Synthesis of High Performance Polyamides Utilizing Copper-Catalyzed Amidation of a Dibromoarene with Different Diamides

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ABSTRACT: A series of diphenylquinoxaline-containing polyamides were prepared from the condensation polymerization of 2,3-bis (4-bromophenyl) quinoxaline (DBQ) with various primary and secondary diamides via copper-catalyzed amidation reaction. The polyamides were characterized with FTIR, NMR, GPC, differential scanning calorimeter, and thermo gravimetric analysis, and their solubility and viscosity were measured. The polyamides synthesized here are amorphous and showed relatively good solubility in polar aprotic solvents and demonstrate the ability to form brownish hard films by solvent casting; their inherent viscosities ranged from 49 to 55 mL/g. The average molecular weights of polyamides were in the range of M_w = 11,950–5592 g/mol (MWD = 1.21–1.87). These polyamides had relatively high thermal stability with T_g values up to 276°C, 10% weight loss temperatures ($T_{10\%}$) in the range of 364–476°C, and char yields at 600°C in N_2 up to 72%. They also exhibit emission in the solid state and in dilute (0.2 g/dL) DMAc solution at 425–484 nm with photoluminescence quantum (Φ_f) yields in the range of 14–23%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1707–1715, 2012

Key words: copper catalysis; coupling polymerization; polyamide; photo physics

INTRODUCTION

Poly(phenylquinoxaline-amide)s form an important class of high performance thermoplastics with exceptional properties such as high T_g, good dimensional stability, low dielectric constant, and tough mechanical properties that make them suitable for diverse applications.[1,2] Polymers containing diphenylquinoxaline moieties are also well-known photo- and electroluminescent materials.[3–7] Among different methods for polymer preparation, one way is C—C coupling reaction by the usage of metal-catalyzed polymerization techniques. Many attempts were made for the synthesis of polymers with different fascinating structural variety through chain-growth condensation polymerization using C—C metal-catalyzed coupling reaction.[8–15] There are informative reviews on the cross-coupling reactions used for the preparation of polymers.[16] Most general and noteworthy synthetic methodology for the formation of C—N bonds in organic synthesis is based on transition-metal-catalyzed approaches which were contributed progressively and independently by Hartwig and coworkers[17] and Wolfe and Buch-

wald,[18] and excellent reviews on this field are also available.[19]

The Pd-catalyzed aryl amination has been applied to polycondensation reactions to give various polyamines.[20–22] Copper-mediated couplings are the reactions of choice for large and industrial scale formation of aryl-heteroatom bonds. In comparison to palladium chemistry, copper catalysts are simple, mild, and avoid the use of air-sensitive and expensive phosphine ligands or additives. Furthermore, there is an economic attractiveness for using copper over noble metals such as palladium. There is a report of preparation of a series of aniline-thiophene copolymers from condensation of 2,5-dibromothiophene or 3,4-dibromothiphene with 1,4-diaminophenylenes under Ullmann conditions in the presence of cuprous iodide and sodium carbonate.[23,24] We have also used copper catalyzed polymerization for the synthesis of polymers from 2,7-dibromo-9,9-dioctylfluorene.[25,26] In the present article, we report synthesis of a series of polyamides by polycondensation of 2,3-bis(4-bromophenyl)quinoxaline with different diamides using copper catalyzed cross-coupling reaction in the presence of CuI and N,N'-dimethylethylene diamine (DMEDA) as catalysts and K_2CO_3 as a base. The polyamides have been fully characterized with FTIR, ^{1}H-NMR, and elemental analysis and some of their physical properties such as viscosity, solubility, molecular weight, photophysical, and thermal stability were determined.

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EXPERIMENTAL

Materials

2,5-Dipiperazinedione, dicarboxylic dichlorides, and all other chemicals were purchased from either Merck or Fluka Co. (Germany). 2,3-bis (4-bromophenyl) quinoxaline quinoxaline, terephthalamide, isophthalamide, adipamide, *N,N'*-dibutylterephthalamide, and *N,N'*-diphenylterephthalamide were prepared according to the procedures given in the following sections. Dimethylformamide (DMF) was purified by distillation over calcium hydride under reduced pressure. Toluene was dried on sodium wire. All other materials were used without further purification.

