

Polycondensation of Diphenyl -2, 2'-diiodobiphenyl-4, 4'-Diglyoxal with Different Di- and Tetra-Aminocompounds

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ABSTRACT

Several potentially thermostable polyquinoxalines are prepared by condensation of 2, 2'-diiodobiphenyl-4, 4'-diglyoxal dihydrate (I) with several aromatic tetraamine compounds (XI-XIII). Polymerizations are carried out either in hexamethylphosphoric triamide solution or as a melt condensation at 300-350°C under nitrogen atmosphere.

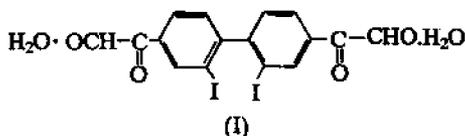
Some model compounds are also prepared from diglyoxal (I) and diaminocompounds (VII-X). All of them show the formation of a quinoxaline ring. The elemental analysis is consistent with the proposed structures. Melting points of all the synthesized polymers are over 340° with high stability at elevated temperatures.

INTRODUCTION

Quinoxaline polymers are known to have excellent thermal stability and high heat resistance but they are extremely expensive and their applications are restricted by their poor solubility in organic solvents [1-6].

Various researches have studied the physical properties of aromatic polymers produced by the introduction of halogen atoms into the aromatic rings. From previous studies, polymers of halogenated aromatic compounds exhibit high fire resistance and thermal stability, as well, relative to that of the non-halogenated analogs [7-11].

Here the preparation scheme of several polyquinoxalines from the reaction of 2, 2'-diiodobiphenyl-4,4'-diglyoxal dihydrate (I) with various aromatic tetraamine compounds (XI-XVIII) in solution or by melt condensations is presented. The physical properties of these polymers are also investigated.



EXPERIMENTAL

Materials and Instruments

All reagents and solvents were of commercial grades and were purchased from Fluka Chemical Co., Aldrich Chemical Co., and Merck Co. Solvents were dried over sodium wires or distilled over phosphorous pentoxide. Melting points were measured on a Gallen-Kamp Melting Apparatus. IR spectra were recorded on a Perkin-Elmer 781 Model spectrophotometer. ¹H-NMR spectra on a Hitachi Perkin Elmer Model R-24B 60 MHz spectrophotometer. Inherent Viscosities were determined by a UST 100/2067 viscometer. Differential thermal analysis (DTA), and thermogravimetric analysis (TGA) were performed with a Mettler TA 20 at a heating rate of 10°C/min under nitrogen.

Preparation of Monomers

First method:

-2,2'-Dinitro-4,4'-diacetylbiophenyl: In a 500 ml three-necked flask equipped with dropping funnel, mechanical stirrer and thermometer, 13.8 g (0.1 mole) of diacetylbiophenyl in 100 ml of 97% sulfuric acid was placed. A mixture of 15 ml fuming sulfuric

acid and 34 ml of fuming nitric acid (65%) was added dropwise to the stirred suspension. The temperature was maintained between -12 and -15°C. After the completion of the addition, the reaction mixture was stirred for 2 hours and then poured, with stirring, into ice. The yellow solid which separated was collected by filtration, washed once with water and recrystallized from ethyl alcohol/isopropanol (1:1) to yield 29.7 g (90%), mp 130-131°C.

- 2,2'-Diamino-4,4'-diacetylphenyl: To a mechanically stirred solution of 2,2'-dinitro-4,4'-diacetylphenyl (20 g, 8.4×10^{-2} mole) in 500 ml of glacial acetic acid 20 g of iron powder were added. This suspension was stirred and refluxed for 4 hr. The cold mixture was filtered and the filtrate was poured into ice water. The yellow precipitate was filtered and washed several times with distilled water. The dry substance was recrystallized from mixture of ethanol/acetone (1:1) and dried in an evacuated desiccator at room temperature. The yellow crystalline product with 74% yield melted at 273°C.

