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### Synthesis and Characterization of Phenylated Poly(Phenylquinoxaline)s

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## NOTES

### SYNTHESIS AND CHARACTERIZATION OF PHENYLATED POLY(PHENYLQUINOXALINE)S

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#### ABSTRACT

*A new bis (phenyl- $\alpha$ -dicarbonyl) monomer 2, 5-bis- (4-phenyl glyoxaloyl)-3, 4-diphenyl thiophene (II) was synthesised and characterised by mass, NMR and IR spectroscopy. A series of poly (phenylquinoxaline)s PPQs was prepared by solution polycondensation of 3-3' diamino-benzidine (DAB) with II and 4-4' oxidibenzil. All these PPQs were obtained in quantitative yields; had reduced viscosity in the range of 0.79 - 0.96 dL/g and were readily soluble in cresol and halogenated hydrocarbons. They showed film forming properties, had no weight loss below 556°C and retain more than 60% weight at 900°C when investigated for TGA under nitrogen atmosphere.*

#### INTRODUCTION

Poly(phenylquinoxaline)s are an important class of high temperature polymers with many desirable properties including excellent thermal stability, low dielectric constant, high T<sub>g</sub>, dimensional stability over a wide temperature range and good mechanical

properties. The synthesis of PPQ involves polycondensation of bis(o-diamine) with a bis(phenyl- $\alpha$ -dicarbonyl) compound<sup>1</sup>.

Several attempts have been made to improve the solubility of PQ and PPQ via synthesis of block copolymers<sup>2,3</sup>, synthesizing polymers with additional functionality like ester<sup>4</sup>, ethers<sup>5,6</sup> carbonyl ether and sulfide<sup>7</sup>, imide amide<sup>8</sup> in PPQ main chain. Introduction of pendent groups or cardo structure along the polymer backbone<sup>9</sup> also imparted greater solubility. In continuation of our earlier reports on tetraphenyl thiophene moiety containing polyamides<sup>10</sup>, polyimide<sup>11</sup>, PBI<sup>12</sup> etc, we now report synthesis of a novel bis(phenyl- $\alpha$ -dicarbonyl) monomer (II) with phenylated structure, its characterisation and PPQs from II which showed enhanced solubility and no appreciable deterioration in thermal stability.

## EXPERIMENTAL

**Materials** : m-cresol, p-xylene, diphenyl ether and dichloromethane (s.d.fine Bombay) were purified following the standard procedures. Phenyl acetyl chloride (Merck) was used as received.

**Synthesis of Monomers** : 3,3' Diamino benzidine (DAB) and 4,4' - oxydibenzil were synthesized in laboratory following literature procedure<sup>13,14</sup>. 2,5-Bis-(4-phenyl glyoxaloyl)-3,4 diphenyl thiophene (II) was synthesized as detailed below.

**A] Synthesis of 2,5 - bis-(4-carbonyl benzyl) -3, 4 - diphenyl thiophene (I)** : In 1000 mL three necked round bottom flask equipped with ice bath, double walled reflux condenser with CaCl<sub>2</sub> tube, thermowell, magnetic stirrer, dropping funnel and N<sub>2</sub> inlet were placed 16.1 g AlCl<sub>3</sub> and 90.7 mL dichloromethane (DCM) and stirred to form suspension. A solution of 23.4856 g (0.06 M) tetraphenyl thiophene and 18.704 g (0.137 M) of phenyl acetyl chloride in 250 mL DCM was added dropwise over a period of 1 hr. while maintaining the temperature between 15-20°C under the purge of N<sub>2</sub>. The resulting reddish brown mixture was stirred at ambient temperature for 18 hrs. and poured onto crushed ice and hydrochloric acid. The organic layer was separated and washed successively with water, aqueous sodium bicarbonate, water and dried over anhydrous magnesium sulphate. Solution was filtered and filtrate was concentrated to 50 mL and filtered, solid washed with benzene and recrystallised from benzene. Product was dried under vacuum, yield 18.59 g (48.98%), mp. 220°C.

**Anal** : Calculated for C<sub>44</sub>H<sub>32</sub>O<sub>2</sub>S                      C,84.64; H,5.13; S,5.31  
Found    C,84.53; H,5.44; S,5.92.

**Mass** : (m/e) 624 (M<sup>+</sup>); 534 base peak, 415, 308, 221, 91

**B] Synthesis of 2,5-bis-(4-phenyl glyoxaloyl) - 3,4 diphenyl thiophene (II)** : In a 250 mL round bottom flask equipped with reflux condenser and magnetic stirrer were placed

5.416 g of selenium dioxide and 74 mL of glacial acetic acid and 15 g (0.024M) of I was added in the reaction flask at 60°C. The reaction mixture stirred at reflux for 24 hrs, followed by hot filtration. The clear yellow filtrate was concentrated to about 25 mL and filtered. The yellow residue was washed with acetic acid (5 mL) dried in air and recrystallised from a mixture of ethyl acetate and hexane to give yellow crystals of (II) yield 11.99 g(76.5%), mp. 260°C.