Monomer synthesis

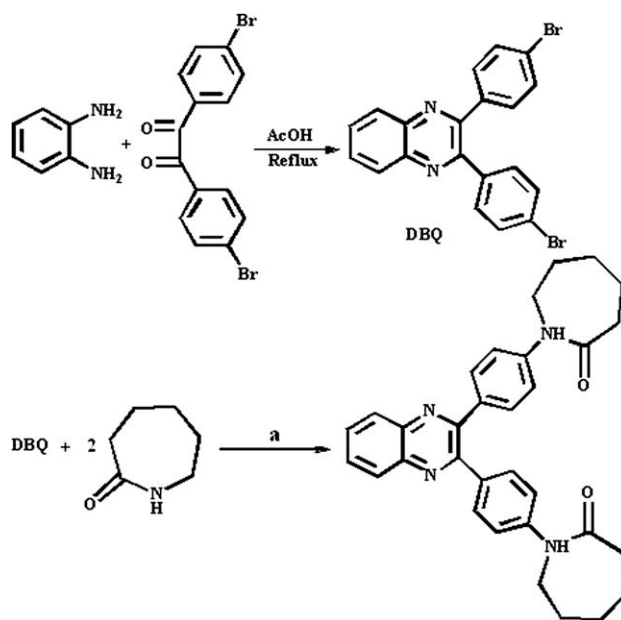#### 2,3-bis (4-bromophenyl) quinoxaline

2,3-bis (4-bromophenyl) quinoxaline (DBQ) was prepared by using almost similar procedure reported in the literature,[27] as shown in Scheme 1. Shortly, in a 25-mL two-necked, round-bottomed flask equipped with a magnetic stirrer bar, 4,4'-dibromobenzil (1 g, 2.72 mmol) was completely dissolved in acetic acid (10 mL). Benzene-1,2-diamine (0.29 g, 2.72 mmol) was then added, and the reaction mixture was heated under reflux for 8 h. While the brown mixture was allowed to cool on its own, the white needles were separated from the mother liquid; 1.15 g (97% crude yield), m.p. = 191–193°C. Anal. Calcd. for $C_{20}H_{12}N_2Br_2$: C, 54.58%; H, 2.75%; N, 6.36%. Found: C, 54.33%; H, 2.79%; N, 6.41%. FTIR (KBr, cm^{-1}): 3028(C—H aromatic), 1608 (C=N aromatic), 1600, 1448 (C=C aromatic). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ = 8.18 (dd, J = 3.2 Hz, 2H), 7.80 (dd, J = 3.6 Hz, 2H), 7.52 (d, J = 8.4 Hz, 4H), 7.42(d, J = 8.4 Hz, 4H). ^{13}C-NMR (400 MHz, DMSO-d_6, ppm): δ = 123.73, 129.20, 130.44, 131.44, 131.70, 137.66, 141.24, 151.91. MS (m/z) calcd: [M$^+$]: 440.1; found: 440.0.

Synthesis of amides

Different primary and secondary diamides were prepared from the reaction between various diacid chlorides such as terephthaloyl chloride, isophthaloyl chloride, and adipoyl chloride and a solution of ammonium or amines such as aniline and *n*-butyl amine by using almost similar procedure reported in the literature.[28] The Products were characterized and the data are given bellow.

Terephthalamide

Yield = 87%, white powder, m.p. = 332°C. Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53%; H, 4.91%; N,

Scheme 1 Preparation of 2,3-bis(4-bromophenyl)quinoxaline (1) and model compound (2). (a: CuI, DMEDA, K_2CO_3, toluene, under argon, at 110–115°C, 12 h).

17.06%. Found: C, 58.61%; H, 4.99%; N, 17.15%. FTIR (KBr, cm^{-1}): 3360, 3158 (N—H aromatic), 1656 (C=O aromatic). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ = 8.08 (s, 2H), 7.9 (s, 4H), 7.52 (s, 2H). ^{13}C-NMR, δ = 128.5, 137.01, 168.

Isophthalamide

Yield = 87%, white powder, m.p. = 262–264°C. Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53%; H, 4.91%; N, 17.06%. Found: C, 58.59%; H, 4.98%; N, 17.12%. FTIR (KBr, cm^{-1}): 3364, 3150 (N—H aromatic), 1658 (C=O aromatic). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ = 8.35 (s, 1H), 8.02 (s, 2H), 7.98–7.91 (m, 2H), 7.87–7.77 (m, 1H), 7.51 (s, 2H). ^{13}C-NMR, δ = 126.9, 129.01, 131.2, 134.5, 68.2.

Adipamide

Yield = 87%, white powder, m.p. = 204–206°C. Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.99%; H, 8.39%; N, 19.43%. Found: C, 49.92%; H, 8.47%; N, 19.48%. FTIR (KBr, cm^{-1}): 3375, 3176 (N—H aromatic), 1668 (C=O aromatic). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ = 7.23 (s, 2H), 6.7(s, 2H), 2.04–1.99 (m, 4H), 1.47–1.42 (m, 4H). ^{13}C-NMR, δ = 25.32, 35.41, 176.66.

N,N'-dibutylterephthalamide (DBTA)

Yield = 87% ,white powder, m.p. = 226–228°C. Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53%; H, 8.75%; N, 10.14%. Found: C, 69.31%; H, 8.58%; N, 10.01%. FTIR (KBr, cm^{-1}): 3313 (N—H aromatic), 2959(C–H

aliphatic),1628 (C=O aromatic). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ = 8.54 (t, J = 5.6 Hz, 2H), 7.89 (s, 4H), 3.26 (q, J = 6.8 Hz, 4H), 1.55–1.47 (m, 4H), 1.37–1.28 (m, 4H), 0.9 (t, J = 7.2 Hz, 6H). ^{13}C-NMR, δ = 14.18, 20.13, 31.66, 42.5, 127.50, 137.21, 165.88.

N,N′-diphenylterephthalamide (DPTA)

Yield = 85%, white powder, m.p. = 349–351°C. Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93%; H, 5.10%; N, 8.85%. Found: C, 75.81%; H, 5.17%; N, 8.65%. FTIR (KBr, cm^{-1}): 3336 (N—H aromatic), 1651 (C=O aromatic). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 10.41 (s, 2H), 8.10 (s, 4H), 7.8 (4H, J = 7.6 Hz, d), 7.38 (m, 4H), 7.13 (m, 2H).^{13}C-NMR, δ = 120.91, 124.37, 128.19, 129.13, 137.90, 139.42, 165.27.

