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Hyperbranched Poly(phenylquinoxaline−ether−ketone) Synthesis in Poly(phosphoric acid)/P_2O_5 Medium: Optimization and Some Interesting Observations

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ABSTRACT: A new self-polymerizable AB_2 monomer, 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid, was synthesized from the double condensation reaction of 4,4′-diphenoxybenzil and 3,4-diaminobenzoic acid. It was polymerized to afford the corresponding hyperbranched poly(phenylquinoxaline) (PPQ) via a diaryl ketone formation from the Friedel−Crafts reaction of the carboxylic acid group (A) and the phenoxy ring (B) in polyphosphoric acid (PPA)/P_2O_5 medium. The polymerization was conducted at (i) 130 and 160 °C and (ii) with and without additional amounts of P_2O_5 and monitored by analyzing the polymerization mixture sampled at certain reaction temperature and time intervals with Fourier transform infrared (FT-IR) spectroscopy and gel-permeation chromatography (GPC). Both FT-IR and GPC results corroborated our previously established optimal conditions: (i) PPA:P_2O_5 ratio of 4:1 and (ii) efficient polymerization temperature ∼130 °C. Furthermore, the series of 10 aliquots taken from the mixture prepared under the optimal conditions, precipitated into water, and stored in the vials for a month showed visually a consistent trend and a transition in the polymer densities and collectively allowed the visualization of a changeover in the macromolecular architecture from a "fanlike" conformation at the early stage of polymerization to a denser, globular conformation at higher molecular weights. The resultant hyperbranched PPQ was thermally stable with 5% weight loss at temperatures over 500 °C in both air and helium atmospheres. It showed UV absorption maxima at 365−370 nm and emission maxima at 433−446 nm. The subsequent chain-end functionality conversion for the parent hyperbranched polymer could be performed in either a one-pot fashion or a two-staged process. Finally, some anomalous dilute-solution behavior (negative or "inverse" polyelectrolyte effect) was observed for the chain-end-modified hyperbranched polymers that appeared to be significantly influenced by the nature of solvents (acidic vs basic) and chain-end groups (polarity).

Introduction

Poly(phenylquinoxaline)s (PPQs) are a well-known class of π-electron-deficient, aromatic heterocyclic polymers, which possess many desirable properties such as good processability, high glass transition temperatures, and excellent thermomechanical properties.[1] Recently, they have also received increasing attention for the possible uses in nonlinear optical[2] and optoelectronic devices such as the electron transport layers in light-emitting diodes.[3] For example, a PPQ that contains thiophene segments has displayed an outstanding electron-transporting capability in the poly(phenylenevinylene)-based light-emitting devices.[4] In general, linear PPQs are prepared by two different polymerization methods. The more traditional method involves condensation between aromatic tetraketones and aromatic tetraamines under acidic conditions.[5] The other methods rely on the aromatic nucleophilic substitution reactions between aromatic dihalides and aromatic bis(phenolate salt)s,[6] or from the self-polymerization of AB monomers,[7] as well as aromatic amide-forming[8,9] and azomethine-forming[10] reactions In the latter cases, a preformed quinoxaline ring is incorporated in the monomer structures.

In comparison to other classes of wholly aromatic hyperbranched polymers,[11] there are only a few examples of phenylquinoxaline (PQ)-containing hyperbranched polymers reported in the literature.[12] They were prepared from either an AB_2 or A_2B monomer with a preformed phenylquinoxaline as the linking group (where A = activated fluoride or CO_2H and B = OH or NH_2) via an aromatic nucleophilic substitution reaction or an activated (direct) amidation reaction under basic or neutral conditions. To our knowledge, prior to the work described herein, there is no reported hyperbranched poly(phenylquinoxaline) that has been prepared from a polymerization process based on an electrophilic-type reaction under acidic conditions. Furthermore, because of our recent work in developing an optimized conditions to effect Friedel−Crafts acylation in PPA/P_2O_5 medium to prepare linear and hyperbranched poly(ether−ketones)[13] from benzene-based AB and A_2B monomers as well as block copolymers[14] and surface modification of carbon nanofibers and nanotubes,[15] we have a continuing interest in defining the scope of the method and therefore its applicability to similar heterocyclic-based monomers.