- 2,2'-Diiodo-4,4'-diacetylphenyl: A magnetically stirred suspension of 2,2'-diamino-4,4'-diacetylphenyl (13.2 g, 5×10^{-2} mol) in a mixture of concentrated hydrochloric acid (50 ml) and distilled water (50 ml) was cooled in an ice-bath to -5°C and diazotized by the addition of a solution of sodium nitrite (10 g) in water (10 ml). The cold reaction mixture was filtered and to the resulting filter cakes a solution of potassium iodide (25 g) in water (50 ml) was added slowly with stirring. Warming the resulting reaction mixture, in a steam bath, resulted a dark brown solid material, which upon addition of sodium hydrogen sulfite, the color changed to yellow. The yellow product was filtered and dried at 100°C. The crude solid product (24.5 g) was dissolved in hot methanol (4 lit) and refluxed for 8 hrs. The hot solution was filtered and then concentrated to about 100 ml on a rotary evaporator which upon cooling afforded white crystals (m.p.154°C, yield 11 g).

- 2,2'-Diiodobiphenyl-4,4'-diglyoxal dihydrate: To a magnetically stirred solution of 4.9 g (1×10^{-2} mol) 2,2'-diiodo-4,4'-diacetylphenyl in 20 ml of concentrated acetic acid in a 100 ml two necked

flask, was added a mixture of 2.22 g of selenium dioxide in 20 ml of concentrated acetic acid and 1 ml of water. The reaction mixture was refluxed for 8 hrs and the warm reaction mixture was filtered. The filtrate was stirred with 0.5 g of charcoal over night. The reaction mixture was filtered and the filtrate was diluted with 30 ml of water, then concentrated to 10 ml upon which yellow crystals were obtained (m.p.165°C, yield 39 g (54.2%)). Anal.Calc. for $C_{16}H_{12}I_2O_6$: C, 34.68%; H, 2.18%; I, 45.81%

Found: C, 34.72%; H, 2.20%; I, 45.74%
Second method:

-4,4'-Biphenyldiglyoxal dihydrate: 4,4'-Diacetyl biphenyl (35 g) was added to a 500 ml two-necked flask and dissolved in 225 ml of concentrated acetic acid by magnetic stirring at a temperature of 60°C. Then selenium dioxide (31.4 g) was added to a 250 ml Erlenmeyer flask and dissolved in 130 ml of glacial acetic acid and 5 ml of water at temperature below 50°C and then charged into a reaction mixture. After several minutes the red material is produced, and after 5 min red selenium changes to the other allotrope of selenium (black selenium).

The reaction mixture was refluxed for 8 hr. After this time the reaction mixture was filtered and the filtrate was decolorized by charcoal. Then it was filtered again and the filtrate was added to 200 ml of water and the precipitate (4,4'-diglyoxalyl dihydrate biphenyl with m.p= 144-145°C, and yield: 17 g (38.3%) was obtained.

-2,2'-Diiodobiphenyl-4,4'-diglyoxal dihydrate: 4,4'-Diglyoxalyl dihydrate (16.3 g) and 120 g of silver sulfate were charged into a 1000 ml three-necked flask equipped with a mechanical stirrer and dissolved in 500 ml of concentrated sulfuric acid. Iodine (122 g) was added to the reaction mixture in several portions. After the addition of iodine the reaction mixture was stirred for 1 hour at room temperature. The reaction temperature was then raised to 80°C and the reaction was continued for 24 hours.

After reaction, the mixture was poured over ice and the yellow solid was filtered. The mixture and excess iodine were removed from the precipitate under vacuum at a temperature of 80°C. The dried solid was extracted in a soxhlet

extractor with ethanol as solvent for 24 hours and the product was crystallized from ethanol solution during extraction. Crystals were collected and recrystallized from ethanol. The final yellow crystals were obtained in 60.0% yield and had a melting point of 165°C.

