Poly(3-phenylquinoxaline): A New Thermally Stable Polymer

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ABSTRACT: A high-performance phenylquinoxaline polymer was prepared by a three-step synthetic route employing a reductive polycyclization process. This method involves in situ generation of the monomer 3,4-diaminobenzil by reducing the precursor 3-nitro-4-aminobenzil. A nearly quantitative yield of poly(3-phenylquinoxaline) was obtained, and its physical properties were similar to those of the known poly[2,2′-(1,4-phenylene)-6,7′-bis(3-phenylquinoxaline)] and isomers. 3,4-Diaminobenzil prepared from dithionite reduction of 3-nitro-4-aminobenzil polycyclized at a rate slower than the classical two-component system.

Introduction

Poly(phenylquinoxalines) (PPQs) constitute a unique class of thermally stable, high-performance thermoplastics currently being used in microelectronics as interlayer dielectrics[1] and having proven potential as high-temperature adhesives for aerospace applications.[2] Although PPQs such as poly[2,2′-(1,4-phenylene)-6,7′-bis(3-phenylquinoxaline)] (and isomers) can be easily prepared by polycyclization of aromatic bis(*o*-diamines) and bis(α-dicarbonyl) compounds, the syntheses of these starting materials usually involve inefficient lengthy steps, and the resulting high cost has prohibited their widespread use as commodity polymers.[3] To overcome this deficiency, 3,4-diaminobenzil, containing both essential reactive groups of the starting materials for the PPQ, was designed and synthesized. This paper presents the first effort to synthesize PPQ from the aminonitrobenzil monomer precursor through a reductive polycyclization process.[4]

Experimental Section

General Procedures. All chemicals were purchased from Aldrich except 4-bromo-2-nitroaniline, which was supplied by Fairfield Chemical Co., Blythewood, SC. 1D and 2D NMR spectra were recorded on a Bruker AC-250 spectrometer equipped with a QNP probe. HPLC analysis was performed on a Waters chromatograph using either a Spectra-Physics RP-8 300-mm column with aqueous acetonitrile (MeCN, 60% to 90% in 3 min) at 3.5 mL/min or a Spectra-Physics Si-300 300-mm column with 95:5 toluene–MeCN isocratic elution at 3 mL/min. GPC analysis was performed on a Waters system using three Ultrastyragel columns (10^4, 10^3, and 500 Å) in series with chloroform at 1.5 mL/min as eluent and UV detection at 265 nm. Polystyrene GPC standards with peak molecular weights of 451 000, 210 000, 50 000, 20 500, 8500, 3600, and 510 served as calibration standards. DSC was performed on a Perkin-Elmer DSC 7 instrument scanning at 10 °C/min. Thermal mechanical analysis (TMA) was performed on a Du Pont 1090 instrument using a tension probe with a 5-g tension load; the coefficient of thermal expansion (CTE) was calibrated by aluminum foil. Film samples were obtained by slow evaporation of a chloroform solution of the polymer. Films were annealed by heating to 380 °C before the measurements were taken. Thermogravimetric analysis (TGA) was performed on a Du Pont 1090 instrument.

2-Nitro-4-(phenylethynyl)aniline (1).[5] 2-Nitro-4-bromoaniline (4.34 g, 20 mmol), triphenylphosphine (0.2 g), cuprous iodide (38 mg), palladium(II) acetate (12 mg), and triethylamine (20 mL) were mixed with mechanical stirring under nitrogen. Phenylacetylene (3.1 g, 30 mmol) was then added, and the mixture was stirred at 100 °C. A white precipitate appeared in 10 min as the color of the mixture darkened. At the end of the reaction the color became yellowish-brown. The course of the reaction was monitored by reverse-phase HPLC, and maximum yield was obtained in ca. 60 min. The triethylamine was then removed under reduced pressure, and the reddish-brown product was washed with water to remove the triethylammonium salt. Drying and recrystallization from dichloromethane afforded pure 2-nitro-4-(phenylethynyl)aniline as bright red crystals: 4.0 g (84%): mp 157–159 °C; ^{1}H NMR ($CDCl_3$) δ 8.34 (d, J = 1.8 Hz, 1 H), 7.52 (m, 3 H), 7.37 (m, 3 H), 6.79 (d, J = 8.7 Hz, 1 H), 6.23 (br s, 2 H).