Therefore, we have designed and synthesized a new but relatively simple phenylquinoxaline-containing AB_2 and evaluated its self-polymerizability with our optimized PPA/P_2O_5 method. This paper reports our results in establishing the efficient polymerization conditions, characterization of the corresponding hyperbranched poly(phenylquinoxaline−ether−

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ketone), and its polymer derivatives that were chain-end functionalized with 3,5-dihydroxyphenylcarbonyl and 3,5-diallyloxyphenylcarbonyl groups.

Experimental Section

Materials. All chemicals and solvents including poly(phosphoric acid) (PPA), assay ≥83% P_2O_5 content, phosphorus pentoxide (P_2O_5), and methanesulfonic acid (MSA) were purchased from Aldrich Chemical Inc. and used as received, unless otherwise specified. 3,4-Diaminobenzoic acid (mp 216−218 °C) was recrystallized from deoxygenated water.

Instrumentation. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured at 270 and 50 MHz on a JEOL-270 spectrometer. Infrared (IR) spectra were recorded on a Beckman FT-2100 Fourier transform spectrophotometer. Elemental analysis and mass spectral analysis were performed by System Support Branch, Materials Directorate, Air Force Research Lab, Dayton, OH. The melting points (mp) of all compounds were determined on a Mel-Temp melting point apparatus and are uncorrected. Viscosities were determined using a Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for methanesulfonic acid (MSA) or *N*-methyl-2-pyrrolidinone (NMP) solution, and polymer concentrations were approximately 0.5−0.1 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) analysis runs were performed in nitrogen with both heating and cooling rate set at 10 °C/min using a Perkin-Elmer DSC7 model thermal analyzer equipped with differential scanning calorimetry cell. Themogravimetric analysis (TGA) was conducted in helium (He) and air atmospheres at a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer. Gel permeation chromatography (GPC) was carried out on a Waters 150-CV equipped with 254, 280, and 420 nm UV detectors. Tetrahydrofuran (THF) was used as the eluting solvent.

1-(2-Methyl-3-butyn-2-ol)-2-(4-phenoxyphenyl)acetylene.[16] Into a 1 L three-necked, round-bottom flask equipped with a magnetic stirrer, a condenser, and nitrogen inlet, 4-bromodiphenyl ether (50.1 g, 201 mmol), freshly distilled 2-methyl-3-butyn-2-ol (64.3 g, 892 mmol), copper(I) iodide (0.11 g, 0.60 mmol), triphenylphosphine (0.33 g, 1.3 mmol), and bis(triphenylphosphine)palladium(II) chloride (1.12 g, 1.6 mmol) were placed. The solids were carefully washed in with triethylamine (500 mL). The mixture was heated under reflux for 24 h. After the reaction mixture had been allowed to cool to room temperature, the solution was filtered through silica gel. The filtrate was poured into 5% hydrochloric acid solution and diluted with methylene chloride. After separation from the aqueous phase, the organic phase was subjected to purification via a silica gel column chromatography with methylene chloride/hexane elution to give 40.5 g (80% yield) of light yellow oil. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93%; H, 6.39%; O, 12.68%. Found: C, 80.88%; H, 6.43%; O, 12.89%. Mass spectrum (*m*/*e*): 252 (M$^+$, 100% relative abundance).

