Hyperbranched Polyphenylquinoxalines from Self-Polymerizable AB_2 and A_2B Monomers

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ABSTRACT: A self-polymerizable AB_2 monomer, 2,3-bis(4-hydroxyphenyl)-6-fluoroquinoxaline, and an A_2B monomer, 2,3-bis(4-fluorophenyl)-6-(4-hydroxyphenoxy)quinoxaline, were prepared and polymerized to afford phenol-terminated and aryl fluoride terminated, hyperbranched polyphenylquinoxalines (**HPPQ**s), respectively. MALDI−TOF analysis showed that intramolecular cyclization was a dominant process for the low molecular weight portion during the polymerizations. After isolation and complete dryness, the phenol-terminated **HPPQ 1** was only soluble in strong organic acids, while the aryl fluoride terminated **HPPQ 2** was soluble in most common organic solvents. **HPPQ 1** was treated with allyl bromide to afford an allyl ether terminated **HPPQ 3,** which was also soluble in most organic solvents. Intrinsic viscosity measurements and SEC analysis indicated that **HPPQ 2** had a much higher M_w and a much broader molecular weight distribution (PDI ∼ 60) than **HPPQ 1** and **HPPQ 3** (PDI ∼ 4). The results also suggested that **HPPQ 1** formed aggregates in solution and that **HPPQ 2** had a much more extended and open conformation. All the **HPPQ**s, which were highly fluorescent, had UV absorption maxima near 375 nm in THF. However, the wavelength of their emission maxima, which ranged from 424 to 466 nm, depended on their end groups.

Introduction

Polyphenylquinoxalines (PPQs) are a well-known class of high performance thermoplastics that have many desirable properties such as good processability, excellent tensile and adhesion properties, and high glass transition temperatures (T_gs).[1] Recently, they have received attention for possible use in photonic applications such as electron transport layers in light emitting diodes.[2] In fact, a PPQ containing thiophene segments has been shown to be far superior to other electron transport layers in PPV-based light emitting devices.[2c] PPQs are prepared by two different methods. The classical method involves the condensation polymerization of aromatic tetraketones with aromatic tetraamines in *m*-cresol.[3] In a more recent approach, aromatic bisphenolate salts are polymerized with activated aromatic dihalides[4] via aromatic nucleophilic substitution reactions in polar aprotic solvents. In this approach, a preformed quinoxaline ring is incorporated in either the bisphenolate salt or the dihalide. This method is currently favored because it is more versatile and potentially less expensive than the first. As part of an effort to further reduce cost, a self-polymerizable AB PPQ monomer was synthesized in this laboratory.[5] The monomer contains a phenolic group and a fluorine atom activated for nucleophilic substitution by a pyrazine ring. The monomer, which exists as two isomers, 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxalne and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline, was self-polymerized in an NMP/toluene mixture to high molecular weight. The PPQ obtained displayed excellent properties.

The overall objective of this work was to use similar chemistry in the preparation of hyperbranched PPQs (**HPPQ**s). Hyperbranched polymers are a new class of materials that display properties distinctly different from those of their linear analogues.[6] For example, hyperbranched systems display lower viscosities and better solubility than their linear analogues with similar molecular weights.[6f,6i] When repeating units themselves are optically active chromophores and incorporated into the hyperbranched polymer molecules, they also display enhanced optical properties. For example, the fluorescent quantum yields of hyperbranched systems are relatively high compared to their linear analogues, presumably due to the efficient physical isolation of the chromophores in polymer molecules by preventing self-quenching.[7] Dendritic system has been developed for light-emitting devices.[8] Related dendrimer systems have been found to be very efficient in light harvesting and energy transfer.[9]

The specific objectives of this work were to synthesize the AB_2 and A_2B monomers 2,3-bis(4-hydroxyphenyl)-6-fluoroquinoxaline[10] and 2,3-bis(4-fluorophenyl)-6-(4-hydroxyphenoxy)quinoxalines.[10b] The monomers were to be self-polymerized to afford the corresponding phenol-terminated and aryl fluoride terminated hyperbranched systems. The new materials were to be thoroughly characterized. In particular, the effects of the terminal groups on the material solubilities, solution viscosities, and their thermal and optical properties were to be determined.

Experimental Section

Reagents and Solvents. All chemicals, unless otherwise mentioned, were purchased from Aldrich Chemical Inc and

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were used as received. *N*-Methyl-2-pyrrolidinone (NMP) (Aldrich) was distilled from phosphorus pentoxide under reduced pressure. All other solvents were purchased from Fisher Scientific Inc and used as received. Dithranol was purchased from ICN Biomedicals, Inc., Aurora, OH.

Instrumentation. Infrared (IR) spectra were obtained with an ATI Mattson Genesis Series FT-IR 5000 spectrophotometer. Solid samples were imbedded in KBr disks. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were obtained at 200 and 50 MHz on a Varian Gemini-200 NMR spectrometer. Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were obtained with a Varian Gemini XL-400 nuclear magnetic spectrometer. Elemental analysis and mass spectral analysis were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points (mp) were measured using a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon Ubbelohde No. 150 and 200 viscometers. The solutions were filtered through a 0.45 μm syringe filter prior to the measurement. Flow times were recorded for *m*-cresol or methanesulfonic acid (MSA) solutions with polymer concentrations of approximately 0.5−0.25 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) analyses were performed in nitrogen with a heating rate of 20 °C/min using a DuPont model 2000 thermal analyzer equipped with differential scanning calorimetry cell. The thermograms were obtained on powder samples after they had been heated to 350 °C and air-cooled to ambient temperature. Glass transition temperatures (T_gs) were taken as the midpoint of the baseline shift. Themogravimetric analyses (TGA) were obtained in nitrogen (N_2) and air atmospheres with a heating rate of 20 °C/min using a TA Hi-Res TGA 2950 themogravimetric analyzer.

A Bruker-Franzen Analytik GMBH, MALDI time-of-fight (TOF) mass spectrometer was employed to determine masses using a reflection mode. Dithranol and potassium trifluoroacetate were used as the UV-absorbing matrix and cationizing salt, respectively. In the case of **HPPQ 1**, size exclusion chromatography (SEC) was carried out on a Waters 490E equipped with UV detector. 0.01 mL samples of the NMP solution were diluted with THF to 2 mL and filtered through a 0.45 μm syringe filter before they were subjected to SEC analysis. In the case of **HPPQ 2**, SEC was carried out on a Waters 150-CV equipped with refractive index, viscosity, and light scattering detectors. Tetrahydrofuran (THF) was used as the elution solvent. UV−visible spectra were obtained on a Hewlett-Packard 8435 UV−visible spectrophotometer. Photoluminescence measurements were performed with a Shimadzu RF-5301PC Spectrofluorophotometer. The excitation wavelength used was that of the UV absorption maximum of each sample. The energy minimized structures and dihedral angles of monomers were carried out by CS Chem 3D Std computational package (Verson 5.0, CambridgeSoft Corporation, Cambridge, MA 02140).

1,2-Bis(4-methoxyphenyl)-2-hydroxyethanone (1).[11] Into a 2 L, three-necked round-bottom flask equipped with an overhead stirrer, a reflux condenser, and a nitrogen inlet were placed 4-methoxybenzaldehyde (209.8 g, 1.541 mol), ethanol (1 L), and a solution of potassium cyanide (105.0 g, 1.622 mol) in water (300 mL). The reaction mixture was heated at reflux for 4 h. The solution changed from light yellow at the initial stage to deep yellow at the final stage. The reaction mixture was allowed to cool to room temperature and poured into 2 L of water. The mixture was very slowly acidified with 200 mL of concentrated HCl (*Caution!* HCN gas was evolved) in an ice bath. Methylene chloride (500 mL) was then added to aid in the workup. The aqueous layer was separated and discarded. The organic layer was washed several times with a large amount of water, separated again from the aqueous layer, and then taken to dryness on the rotary evaporator. The viscous residue was taken up in acetone, filtered, and again taken to dryness on a rotary evaporator. The yellow oil was dissolved in hot 95% ethanol or glacial acetic acid and then stored in a refrigerator to obtain 140.6 g (67%) of yellow crystals: mp 111−112 °C (lit.[11d] mp 111−112 °C); ^{1}H NMR ($CDCl_3$) δ 4.75 (s, 3H, OCH_3), 4.80 (s, 3H, OCH_3), 4.58 (d, 1H, CH), 5.85 (d, 1H, OH), 6.85 (dd, 4H, Ar), 7.20 (d, 2H, Ar), and 7.90 ppm (d, 2H, Ar).