1,1′-(4,4′-(quinoxaline-2,3-diyl)bis(1,4-phenylene))diazepan-2-one (model compound, QBD)

A 25-mL two-necked flask equipped with a magnetic stirrer, a condenser, and an argon inlet/outlet tube was charged with CuI (0.0192 g, 0.1 mmol, 10 mol %), DBQ (0.219 g, 0.5 mmol), caprolactam (0.141 g, 1.25 mmol), and K_2CO_3 (0.28 g, 2.03 mmol). DMEDA (0.021 mL, 0.2 mmol) and toluene (5 mL) were added to the mixture under argon. The flask was briefly evacuated and backfilled with argon. The reaction mixture was stirred at 110–115°C for 12 h. The resulting suspension was allowed to reach room temperature and then filtered through a 0.5 × 1 cm^2 pad of silica gel eluting with 1 : 1 ethyl acetate/dichloromethane (10 mL). The filtrate was evaporated and then purified with column chromatography (SiO$_2$, 1 : 4 ethyl acetate/dichloromethane). QBD was a yellow, crystalline product with yield = 92% and T_m = 226–228°C. The reaction for the synthesis of the model compound is shown in Scheme 1. Anal. Calcd. for $C_{32}H_{32}N_4O_2$: C, 76.16%; H, 6.39%; N, 11.10%. Found: C, 76.34%; H, 6.43%; N, 11.02%. FTIR (KBr, cm^{-1}): 3036 (C—H aromatic), 2945 (C—H aliphatic), 1658 (C=O), 1598 (C=N aromatic), 1405 (C—N). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ = 8.16 (dd, J = 3.2 Hz, 2H), 7.78 (dd, J = 3.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 4H), 7.27(d, J = 8.8 Hz, 4H), 3.78 (m, brs, 2H), 2.73 (m, brs, 2H), 1.7 (m, brs, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6, ppm): δ = 23.49, 28.96, 29.80, 37.86, 52.89, 125.93, 129.17, 129.98, 130.50, 136.68, 141.17, 145.12, 152.51, 175.41. MS (m/z) calcd: [M$^+$] : 504.4; found [M$^+$-C_2H_4]: 476.4.

Polymer synthesis

A 50-mL, two-necked flask equipped with a magnetic stirrer bar, a condenser, and an argon inlet/outlet tube was charged with CuI (0.076 g, 0.40 mmol, 40 mol %), DBQ (0.8763 g, 2 mmol), a dia-
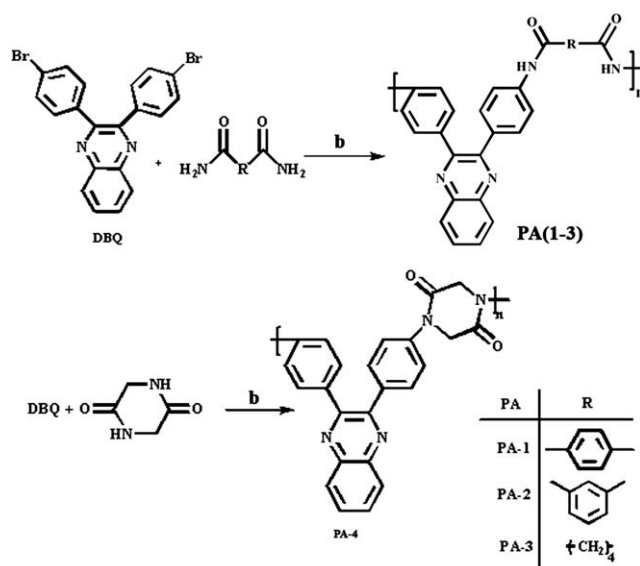
Scheme 2 Synthesis procedure for preparation of polyamides. (b: CuI, DMEDA, K_2CO_3, DMF, under argon, at 110–115°C, 24 h).

mide (2.5 mmol), and K_2CO_3 (1.12 g, 8.12 mmol). DMEDA (0.086 mL, 0.80 mmol) and DMF (15 mL) were added to the mixture under argon. The flask was briefly evacuated and backfilled with argon. The reaction mixture was stirred at 110–115°C for 24 h. The resulting viscous solution was allowed to reach room temperature, diluted with 5 mL DMF, and then filtered through a 0.5 × 1 cm^2 pad of silica gel. The resulting solution was poured into 100 mL of water; the polymer was filtered, purified with refluxing in methanol for 1 h and dried in a vacuum oven at 100°C. The synthesis and designation of polyamides is shown in Scheme 2.

PA-1

Yield: 93% and η_{inh} = 0.55 dL/g. FTIR (KBr, cm^{-1}): 3348 (N—H stretching), 3044 (Ar—H stretching), 1662 (C=O stretching), 1601 (C=C aromatic), 1594 (C=N stretching), 1526 (N—H bending). ^{1}H-NMR [DMSO-d_6, δ ppm]: 10.56 (2H, amidic protons), 7.45–8.13 (16H, aromatic protons). Anal. Calcd. for $(C_{28}H_{18}N_4O_2)_n$: C, 76.01%; H, 4.10%; N, 12.66%. Found: C, 76.12%; H, 4.22%; N, 12.44%.

PA-2

Yield: 91% and η_{inh} = 0.55 dL/g. FTIR (KBr, cm^{-1}): 3330 (N—H stretching), 3053 (Ar—H stretching), 1673(C=O streching), 1611 (C=C aromatic), 1599 (C=N aromatic), 1520 (N—H bending). ^{1}H-NMR [DMSO-d_6, δ ppm]: 10.57 (2H, amidic protons), 7.53–8.55 (16H, aromatic protons). Anal. Calcd. for $(C_{28}H_{18}N_4O_2)_n$: C, 76.01%; H, 4.10%; N, 12.66%. Found: C, 76.14%; H, 4.31%; N, 12.39%.