Anal. Calc. for $C_{16}H_{12}I_2O_6$: C, 34.66%; H, 2.17%; I, 45.85%

Found: C, 34.70%; H, 2.12%; I, 45.69%

Model Compounds

General procedures for the condensation of 2, 2'-diiodobiphenyl-4,4'-diglyoxalyl dihydrate with different diamine. 2,2'-Diiodobiphenyl-4,4'-diglyoxalyl dihydrate (1 mmole) was dissolved in dry ethanol (20 ml) in a 100 ml two-necked round bottom flask, equipped with a magnetic stirrer, a condenser and dropping funnel and an inlet of nitrogen gas. A diamine was dissolved in 15-20 ml absolute ethanol or glacial acetic acid, and was added to the diglyoxal solution during 10 min. The reaction mixture was refluxed for 4 hours. After 30 min the colored suspension appeared. The mixture was cooled, the precipitate was filtered, washed with ether and dried at 40°C under vacuum. The detailed experimental conditions are given in Table 1.

Polymers

General procedures for the condensation of 2, 2'-diiodobiphenyl-4,4'-diglyoxalyl dihydrate with different tetraamines.

a) By solution condensation:

To a magnetically stirred solution of a tetraamine in dry hexamethylenephosphoramide (HMPA) in a 100 ml three-necked flask, equipped with a condenser, separatory funnel, a solution of fresh 2,2'-diiodobiphenyldiglyoxalyl dihydrate was added during 30 min. The mixture was heated under nitrogen at 180°C for 4 hours. The resulting polymer was separated by filtration, washed with methanol and dried under vacuum. The dry material was pulverized and reheated at 250-375°C for 3-4 hours, to obtain the desired polymeric materials (Table 2).

b) By melt condensation:

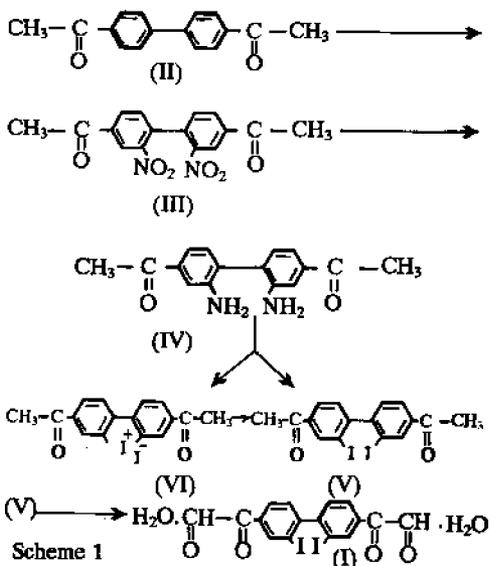
Equimolar of a tetraamines and diglyoxal was

mixed and melted for 3-4 hours. The resulting polymer was washed with methanol and dried in vacuum. The resulting powdered prepolymer was heated at 250-375°C to afford the desired polymer (Table 2).

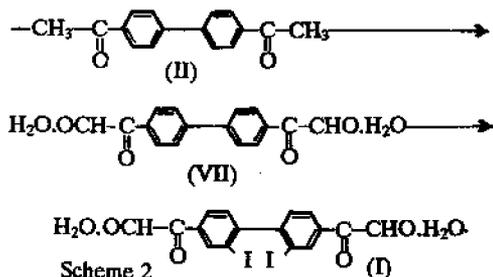
RESULTS AND DISCUSSION

The synthesis of 2,2'-diiodobiphenyl-4,4'-diglyoxal dihydrate (I) was performed for the first time in our laboratories. The synthesis was carried out by two different routes (schemes 1 and 2).

In both syntheses the starting material was 4,4'-diacetyl biphenyl (II). In the first route (scheme 1), compound II was nitrated in fuming sulfuric and nitric acids at -12°C to afford the proper nitrated compound III in 100% yield. Reduction of compound III in acetic acid in the presence of iron powder gave the corresponding diamine (IV) in 74% yield. Diazotization followed by potassium iodide addition produced two different compounds; 2,2'-diiodo-4,4'-diacetyl biphenyl (V) which had a melting point of 154°C and an iodonium iodide compound (VI) which in turn was converted to the proper diiodocompound (V) at 200°C. The diiodocompound was oxidized in the presence of selenium dioxide in acetic acid to give compound I in a reasonable yield (54.3%).