1,2-Bis(4-methoxyphenyl)ethanedione (2).[12] **Method I.** Into a 1 L, three-necked, round-bottom flask equipped with a reflux condenser, an overhead stirrer, and a nitrogen inlet were placed desoxyanisoin (103.2 g, 0.4025 mol), copper(II) bromide (200.0 g, 0.8955 mol), 300 mL of DMSO, and 300 mL of ethyl acetate. The mixture was heated at reflux for 7 h. After the solution was allowed to cool to room temperature, it was poured into 3 L of ice water. Methylene chloride (1 L) was then added. The aqueous layer was separated and discarded. The organic layer was washed several times with water until the aqueous layer was no longer green. The organic layer was again separated and filtered to remove the silverlike solid that precipitated. The solvent was removed on a rotary evaporator. The yellow residue was dissolved in hot ethanol. The solution was filtered to remove any insoluble solid and then allowed to cool to room temperature to afford 101.2 g (93%) of bright yellow needles: mp 133−134 °C (lit.[12c] mp 132−134 °C); FT-IR (KBr, cm^{-1}) 1655 (carbonyl); ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, OCH_3), 6.97 (d, 4H, Ar), and 7.97 ppm (d, 4H, Ar).

Method II. A solution of anisoin (100.0 g, 0.3593 mol) in 350 mL of DMSO was stirred in a 1 L, three-necked, round-bottom flask equipped with an overhead stirrer, a reflux condenser, a nitrogen inlet, and an addition funnel. Hydrobromic acid (48%, 200 mL) was then added slowly over 1 h. The reaction mixture was heated to 50 °C for 4−5 h. During this period, the exothermic reaction evolved a large amount of gas bubbles. The reaction flask was occasionally cooled in a cold water bath. After the evolution of bubbles subsided, the reaction mixture was slowly heated to 90 °C and maintained at that temperature overnight. After the reaction mixture was allowed to cool to room temperature, it was poured into a 2 L slurry of ice and water. The precipitate that formed was collected by filtration, washed with a large amount of water, and dried in air. The yellow solid was dissolved in boiling methanol or ethanol. The solution was filtered and then allowed to cool to room temperature to give 90.4 g (91%) of bright yellow needles: mp 133−134 °C (lit.[12c] 132−134 °C); FT-IR (KBr, cm^{-1}) 1655 (carbonyl); ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, OCH_3), 6.97 (d, 4H, Ar), and 7.97 ppm (d, 4H, Ar).

5-Fluoro-2-nitroaniline (6).[13] Into a 3 L, three-necked, round-bottom flask equipped with an overhead stirrer, a reflux condenser, an addition funnel, and a nitrogen inlet were placed 2,4-difluoronitrobenzene (100.0 g, 0.629 mol) and NMP (475 mL). After ammonium hydroxide (127 mL) was added dropwise over 1 h, the solution was stirred for 24 h. Thin-layer chromatography (TLC) showed that only a trace of 2,4-difluoronitrobenzene remained. The slurry was cooled in an ice bath and diluted to 2.5 L by dropwise addition of deoxygenated water. The resulting yellow solid was collected by suction filtration and washed with deoxygenated water. The compound was recrystallized from deoxygenated aqueous 2-propanol to give 94.2 g (96% based on 2,4-difluoronitrobenzene) of bright yellow needles: mp 95−97 °C (lit.[13] mp 97 °C); FT-IR (KBr, cm^{-1}) 1255 (Ar−F), 1571 (Ar−NO_2), 3368 (Ar−NH_2); ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 2H, NH_2), 6.40−6.55 (m, 2H, Ar), and 8.17 ppm (dd, 1H, Ar).

4-Fluoro-1,2-phenylenediamine (4).[14] **Method I.** A solution of 4-fluoro-2-nitroaniline (33.0 g, 0.211 mol) in 150 mL of deoxygenated ethyl acetate containing 5% palladium on activated carbon (0.53 g) was placed in a hydrogenation apparatus. Hydrogen was charged and discharged five times. The mixture was agitated under hydrogen (55−65 psi) at room temperature 12 h. The solution was filtered through Celite to remove the catalyst. The filtrate was reduced to dryness on a rotary evaporator. After the gray solid residue was dissolved in hot toluene, the solution was allowed to cool to room temperature to give 25.5 g (96%) of gray crystals: mp 89−91 °C (lit.[14] mp 89−91 °C).

Method II. The compound was prepared from 5-fluoro-2-nitroaniline (60.0 g, 0.384 mol) using the procedure described for method I. The gray solid was recrystallized from toluene to give 47.5 g (98%) of white crystals: mp 89−91 °C (lit.[14] mp 89−91 °C).

4,4′-Dihydroxybenzil (3). Into a 1 L, three-necked, round-bottom flask equipped with an overhead stirrer, a reflux condenser, and a nitrogen inlet were placed 50.0 g (0.184 mol) of 4,4-dimethoxybenzil, 250 mL of acetic acid, and 250 mL of 48% hydrobromic acid or 300 g of freshly prepared pyridine hydrochloride (py·HCl). The suspension was heated at reflux with vigorous stirring until it became homogeneous. This usually took about 5−6 h. The crystals that formed during cooling was collected by filtration and washed with water to afford 32.8 g (85%) of yellow needles: mp 254−256 °C (lit.[15] mp 248−250 °C); ^{1}H NMR (acetone-d_6) δ 6.97−7.01 (dd, 4H, Ar), 7.80−7.85 (dd, 4H, Ar), and 9.65 ppm (s, 2H, OH).

1,2-Bis(4-fluorophenyl)-2-hydroxyetnanone (9). The compound was prepared from 4-fluorobenzaldehyde (250.0 g, 2.014 mol) according to the procedure described for the synthesis of 4,4-dimethoxybenzoin. The yellow solid was recrystallized from 90% ethanol or aqueous acetic acid to yield 163.0 g (65%) of yellow crystals: mp 81−83 °C (lit.[16] mp 80−82 °C). FT-IR (KBr, cm^{-1}): 1235 (Ar−F), 1682 (carbonyl), 3478 (Ar−OH).

4,4′-Difluorobenzil (10). The compound was prepared from 4,4′-difluorobenzoin (60.0 g, 0.242 mol) using the procedure described for the oxidation of 4,4′-dimethoxybenzoin. The yellow solid was recrystallized from methanol or ethanol to give 57.3 g (96%) of bright yellow flakes: mp 121.5−123 °C (lit.[17] mp 121−122 °C); FT-IR (KBr, cm^{-1}) 1231 (Ar−F), 1670 (carbonyl). ^{1}H NMR ($CDCl_3$, ppm) δ 7.16−7.26 (td, 4H, Ar), 7.99−8.06 (td, 4H, Ar); ^{13}C NMR ($CDCl_3$, ppm) δ 116.31, 116.63, 129.41, 132.75, 132.90, 164.98, 168.78, 192.22.

3-Amino-4-nitro-4′-hydroxydiphenyl Ether (7). Into a 1 L, three-necked, round-bottom flask equipped with an overhead stirrer, a Dean−Stark trap with a reflux condenser, and a nitrogen inlet and outlet were placed hydroquinone (110.1 g, 1.000 mol), potassium hydroxide (56.1 g, 1.00 mol), 75 mL of toluene, and 300 mL of DMAc. The reaction mixture was heated at 160 °C overnight. During this period, the water that was generated was removed as a toluene azeotrope. After cooling to 130 °C, 5-fluoro-2-nitroaniline (40.0 g, 0.256 mol) was added. The mixture was heated at 130 °C for 4 h with stirring, allowed to cool to room temperature, and poured into a 1.5 L slurry of ice water containing 100 mL of concentrated hydrochloric acid. The precipitate that formed was collected by filtration, washed with water, and dissolved in hot ethanol. The solution was filtered to remove insoluble solid and then allowed to cool to room temperature to afford 54.8 g (87% based on 5-fluoro-2-nitroaniline) of brown crystals: mp 210−211 °C (lit.[18] mp not reported); ^{1}H NMR (DMSO-d_6, ppm) δ 6.22−6.28 (dd, 2H, Ar), 6.80−6.84 (d, 2H, Ar), 6.95−6.99 (d, 2H, Ar), 7.45 (s, 2H, NH_2), 7.94−7.99 (d, 1H, Ar), and 9.54 (s, 1H, OH). Anal. Calcd for $C_{12}H_{10}N_2O_4$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.33; H, 4.33; N, 11.27. Mass spectrum (*m*/*e*): 246 (M$^+$, 100% relative abundance).

