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A new synthesis of bisbenzils and novel poly(phenylquinoxaline)s therefrom

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A novel synthesis of bisbenzils has been investigated and used to prepare several monomers for the synthesis of poly(phenylquinoxaline)s (PPQs). PPQs incorporating 2-naphthalenyl moieties in the pendent position have been prepared. The polymers are amorphous but exhibit excellent resistance to most organic solvents, and are soluble in only *m*-cresol and concentrated sulfuric acid. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(phenylquinoxaline); thermally stable; solvent resistant)

INTRODUCTION

Poly(phenylquinoxaline)s (PPQs) are engineering thermoplastics that are known for their high thermal and hydrolytic stability[1]. They have attracted much interest for applications such as adhesives, packaging in electronics and as insulation for electrical wiring[2]. PPQs have been synthesized via quinoxaline ring forming polymerization and via nucleophilic displacement of activated halides[3].

A significant effort has been made to modify PPQs in order to produce processable materials with desirable properties[3]. The work includes modifying the polymer backbone or altering the nature of the pendent groups[3]. The pendent groups can be altered through the synthesis of novel bisbenzils. Many of these compounds can be prepared via the method reported by Wrasidlo and Augl, which involves Friedel–Crafts reaction of phenylacetyl chlorides to give deoxybenzoin intermediates[4]. Other synthetic routes to novel bisbenzils have been investigated in an attempt to make the synthesis of these compounds more attractive[5–8].

We have recently developed a novel synthesis of bisbenzils by the reaction of an aromatic Schiff base with bistertiary amines. This chemistry is versatile and can be used to insert a variety of aromatic and heterocyclic groups into the pendent position of the bisbenzil, depending on the Schiff base employed. Four bisbenzil monomers have been prepared by this methodology and polymerized with 1,1′,2,2′-tetraaminobiphenyl (DAB) to produce PPQs. The synthesis and properties of these monomers and polymers will be discussed.

EXPERIMENTAL

Materials

Aniline, potassium carbonate (A&C Chemicals), benzaldehyde, 2-naphthaldehyde, *N*-ethylaniline, α,α'-dichloro-*p*-xylene, α,α'-dichloro-*m*-xylene, *m*-cresol and potassium butoxide (Aldrich) were used as received. Dimethylformamide (DMF) (ACP) was distilled from calcium hydride and stored over 4 Å molecular sieves. 1,1′,2,2′-Tetraaminobiphenyl (Aldrich) was recrystallized under nitrogen from deoxygenated, distilled, deionized water containing a pinch of sodium hydrosulfite.

General methods

^1H and ^{13}C nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Unity-500 spectrometer and were referenced internally to tetramethylsilane (TMS). Mass spectrometry (m.s.) was performed on a DuPont 21-492B instrument. Melting points were obtained using a Fisher–Johns melting point (m.p.) apparatus. Inherent viscosity data were obtained using *m*-cresol solutions with a concentration of 0.5 g dl^{-1} in a calibrated 1 Å (176) Ubbelohde dilution viscometer at 25°C. The bath temperature was controlled using a Julabo (model PC) heater.

Apparent molecular weights were determined by gel permeation chromatography (g.p.c.) using a calibration curve constructed with monodisperse polystyrene standards. The polymers were analysed with a Waters 510 HPLC with an ultraviolet (u.v.) detector ($\lambda = 254$ nm) and four ultra-styragel columns (10^5, 10^4, 500 and 100 Å) in series. The mobile phase used was chloroform.

Polymer samples for thermal characterization were dried at 200°C in a vacuum oven (1 mmHg) for 18 h before use. Each polymer was pressed into pellets under 5 tons of pressure using a KBr pellet die. Glass transition temperatures (T_g) were obtained by differential scanning calorimetry (d.s.c.) using a Seiko 220 DSC at a heating rate of 20°C min^{-1} under a nitrogen atmosphere. The T_g was taken as the midpoint of the change in slope of the baseline. All values reported are from the second scan.

Thermogravimetric analysis (t.g.a.) was performed using a Seiko 220 TG/DTA instrument. The 5% weight loss temperatures were recorded using a heating rate of 10°C min^{-1} under atmospheres of nitrogen and air.

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Young's moduli were recorded using a Seiko TMA/SS120 instrument. The polymer films used for these measurements were prepared from 150 mg of polymer dissolved in 3 ml of chloroform. The chloroform solution was cast onto a glass plate using circular glass moulds 2.5 cm in diameter. The chloroform was allowed to evaporate at room temperature and the films were then dried at 85°C for 18 h in a forced air oven and under vacuum (1 mmHg) at 100°C for 18 h.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Schiff base

N-Phenylmethylenebenzeneamine **1a** and *N*-(2-naphthalenylmethylene)benzeneamine **1b** were prepared as described in the literature[9].