In the second route of synthesis (scheme 2), the diacetyl (II) was oxidized first with selenium dioxide in the presence of acetic acid to give dihydrated 4,4'-biphenyl diglyoxal (VII) 38% yield. Iodination of compound VII in the presence of silver sulfate, iodine and sulfuric acid at 80°C afforded the dihydrated diiodide (I) 60% yield.



The structure and composition of the glyoxal, identified by IR, ¹HNMR spectroscopy and elemental analysis, are quite consistent with the proposed molecular structure and composition. In the IR spectrum, a broad band at 3500-2500 cm⁻¹ for the water molecules associated with compound I which obscures the absorption of aldehyde carbon hydrogen band and a strong carbonyl group absorption at 1680 cm⁻¹ were observed (Fig.1). Its

NMR spectrum in dimethylsulfoxide shows a doublet of doublet at $\delta=3.2, 8.05$ which is an indication of an AB system in the aromatic region, and a singlet at $\delta=8.46$ which shows an aromatic proton located between iodine atom and carbonyl group, and a singlet at $\delta=9.95$, which shows the presence of -CHO group (Fig.2).

Model Compounds

Different model compounds were prepared by the condensation of biphenylbisglyoxalyl dihydrate (I) with 2-phenylenediamine, 3,4-diaminobenzoic acid, and 3,4-diaminopyridine in ethanol or acetic acid under reflux conditions. The structures of these model compounds are shown below (structure VIII through X). IR spectra of the

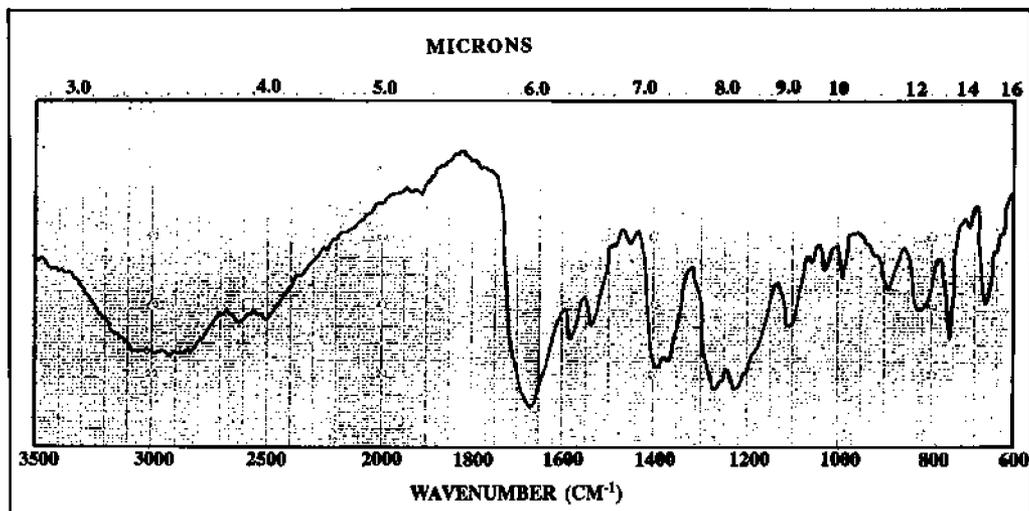
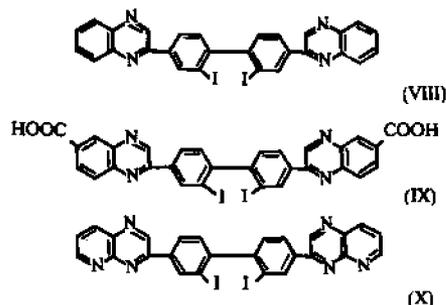


Figure 1: IR spectrum of 2,2'-diiodobiphenyl-4,4'- diglyoxalyl dihydrate (Compound I)



Figure 2: NMR spectrum of 2,2'-diiodobiphenyl-4,4'-diglyoxal dihydrate (Compound I)

prepared compounds showed an absorption band at 1670 cm^{-1} which indicates the formation of C=N. Elemental analysis of the model compounds is also consistent with their structures. The structure, solvents, yields, melting points, reaction times and elemental analysis are given in Table 1.