3-Nitro-4-aminobenzil (2). 2-Nitro-4-(phenylethynyl)aniline (12 g, 50 mmol) was heated to dissolve in dichloromethane (250 mL). To this solution were added the following: Adogen 464 (1.0 g), water (250 mL), sodium bicarbonate (4.2 g), and potassium permanganate (21 g). The mixture was stirred vigorously at room temperature. A slight exotherm indicated the progress of the oxidation, and the reaction was completed in 2 h as indicated by normal-phase HPLC. Sodium bisulfite (43 g) and hydrochloric acid (15 mL) were added slowly to reduce excess permanganate and manganese dioxide. The yellowish-brown dichloromethanne solution was saturated with 3-nitro-4-aminobenzil, and filtration afforded a mixture of manganese sulfite and the product as a gray powder. Addition of dilute HCl (3 N, 20 mL) liberated 6.95 g of 3-nitro-4-aminobenzil from the manganese sulfite salt as a yellow powder. After drying (magnesium sulfate) and solvent removal, an additional 2.50 g of the product was recovered from the dichloromethane layer. Recrystallization from DMF afforded pure 3-nitro-4-aminobenzil as yellow crystals: mp 189 °C; ^{1}H NMR ($CDCl_3$) δ 8.73 (d, J = 2.0 Hz, 1 H), 8.01 (m, 3 H), 7.64 (m, 1 H), 7.56 (m, 2 H), 6.91 (d, J = 8.8 Hz, 1 H), 6.65 (br s, 2 H); ^{13}C NMR (DMSO) δ 194.31 (s), 191.01 (s), 150.15 (s), 135.34 (d), 134.09 (d), 132.41 (s), 130.20 (d), 129.74 (s), 129.66 (d), 129.37 (d), 120.20 (d), 119.50 (s); MS (CI, CH_4) m/e 271 (100, M + H), 241 (10), 165 (6), 105 (7). Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.14; H, 3.71; N, 10.53.

3,4-Diaminobenzil (3). A reducing solution made from sodium dithionite (3.2 g), NaOH (1.5 g), and water (40 mL) was stirred under nitrogen. 3-Nitro-4-aminobenzil (1.08 g, 4 mmol) dissolved in tetrahydrofuran (16 mL) was added to the reduction solution. The color changed from pale yellow to dark brown, indicating the progress of the reduction. The reaction was completed in 35 min (monitored by HPLC), and extraction by dichloromethane removed the organic layer. Drying (magnesium sulfate) and solvent removal afforded the crude 3 as a semisolid that solidified to a brown mass upon standing overnight in a freezer (64% yield). Recrystallization in an acetonitrile/methanol mixture gave a yellowish-brown powder: mp 157–158 °C; ^{1}H NMR ($CDCl_3$) δ 7.96 (m, 2 H), 7.67 (m, 1 H), 7.51 (m, 2 H), 7.39 (m, 2 H), 6.70 (d, 1 H, J = 8.1 Hz), 4.16 (br s, 2 H), 3.40 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 195.42 (s), 193.25 (s), 143.27 (s), 134.50 (d), 133.41 (s), 133.25 (s), 129.87 (d), 128.84 (d), 125.66 (d), 124.44 (s), 117.79 (d), 114.53 (d). The structure was further confirmed by C–H COSY (see Figure 2).

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Poly(phenylquinoxaline) 4 from 3,4-Diaminobenzil. 3,4-Diaminobenzil (50 mg) was dissolved in *m*-cresol (530 mg), and the solution was heated at 42 °C in a sealed tube under nitrogen. Polymerization was indicated by slow bleaching of the reddish-brown monomer to yellowish-brown oligomers. The monomer concentration decreased to half the original after 40 min and to <1% after 24 h. The number-average molecular weight (M_n) of the polymer was 1980: ^{1}H NMR ($CDCl_3$) δ 8.50 (br s, 1 H), 8.10 (br s, 1 H), 7.86 (br s, 1 H), 7.62 (m, 2 H), 7.43 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.84, 152.47, 141.30, 141.16, 140.87, 138.33, 131.74, 131.49, 130.85, 129.87, 129.33, 128.95, 128.57.

Reductive Polycyclization of 3-Nitro-4-aminobenzil. A mixture of 3-nitro-4-aminobenzil (250 mg, 0.925 mmol), iron fillings (0.15 g), acetic acid (1 mL), and *m*-cresol (3 mL) was heated under reflux under nitrogen for 16 h. The mixture was poured into methanol (50 mL) and filtered. The polymer was further washed with water and methanol to remove iron salt and oligomers. Drying at 100 °C afforded pale yellow polymer in 160 mg (85%). An optimized condition was established by using a mixture of 4/Fe/HOAc/*m*-cresol in a 1.4:1:2:6 weight ratio at 140 °C. The yield of PPQ 4 was quantitative.