1,4-Bis[(N-ethyl-N-phenyl)methanamine]benzene **8a**

A 100 ml flask was charged with acetonitrile (500 ml), *N*-ethylaniline **7** (12.1 g, 0.10 mol), α,α'-dichloro-*p*-xylene **6a** (8.75 g, 0.05 mol) and K_2CO_3 (55.3 g, 0.4 mol). The crude solid was recrystallized from methanol to give **8a** (13.5 g, 78.5%) as white needles (m.p. 127–128°C). ^1H n.m.r. (200 MHz, $CDCl_3$), δ (ppm) 7.19–7.26 (m, 8H), 6.67–6.71 (m, 6H), 4.5 (s, 4H), 3.40–3.55 (q, $J = 6.98$ Hz, 4H), 1.17–1.24 (t, $J = 7.02$ Hz, 6H). ^{13}C n.m.r. (125 MHz, $CDCl_3$), δ (ppm) 149.5, 138.2, 129.6, 127.2, 116.4, 112.5, 54.1, 45.5, 12.5. M.s. (direct inlet electron impact, 100°C), m/e 345 (14.0, $M^{+\cdot} + 1$), 344 (52.2, $M^{+\cdot}$), 244 (100), 157 (13.8), 104 (31.9), 16.1 (3.7). Calculated for $C_{24}H_{24}N_2$: C, 84.31; H, 7.44; N, 8.21. Found: C, 84.67; H, 7.11; N, 8.23.

1,3-Bis[(N-ethyl-N-phenyl)methanamine]benzene **8b**

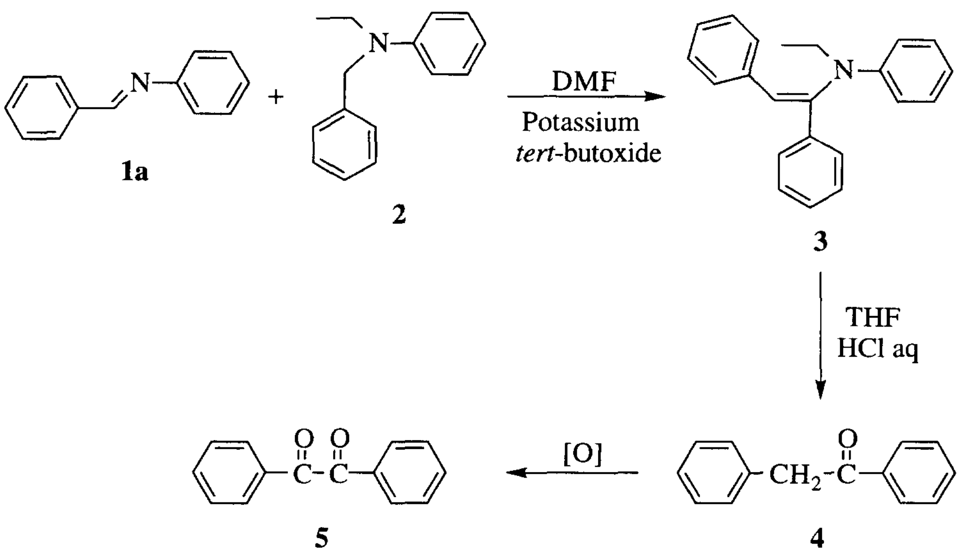
Compound **8b** was prepared in the same manner as described for **8a**. The reactants were *N*-ethylaniline **7** (12.1 g, 0.10 mol) and α,α'-dichloro-*m*-xylene **6b** (8.75 g, 0.05 mol). The crude solid was recrystallized from methanol to give **8b** (14.1 g, 82%) as white needles (m.p. 82–83°C). ^1H n.m.r. (500 MHz, $CDCl_3$), δ (ppm) 7.09–7.24 (m, 5H), 6.63–6.68 (m, 5H), 4.47 (s, 4H), 3.42 (q, $J = 6.5$ Hz, 4H), 1.19 (t, $J = 6.6$ Hz). ^{13}C n.m.r. (125 MHz, $CDCl_3$), δ (ppm) 148.41, 139.59, 129.14, 128.71, 124.94, 124.70, 115.93, 112.12, 52.89, 45.08, 12.04. M.s. (direct inlet EI, 100°C), m/e 345 (17.4), 344 (65.2), 330 (6.4), 329 (24.9), 315 (3.8), 225 (12.0), 224 (28.5), 157 (20.3), 105 (100), 77 (12.8). Calculated for $C_{24}H_{28}N_2$: C, 83.68, H, 8.19; N, 8.13. Found: C, 83.59; H, 8.22; N, 8.07.