3,4-Diamino-4′-hydroxydiphenyl Ether (8). A solution of 3-amino-4-nitro-4′-hydroxydiphenyl ether (18.5 g, 7.51 mmol) in 150 mL of deoxygenated ethanol containing 5% palladium on activated carbon (0.80 g) was placed in a hydrogenation apparatus. The mixture was agitated under hydrogen (55−65 psi) at room temperature overnight. The solution was filtered through Celite to remove the catalyst. Deoxygenated water was added to the filtrate, which was stored in a refrigerator, to give 15.9 g (98%) of brown crystals: mp 220−221 °C (lit.[19] mp not reported). FT-IR (KBr, cm^{-1}): 1213 (Ar−O−Ar), 3347 (Ar−NH2), 3410 (Ar−OH). ^{1}H NMR (DMSO-d_6, ppm): δ 4.81 (s, 2H, NH_2), 5.08 (s, 2H, NH_2), 6.20−6.42 (m, 4H, Ar), 6.61−6.74 (m, 3H, Ar), and 9.55 (s, 1H, OH). Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.33; H, 5.63; N, 12.77. Mass spectrum (*m*/*e*): 216 (M$^+$, 100% relative abundance).

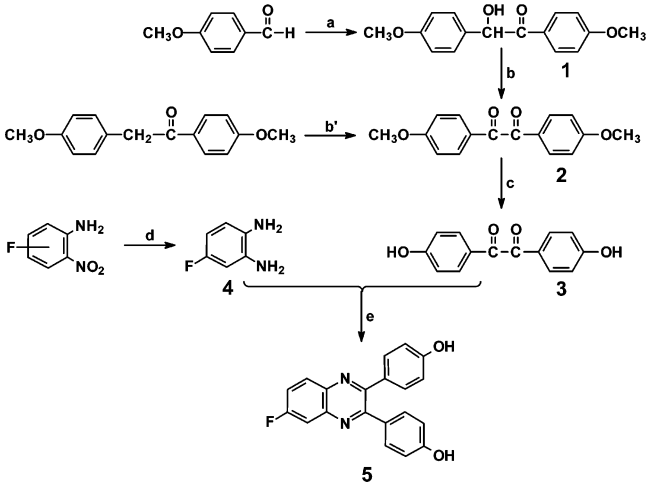
2,3-Bis(4-hydroxyphenyl)-6-fluoroquinoxaline (5).[10] A 500 mL, round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, a Dean−Stark trap, and a nitrogen inlet was charged with 4,4′-dihydroxybenzil (12.0 g, 4.95 mol), 4-fluoro-1,2-phenylenediamine (6.25 g, 4.96 mmol), toluene (75 mL), and deoxygenated acetic acid (250 mL). The reaction mixture was stirred and gently heated at reflux overnight. The water that was generated was removed as a toluene azeotrope. The reaction mixture was then allowed to cool to room temperature and poured into a 1 L slurry of ice and water containing 50 mL of concentrated hydrochloric acid. The precipitate that formed was collected by suction filtration, washed with water, and dissolved in hot aqueous ethanol containing charcoal. The solution was filtered and then allowed to cool to room temperature to give 15.6 g (95% based on 4,4′-dihydroxybenzil) of yellow crystals: mp 142 °C and 238 °C (DSC) (lit.[10a] mp not reported); FT-IR (KBr, cm^{-1}) 1209 (Ar−F), 3259 (Ar−OH). ^{1}H NMR (acetone-d_6, ppm) δ 6.80−6.86 (d, 4H, Ar), 7.40−7.46 (dd, 4H, Ar), 7.58−7.73 (m, 2H, Ar), 8.06−8.13 (t, 1H, Ar), and 8.83 ppm (s, 2H, OH); ^{13}C NMR (acetone-d_6, ppm) δ 114.54, 114.97, 117.70, 121.79, 122.31, 133.21, 133.36, 133.84, 134.05, 134.24, 140.82, 156.73, 161.06, 161.24, 162.74, and 167.68. Anal. Calcd for $C_{20}H_{13}FN_2O_2$: C, 72.28; H, 3.94; N, 8.43. Found: C, 72.18; H, 4.06; N, 8.29. Mass spectrum (*m*/*e*): 332 (M$^+$, 100% relative abundance).

2,3-Bis(4-fluorophenyl)-6-(4-hydroxyphenoxy)quinoxaline (11). The monomer was prepared from 4,4′-difluorobenzil (20.0 g, 81.2 mmol) and 3,4-diamino-4-hydroxydiphenyl ether (17.6 g, 81.3 mmol) using the procedure described for 2,3-bis-(4-hydroxyphenyl)-6-fluoroquinoxaline. The yellow product was recrystallized from aqueous acetic acid containing charcoal to give 28.8 g (83% based on 4,4′-difluorobenzil) of bright yellow crystals: mp 223 °C (DSC); FT-IR (KBr, cm^{-1}) 1229 (Ar−F), 3429 (Ar−OH). ^{1}H NMR (DMSO-d_6, ppm) δ 6.83−6.91 (d, 2H, Ar), 7.06−7.12 (d, 2H, Ar), 7.14−7.22 (m, 5H, Ar), 7.43−7.51 (m, 4H, Ar), 7.60−7.62 (d, 1H, Ar), 8.12−8.15 (d, 1H, Ar), 9.54 (s, 1H, Ar). Anal. Calcd for $C_{26}H_{16}F_2N_2O_2$: C, 73.23; H, 3.78; N, 6.57. Found: C, 73.45; H, 4.35; 6.23. Mass spectrum (*m*/*e*): 426 (M$^+$, 100% relative abundance).

Preparation of HPPQ 1 and HPPQ 2. A typical synthesis of a **HPPQ** was conducted in a three-necked, round-bottom flask equipped with an overhead stirrer, a Dean−Stark trap with a reflux condenser, and a nitrogen inlet and outlet. The flask was charged with monomer (20 wt %) and potassium carbonate (20 mol % excess to hydroxyl group). The solids were carefully washed in with a mixture of toluene and NMP. The mixture was heated until the toluene began to reflux, and then it was maintained at 150−160 °C until water could no longer be observed in the Dean−Stark trap, which typically took about 3−5 h. The dried solution was slowly heated to 180 °C over 1 h under a strong nitrogen flow. The solution was then heated to reflux and maintained at reflux until the solution viscosity began to noticeably increase. In the case of **HPPQ 1**, the solution became elastic gels and was no longer able to be efficiently stirred due to the large number of phenolate salts. This usually took approximately 30−40 min at NMP boiling temperature. The gel was added to large excess of water containing 5 wt % hydrochloric acid (1 L) to precipitate. In the case of **HPPQ 2**, the reaction mixture was diluted with NMP, allowed to cool to room temperature, and poured into a large quantity (1 L) of water containing 5 wt % hydrochloric acid (1 L) to precipitate. The polymer that precipitated was collected by filtration and air-dried overnight. The polymers were dissolved in MSA or NMP and passed through a pressurized filter to remove any insoluble salts. The filtrates were again poured into methanol/water (9/1, v/v) mixture and boiled for several h to remove any trapped salts and Soxhlet extracted for a week with water (**HPPQ 1**) and 3 days with water and 4 days with methanol (**HPPQ 2**). The polymers were collected and dried at 200 °C over phosphorus pentoxide at reduced pressure (1 mmHg) for approximately 48 h. The yields were 98%+: **HPPQ 1** [η] = 0.60 dL/g (MSA, 30 ± 0.1 °C) and T_g = 308 °C (DSC). Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97. Found: C, 71.14; H, 4.37; N, 8.04; **HPPQ 2** [η] = 1.13 dL/g (*m*-cresol, 30 ± 0.1 °C) and T_g = 225 °C (DSC). Anal. Calcd for $C_{26}H_{15}FN_2O_2$: C, 76.84; H, 3.72; N, 6.89. Found: C, 76.55; H, 3.77; N, 6.74.