4-Phenoxyphenylacetylene.[16] Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and nitrogen inlet, 1-(2-methyl-3-butyn-2-ol)-2-(4-phenoxyphenyl)acetylene (40.0 g, 159 mmol) was dissolved in toluene (700 mL). A solution of potassium hydroxide (2.2 g, 39.2 mmol) in methanol (40 mL) was added. The mixture was heated under reflux 14 h. The solution was concentrated to ∼100 mL and then purified by silica gel column chromatography with pentane elution to give 28.0 g (90% yield) of light yellow oil. Anal. Calcd for $C_{14}H_{10}O$: C, 86.57%; H, 5.19%; O, 8.24%. Found: C, 86.52%; H, 5.25%; O, 8.29%. Mass spectrum (*m*/*e*): 194 (M$^+$, 100% relative abundance).

1,2-Bis(4-phenoxyphenyl)acetylene[17,18] **(1).** Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and nitrogen inlet, (4-phenoxyphenyl)acetylene (28.0 g, 144 mmol), 4-bromodiphenyl ether (27.7 g, 151 mmol), copper(I) iodide (0.10 g, 0.53 mmol), triphenylphosphine (0.30 g, 1.1 mmol), and bis(triphenylphosphine)palladium(II) chloride (1.00 g, 1.4 mmol) were placed. The solids were carefully washed in with triethylamine (500 mL). The mixture was then heated under reflux for 24 h. After the reaction mixture had been allowed to cool to room temperature, the solution was filtered through silica gel. The filtrate was poured into 5% hydrochloric acid solution and diluted with methylene chloride. After separation from the aqueous phase, the organic phase was subjected to a silica gel column chromatography with petroleum ether to remove the excess 4-bromodiphenyl ether and then methylene chloride/hexane (33/67, v/v) elution to give 42.3 g (81% yield) of white crystals. It was again recrystallized from toluene to give 32.1 g (62% yield) of white flakes; mp173−174 °C, lit.[19] 167−168 °C. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.17%; H, 5.01%; O, 8.83%. Found: C, 86.13%; H, 5.40%; O, 8.43%. FT-IR (KBr, cm^{-1}): 738, 3039, 3061. Mass spectrum (*m*/*e*): 362 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-*d*$_6$, δ in ppm): 6.97−7.00 (dd, 4H, Ar), 7.04−7.08 (m, 4H, Ar), 7.15−7.21 (t, 2H, Ar), 7.38−7.44 (t, 4H, Ar), 7.49−7.52 (d, 4H, Ar).

1,2-Bis(4-phenoxyphenyl)benzil[18,19] **(2). Method 1.** Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, dropping funnel, and nitrogen inlet, 1,2-bis(4-phenyloxyphenyl)acetylene (4.0 g, 11.0 mmol) and trialkylmethylammonium chlorides (Adogen 454, 1.25 g) were dissolved in methylene chloride (200 mL). A solution of potassium permanganate (16.0 g, 101 mmol) in acetic acid (30 mL) and water (500 mL) was slowly added through a dropping funnel. The mixture was gently heated under reflux for 10 h. After cooling to room temperature, the mixture was poured in large flask, potassium bisulfate was added until the mixture became clear, and then a small amount of sodium bicarbonate was added. The organic layer was then separated, dried over magnesium sulfate, and filtered, and solvent was removed under the reduced pressure to give 4.22 g of light yellow solid, which was redissolved in hot ethanol or heptane and allowed to cool to room temperature to give 3.88 g (89% yield) of light yellow powder; mp 119−120 °C, lit.[19] 113−114 °C. Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17%; H, 4.60%. Found: C, 79.83%; H, 4.89%. FT-IR (KBr, cm^{-1}): 1667. Mass spectrum (*m*/*e*): 394 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-*d*$_6$, δ in ppm): 7.00−7.06 (dd, 4H, Ar), 7.06−7.11 (m, 4H, Ar), 7.20−7.25 (t, 2H, Ar), 7.37−7.44 (t, 4H, Ar), 7.78−7.96 (dd, 4H, Ar). ^{13}C NMR (DMSO-*d*$_6$, δ in ppm): 117.43, 120.49, 125.09, 127.54, 130.16, 132.23, 154.87, 163.56, 193.14.

