us [1, 2]. Since most of the polynaphthoquinoneazines are either partially soluble or insoluble in DMF, they can be assumed to show polycondensation degrees higher than those of these oligomers.

The polyazine structure of these products was confirmed by the i.r. spectra. The $\nu_{C=N}$ absorption



band appeared between 1625 and 1630 cm^{-1} for the products obtained with hydrazine hydrate and at 1615 cm^{-1} for those synthesized with disulphinylhydrazine. All the products had a free carbonyl group at the chain end; only in the spectrum of poly-1,2-naphthoquinoneazine obtained with disulphinyhydrazine, the absorption band characteristic of the sulphinyl residue was found.

Properties of polyazines

Thermal stability. The thermal behaviour was examined by thermodifferential analysis in the 20–1000° range, at a heating rate of 10°/min in air. The thermal destruction of polynaphthoquinoneazines proceeds in two stages, viz. nitrogen elimination which might be explained by means of azo–azinic tautomerism =N—N= ⇄ —N=N—, and the destruction of the naphthalene residue (Table 3). The nitrogen is eliminated over a much wider temperature range than with the other polyquinoneazine [17].

Electrical properties. The electrical conductivity was measured on pellets formed under a pressure of 10 t/cm^3 over the 30–140° range. The values are of about the same order of magnitude (10^{-15}–10^{-13} $ohm^{-1} cm^{-1}$) as for the polyaldazines [3, 4] and polyacenaphthenequinoneazines [1], polyphenanthrenequinoneazines, polyanthraquinoneazines [2] and polyketazines being higher.

Table 2. Characteristics of poly-1,2-naphthoquinoneazines

No.	Hydrazine	Solvent	Catalyst	Quinone–hydrazine mole ratio	Time (hr)	Product insoluble in the reaction medium: Yield (%)	Product insoluble in the reaction medium: m.p. (°C)	Product soluble in the reaction medium: Yield (%)	Product soluble in the reaction medium: m.p. (°C)
1.	$H_2N—NH_2 \cdot H_2O$	CH_3COOH	H_2SO_4	1:1	10	30.70	>300	32.46	185–190
2.	$H_2N—NH_2 \cdot H_2O$	CH_3COOH	—	1:1	10	5.17	230 decomp.	48.77	210–215
3.	$H_2N—NH_2 \cdot H_2O$	*o*-Xylene	$ZnCl_2$	1:1	10	42.80	>300	—	—
4.	$H_2N—NH_2 \cdot H_2O$	DMF	$ZnCl_2$	1:1	10	—	—	44.74	165–170
5.	O=S=N—N=S=O	Pyridine	Pyridine	1:2	20	—	—	25.87	245–250

Table 3. Thermal properties of polynaphthoquinoneazines

No.	Quinone	Hydrazine	Solvent	Catalyst	Stages of thermal degradation I: Temperature range (°C)	I: Weight losses (%)	II: Temperature range (°C)	II: Weight losses (%)
1.	1,2-Naphthoquinone	$H_2N—NH_2 \cdot H_2O$	CH_3COOH	H_2SO_4	230–337	11.40	337–810	87.14
2.	1,4-Naphthoquinone	$H_2N-NH_2 \cdot H_2O$	CH_3COOH	H_2SO_4	237–440	11.95	440–830	87.87
3.	1,2-Naphthoquinone	$H_2N-NH_2 \cdot H_2O$	Xylene	$ZnCl_2$	240–395	12.10	395–790	87.82
4.	1,4-Naphthoquinone	$H_2N—NH_2 \cdot H_2O$	Xylene	$ZnCl_2$	215–470	11.38	470–830	88.50
5.	1,2-Naphthoquinone	$H_2N—NH_2 \cdot H_2O$	DMF	$ZnCl_2$	250–460	11.31	460–850	88.63
6.	1,2-Naphthoquinone	O=S=N– N=S=O	Pyridine	Pyridine	180–360	11.91	360–740	88.04
7.	1,4-Naphthoquinone	O=S=N–N=S=O	Pyridine	Pyridine	235–375	11.69	375–870	88.25

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