Spin–Lattice Relaxation Time (T_1) Measurements. A 5% (w/w) solution of PPQ 4 in deuteriochloroform was subjected to five cycles of freeze–pump–thaw–degas before being flame-sealed in an NMR tube. An inversion–recovery pulse sequence was used with delays up to 5 s. The T_1s were calculated by using Bruker standard software.

2D C–H COSY Measurements. The 2D C–H COSY experiments were performed at 298 K using quadrature detection with the carrier frequency set in the center of the spectrum. A total of 256 scans were accumulated over 128 t_1 increments with a relaxation delay of 4 s. The initial matrix size was 10 000 Hz (2K) and 2000 Hz (128 words) in F_2 and F_1, respectively. A sine-bell apodization function without phase shift was applied in both dimensions prior to Fourier transformation. The delay times Δ_1 and Δ_2 were set at 4 and 2 ms, respectively. The digital resolutions after zero-filling in F_1 were 9.77 Hz/point in F_2 and 7.81 Hz/point in F_1.

COLOC Experiments. The long-range C–H COSY (or COLOC)[6] experiments were run with two sets of slightly different delay times (Δ_2 = 30 and 32 ms and Δ_3 = 25 and 24 ms). The remaining parameters were similar to those used in the C–H COSY experiments.

Results and Discussion

Properties of the Monomer. 3,4-Diaminobenzil (3), which contains both essential reactive groups for forming PPQ 4, was successfully synthesized in 40% overall yield (Figure 1). The 2D C–H COSY spectrum readily confirms the structure (Figure 2). The stability of 3 is surprisingly high; no detectable reaction was found for a sample left in ambient laboratory environments for over 6 months. The DSC thermogram of 3 shows a melting endotherm at 158 °C, followed by a polycyclization exotherm at 161 °C with an enthalpy of ca. −45 J/g (Figure 3). The interfering melting endotherm prevents an accurate measurement. Although a chloroform solution of 3 is also quite stable and no appreciable polycyclization reaction can be detected at room temperature, polycyclization did proceed slowly at room temperature in more acidic solvents such as cresol. An overnight reaction performed at 42 °C in cresol afforded only oligomers (M_w = 4470, M_n = 1980). When similar conditions were applied on a mixture of 3,3′-diaminobenzidine and 1,4-bis(phenylglyoxaloyl)benzene, it afforded a much higher molecular weight PPQ 5 (M_w = 21 340, M_n = 3595) in <1 h at room temperature.[7] The higher activation energy for the formation of PPQ 4 is expected. In the two-component system, both the tetraamine and tetraketone are free to move until a preferred orientation to form the quinoxaline ring is met. In the one-component system, however, both reactive groups are tethered by chemical bonds within the same molecule, and access to a preferred orientation by another monomer molecule is therefore much more restricted. The proximity of the bulky phenyl ring to the diamino groups interferes with

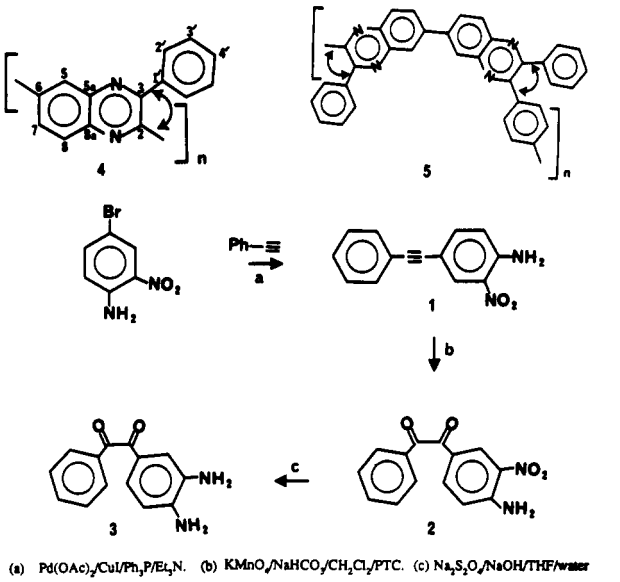


Figure 1. Synthetic scheme for 3,4-diaminobenzil and structures of poly(3-phenylquinoxaline) (4) and poly[2,2′-(1,4-phenylene)-6,7′-bis(3-phenylquinoxaline)] (5). The numbering of 4 shown is used throughout this paper.