Method 2. Into a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, dropping funnel, and nitrogen inlet, phenol (8.0 g, 85.0 mmol) and potassium carbonate (13.5 g, 98 mmol) were dispersed in NMP (100 mL). Then the mixture was heated at 150 °C overnight. After the reaction mixture had been allowed to cool to 130 °C, a solution of 4,4′-difluorobenzil (10.0 g, 40.6 mmol) in NMP (50 mL) was slowly added through a dropping funnel. The mixture was heated at 145 °C for 10 h. Upon cooling to room temperature, the mixture was filtered and the filtrate was poured into 5% hydrochloric acid. The resulting precipitate was collected, air-dried, and dissolved in hot ethanol or heptane and allowed to cooled to room temperature to give 13.6 g (85% yield) of light yellow powder; mp 120−122 °C, lit.[19] 113−114 °C. Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17%; H, 4.60%. Found: C, 79.19%; H, 4.75%. FT-IR (KBr, cm^{-1}): 1666. Mass spectrum (*m*/*e*): 394 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-*d*$_6$, δ in ppm): 7.01−7.05 (dd, 4H, Ar), 7.05−7.10 (m, 4H, Ar), 7.19−7.26 (t, 2H, Ar), 7.36−7.44 (t, 4H, Ar), 7.78−7.95 (dd, 4H, Ar). ^{13}C NMR (DMSO-*d*$_6$, δ in ppm): 117.40, 120.46, 125.06, 127.51, 130.16, 132.20, 154.84, 163.56, 193.11.

2,3-Bis(4-phenoxyphenyl)quinoxaline-6-carboxylic Acid (3). Into a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and nitrogen inlet, 3,4-diaminobenzoic acid (2,65 g, 17.4 mmol) was dissolved in acetic acid (150 mL). 4,4′-Diphenyloxybenzil (6.55 g, 16.6 mmol) was then added and heated under reflux for 12 h. Upon cooling to room temperature, the resulting dark red solution was filtered, and the filtrate was poured into 5% hydrochloric acid. The resulting light yellow precipitate was collected by suction filtration and air-dried. It was recrystallized from ethanol to give 7.0 g (83% yield) of bright yellow powder; mp 224−226 °C. Anal. Calcd for $C_{33}H_{22}N_2O_4$: C,