PA-3

Yield: 88% and η_{inh} = 0.49 dL/g. FTIR (KBr, cm^{-1}): 3347 (N—H streching), 3060 (Ar—H stretching), 2927 (C—H stretching), 1674 (C=O stretching), 1609 (C=N aromatic), 1527 (N—H bending). ^{1}H-NMR [DMSO-d_6, δ ppm]: 10.01 (2H, amidic protons), 7.41–8.08 (12H, aromatic protons), 1.59–2.49 (8H, aliphatic protons). Anal. Calcd. for $(C_{26}H_{22}N_4O_2)_n$: C, 72.80%; H, 5.86%; N, 13.58%. Found: C, 72.91%; H, 5.98%; N, 13.51%.

PA-4

Yield: 87% and η_{inh} = 0.51 dL/g. FTIR (KBr, cm^{-1}): 3063 (Ar—H stretching), 1685 (C=O stretching), 1610 (C=N aromatic). ^{1}H-NMR [DMSO-d_6, δ ppm]: 7.32–8.17 (12H, aromatic protons), 4.58 (aliphatic protons). Anal. Calcd. for $(C_{24}H_{16}N_4O_2)_n$: C, 73.46%; H, 4.11%; N, 14.28%. Found: C, 73.52%; H, 4.34%; N, 14.20%.

Polymer film preparation

A solution of polymer was made by dissolving 0.50 g of a polyamide sample in 6 mL DMAc. The homogeneous solution was poured into a 5-cm glass Petri dish, which was heated at 50°C for 1 h, 100°C for 2 h, and 160°C for 5 h to slowly vaporize the solvent under vacuum.

Measurement

The FTIR spectra were recorded on a Bruker Tensor 27 spectrometer using KBr pellets. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DRX 400 MHz Advance instrument, with DMSO-d_6 as solvent. Elemental analysis was performed by using a CHN-600 Leco elemental analyzer. Melting point (uncorrected) was measured by a Barnstead Electrothermal engineering LTD 9200 apparatus. Inherent viscosities (at a concentration of 0.5 g/dL) were measured by an Ubbelohde suspended-level viscometer at 25°C using NMP as solvent. Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. The UV–visible absorption and fluorescence emission spectra were recorded on a Cecil 5503 spectrophotometer and a Perkin–Elmer LS-50B spectrofluorimeter, respectively. Mass spectra were obtained on an Agilent 7890A/5975C GC/MSD spectrometer. Thermo gravimetric analysis (TGA) was performed by Du Pont Instruments (TGA 951) analyzer well equipped with a PC at a heating rate of 10 °C/min under nitrogen atmosphere (20 cm^3/min) and in the temperature range of 30–600°C. Differential scanning calorimeter (DSC) was recorded on a Perkin–Elmer pyres 6 DSC at a heating rate of 10°C under nitrogen atmosphere (20 cm^3/min). X-ray powder diffraction (XRD) patterns of polymers were recorded by an X-ray diffractometer (XRD, GBC MMA Instrument)
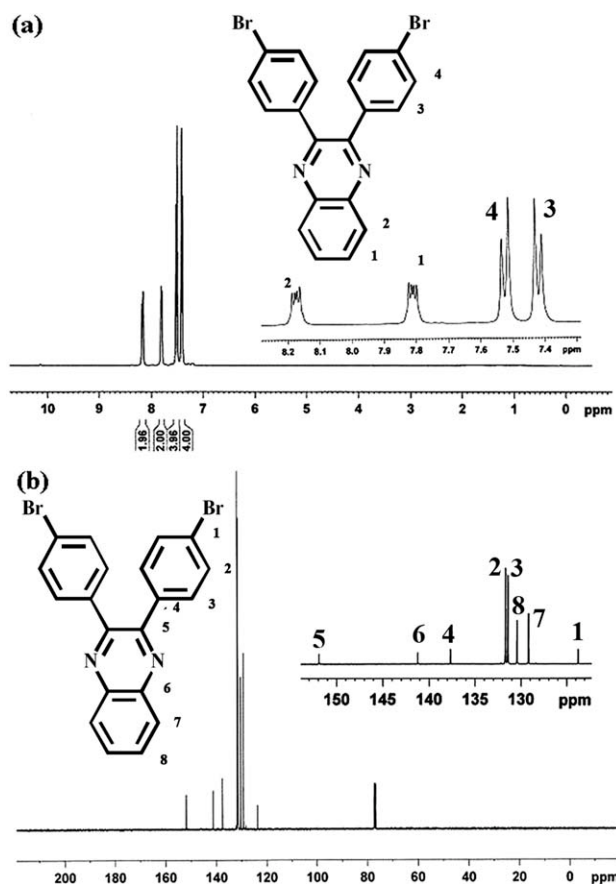
Figure 1 ^{1}H and ^{13}C-NMR spectra of 2,3-bis(4-bromophenyl)quinoxaline.

with Be-filtered Cu Kα radiation (1.5418 Angstrom) operating at 35.4 kV and 28 mA. The scanning range of 2θ was set between 5° and 40° with a scan rate of 0.05 degree/s. Molar mass distributions were determined using a Perkin–Elmer instrument equipped with a differential refractometer detector. The measurements were performed at 30°C using columns were packed with a polystyrene/divinylbenzene copolymer (PL gel MIXED-B from Polymer Laboratories) with DMF as fluent at a flow rate of 1 mL/min. Calibration of the instrument was done with monodisperse polystyrene standards.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

Since we were interested in using diphenylquinoxaline as building block in the polyamide chains, thus DBQ was synthesized by a one-step addition–elimination reaction, as outlined in Scheme 1. The reaction was carried out by dissolving 4, 4′-dibromobenzil in acetic acid and then refluxing with benzene-1, 2-diamine for 8 h. The progress of reaction was checked by TLC measurements. The ^{1}H and ^{13}C-NMR spectra of DBQ are shown in Figure 1. The