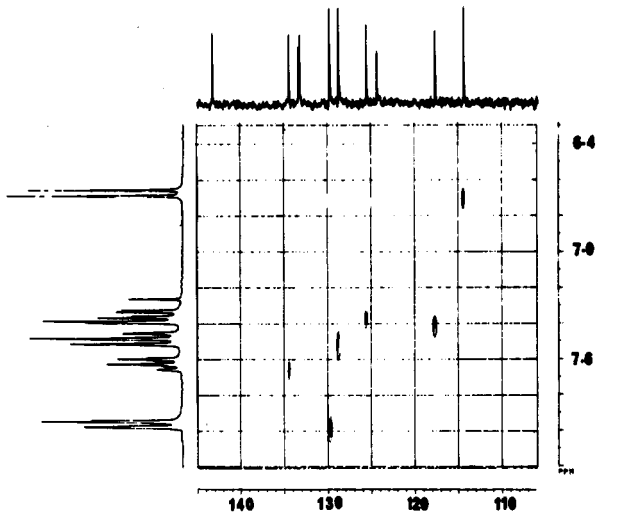


Figure 2. Two-dimensional ^{13}C–^{1}H COSY spectrum of 3,4-diaminobenzil in deuteriochloroform with the respective 1D spectra plotted on the F_2 and F_1 projections. Only the aromatic region is shown. ^{13}C signals without cross-peaks are quaternary carbons.

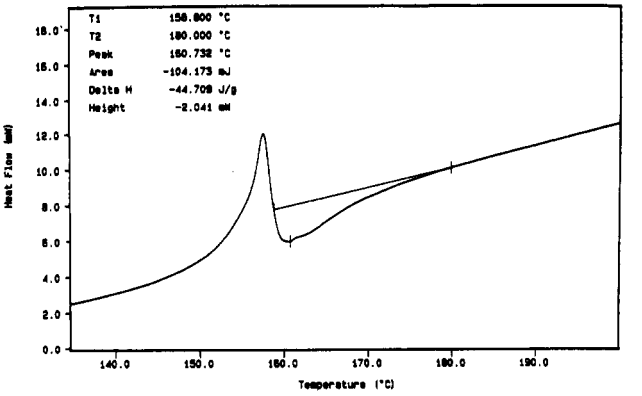


Figure 3. DSC thermogram of 3,4-diaminobenzil. Due to the interfering melting endotherm, the polycyclization exotherm cannot be determined accurately.

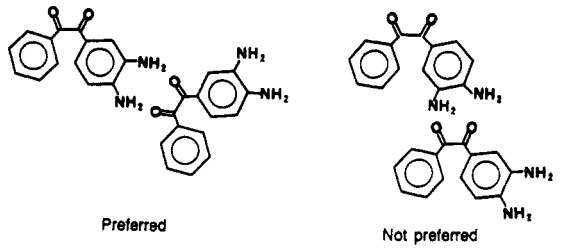


Figure 4. Preferred and nonpreferred prepolymerization configurations of diaminobenzil.

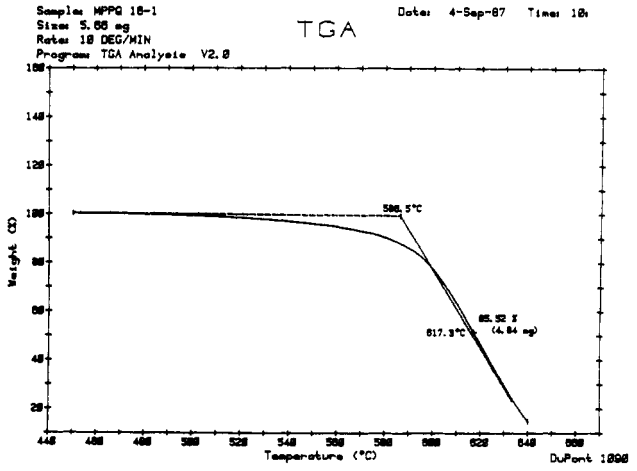


Figure 5. Dynamic TGA of PPQ 4 taken at 10 °C/min in air.

the approach of the dicarbonyl of the monomer (or even worse, the dicarbonyl of the oligomers) to form the quinoxaline ring. Only one of the two preferred conformers of diaminobenzil would have a significant contribution to the polycyclization reaction (Figure 4). Polymer formed by this prepolymerization configuration would have H7 and H8 exposed to the ring current generated by the adjacent phenyl group, thus resulting in the high-field shifts of these protons in the NMR spectrum (vide infra). Unfortunately, the 2D NOESY experiments carried out under a wide range of mixing times (10 ms to 1.5 s) and different temperatures did not give any non-J-related cross-peaks between H2′ or H3′ and H5, H7, or H8. Therefore a detailed conformation between the two aromatic planes in the polymer chain can not be deduced.