Preparation of HPPQ 3. Into a 50 mL one-necked, round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet were placed **HPPQ 1** (1.0 g, 3.2 mmol, repeat unit), potassium carbonate (1.0 g, 7.2 mmol), allyl bromide (0.5 g, 4.1 mmol), and NMP (20 mL). The reaction mixture was then heated and maintained at 90 °C for 10 h. During this time

Scheme 1. Synthesis of AB_2 Monomer 5[a]



[a] Key: (a) KCN, aqueous EtOH, reflux; (b) HBr (48%), DMSO, 50 °C; (b′) $CuBr_2$, EtOAc/DMSO, reflux; (c) HBr (48%), AcOH, reflux or pyridine hydrochloride (py·HCl), reflux; (d) H_2 (65−70 psi), Pd−C, EtOAc, room temperature; (e) AcOH/toluene, reflux.

period, the red mixture became light yellow and homogeneous. After the solution had been allowed to cool to room temperature, it was filtered through Celite 545 to remove any insoluble salts. The filtrate was poured into water containing 5% hydrochloric acid (200 mL). The resulting light yellow powder was collected by filtration and dried. The sample was precipitated twice from chloroform with methanol, Soxhlet extracted with water for 3 days and methanol for 4 days, and dried under reduced pressure (1 mmHg) over phosphorus pentoxide at 100 °C for 48 h. The yield was essentially quantitative. $[\eta] = 0.31$ dL/g (NMP at 30.0 ± 0.1 °C). Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.39; H, 4.58; N, 7.95; O, 9.08. Found: C, 77.94; H, 4.83; N, 7.93, O, 9.14. ^{1}H NMR ($CDCl_3$, δ in ppm): 4.73 (−C***H*****$_2$**−CH=CH_2), 5.27−5.46 (−CH_2−CH=C***H*****$_2$**), 6.05 (−CH_2−C***H***=CH_2), and 7.06−8.13 (Ar−***H***).

Results and Discussion

Synthesis of Self-Polymerizable AB_2 and A_2B Monomers. The AB_2 monomer 2,3-bis(4-hydroxyphenyl)-6-fluoroquinoxaline (**5**) was prepared by the sequence shown in Scheme 1. Thus, the benzoin condensation of 4-anisaldehyde gave 4,4′-dimethoxybenzoin (**1**), which was oxidized with hydrobromic acid in DMSO to afford 4,4′-dimethoxybenzil (**2**). Intermediate **2** was also prepared by the oxidation of 4-methyoxybenzyl-4′-methoxyphenyl ketone (desoxyanisoin) with copper(II) bromide in a DMSO/ethyl acetate mixture. 4,4′-Dimethoxybenzil was demethylated by treatment with 48% HBr in acetic acid or by treatment with pyridine hydrochloride (py·HCl) to give 4,4′-dihydroxybenzil (**3**). This intermediate was treated with 4-fluoro-1,2-phenylenediamine (**4**), which was prepared by reduction of 4-fluoro-2-nitroaniline, to give the AB_2 monomer. The structure of the monomer, which was recrystallized from aqueous ethanol, was ascertained by FT-IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and mass spectroscopy. The DSC thermogram of **5** contained two melting endotherms with minima at 142 and 238 °C. This behavior, which has been observed previously with analogous AB monomers, has been attributed to two different crystalline forms. Energy minimization of a space-filling molecular model showed that the pendent phenyl groups are twisted with regards to each other so that they are approximately 40° out of the plane of the quinoxaline ring (Figure 1). This AB_2 monomer was also prepared and polymerized by Hedrick and co-workers during the course of this research.[10a]

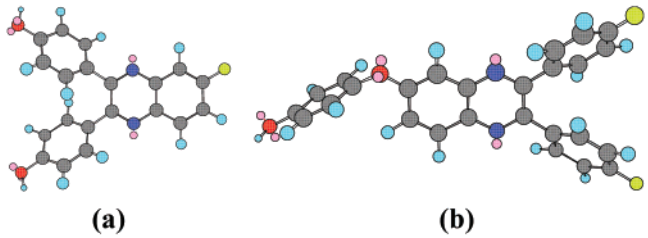
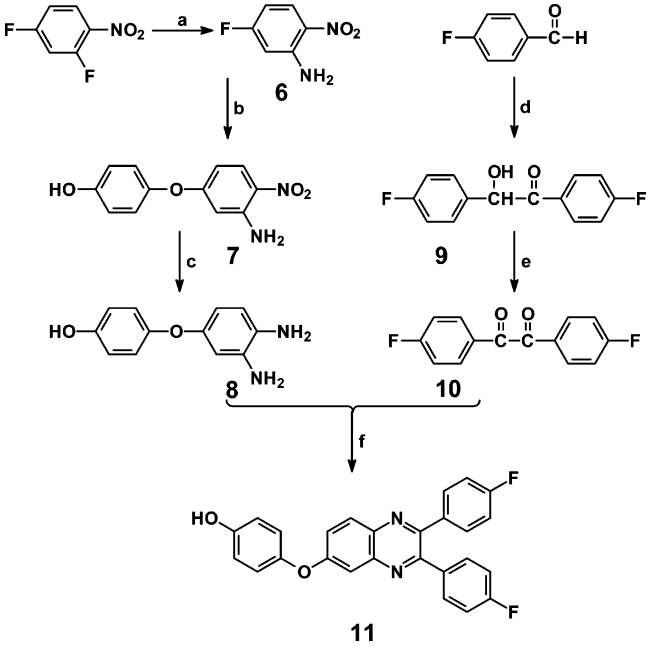


Figure 1. Energy minimized structures (CS ChemBats3D Std V5.0): (a) **5**; (b) **11**.

Scheme 2. Synthesis of A_2B Monomer 11[a]



[a] Key: (a) NH_4OH, NMP, room temperature; (b) Excess hydroquinone, K_2CO_3, NMP/toluene, 140−150 °C; (c) H_2 (65−70 psi), Pd−C, EtOH, room temperature; (d) KCN, aqueous EtOH, reflux; (e) HBr (48%), DMSO, 50 °C; (f) AcOH/toluene, reflux.

The new extended A_2B monomer 2,3-bis(4-fluorophenyl)-6-(4-hydroxyphenoxy)quinoxaline (**11**) was prepared by the synthetic route shown in Scheme 2. Thus, the benzoin condensation of 4-fluorobenzaldehyde in aqueous ethanol in the presence of potassium cyanide gave 4,4′-difluorobenzoin (**9**), which was oxidized to 4,4′-difluorobenzil (**10**) with hydrobromic acid in DMSO in over 90% yield. 3,4-Diamino-4′-hydroxydiphenyl ether (**8**) was prepared by catalytic reduction of 3-amino-4-nitro-4′-hydroxydiphenyl ether (**7**) with hydrogen over palladium on activated carbon. To synthesize the intermediate **7**, 2,4-difluoronitrobenzene was initially treated with ammonium hydroxide in NMP to give 5-fluoro-2-nitroaniline (**6**) in >95% yield[13] and the compound **6** was treated with a 3 M excess of hydroquinone in the presence of potassium carbonate to give 3-amino-4-nitro-4′-hydroxydiphenyl ether (**7**).[18] Condensation of **8** with **10** in an acetic acid/toluene mixture gave the A_2B monomer **11**.

The ^{19}F NMR spectra of **5** and **11** are shown in Figure 2. The single absorption peak in the spectrum of **5** appears at 109.85 ppm, very close to the absorption peak in the spectrum of the corresponding AB monomer isomer (−109.50 ppm, Figure 2a).[5g] Thus, the chemical

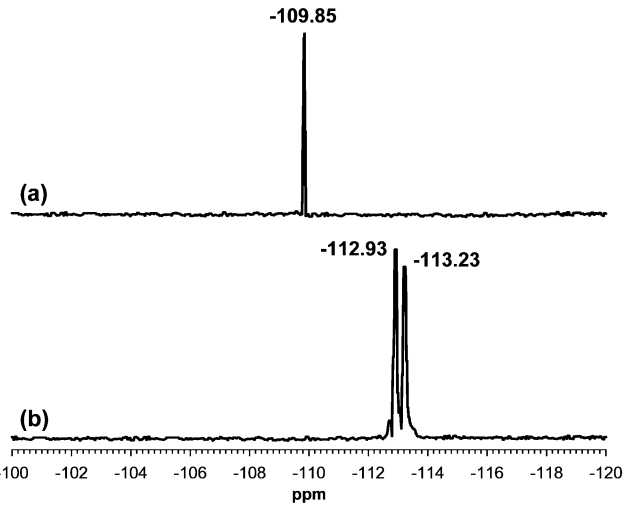


Figure 2. ^{19}F NMR spectra of monomers: (a) **5**; (b) **11**.