1,1′-(1,4-Phenylene)bis(2-phenylethanedione) **11a**

A 250 ml, three-necked flask was charged with *N*-phenylmethylenebenzeneamine **1a** (6.94 g, 38.3 mmol), 1,4-bis[(*N*-ethyl-*N*-phenyl)methanamine]benzene **8a** (6.00 g, 17.4 mmol) and DMF (75 ml). The flask was flushed with nitrogen gas and the solution was heated to 75°C. Potassium butoxide (19.8 g, 176.2 mmol) was added to the flask and the solution was stirred for 30 min. The reaction was quenched into distilled water (300 ml) and the crude solid was recovered by filtration. The solid was digested in methanol for 2 h, filtered and dried. The resulting yellow powder was dissolved in tetrahydrofuran (THF) (100 ml). Distilled water (20 ml) and concentrated HCl (5 ml) were added. The solution was refluxed for 3 h, cooled and diluted with distilled water (200 ml). The aqueous solution was extracted with methylene chloride; the organic phase was separated, washed with 10% K_2CO_3 solution, dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The crude solid was dissolved in dimethyl sulfoxide (DMSO) (200 ml) and HBr (48% aqueous, 10 ml). The solution was stirred at 55°C for 24 h. The aqueous solution was extracted with methylene chloride and the solvent was removed under reduced pressure. The crude solid was recrystallized from ethanol to yield **11a** (2.8 g, 48%) as fine yellow needles (m.p. 124–125°C; literature value[10] 126°C).

1,1′-(1,3-Phenylene)bis(2-phenylethanedione) **11b**

Compound **11b** was prepared in the same manner as described for **11a**. The reactants were 1,3-bis[(*N*-ethyl-*N*-phenyl)methanamine]benzene **8b** (6.00 g, 17.4 mmol) and *N*-phenylmethylenebenzeneamine **1a** (6.94 g, 38.3 mmol). The crude product was recrystallized from ethanol to yield **11b** (3.0 g, 51%) as pale yellow needles (m.p. 98–99.5°C; literature value[11] 99–100°C).



Scheme 1

1,1′-(1,4-Phenylene)bis[2-(-naphthalenyl)ethanedione] 11c

Compound **11c** was prepared in the same manner as described for **11a**. The reactants were 1,4-bis[(*N*-ethyl-*N*-phenyl)methanamine]benzene **8a** (6.00 g, 17.4 mmol) and *N*-(2-naphthalenylmethylene)benzeneamine **1b** (8.86 g, 38.3 mmol). The crude product was recrystallized from THF to yield **11c** (4.1 g, 53%) as a pale yellow powder (m.p. 203–204°C). ^{1}H n.m.r. (500 MHz, $CDCl_3$), δ (ppm) 8.41 (s, 2H), 8.18 (s, 4H), 8.08–8.10 (m, 2H), 7.98–7.99 (m, 2H), 7.90–7.94 (m, 4H), 7.56–7.68 (m, 4H). ^{13}C n.m.r. (500 MHz, $CDCl_3$), δ (ppm) 193.51, 193.39, 137.28, 136.52, 133.78, 132.29, 130.38, 130.00, 129.90, 129.82, 129.38, 128.00, 127.35, 123.57. M.s. (direct inlet EI, 150°C), *m/e* 442 (8.1, $M^{+\cdot}$), 156 (16.1), 155 (100), 128 (6.1), 127 (31.8). Calculated for $C_{30}H_{18}O_4$: C, 81.44; H, 4.10. Found: C, 81.41; H, 4.13.