¹H-NMR spectrum shows signals in the region of 8.18 and 7.80 ppm, related to the protons of the quinoxaline ring and in the region of 7.52 and 7.42 ppm, related to the protons of the diphenyl rings. The spectroscopy and mass spectrometer data in the synthesis section are confirmations of DBQ structure. We were also interested in using different primary and secondary diamides in coupling polymerization with DBQ. Cyclic diamide of 2, 5-dipiperazinedione is commercially available, and different primary and secondary diamides were synthesized. FTIR spectra of the primary diamides showed characteristic peaks around 3365 and 3160 cm^{-1} related to the primary amine and at 1665 cm^{-1} related to the amide carbonyl group. Secondary diamides showed absorptions at 1405 cm^{-1} and at 1628–1651 cm^{-1} related to C—N bond and carbonyl group, respectively. The reaction between DBQ and caprolactam for preparation of the model compound (QBD) was conducted in toluene in the presence of CuI, DMEDA ligand, and K$_2$CO$_3$ as base at 110–115°C under argon atmosphere, as shown in Scheme 1. The structure of QBD was confirmed by using elemental analysis, FTIR, NMR, and MS, measurements. FTIR spectrum of QBD shows peaks at ∼ 3036 cm^{-1} related to aromatic C—H stretching, at ∼ 1658 cm^{-1} related to C=O, at ∼ 1600 and 1470 cm^{-1} related to aromatic C=C, and at 1405 cm^{-1} related to C=N stretching. The elemental analysis values of QBD generally agreed well with the calculated values for the proposed structure. ¹H-NMR spectrum of QBD is shown in Figure 2(a). The characteristic signals at 1.7, 2.73, and 3.78 ppm are related to the protons of CH$_2$ groups of the cycloaliphatic ring. The ¹³C-NMR spectrum in Figure 2(b) shows the characteristic signals at 23.49, 28.96, 29.80, 37.86, 52.89 ppm related to the carbons of cycloaliphatic ring and at 175.41 ppm which is related to the carbon of carbonyl group.

Polymer synthesis and characterization

A series of polyamides PA (1–4), as illustrated in Scheme 2, was successfully synthesized in relatively good yields (87–93%) by a cross-coupling reaction between DBQ and four diamides in the presence of inexpensive and air-stable CuI as the catalyst and DMEDA as a ligand at 110–115°C. The mechanism of the catalytic C—N bond formation depends on the nature of the metal involved. The reaction in general involves the transition metal catalyzed oxidative addition reaction across the C—X bond of an electrophile, *trans*-metallation with a main group organometallic nucleophile, followed by reductive elimination step leading to C—N bond formation and the active catalyst is regenerated. The inherent viscosity of the polyamide (PA-1), as a suitable criterion for evaluation of molecular weight, was measured for
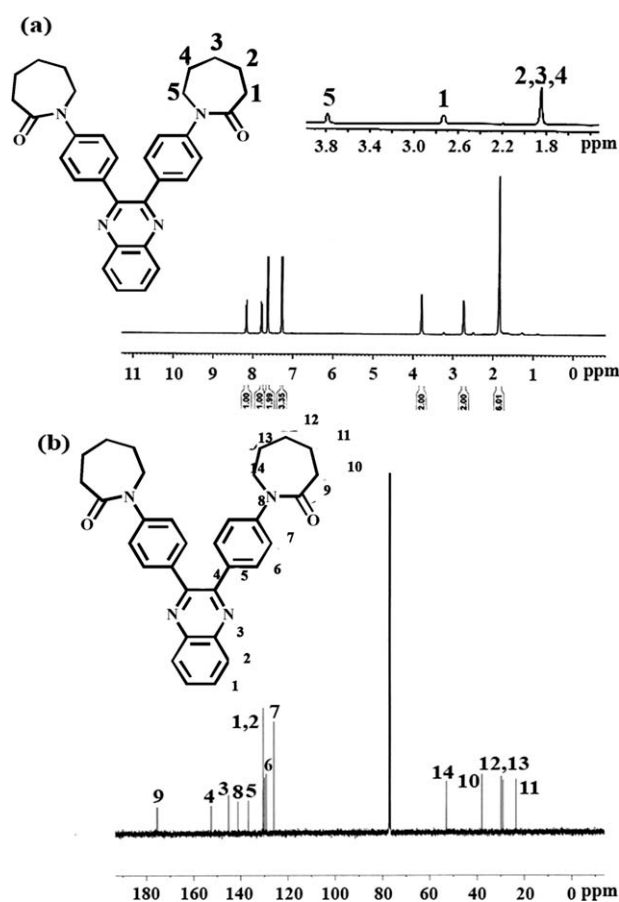

Figure 2 ¹H and ¹³C-NMR spectra of model compound.