**Anal** : Calculated for  $C_{44}H_{28}O_4S$  C,88.98; H,4.29  
Found C,88.79; H,4.41

**Mass** : (m/e) 652 ( $M^+$ ), 547, 414, 105, 77.

**PMR** : 7.94, dd (4H); 7.84, d (4H); 7.75, t (2H); 7.52, t (4H);  
7.73 d (4H); 7.18, t+d (4H + 2H); 7.00 t (2H).

Each peak showed fine ABC/AB type complex splitting.

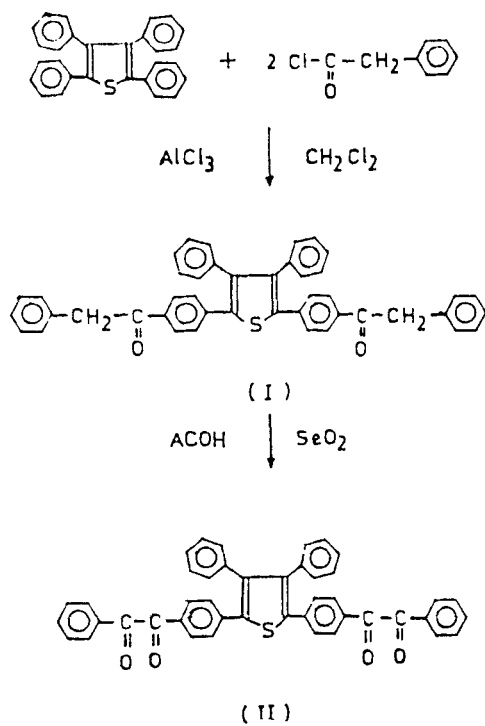
**Polymerization (Preparation of PQ.5)** : In a 100 mL 3 necked round botom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube were placed 0.214 g (0.001 M) of finely powdered DAB and 4.5 mL of 1:1 mixture of m-cresol and p-xylene. The reaction mixture was stirred at 20°C for five minutes and 0.434 g(0.001 M) of finely powdered oxidibenzil was added in two lots in 10 minutes interval and stirred at 20°C for 24 hrs. A portion of the viscous solution was used to cast polymer film on a glass plate which was dried at 80°C/2h and 130°C/15h to get tough, transparent, flexible, slightly yellow to brown coloured film. The remaining reaction mixture was poured in methanol to precipitate the PPQ. It was filtered, washed with methanol and dried under vacuum at 70°C for several hours. The PPQ had viscosity ( $\eta_{sp/c}$ ) of 0.79 dL/g in m-cresol. The other PPQs, PQ1 to PQ4, were synthesized by following similar procedure.

**Measurements** : The reduced visosities ( $\eta_{red}$ ) were measured with 0.5% concentration in m-cresol at 30°C using suspended type Ubbelohde viscometer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as nujol mull or polymer films. H 1 NMR were recorded in  $CDCl_3$  on Brucker 200 MHz spectrophotometer using TMS as an internal reference. Thermogravimetric analysis were performed on Perkin-Elmer TGA-7 at a heating rate of 10°C/min. The mass spectra were recorded on II MS 30, double beam mass spectrometer. Elemental analysis were run in Perkin-Elmer model 2400 - CHN analyser.

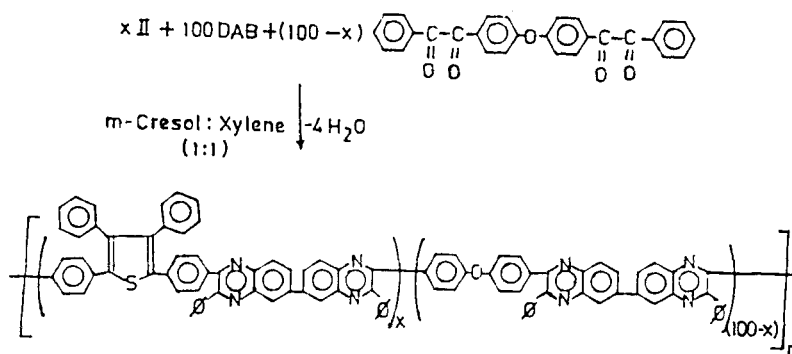
## RESULTS AND DISCUSSION

The new bis-(phenyl- $\alpha$ -dicarbonyl) monomer (II) was synthesized in two steps; involving the FC acylation of tetraphenyl thiophene by phenyl acetyl chloride to give 2,5-Bis-(4-carbonyl benzyl)-3,4-dipheyl thiophene followed by oxidation using selenium dioxide to give (II).