Thermal Properties of PPQ 4. The thermal stability of 3-(phenylquinoxaline) polymer was first discussed in a theoretical paper by Sun[8] et al. in 1981. Using HMO calculations they concluded that poly(3-phenylquinoxaline) is slightly more stable than the conventional PPQ 5. This conclusion was confirmed by both TMA and thermal aging experiments. An isothermal aging experiment performed at 371 °C showed that PPQ 4 lost 5.3% of its original weight after heating in air for 33 h, while under similar conditions PPQ 5 lost 6.9% of its weight after 25 h.[9] Dynamic TGA experiments run at 10 °C/min in air showed that PPQ 4 lost 10% of its weight at 586.5 °C (Figure 5). The glass transition temperature (T_g) of PPQ 4 was not sharp enough to be measured accurately by DSC. T_gs in the range 326–332 °C were obtained by DSC for a sample with M_w = 59 000 and a polydispersity of 2.9. In contrast, the T_g measured by TMA was quite reproducible, and a value of 354 °C was obtained for the same sample. A commercial sample of PPQ 5 with M_w = 77 000 and a polydispersity of 3.0 gave a T_g of 345 °C by TMA. The coefficient of thermal expansion (CTE) of PPQ 4 may be expected to be different from that of PPQ 5, because PPQ 4 lacks the p-phenylene spacer group in the

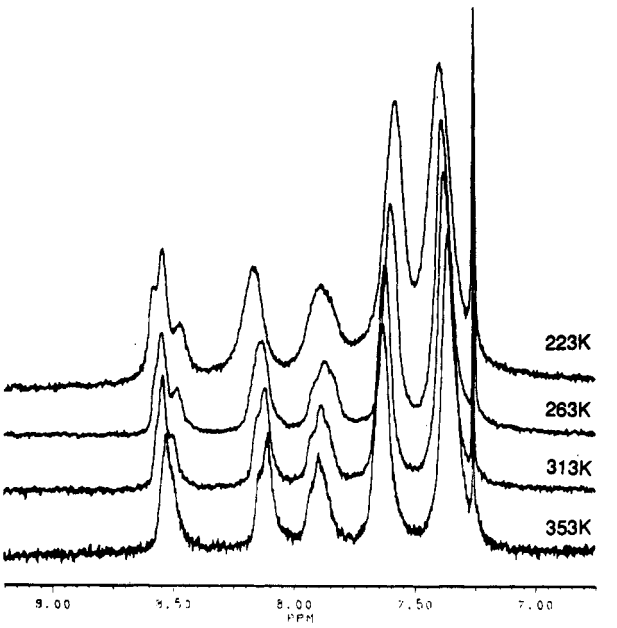


Figure 6. Temperature-dependent ^{1}H spectra of PPQ 4.

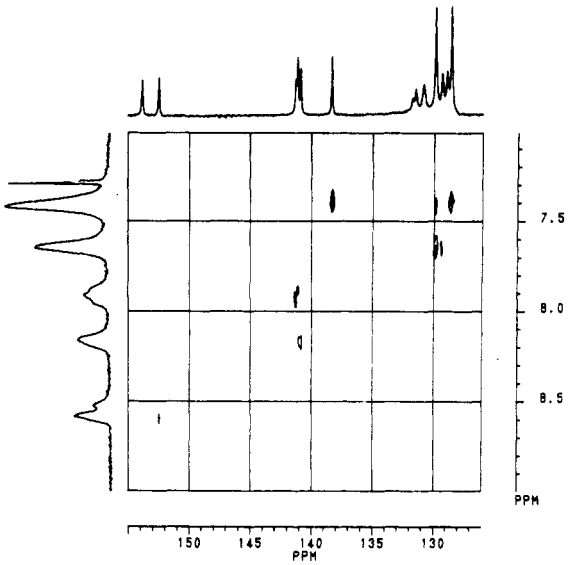


Figure 7. Long-range C–H COSY (COLOC) spectrum of PPQ 4. The spectrum was taken using Δ_2 = 30 ms and Δ_3 = 25 ms. The weak cross-peak of C2 and H5 clears the assignment for the two low-field quaternary carbons.