different polymerization times. The viscosity increased with time of polymerization, from 21 mL/g after 8 h to 35 mL/g after 14 h and changed to 55 mL/g when the reaction time increased up to 24 h. The polyamides PA(1–4) had inherent viscosities in the range of 49–55 mL/g, and GPC analysis with polystyrene standards and using DMF as solvent showed M_ws of 11,950, 8730, and 5592 g/mol for PA-1, PA-2, and PA-3 with polydispersity index of 1.87, 1.41, and 1.21, respectively. The molecular weight of PA-4 was not determined because this polymer did not dissolve in DMF at room temperature. The molecular weight of these polyamides are lower than the molecular weight of the polyamides obtained from 2,7-dibromo-9,9-dioctylfluorene using the same procedure.[25,26] This can be due to better solubility of the oligomers in the reaction media because of the presence of diocty moiety at the 9 position of fluorene ring. However, these polyamides had molecular weight comparable to other polymers obtained through coupling reactions by other researchers.[3,8,16,27] The structures of the polymers were verified by FTIR, ¹H-NMR spectroscopy, and elemental analysis. FTIR spectra of the polymers displayed absorption features that are consistent with their structures, at about 2927 (C—H aliphatic),
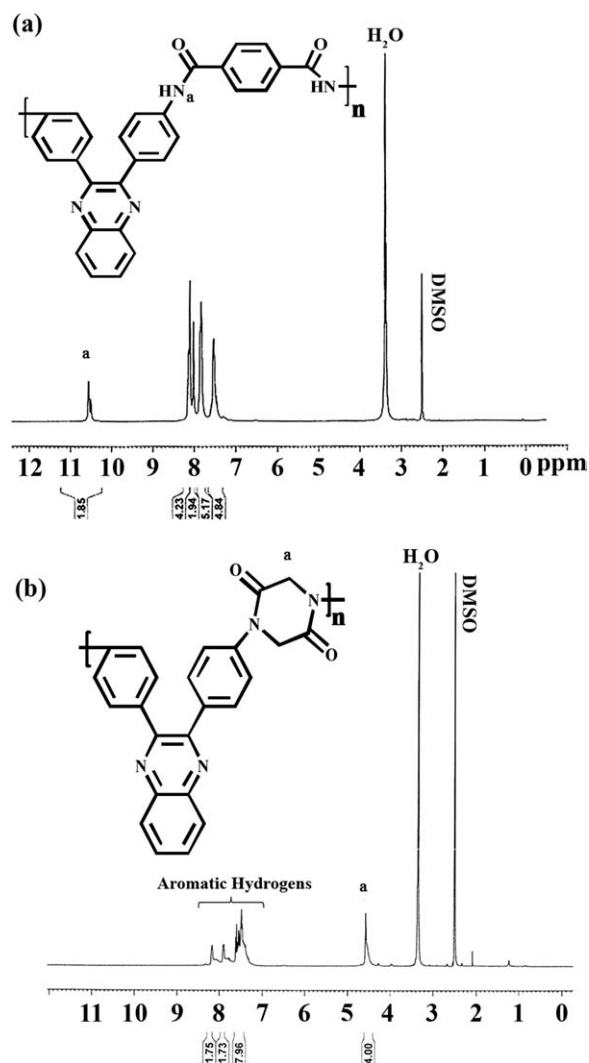
Figure 3 ¹H-NMR spectra of the representative polyamides; (a) PA-1 and (b) PA-4.

3045 (C—H aromatic), 1645 (C=O), 1610 (C=C), 3350 (N—H stretching), and 1600 (C=N) cm⁻¹. ¹H-NMR spectra of the polymers exhibited peaks at about 7.45–8.55 (aromatic protons), 10.01–10.57 (amidic protons), 1.59–2.49 (aliphatic protons in PA-3), and 4.58 ppm (alicyclic protons in PA-4). In addition, no peak was observed at 10.01–10.57 ppm for PA-4, indicating the absence of secondary amide groups. Figure 3 shows the ¹H-NMR spectra of the representative polymers. However, the reaction between DBQ and secondary diamides such as *N,N'*-diphenylterephthalamide (DPTA) and *N,N'*-dibutyl-terephthalamide (DBTA) did not lead to polymer formation. This can be related to the steric hindrance due to free motion of butyl and phenyl group on nitrogen atom of these diamides in comparison with the secondary alicyclic diamide of 2,5-dipiperazine-dione which yielded polymer PA-4 with $\eta_{inh} = 51$ mL/g.

Polymer properties

Wide-angle X-ray diffraction and solubility

The wide-angle X-ray diffraction test revealed essentially amorphous patterns for all the polymers, except PA-4 with margin crystallinity as shown in Figure 4. Obviously, the bulky diphenylquinoxaline groups hindered chain packing and reduced the level of ordering, thus leading to the amorphous nature of the polymer. The margin cristallinity in PA-4 may be due to the presence of low molecular weight crystallizable oligomers which was not washed out by refluxing polymer in methanol. The solubility behavior of the polyamides was determined at a concentration of 5% (W/V) in a number of solvents and the results are tabulated in Table I. The solubility of polymers varied depending upon the diamide used. PA-1, PA-2, and PA-3 which were produced from primary amides and having secondary amide groups in the backbone are readily soluble in polar aprotic solvents such as NMP, DMAc, DMF, DMSO, and pyridine at room temperature. The good solubility of these polyamides should be the result of H-binding with polar solvent molecules and also the amorphous nature of these polymers was also reflected in their good solubility. The disturbed packing of macromolecular chains facilitates the diffusion of small solvent molecules between the polymer chains, resulting in a better solubility. The semi-aliphatic polyamide (PA-3) showed better solubility in comparison with the aromatic polyamides due to presence of methylene groups in the backbone which increased flexibility and also disturbed the planarity of aromatic units resulting in a reduction of the close packing. PA-4 showed good solubility in NMP at room temperature and dissolved in DMAc, DMF, DMSO, and pyridine only by heating at 60°C. The different solubility behavior of PA-4 in comparison with the other prepared polyamides can be due to margin crystallinity of this polymer, as indicated by the X-ray diffraction patterns, and the absence of H-binding between the amide groups in the backbone of this polymer and polar solvent molecules. In
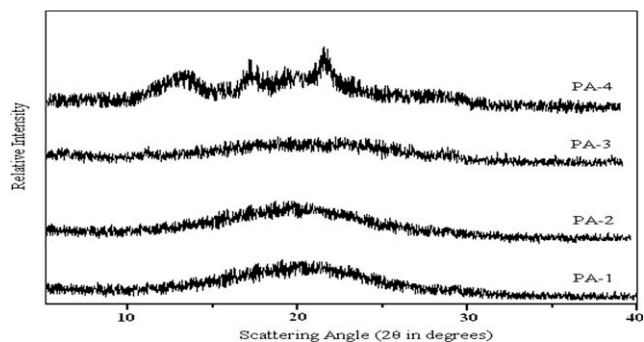

Figure 4 X-ray diffraction patterns of polyamides.