1,1′-(1,3-Phenylene)bis[2-(2-naphthalenyl)ethanone] 11d

Compound **11d** was prepared in the same manner as described for **11a**. The reactants were 1,3-bis[(*N*-ethyl-*N*-phenyl)methanamine]benzene **8b** (6.00 g, 17.4 mmol) and *N*-(2-naphthalenylmethylene)benzeneamine **1b** (8.85 g, 38.3 mmol). The solid was recrystallized from THF to yield **11d** (3.7 g, 48%) as pale yellow plates (m.p. 177–178°C). ^{1}H n.m.r. (500 MHz, DMSO-d_6), δ (ppm) 8.68 (t, $J = 1.5\,H_2$, 1H), 8.33–8.35 (dd, $J = 1.5$ and $8\,H_2$, 2H), 7.79–7.90 (m, 8H), 7.72–7.75 (t, $J = 8\,H_2$, 1H), 7.42–7.51 (m, 6H), 4.67 (s, 4H). ^{13}C n.m.r. (500 MHz, DMSO-d_6), δ (ppm) 198.2, 137.6, 133.8, 133.6, 133.46, 133.43, 132.6, 129.08, 129.05, 128.9, 128.8, 128.5, 128.3, 128.2, 126.9, 126.5, 45.8. M.s. (direct inlet EI, 180°C), *m/e* 414 (22.1, $M^{+\cdot}$), 274 (21.1), 273 (100), 141 (37.7). Calculated for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.89; H, 5.37.

Polymer synthesis

A general procedure for the preparation of the polymers **13a**–**13d** is given. A 100 ml, three-necked flask was flushed with nitrogen gas and charged with 1,1′-(1,4-phenylene)bis(2-phenylethanedione) **11a** (1.00 g, 2.92 mmol), *m*-cresol (8 ml) and xylene (8 ml). 1,1′,2,2′-Tetraaminobiphenyl **12** (0.6259 g, 2.92 mmol) was crushed to a fine powder and added to the flask over 5 min. The reaction mixture was stirred at room temperature for 24 h, and then heated to 90°C for 2 h. The solution was diluted with xylene (10 ml) and the polymer was coagulated into aqueous methanol. The crude polymer was stirred in boiling water for 2 h to extract trapped solvent, recovered by filtration and dried in air. The solid was dissolved in chloroform (100 ml) and the solution was filtered through celite. The solution was then concentrated and the polymer was reprecipitated into methanol. The polymer was dried under vacuum for 24 h at 90°C.

RESULTS AND DISCUSSION

We have previously reported[12] the reaction of aromatic Schiff base **1a** with tertiary amine **2** to form enamine **3**. The hydrolysis of enamine **3** produced deoxybenzoin **4** which could then be oxidized to benzil **5** (*Scheme 1*). This serves as an excellent model reaction for the preparation of bisbenzils.

Bistertiary amines **8a** and **8b** were prepared from *N*-ethylaniline **7** and α,α'-dichloroxylenes **6a** and **6b** (*Scheme 2*)[12]. Compounds **8a** and **8b** were reacted with two equivalents of aromatic Schiff bases **1a** and **1b** to produce bisenamines **9a**–**9d** (*Scheme 3*). The hydrolysis of **9a**–**9d** gave diketones **10a**–**10d** which were then oxidized, readily to the tetraketone monomers **11a**–**11d** (*Scheme 3*)[13]. We were able successfully to prepare monomers **11a**–**11d** in 48–53% overall yield. A wide variety of bisbenzils can potentially be prepared by this route.

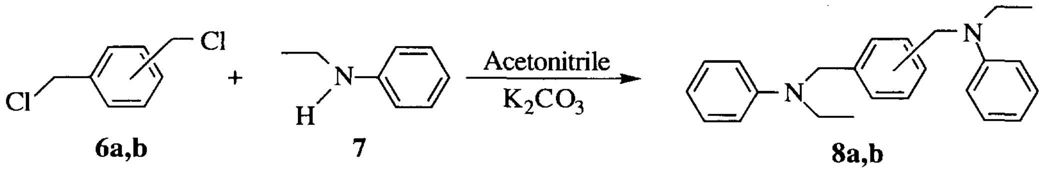
Monomers **11a**–**11d** were polymerized with 1,1′,2,2′-tetraaminobiphenyl **12** (DAB) in *m*-cresol, following the method of Hergenrother[14], to give high molecular weight PPQ polymers **13a**–**13d** (*Scheme 4*).

Table 1 presents the physical and mechanical properties of polymers **13a**–**13d**. Polymers **13a** and **13b**, which have been synthesized previously[3], have been included for comparison. The glass transition temperatures and thermal stabilities, as measured by t.g.a., are comparable to those reported previously[3].