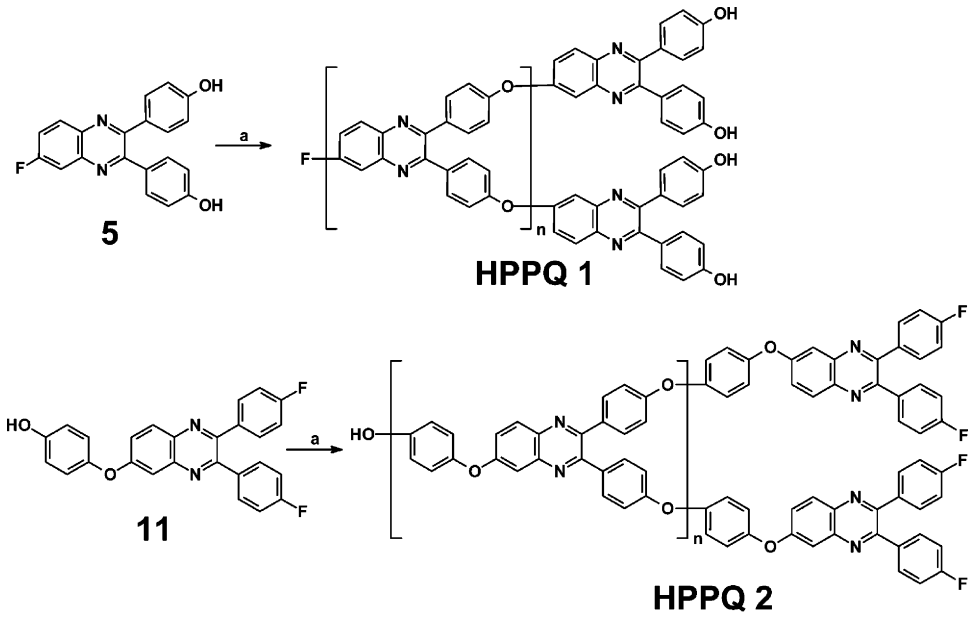
shift is not significantly affected by the hydroxyl group on the phenyl substitutent in the quinoxalines 3-position. This group cannot participate in resonance that directly affects the 6-position. The spectrum of **11** (Figure 2b) contains two peaks at −112.93 and −113.23 ppm due to differences in the electronic environments of the fluorine atoms on the aromatic rings in the quinoxaline's 2- and 3-positions. Since the fluorine atom on the 2-aryl substituent can be deshielded by resonance with the phenoxy substitutent at the 6-position, the peak at −113.23 ppm can be assigned to this substitution pattern.

Self-Polymerization of the AB_2 and A_2B Monomers. Monomers **5** and **11** were self-polymerized in an NMP/toluene mixture in the presence of potassium carbonate to afford the phenol-terminated **HPPQ 1** and the aryl fluoride terminated **HPPQ 2**, respectively (Scheme 3). The solution of **HPPQ 1** became very viscous and then set to a dark elastic gel. The gelation phenomenon could be related to ionic interaction between the large number of phenolate salts at chain ends. The gel was added to a large excess of water containing 5 wt % hydrochloric acid to precipitate the product. A small portion of the polymerization mixture was removed, acidified, collected, air-dried, dissolved in NMP, and diluted with THF prior to precipitation. The sample was used for SEC and spectroscopic analysis. The solution of **HPPQ 2**, which became quite viscous but did not gel, was also added to water containing 5 wt % hydrochloric acid to precipitate the product. Both samples were further purified by Soxhlet extraction for a week with water and/or methanol.

The polymerization rates of the monomers were much faster than that of an AB analogue. High molecular weight polymer was obtained in approximately 0.5−1 h, in refluxing NMP, while it took approximately 3−5 h for a linear polymer under similar conditions.[5] This is because the number of B functional groups (DP + 1) per molecules increased as the polymerization proceeded.

Initial attempts to dry **HPPQ 1** at 200 °C under reduced pressure (1 mmHg) were unsuccessful. TGA showed that the polymer tenaciously retained approximately 5 wt % NMP (Figure 3). Samples containing residual solvent were soluble in ether solvents such as THF and most polar aprotic solvents. To remove the residual NMP, the following procedure was carried out. The polymer was reprecipitated twice from THF with hexane. After it was extracted with water for a week, it was dried over phosphorus pentoxide at 200 °C under reduced pressure (1 mmHg) for approximately 48 h. The orange polymer particles, which showed no weight losses below 390 °C when subjected to TGA (Figure 3), could only be swollen in organic solvents. This behavior is in marked contrast to that of the previously described sample of this material, which displayed solubility in *N,N*-dimethylpropyleneurea (DMPU).[10a] It is postulated that the sample may not have been dried sufficiently and, thus, retained residual DMPU. This behavior is also much different than that of the linear PPQ analogue of **HPPQ 1**, which is soluble in chlorinated and polar aprotic solvents. It is postulated that once all the residual solvent was completely removed, strong inter- and intramolecular hydrogen bonds formed between the

Scheme 3. Synthesis of HPPQ 1 and HPPQ 2[a]



[a] Key: (a) K_2CO_3, NMP/toluene, 150−160, 180, and 202°C.

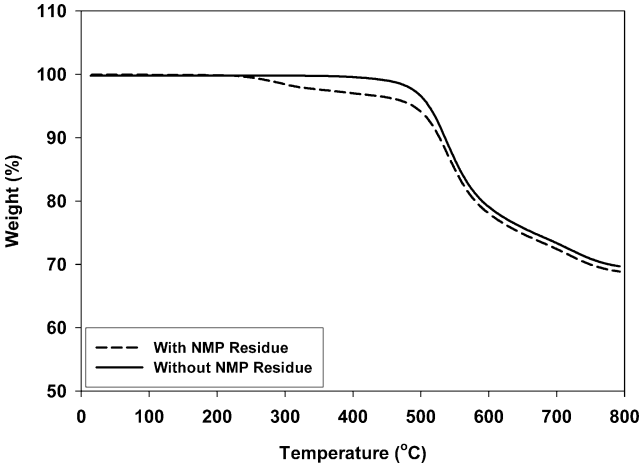


Figure 3. TGA thermograms of **HPPQ 1** with hearing rate of 20 °C/min.

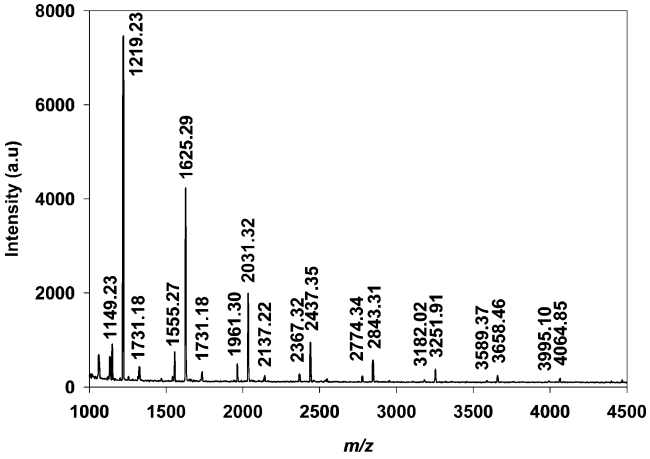


Figure 4. MALDI−TOF mass spectrum of **HPPQ 2**.

terminal hydroxyl groups, which prevented solvation. **HPPQ 1** could only be dissolved in strong acids such as methanesulfonic acid (MSA) and sulfuric acid at room temperature. High molecular weight, phenol-terminated, hyperbranched poly(aryl ether sulfones) are also insoluble in organic solvents, while their aryl fluoride terminated analogues display excellent solubility.[20]

The light yellow powder sample of **HPPQ 2** was dried over phosphorus pentoxide at 200 °C under reduced pressure (1 mmHg) for approximately 48 h. Although TGA indicated that all the NMP was removed by this treatment, to be consistent with the handling of **HPPQ 1**, the sample was extracted with methanol and water for 1 week and then dried over phosphorus pentoxide at 200 °C for 48 h. The aryl fluoride terminated **HPPQ 2** was soluble in polar aprotic solvents (DMF, DMAc, DMSO, NMP, sulfolane), ether solvents (THF), chlorinated solvents (methylene chloride, chloroform), phenolic solvents (*m*-cresol), and strong acids (sulfuric acid, MSA).