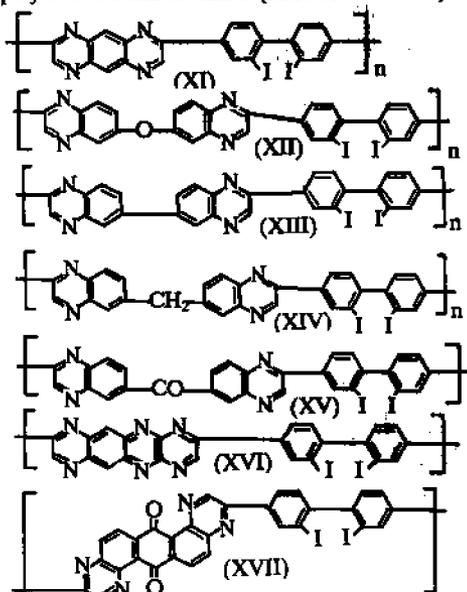
Polymers

Polyquinoxalines were prepared from 2,2'-diiodobiphenyl-4,4'-diglyoxal (I) and 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminobiphenylether, 3,3'-diaminobenzidine, 3,3',4,4'-tetra-aminobiphenylmethane, 3,3',4,4'-

No	Solvent	Yield	m.p. °C	Time hr.	Elemental Analysis							
					Calculation				Found			
					C	H	I	N	C	H	I	N
VIII	EtOH	85.5	205	4	50.78	2.43	38.32	8.46	50.70	2.40	38.10	8.40
IX	EtOH	90.4	>320	4	47.09	2.12	38.21	12.65	46.80	2.08	38.0	12.30
X	AcOH	95	320	3	48.02	2.15	33.83	7.47	47.91	2.20	33.2	7.2

Table 1: Experimental conditions, yields, and elemental analysis of polycondensations of diglyoxal with diamino compounds (VIII-X).

tetraaminobiphenylketone, 2,3,6,7-tetraaminoquinoxaline, and 1,2,6,7-tetraaminoanthraquinone. The structures of these polymers are shown below (structure XI-XVII).



Prepolymerizations were carried out either in HMPA solution at 200-240°C or under melt condition. The desired prepolymers were isolated and then melt condensation was carried out under nitrogen atmosphere at 300-350°C.

Table 2: Experimental conditions, viscosities, and elemental analysis of polycondensed diglyoxal 1 with tetraamino compounds (XI-XVII).

Polymers	Prim. step temp. °C	Time hr	Sec. step temp °C	Yield	[η] ^{**} dl.g ⁻¹	Elemental Analysis							
						Calculated				Found			
						C	H	I	N	C	H	I	N
XI	250	4	310	100	0.15	47.40	1.66	41.37	9.21	48.20	1.52	39.60	8.80
XII	235	4	360	70	0.25	49.73	2.09	37.53	8.28	48.10	1.85	36.20	8.01
XIII	180	4	350	100	0.35	50.93	2.14	38.44	8.49	49.74	1.98	37.20	8.12
XIV	250	4*	330	100	0.22	51.66	2.39	37.64	8.31	59.22	1.28	36.34	8.25
XV	250	4	310	100	0.31	50.61	2.05	36.88	8.14	49.21	1.86	35.30	7.93
XVI	250	4	375	90	0.15	45.31	1.58	39.89	13.21	46.62	1.70	39.23	11.30
XVII	250	3	350	85	0.20	50.45	1.69	35.53	7.84	51.86	1.62	34.90	7.02

The isolated polymers are colored powder materials and their melting points are above 340°C. They are neither soluble in common organic solvents nor soluble in hexamethylene-phosphoramidate, trifluoroacetic acid, dimethyl-formamide, dimethylsulfoxide. These polymers are slightly soluble in concentrated sulfuric acid. They all show low inherent viscosities and infinitesimal weight loss was observed at 400°C, with the heating rate of 150°C/hr under nitrogen atmosphere..

The preparation conditions, yields and elemental analysis of the isolated polymers are summarized in Table 2.

* in hexamethylenephosphoramidate

** Measured at a polymer concentration of 0.2 g/dl in conc. H₂SO₄ at 25°C.

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