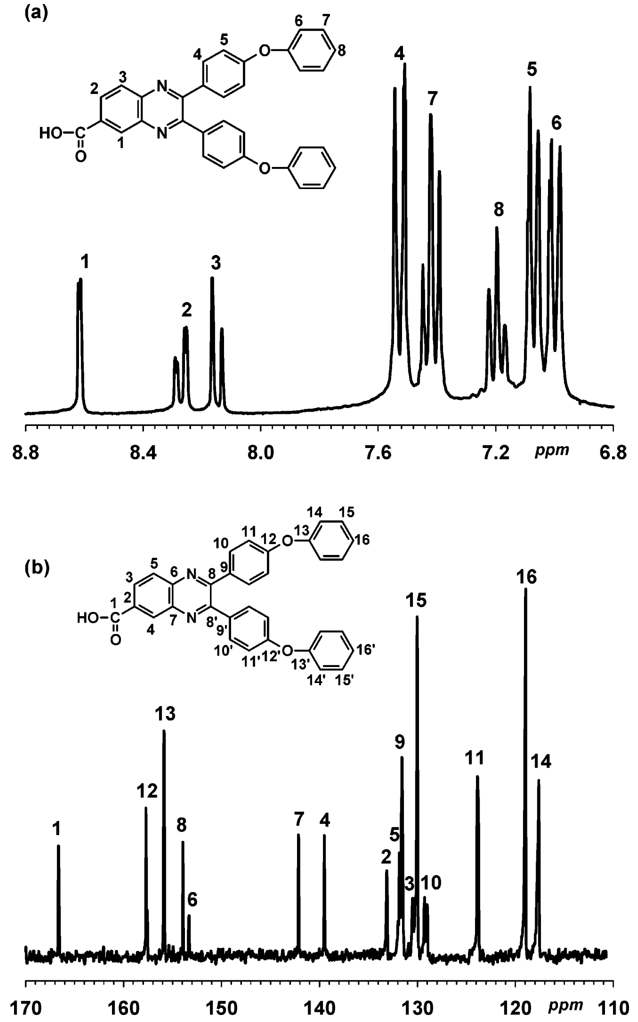


Figure 1. ^{1}H and ^{13}C NMR spectra of monomer **3** with tentative peak assignments: (a) proton; (b) carbon.

77.63%; H, 4.34%; N, 5.49%; O, 12.54%. Found: C, 77.71%; H, 4.39%; N, 5.27%; O, 12.41%: FT-IR (KBr, cm^{-1}): 1242, 1488, 1588, 1697. Mass spectrum (*m*/*e*): 510 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm); see Figure 1 for labeling of the protons: 6.99−7.02 (d, $J_{67} \sim 8.2$ Hz; 4H, Ar), 7.06−7.09 (d, $J_{54} \sim 7.7$ Hz; 4H, Ar), 7.17−7.22 (t, $J_{87} \sim 7.2$ Hz; 2H, Ar), 7.39−7.45 (t, $J_{76} \sim 8.2$, $J_{78} \sim 7.7$ Hz; 4H, Ar), 7.52−7.55 (d, $J_{45} \sim 7.7$ Hz; 4H, Ar), 8.14−8.17 (d, $J_{23} \sim 2$; 1H, Ar), 8.26−8.29 (dd, $J_{13} \sim 2$ Hz, $J_{12} \sim 8.7$ Hz; 1H, Ar), 8.61−8.62 (d, $J_{31} \sim 2$ Hz; 1H, Ar). ^{13}C NMR (DMSO-d_6, δ in ppm): 117.72, 119.10, 123.94, 129.03, 130.08, 131.57, 131.66, 131.83, 133.19, 139.55, 142.20, 153.23, 153.83, 155.82, 157.69, 166.53.

Self-Polymerization of AB$_2$ Monomer in PPA (83 wt % P$_2$O$_5$ Content) at 160 °C (4a). Into 250 mL resin flask equipped with a high-torque mechanical stirrer and nitrogen inlet and outlet, pressure regulator, and side opening for additions, poly(phosphoric acid) (PPA, 60 g) was charged. PPA was degassed under reduced pressure by freezing in liquid nitrogen and melt in warm water several times. Then the monomer, 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid (3.0 g, 5.9 mmol), was introduced. As soon as the monomer was added and the stirring started, the mixture became deep blue-purple. The mixture was heated to 160 °C for 48 h. Although the mixture had become deep red, its viscosity was not significantly increased. Water was added into the mixture and warmed at 60−70 °C overnight under the nitrogen. The resulting bright yellow solids were collected by suction filtration and washed with diluted ammonium hydroxide and a large amount of water. The polymer was finally dried under reduced pressure (0.05 mmHg) at 200 °C for 150 h to give essentially quantitative yield. Its intrinsic viscosity was determined to be 0.07 dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Anal. Calcd for $C_{33}H_{20}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%; O, 9.75%. Found: C, 78.69%; H, 4.34%; N, 5.27%; O, 10.81%.