Table I
NMR Peak Assignments and ^{13}C T_1 of PPQ 4

^{13}C, δ	assignment	^{1}H, δ	assignment	^{13}C T_1, s
128.57	C3′	7.43	H3′	0.14 ± 0.04
128.95	C8	8.10	H8	0.13 ± 0.04
129.33	C4′	7.43	H4′	0.13 ± 0.04
129.87	C2′	7.62	H2′	0.14 ± 0.05
130.85	C5	8.50	H5	0.14 ± 0.05
131.49	C7	7.86	H7	0.12 ± 0.06
131.74	C7[a]	7.86	H7[a]	0.11 ± 0.05
138.33	C1′			1.17 ± 0.05
140.87	C5a			1.03 ± 0.06
141.16	C6 + C8a[a]			1.15 ± 0.06
141.30	C8a			1.27 ± 0.02
152.47	C2			1.19 ± 0.07
153.84	C3			1.25 ± 0.07

[a] Isomeric peaks.

polymer chain. The measured CTEs of both quinoxaline polymers are, however, quite similar, 35 and 33 ppm/°C for PPQ 4 and PPQ 5, respectively, averaged from 50 to

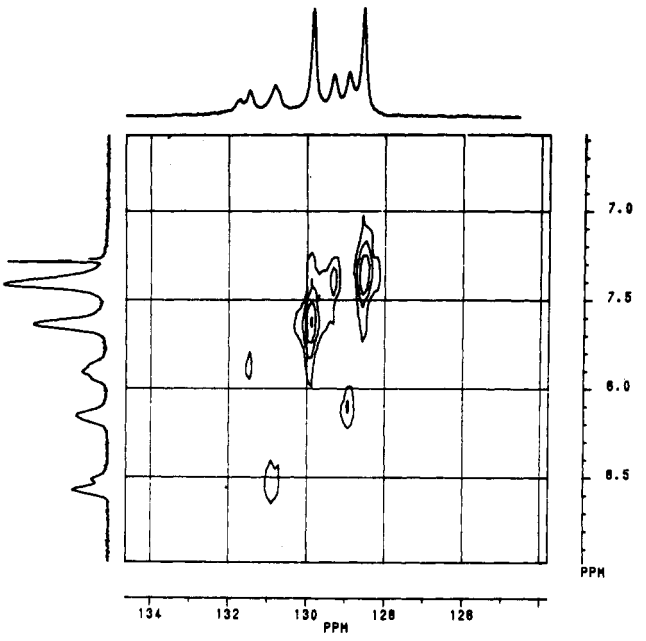


Figure 8. C–H COSY spectrum of PPQ 4. The composite peak of H3′ and H4′ at δ 7.43 is readily separated into two cross-peaks by the different chemical shifts of the respective carbons they are attached to. The two isomeric peaks at δ 131.49 and 131.74 give only one weak cross-peak with H7 at δ 7.86.

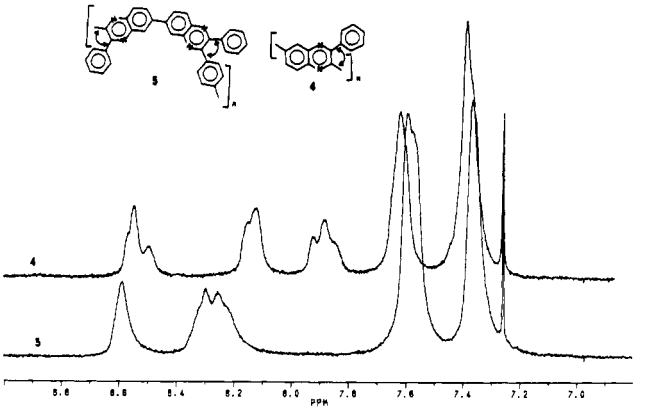


Figure 9. Comparison of the ^{1}H NMR spectra of the two PPQ polymers in deuteriochloroform.