TABLE I
Viscosity, Average Molar Mass, and Solubility Behavior of Polyamides

Polymer	Yield (%)	η_{inh} (dL/g)	M_w (MWD) (g/mol)	NMP	DMAc	DMF	DMSO	PY	THF	DO	TCE
PA-1	93	0.55	11950 (1.87)	++	++	++	++	++	±	±	−
PA-2	91	0.55	8730 (1.41)	++	++	++	++	++	+	+	−
PA-3	88	0.49	5592 (1.21)	++	++	++	++	++	+	+	−
PA-4	87	0.51	−	++	+	+	+	+	−	−	−

The solubility was determined by using 5 g sample in 100 mL of solvent.
DMAc: N,N-dimethyl acetamide; DMF: N,N-dimethyl formamide; NMP: N-methyl pyrrolidone; DMSO: dimethyl sulfoxide; DO: dioxan; PY: pyridine; THF: tetrahydrofuran; TCE: tetrachloroethane.
++: Soluble at room temperature; +: Soluble on heating at 60°C; ± partially soluble on heating at 60°C; − Insoluble on heating at 60°C).
Viscosity was measured at a polymer concentration of 0.5 g/dL in NMP at 25°C.
Molecular mass average was determined via GPC using DMF as fluent at a flow rate of 1 mL/min.

general, these polymers showed less solubility in common aprotic organic solvents in comparison with the solubility of polymers reported previously obtained by the same reaction protocol.[25,26] The better solubility of those polymers can be due to presence of dioctyl units at the 9-position of the fluorene ring.

Photophysical properties

The optical absorption and photoluminescence (PL) emission spectra of the polymers in dilute (0.2 g/dL) DMAc solution are shown in Figure 5. All polymers showed a narrow low-energy absorption band in the range of 300–400 nm, typical of the π-π* transition of the aromatic rings. Absorption peak at 380 nm is related to the one quinoxaline unit in the backbone and at 300 nm is related to the phenyl ring.[27] Overall, we note that the absorption features in all four polymers are blue-shifted compared to typical dialkoxysubstituted polymers,[29] indicating that the conjugation length is decreased by inserting the quinoxaline moieties in the main chain. The spectral data for the polymer solution and in solid state are listed in Table II. These polymers emit in the blue region in solution and in solid with maxima in the range of 425–491 nm when excited at maximum

absorption wavelength. These polymers possess a rigid quinoxaline structure and a large band gap, thus they should favor blue-light-emitting properties, as shown in Figure 5. In general, the presence of a well-defined vibronic structure in the emission spectra indicates that the polymers have a rigid and well-defined backbone.[30,31] The fluorescence emission intensity of aliphatic polyamides PA-3 and PA-4 is higher than the aromatic polyamides PA-1 and PA-2. This could be attributed to the effectively reduced conjugation and capability of charge-transfer-complex formation by aliphatic diamide in comparison with the electron-donating amido unit and the strongly electron-accepting aromatic diamide unit.[32] Comparing the emission spectra of PA-4 and the polyamide reported in our previous work,[26] the previously reported polyamide emitted at the higher wavelength which can be due to presence of fluorene system in the polymer backbone.

Thermal properties

The thermal behavior of these polyamides was investigated by DSC at a heating rate of 10 °C/min under N$_2$. DSC curves of the polyamides up to

Figure 5 Absorption (a) and emission (b) spectra of polyamides in DMAc solution.

TABLE II
Absorption and Emission Spectral Data of the Polymers in Solution and in Thin Films

Polymers	$\lambda_{a.max}$ (nm)		$\lambda_{e.max}$ (nm)		
	Solution[a]	Film[b]	Solution	Film	Φ_f^c (%)
PA-1	297	301	484	491	15
PA-2	295	300	475	483	14
PA-3	289	304	468	478	23
PA-4	290	305	425	436	21

$\lambda_{a.max}$, maximum absorption wavelength; $\lambda_{e.max}$, maximum emission wavelength.
The excitation wavelength was 315 nm.
[a] Polymer concentration of 0.20 g/100 mL in DMAc.
[b] Polymers film for the spectra were drop-coated from DMAc solutions (0.2 g/dL) onto quartz substrates.
[c] Fluorescence quantum yield relative to $10^{-5}M$ quinine sulfate in 1N H$_2$SO$_4$ (aq) ($\Phi_f = 0.55$) as a standard.
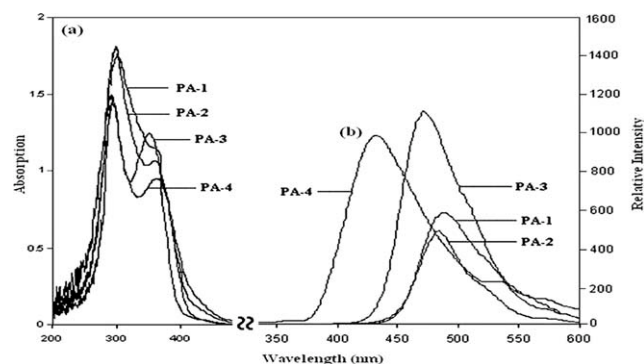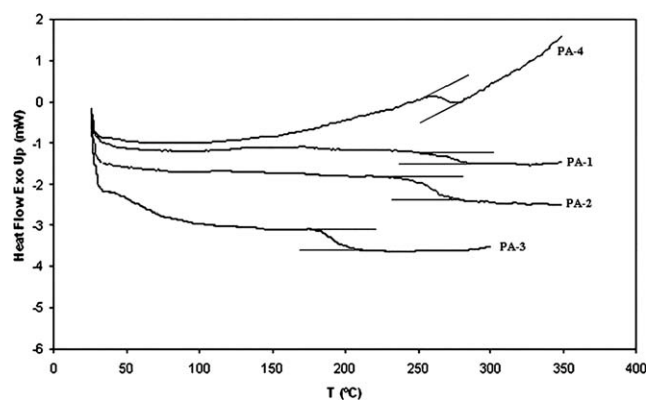
Figure 6 DSC curves of polyamides.