MALDI—TOF Analysis of HPPQ 2. Considerable research has been carried out to determine the presence or absence of a unique focal point group in hyperbranched polymers.[21] MALDI−TOF analysis of a previously prepared sample of **HPPQ 1** indicated the absence of a fluorine at focal point.[10a] Thus, intramolecular ring closure was a dominant process in the material preparation at lower molecular region. A single hydroxyl group at the focal point of the **HPPQ 2** should have also been present if no intramolecular cyclization occurred during its polymerization. The MALDI−TOF mass spectrum of **HPPQ 2** is dominated by one series of peaks separated by 406 amu and containing exclusively protonated ions due to the high basicity of the quinoxaline moiety of polymer. The value of 20 amu corresponding to a loss of HF is lower than that expected based on the repeat unit molecular weight up to 8000 *m/z* (Figure 4). This means all **HPPQ 2** oligomers have undergone intramolecular cyclization and lost their unique hydroxyl focal point. Acidic hydrogen atom from hydroxyl group at focal point is reacted with potassium carbonate producing phenolate salt and potassium bicarbonate, which attacks one of activated DP + 1 fluorines at chain ends forming macrocyclic oligomer and loosing focal point. A series of $[C_{26}H_{15}N_2O_2]_nH^+$ macrocyclic oligomers were formed with $n = 3-10$. A minor series of peaks appeared 70 amu below the major series of peaks is proposed to originate from Na^+ adducts of defective oligomers, containing one monomer unit without the 4-hydroxyphenyl substituent. The formation of many hyperbranched systems has been found to proceed with the formation of cyclics. Since the sensitivity of the MALDI−TOF measurements were limited to molecular weights less than 10000 amu, the possibility that the hyperbranched macromolecules with higher molecular weights had a focal point cannot be ruled out.

Table 1. Properties of HPPQs

		GPC[a]				TGA[c]	
polymer	$[\eta]$ (dL/g)	M_n (g/mol)	M_w (g/mol)	PDI	T_g[b] (°C)	$T_{d5\%}$ in N_2 (°C)	char % at 800 °C
HPPQ 1	0.60[d]	87100[e]	322000	3.70	308	511	70
HPPQ 2	1.13[f]	44000[g]	2643000	60.07	225	575	68
HPPQ 3	0.31[h]	55700[g]	243000	4.36		523 (He)	73

[a] Data from refractive index response. [b] Inflection in baseline on DSC thermogram obtained in N_2 with a heating rate of 20 °C/min. [c] Temperature at which 5% weight loss occurred on TGA thermogram obtained with a heating rate of 20 °C/min. [d] Intrinsic viscosity measured in MSA at 30.0 ± 0.1 °C. [e] Determined in THF containing less than 1 vol % NMP. [f] Intrinsic viscosity measured in *m*-cresol at 30.0 ± 0.1 °C. [g] Determined in THF. [h] Determined in NMP at 30.0 ± 0.1 °C.

Solution Properties of HPPQ 1 and HPPQ 2. The intrinsic viscosities of **HPPQ 1** and **HPPQ 2** were 0.60 dL/g (MSA at 30.0 ±0.1 °C) and 1.13 dL/g (*m*-cresol at 30.0 ±0.1 °C), respectively (Table 1). Although a direct comparison cannot be made due to the different solvents used, the viscosity of **HPPQ 2** was almost twice that of **HPPQ 2**. While this is most likely due to a large difference in molecular weight, this may also be an indication of the differences in the conformations of the polymers in solution. Intramolecular hydrogen bonding superior to structural rigidity in **HPPQ 1** and the interaction between polymer and solvent could lead to a compact structure, while the van der Waals interaction between the terminal dipoles in **HPPQ 2** inferior to the structural rigidity of polymer chain and the interaction between polymer and solvent could lead to an open, solvated, extended structure. The large viscosity of **HPPQ 2** is unusual in that hyperbranched systems typically display viscosities well below one.

Thermal Properties of HPPQ 1 and HPPQ 2. The **HPPQ 1** displayed a T_g of 308 °C (Figure 5a, Table 1). This is more than 50 °C higher than that of the analogous linear PPQ (252−256 °C).[5] It is postulated that this is due to strong inter- and intramolecular hydrogen bonding between the hydroxyl chain ends.

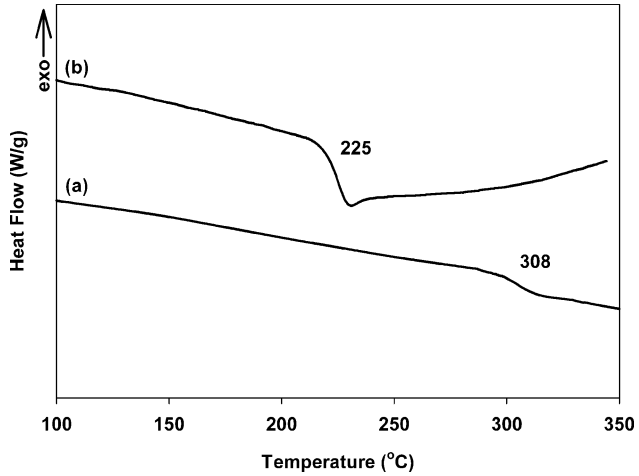


Figure 5. DSC thermograms of polymers with heating rate of 20 °C/min: (a) **HPPQ 1**; (b) **HPPQ 2**.

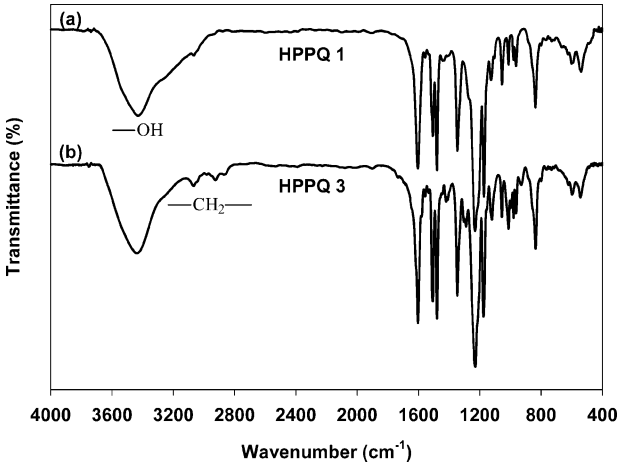


Figure 6. FT-IR (KBr) spectra: (a) **HPPQ 1**; (b) **HPPQ 3**.

Surprisingly, the T_g was also more than 50 °C higher than that reported for a previously prepared sample of **HPPQ 1** (255 °C),[10a] which is similar to that of the linear analogue.[5] This may be further evidence that the previous sample contained residual solvent (see Figure 3), which could have been difficult to completely remove, served as a plasticizer, and lowered the T_g. The other reason may be due to a lower molecular weight polymer. The T_g of **HPPQ 2** was 225 °C (Figure 5b, Table 1), which was not significantly different from that of the analogous linear **PPQ** (220 °C) with the same repeating unit.[22] The much lower T_g of **HPPQ 2** compared to **HPPQ 1** can be attributed to the extra flexible units in the repeating unit, to no hydrogen bonding, and also to its apparent extended, open conformation. The T_gs of phenol-terminated, hyperbranched poly(aryl ether sulfones) are considerably higher than those of their aryl fluoride terminated counterparts.[20]

Powder samples of **HPPQ 1** and **HPPQ 2** underwent 5% weight losses at 511 and 575 °C, respectively, when they were subjected to TGA in N_2 with heating rate of 20/min. The reduced stability of **HPPQ 1** is most likely due to the lower stability of the terminal phenol groups. Phenol-terminated, hyperbranched poly(aryl ether sulfones) are also less thermally stable than their aryl fluoride terminated counterparts.[20]