320 °C. This suggests that the phenylene spacer does not contribute significantly to the overall chain mobility in the quinoxaline polymer. The similarity of PPQ 4 and 5 in their solubility behavior is no surprise, since structurally they are quite similar. Both are soluble in phenolic solvents (phenol, cresol, guaiacol) and halogenated hydrocarbons (chloroform, bromoform, tetrachloroethane) as well as in sulfuric acid. The brown solution of PPQ 4 in a 2:1 cresol–xylene mixture can be readily spin-coated onto a silicon wafer, forming a very low stress (1.6×10^7 dyn/cm^2, 1 order of magnitude lower than those of polyimides), low dielectric constant (2.44, 100 kHz to 10 MHz) insulation layer. PPQ 4 does not give resolved peaks in the wide-angle X-ray diffractogram and therefore is considered to be amorphous, similar to PPQ 5.

Temperature-Dependent Spectra of PPQ 4. Molecular models revealed that the phenyl ring located in the proximity of the quinoxaline ring is subject to steric interactions, and the rotation of the phenyl ring is therefore restricted. Figure 6 shows four ^{1}H spectra of PPQ 4 taken between 223 and 353 K. The splitting at ca. δ 8.50 at low temperatures indicates that at least three different H5 protons are in the polymer chain. Attempts to measure

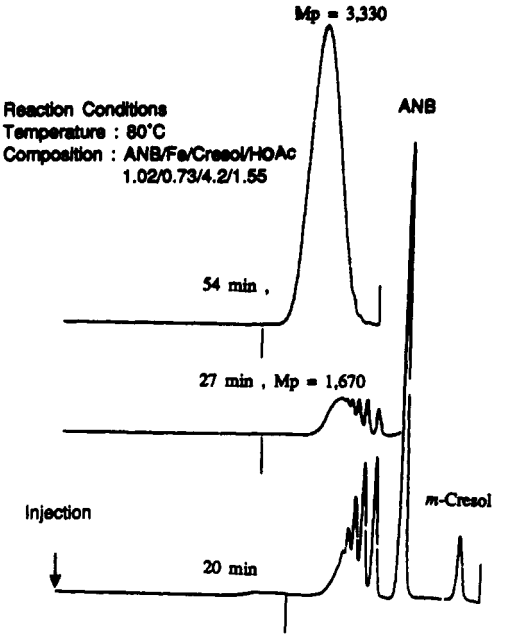
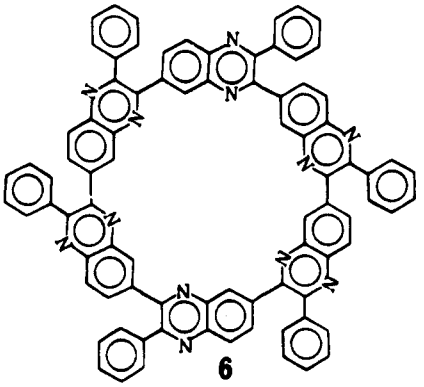


Figure 10. Chromatograms of reductive polycyclization of 3-nitro-4-aminobenzil conducted at 80 °C. Peak molecular weights (M_p) are shown.

the rotational barrier failed due to the absence of clear coalescence points in this temperature range. The complex spectral patterns of different isomeric origins also made the measurement harder than in the other system. The restricted phenyl rotation is also consistent with the ^{13}C T_1 measurements. The T_1 values of proton-bearing carbons in the phenyl ring are quite similar, ranging from 0.14 (C2′ and C3′) to 0.13 s (C4′) at 40 °C (see Table I), indicative of no anisotropic phenyl rotation.[10] In contrast to the dynamic nature of the ^{1}H NMR spectra of PPQ 4, the ^{13}C spectrum of PPQ 4 is temperature independent up to 50 °C. Apparently, the small conformational change does not induce observable effects on the ^{13}C chemical shifts of this polymer.