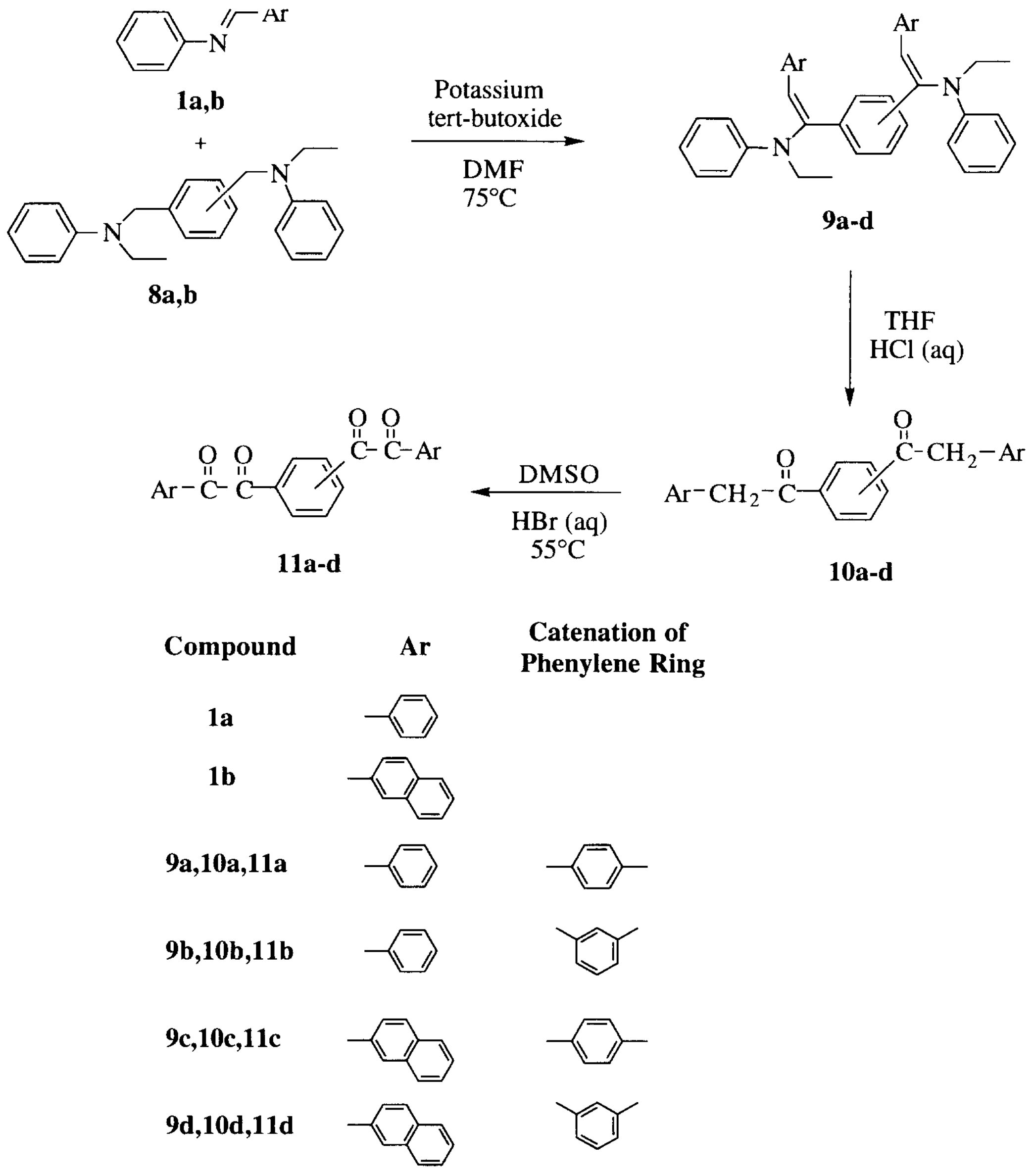
In polymers **13c** and **13d**, the pendent phenyl groups of polymers **13a** and **13b** have been replaced with 2-naphthalenyl groups. We speculated that the larger 2-naphthalenyl moieties might result in a polymer with a higher T_g. The bulky 2-naphthalenyl groups might be expected to increase the resistance to the 'jump rope' motions of the polymer chains as they approached the polymer T_g, thus increasing the T_g of the polymer[15]. The data in *Table 1* show that no significant difference was observed between the T_g values of polymers **13a** and **13c** or polymers **13b** and **13d**.

The thermal stabilities and mechanical properties of polymers **13a** and **13b** are not significantly different from those of polymers **13c** and **13d**. All polymers showed 5% weight loss temperatures in excess of 550°C (by t.g.a.) in nitrogen and air. The Young's moduli at 25 and 200°C are also comparable.