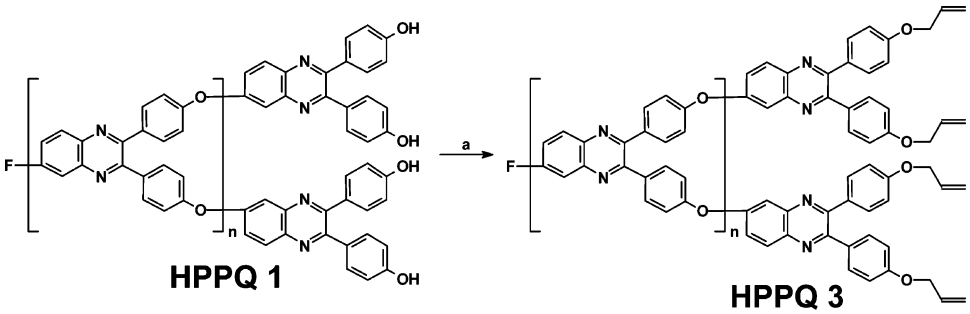
Functionalization of HPPQ 1. HPPQ 1 was treated with allyl bromide in NMP to afford an allyl ether-terminated **HPPQ 3** (Scheme 4). Although dried **HPPQ 1** was only swollen in NMP, it gradually went into solution as the functionalization proceeded. The conversion were followed with ^{1}H NMR by the disappearance of the hydroxyl proton absorption at 8.4−9.5 ppm and with FT-IR by the appearance of the absorption bands at 2918 and 3064 cm^{-1} (Figure 6).

In contrast to its parent,**HPPQ 3** was soluble in polar aprotic solvents (DMF, DMAc, DMSO, NMP, sulfolane), chlorinated solvents (dichloromethane, chloroform), and ether solvents (diethyl ether, THF). It displayed an intrinsic viscosity of 0.31 dL/g (NMP at 30 ± 0.1 °C), which is considerably lower than that of its parent ([η] = 0.60 dL/g in MSA at 30 ± 0.1 °C). This is most likely due to the change in the end groups from hydroxyl groups, which could form hydrogen bonds with the MSA solvent and promote aggregation, to relatively nonpolar hydrocarbon residues.

A DSC thermogram was obtained on a powder sample of **HPPQ 3** after it had been heated to 200 °C and air-cooled to ambient temperature. The thermogram contained a major exotherm with a maximum at 303 °C (ΔH_{exo} = 88 J/g) and a very minor exotherm with a maximum at 379 °C (ΔH_{exo1} = 2.6 J/g). The major exotherm is most likely due to the Claisen rearrangement of the allyl ether end groups and their subsequent polymerization. Similar behavior has been observed with polybenzoxazoles containing pendent oxyallyl substitutents.[23] TGA analysis of powder samples of **HPPQ 3** showed 5% weight losses at 523 °C in helium and at 512 °C in air.

SEC Analysis of HPPQs. To obtain a solution of the phenol-terminated **HPPQ 1** for SEC analysis, an aliquot of the NMP polymerization solution was diluted with THF. The trace obtained showed a multimodal molecular weight distribution with a weight-average molecular weight (M_w) of 322000 and a polydispersity index (PDI) of 3.70 (Figure 8a, Table 1). It appears that a portion of the very high molecular weight fractions were

Scheme 4. Functionalization of HPPQ 1 To Afford HPPQ 3[a]



[a] Key: (a) CH_2=$CHCH_2$−Br, K_2CO_3, NMP, 90 °C.

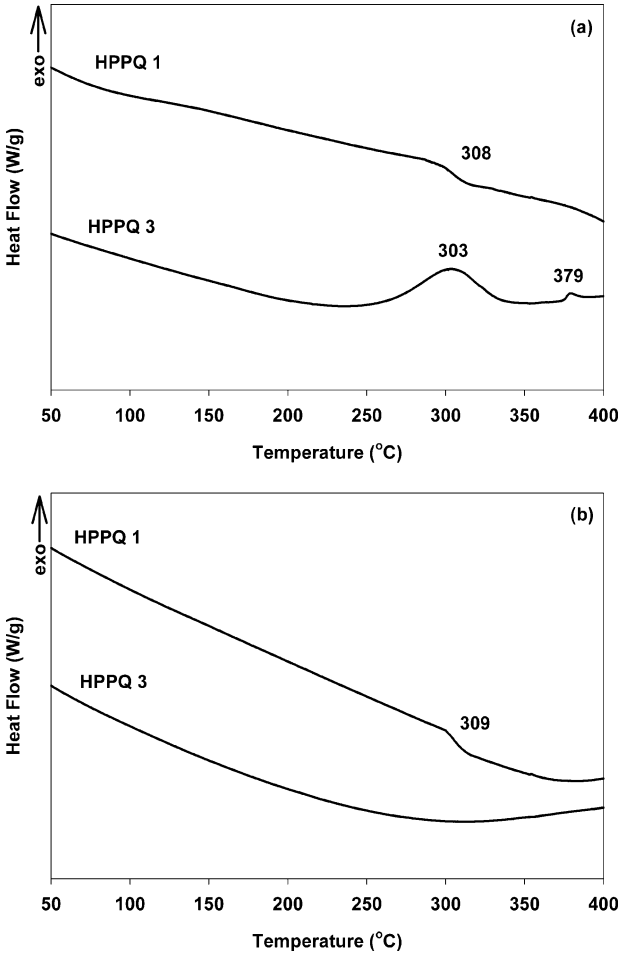


Figure 7. DSC thermograms of **HPPQ 1** and **HPPQ 3** with heating rate of 20 °C/min: (a) first heating scan; (b) second heating scan.

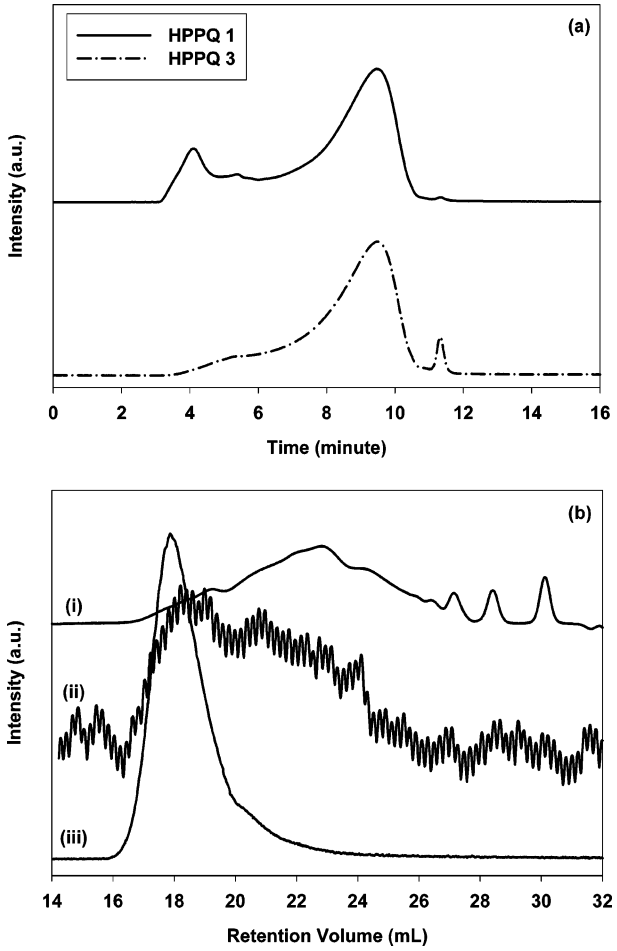


Figure 8. GPC traces: (a) **HPPQ 1** and **HPPQ 3**; (b) **HPPQ 2** (i) refractive index response, (ii) viscosity response, and (iii) light scattering response.

agglomerates, because when this polymer was functionalized with allyl groups, most of these fractions could not be detected. Although the dilute solution of **HPPQ 1** was passed through a 0.45 μm filter prior to injection into the SEC, it is possible that some physical aggregates remained. It is also possible that the molecules simply aggregated due to hydrogen bonding. High molecular weight polymers that contain large amounts of hydroxyl groups have a tendency to aggregate in poor solvents. The M_w of the allyl ether-terminated **HPPQ 3** was 243000 and the PDI was 4.36 (Figure 8a, Table 1). The functionalization not only removed the terminal hydroxyl groups but also afforded solubility in THF.