## SYNTHESIS OF MONOMER (II)



## POLYMERIZATION



X =	100	75	50	25	00
PQ	1	2	3	4	5

The structure of I and II were confirmed by spectroscopic and elemental analysis. Infrared (IR) spectrum of I showed a strong absorption band at  $1684\text{ cm}^{-1}$  ( $\nu_{\text{C}} = 0$ ) for arylalkyl carbonyl structure.  $^1\text{H}$  NMR of I could not be taken due to insolubility of the compound I even in chloroform, dimethyl sulfoxide or trifluoroacetic acid. Mass spectrum of the I showed  $\text{M}^+$  at  $m/e$  624 and base peak at  $m/e$  534 (M-90) for loss of -CHPh. Fragmentation of  $\text{COCH}_2\text{Ph}$  additionally gave (M-90-119) peak at  $m/e$  415 and the peak at  $m/e$  308 resulted by loss of one more CPh. Peak at  $m/e$  91 is due to trophylidium ion formation. IR spectrum of II showed two strong absorption bands at  $1674\text{ cm}^{-1}$  and  $1664\text{ cm}^{-1}$  corresponding to the two carbonyl groups of  $\alpha$ -diketo group. The PMR spectrum of II conforms the structure assigned as evidenced by the chemical shift (all aromatic protons 8.1 to 6.8  $\delta$ ); number of NMR signals and expected multiplicity of the peaks with appropriate integration and no signals due to  $-\text{CH}_2-$  in the range of 1 to 6 ppm. Mass spectrum of II showed ( $\text{M}^+$ ) peak at  $m/e$  652 as expected with fragmental peaks at  $m/e$  547 (loss of PhCO, M-105), 414 (loss of 2 PhCO and CO). Peaks at  $m/e$  77 and 105 are due to Ph and PhCO ions. Absence of peak at  $m/e$  91 in mass spectrum of II indicate absence of trophylidium ion formation confirming complete oxidation of I into II.

Poly(phenylquinoxaline)s and copoly(phenylquinoxaline)s were synthesized by polycondensation of DAB with II and/or ODB by solution polymerization method. The polymers were synthesized in almost quantitative yield and showed reduced viscosity in the range of 0.79 to 0.96 dL/g at  $30^\circ\text{C}$  (Table I). The formation of polymer was confirmed by IR spectroscopy. IR spectrum of PPQ showed absence of absorption at  $1674$  and  $1664\text{ cm}^{-1}$  indicating ketonic functionalities of II/ODB reacted completely to form poly(phenylquinoxaline). Similarly absorption at  $3400\text{--}3000\text{ cm}^{-1}$  due to NH (stretch) were absent. A tough, flexible and transparent film could be cast from all the reaction mixtures. It is observed that in copoly(phenylquinoxaline)s as the amount of II increases the viscosity of the polymer also increases (PQ5 to PQ1).

Thermal properties of these polymers were evaluated by thermogravimetry and results are given in Table I. The polymers showed the initial decomposition temperature between  $556$  to  $572^\circ\text{C}$  and  $T_{\text{max}}$   $580$  to  $603^\circ\text{C}$  where as the residual weight at  $900^\circ\text{C}$  was in the range of 60 to 68% of the initial weight indicating that the polymers are highly thermally stable.

All these PPQs were soluble in chloroform, tetrachloroethane and *m*-cresol etc. However, they are partly soluble in aprotic polar solvents such as DMAc, DMF, NMP. The polymers were insoluble in DMSO. A 1% solution was taken as criterion for solubility. On qualitative comparison it was observed that the polymers containing higher % of II (PQ4 to PQ1) were more easily soluble than PQ5.

Table - I : YIELD, VISCOSITY AND THERMAL PROPERTIES OF COPOLY (PHENYLQUINOXALINE)S FROM DAB.

Polymer Code	Bis( $\alpha$ -dicarbonyl) (Mol%)		Yield (%)	$\eta_{sp}/c$ (dL/g)	$T_i$ ( $^{\circ}\text{C}$ )	$T_{max}$ ( $^{\circ}\text{C}$ )	Residual Weight at $900^{\circ}\text{C}$ (%)
	II	ODB					
PQ1	100	---	98.76	0.96	556	580	60.76
PQ2	75	25	99.30	0.91	572	607	62.62
PQ3	50	50	99.27	0.88	602	623	-----
PQ4	25	75	99.20	0.80	588	615	61.46
PQ5	---	100	98.95	0.79	572	603	68.05

## CONCLUSIONS

A novel bis-(phenyl- $\alpha$ -dicarbonyl) monomer, 2,5-bis-(4-phenyl glyoxaloyl)-3, 4-diphenyl thiophene has been synthesized and utilized as comonomer to obtain high molecular weight poly(phenylquinoxaline)s. The resulting polymers were highly thermally stable and soluble in some organic solvents. A tough, flexible and transparent film could be cast from the polymerization reaction mixture itself. These PPQs have excellent potential for use in high temperature applications.

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