Polymers **13a** and **13b** were soluble in *m*-cresol, concentrated sulfuric acid and chlorinated solvents such as chloroform. A significant change in polymer solubility is observed for polymers **13c** and **13d**, which were soluble only in *m*-cresol and concentrated sulfuric acid. The improved solvent resistance is not a result of Schiff base crosslinks, which can occur during the polymerization reaction[16]. The polymers did not show any decrease in inherent viscosity after 18 h in an aqueous sulfuric acid solution; any decrease would have indicated the hydrolysis of Schiff base moieties[16].



Scheme 2

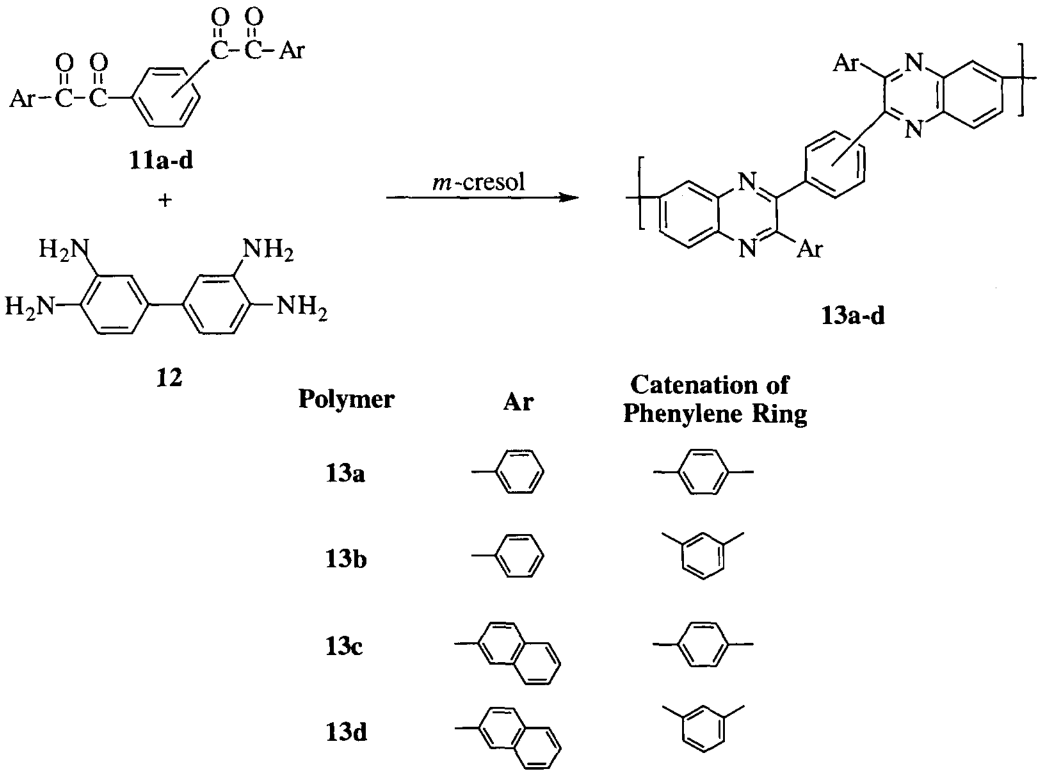


Scheme 3

Table 1 Properties of the polymers

Polymer	Inherent viscosity[a] (dl g^{-1})	T_g[b] (°C)	Temperature of 5% weight loss[c] (°C)		Young's modulus (GPa)		tan δ
			N_2	Air	25°C	200°C	
13a	1.2	333	564	555	1.93	1.21	326
13b	0.98	319	588	568	1.88	1.23	309
13c	1.0	333	600	577	1.96	1.17	325
13d	0.88	317	581	564	1.85	1.25	308

[a] At 0.5 g dl^{-1} in $CHCl_3$ at 25°C
[b] Heating rate of 20°C min^{-1}
[c] Heating rate of 10°C min^{-1}



Scheme 4

CONCLUSIONS

A new synthesis of bisbenzil monomers for phenylquinoxaline polymers has been reported. Four bisbenzils have been prepared and successfully polymerized with 1,1′, 2,2′-tetraaminobiphenyl. Two polymers incorporating 2-naphthalenyl moieties in the pendent position have been prepared. The presence of the pendent 2-naphthalenyl moieties was found to increase solvent resistance, resulting in polymers which were soluble in only *m*-cresol and concentrated sulfuric acid. No other significant changes to the physical and mechanical properties of the polymers, as compared to previously reported PPQs were observed.

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