HPPQ 2, which was very soluble in THF, was analyzed with SEC using a refractive index detector, a viscosity detector, and a light scattering detector (Figure 8b, Table 1). The trace obtained with the refractive index detector (top curve, Figure 8b) showed a very broad molecular weight distribution (PDI $\sim$ 60). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 44000 and 2643000 g mol^{-1}, respectively. Although a PDI of approximately 60 has been predicted for hyperbranched polymers from AB_2 monomers,[24] there have been few previous reports of PDIs approaching such a high value.[25] The use of the viscosity detector resulted in the number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 68000 and 2992000 g mol^{-1}, respectively with a PDI of 44. Analysis with the light scattering detector indicated a much higher molecular weights with the number-average molecular weight (M_n) of 1876000 g mol^{-1}, weight-average molecular weight (M_w) of 24388000 g mol^{-1}, and PDI of **HPPQ 2**. The radius of gyration was 14.07 nm. The narrower molecular weight distribution is most likely due to the better sensitivity of the light scattering detector in the higher molecular weight regions. The high molecular weight response in all these analyses is postulated to be due to an extended molecular conformation due to van der Waals interaction of the aryl fluoride groups at the chain ends is not strong enough to overcome the structural rigidity of polymer chains and the interaction between polymer and solvent. This result is opposite to that for the fluoride terminated hyperbranched poly(ether ketone).[26]

Optical Properties of Monomers and HPPQs. The monomers and polymers prepared in this study were highly fluorescent. Monomer **5** displayed a major UV absorption peak with a maximum at 376 nm and a fluorescence emission peak with a maximum at 441 nm in THF. **HPPQ 1** and **HPPQ 3** had absorption maxima of 378 and 376 nm, respectively and emission maxima of 466 and 458 nm, respectively (Figure 9a, Table 2). The absorption maximum of the phenol-terminated **HPPQ 1** was almost identical to that of its monomer, but its emission peak maximum was red-shifted 25 nm. The emission maximum of **HPPQ 3** was slightly blue-shifted (7−8 nm) from its parent. The absorption and emission maxima of monomer **11** were at 369 and 416 nm, respectively (Figure 9b, Table 2). The absorption and the emission maxima of the **HPPQ 2** prepared from

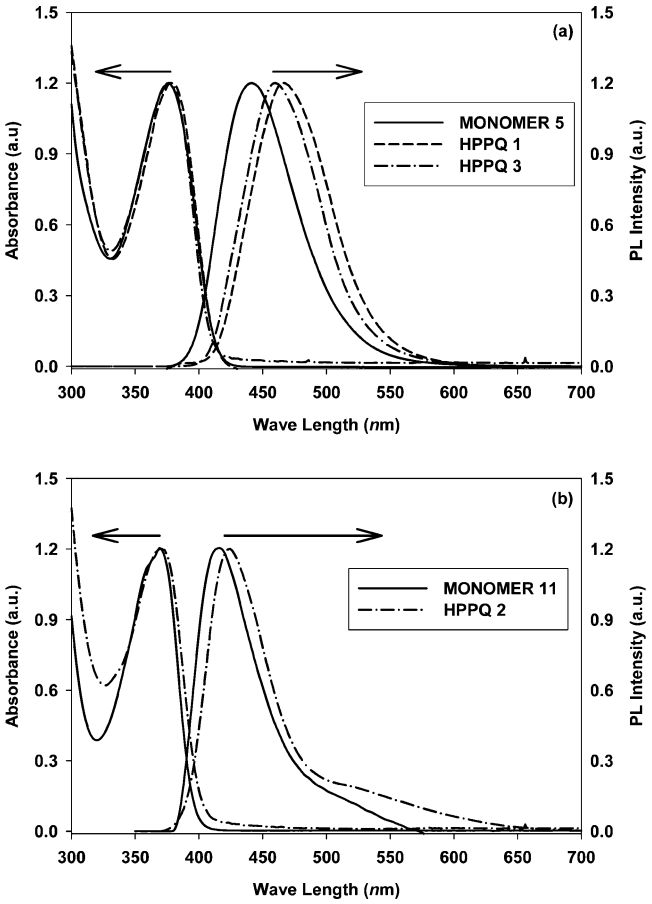


Figure 9. UV-absorption and emission spectra in THF solutions: (a) **5**, **HPPQ 1**, **HPPQ 3**; (b) **11, HPPQ 2**.

Table 2. Optical Properties of Monomers and Polymers

compound	$\lambda_{ab}{}^{a}$ (nm)	$\lambda_{em}{}^{a}$ (nm)
monomer **5**	376	441
monomer **11**	369	416
HPPQ 1	378[b]	466[b]
HPPQ 2	371	424
HPPQ 3	376	460

[a] Determined in THF with a concentration of 10^{-4}–10^{-6} g/L. [b] Determined in THF containing 8% of **HPPQ 1** solution in NMP with a concentration of 10^{-3}–10^{-5} g/L.

this monomer **11** were at 371 and 424 nm, respectively (Figure 9b). Thus, the absorption maximum of the polymer was also almost identical to that of its monomer, while the emission maximum was red-shifted. Interestingly, the absorption maxima of the monomers and the polymers prepared from them occurred at almost identical wavelengths, while the fluorescence emission maxima varied depending on the end group. Similarly, an emission peak shift depending on solvent polarity was reported. The emission maxima of organic dyes attached on dendrimer varied by solvent polarity.[27]

Both the absorption and emission intensities of the **HPPQ**s in THF were linearly dependent on the polymer concentrations from 1.00×10^{-6} to 1.00×10^{-4} g/L. At concentration above 1.00×10^{-4} g/L the intensity of the fluorescence emission was off the scale of the instrumentation. This behavior indicates that the quinoxaline chromophores in each repeating unit are physically well isolated from each other and not subject to π–π electron quenching via aggregate excimer formation and self-quenching. Meanwhile, emission intensities of **HPPQ 2** and **HPPQ 3** were approximately twice as strong as **HPPQ 1** at the same concentration.

Surprisingly, the aryl fluoride terminated **HPPQ 2** emitted a strong blue-green fluorescence when excited at 360 nm in the solid state, while **HPPQ 1** was not active.[28] This is further evidence that the hydroxyl-terminated system is much more compact and subject to internal aggregate excimer formation and self-quenching due to intramolecular hydrogen bonding between the end groups.

Conclusions

There are limited examples in the literature showing that the polarity of surface groups on hyperbranched polymers with similar structure is of great influence on properties of hyperbranched polymers.[26] To study the influence of surface groups on hyperbranched polymer, known AB_2 and novel A_2B monomers can be prepared and self-polymerized via aromatic nucleophilic substitute (S_NAr) reactions to very high molecular weight **HPPQ**s. Corresponding **HPPQ**s are fully worked-up until no residual solvents are detected and used for characterization. Some properties of known **HPPQ 1** displays quite different T_g and solubility compared to reported **HPPQ 1**[10a] and **HPPQ**s prepared in this manner dramatically depend on the nature of end groups. Thus, our work firmly suggests several points of fundamental significance. First, it indicates that thoughtful workup is very important to get rid of unnecessary factors that can affect properties of new synthesized polymer, although a lot of researchers often ignore this point. In particular, we believe extra attention is required for dealing with polar amorphous polymers. Their properties could be more significantly influenced by residual impurity such as solvents. It is noteworthy that the interaction between polar hyperbranched polymer and polar solvent is too strong, resulting in removal of the residual solvent entrapped in polymer matrix being not such a simple process, and thus one needs to pay careful attention to final workup to purify the polymer. Second, depending on the surface group nature of hyperbranched polymers, their properties such as T_g, degradation temperature, solution behavior, molecular weight, molecular weight distribution, and optical properties have been also greatly influenced, since the number [DP + (1)] of periphery groups on hyperbranched polymer are additional major parameters beside molecular weight, molecular weight distribution, and the backbone nature of polymer. Last but not least, a rare example of solid-state fluorescence from fluoride-terminated **HPPQ 2** is also demonnstrated whereas hydroxyl-terminated **HPPQ 1** does not. This fact is currently being investigated.

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Supporting Information Available: Color photographs showing the sample vials containing **HPPQ 1** and **HPPQ 2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Color photographs showing the sample vials containing **HPPQ 1** and **HPPQ 2** are provided as Supporting Information.

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