Figure 7 TGA curves of polyamides.

350°C are shown in Figure 6. The absence of melting peak in the DSC curves and the results obtained from WAXD test supported the generally amorphous nature of these polymers. T_g of the polymers extracted from DSC curves and listed in Table III, ranged from 196 to 276°C. The absence of melting and the relatively high T_g reflect their high barrier for segmental mobility as a result of the bulky quinoxaline moieties per repeat unit. Similar enhancements of T_g were observed for polyfluorenes with the incorporation of the quinoxaline units in their main chains.[9] The decreasing trend of T_g is comparable to the decreasing order of stiffness and chain rigidity. For example, PA-1 which is based on terephthalic amide showed the highest T_g value because of the highest rigidity, which inhibited the molecular motion and the lower T_g value of PA-3 is mainly due to low rotation barrier of the incorporated flexible aliphatic units in the main chain. Thermal stability of these polymers was evaluated by TGA in N_2 at a heating rate 20 °C/min. TGA curves, in Figure 7, reveal good thermal stability of these polymers. As shown in Table III, these polymers possess excellent thermal stability with the onset decomposition temperature (T_i) ranging from 335 to 446°C, T_{10} from

364 to 476°C, and the char yields at 600°C varied from 61 to 72% depending on the structure of diamide component in the polymer backbone. The good thermal stability of these polyamides and particularly the relatively high char yield of semialiphatic PA-3 may be attributed to the condensed aromatic moiety of the diphenylquinoxaline unit in the polymer chains. In general, the lower thermal stability of PA-3 in comparison with the aromatic polyamides is related to introduction of aliphatic units in the polyamide backbone. In general, these polymers showed higher thermal stability in regard of values of T_g and T_{10} in comparison with these values of our previously reported polyamides obtained by using the same reaction protocol.[25,26] This difference in thermal stability can be due to the presence of bulky quinoxaline unit in the backbone of the present polymers. Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation.[33] LOI = 17.5 + 0.4CR where CR = char yield. For all the polymers LOI values were calculated based on their char yield at 600°C. According to Table III, it is clear that polymers based on aromatic have better thermal stability and higher LOI as compared to semis-aliphatic polyamides. It could be pertained to aromatic, rigid structure of diamides compared to aliphatic, flexible structure of diamide.

TABLE III
Thermal Properties of Polyamides

Polymer	LOI	T_g (°C)[a]	T_i (°C)	T_{10} (°C)	C. Y. (%)[b]
PA-1	46.34	276	446	476	72.1
PA-2	45.22	259	428	465	69.3
PA-3	44.46	196	335	364	67.4
PA-4	41.94	260	389	417	61.1

[a] Midpoint temperature of baseline shift on the second DSC heating trace (10 °C/min, under N_2: 20 cm³/min) of the sample after quenching from 350°C.
[b] (Char yield): Residual weight percentage at 600°C in N_2.
T_g: glass transition temperature; T_i: decomposition temperature, recorded via TGA at a heating rate of 10 °C/min under N_2 (20 cm³/min); T_{10}: temperature for 10% weight loss.
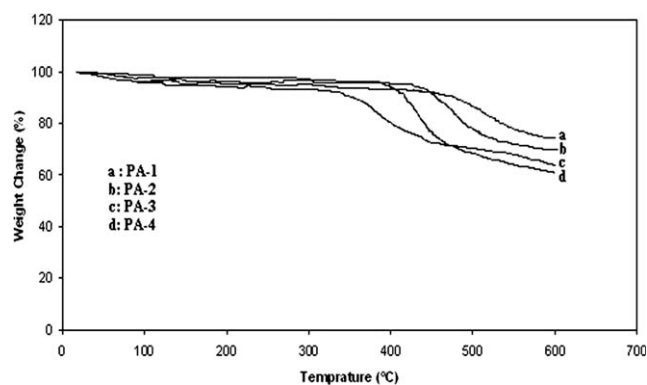LOI: limiting oxygen index.

CONCLUSIONS

The present article describes preparation of polyamides containing diphenylquinoxaline moieties in the main chain using copper-catalyzed amidation reaction between 2,3-bis (4-bromophenyl) quinoxaline and various diamides. The results showed successful polymer preparation with primary diamides of aliphatic and aromatic units and also with a secondary alicyclic diamide, but this method was not successful with the secondary linear diamides due to steric hindrance. The prepared polyamides of this method exhibited M_ws up to 12,000 g/mol, good solubility in

common organic solvents, and satisfactory thermal stability with T_g and 10% weight loss temperatures of up to 276°C and 476°C, respectively. A noteworthy advantage of this method is that we can synthesize soluble and thermally stable polyamides without using diacids or diacid chlorides, the synthesis and purification of which are usually difficult.

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