Structural Characterization of PPQ 4. Although unresolved peaks were found in the ^{1}H NMR spectrum, the ^{13}C spectrum of PPQ 4 revealed the expected pattern in the chemical shift range of 128–154 ppm. Peak assignment was aided mainly by ^{13}C–^{1}H COSY and COLOC experiments (Figures 7 and 8). The COLOC experiments clear up the ambiguity in the quaternary carbon assignments. A total of 13 resolved peaks were found instead of the expected 12 in the ^{13}C spectrum, suggesting the presence of more than one isomeric segment in PPQ 4. Evidence of structural isomerism in PPQs with ether linkage has been reported.[11] The isomeric structures of PPQ 5, although speculated about since the first preparation of PPQ in 1967, have never been observed experimentally. The two carbon peaks of PPQ 4 at δ 131.49 and 131.74 shared a common cross-peak with the unresolved proton peak at δ 7.86 in the C–H COSY spectrum and identified themselves as carbons in a structurally similar isomeric fashion. The intensity ratio between these two carbons matches the ratio of the barely resolved proton peaks at ca. δ 8.50 (split at 223 K to three peaks at δ 8.46, 8.53, and 8.57), although the chemical shift direction is reversed; i.e., the minor component has a low-field absorption in the ^{13}C spectrum while the same component in the ^{1}H spectrum is a high-field peak. It is likely that the minimum-energy conformation of PPQ 4 in chloroform requires that the phenyl ring be perpendicular to the quinoxaline plane so that the major conformer has proton H7

pointing to the center of the phenyl ring. This conformation explains the high-field-shifted nature in the ^1H NMR spectrum. As compared to the respective protons in PPQ 5, H7 is shifted to higher field by 0.4 ppm and H8 is shifted to higher field by 0.2 ppm (Figure 9), due to the ring current effect contributing from the nearby orthogonal benzene ring. The absence of any peaks between δ 8.2 and δ 8.4 in polymer 4 suggests that the conformer having H5 pointing to the phenyl ring does not exist in solution. The other possible conformation is the structure with two parallel aromatic planes facing each other. Quadrupolar repulsion between the two aromatic rings is a factor against this conformation, and probably this conformation only accounts for a minor contribution. In addition to the conformational isomerism, cis to trans geometric isomerism of the propagating polymeric chain also plays an important role in the PPQ chain structure. The steric interactions in the growth of the cis polymer segments is a factor against building up high molecular weight polymer. Successive cis chain growth would generate a cyclic quinoxaline hexamer 6, which has yet to be detected experimentally. Most likely, interruption of the major trans segments by occasional cis linkages would be a proper structural description of this quinoxaline polymer.[12]



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Reductive Polycyclization. The low yield in sodium dithionite reduction of 3-nitro-4-aminobenzil (2) prompted a circumvention of this nonselective reaction.[13] A literature search revealed precedence of the in situ reductive cyclization of carbonyl-containing nitro compounds.[14] The application of this process in polycyclization, however, has rarely been exploited.[15] Preliminary experiments showed that oligomers of phenylquinoxaline were produced when 2 was refluxed with iron powder in acetic acid. Increasing the solubility of the oligomers in the reaction media by adding a good solvent, thus preventing a premature phase separation, produced a higher molecular weight polymer. In addition to being a good solvent for PPQ, cresols also help to form the preferred cis conformer of the benzil through hydrogen bonding.[16] The optimum reaction conditions were found using a mixture of 2/Fe/HOAc/*m*-cresol in a 1.4:1:2:6 weight ratio at 140 °C. Purification by washing with acetic acid and water afforded the desired polymer as a yellowish-brown powder in a nearly quantitative yield. The acidity of the reaction mixture is an important factor influencing the polymer yield and molecular weight distribution. Acids of different pK_a produced different results owing to the subtle balance between the available equilibrium diamine concentration (vanished with increasing acidity) and the subsequent acid-catalyzed dehydration step (accelerated with increasing acidity), similar to that of the oxime formation reaction.[17] The reductive polycyclization was monitored carefully by GPC at two temperatures (80 and 140 °C), and the chain propagation rates were calculated. An apparent activtion energy of 17 kcal/mol for this polycyclization was obtained. In the early reaction stage at low temperatures, resolved oligomer peaks up to hexamers were detected (Figure 10). The polymer obtained by this method was identical with that produced by polycyclization of 3,4-diaminobenzil, thus reflecting a polymer yield improvement of 30% over the indirect route.

Conclusion

We have shown that a new phenylquinoxaline polymer with high thermal stability can be prepared from 3-nitro-4-aminobenzil via reductive polycyclization. The relatively simple reactions involve no known carcinogens[18] and no expensive starting materials,[19] in contrast to the existing system. This new polymer can be used to replace the high-cost, two-component poly(phenylquinoxalines) with the advantages of a higher thermal stability and a lower dielectric constant.

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References and Notes

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Registry No. 1, 120703-28-8; 2, 120703-29-9; 2 (homopolymer), 130434-98-9; 3, 120703-30-2; 4 (homopolymer), 120704-84-9; 4 (SRU), 130495-43-1; Fe, 7439-89-6.