Self-Polymerization of AB$_2$ Monomer in PPA/P$_2$O$_5$ (4/1, w/w) at 130 °C (4b). Into a 250 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, and pressure regulator, PPA (83% assay, 80 g) was placed and stirred with dried nitrogen purging at 100 °C for 10 h. The monomer 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid (4.0 g) was added and heated to 130 °C until it become a homogeneous mixture. It usually took about 1 h. The color of mixture became dark brown. P$_2$O$_5$ (20.0 g; 25 wt % relative to PPA) was then added in one portion, and the temperature was maintained 130 °C for 24 h. The mixture became very viscous after 2 h at 130 °C and started to stick to stirring rod. At the end of the reaction, water was added into the flask. The resulting precipitates were collected by suction filtration, washed with diluted ammonium hydroxide and then with large amounts of water, stirred in boiling water for 100 h, and finally dried in the presence of phosphorus pentoxide under reduced pressure (1 mmHg) at 200 °C for 48 h. The yield was essentially quantitative (>99% yield). Its intrinsic viscosity is 0.56 dL/g (MSA, 30 ± 0.1 °C). Anal. Calcd for $C_{33}H_{19}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%; O, 9.75%. Found: C, 80.08%; H, 4.57%; N, 3.69%; O, 10.34%.

Self-Polymerization of AB$_2$ Monomer in PPA/P$_2$O$_5$ (4/1, w/w) at 160 °C (4c). Into a 100 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, and pressure regulator, PPA (83% assay, 40 g) was placed and stirred with dried nitrogen purging at 100 °C for 10 h. The monomer, 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid (1.80 g, 3.5 mmol), and P$_2$O$_5$ (4.0 g) were added, and the mixture was heated to130 °C until it become a homogeneous mixture. It took about 3 h. The mixture was then heated at 160 °C, and it soon stuck to the stirring rod, rendering further efficient stirring/mixing impossible. It took around 3 h. At the end of the reaction, water was added into the flask. The resulting clusters were taken into a Waring blender and the bundles chopped, collected by suction filtration, washed with diluted ammonium hydroxide and then with a large amount of water, stirred in boiling water for 100 h, and finally dried in the presence of phosphorus pentoxide under reduced pressure (1 mmHg) at 200 °C for 48 h. The yield was essentially quantitative (>99% yield). The polymer was insoluble in most organic solvents and only formed gel in methanesulfonic acid. Anal. Calcd for $C_{33}H_{19}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%. Found: C, 78.34%; H, 4.34%; N, 5.27%.

Self-Polymerization of AB$_2$ Monomer in PPMA at 110 °C (4d). Into a 100 mL three-necked, round-bottom flask equipped with a mechanical stirrer and nitrogen inlet and outlet, the monomer 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid (1.0 g, 1.96 mmol) and PPMA (10 mL) were added and heated to 110 °C for 8 h. The color of mixture became dark purple. The mixture was poured into ice water. The resulting purple precipitates were collected by suction filtration, washed with diluted ammonium hydroxide and then with a large amount of water, stirred in boiling water for 48 h, and finally dried in the presence of phosphorus pentoxide under reduced pressure (1 mmHg) at 200 °C for 48 h. The yield was essentially quantitative (>99% yield). Its intrinsic viscosity was 0.50 dL/g (MSA, 30 ± 0.1 °C). Anal. Calcd for $C_{33}H_{19}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%; O, 9.75%. Found: C, 78,12%; H, 4.33%; N, 5.27%; O, 10.77%.

Preparation of Star-Block Poly(phenylquinoxaline−ether−ketone)-*block*-meta-poly(ether−ketone) (5). Into a 250 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, and a pressure regulator, PPA (83% assay, 80 g) and P$_2$O$_5$ (25 wt % to PPA 20.0 g) were placed and heated to 130 °C until it became a homogeneous mixture. After the PPA medium had been allowed to cool to 100 °C, the monomer 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid (0.4 g, 0.78 mmol) was added. The color of resulting mixture became deep purple. The mixture was heated to 130 °C for 6 h, and then 3-phenoxybenzoic acid (3.6 g, 16.8 mmol) was added. The mixture was stirred at 130 °C for 18 h. It was moderately viscous and allowed to cool to ∼100 °C and poured into water. The resulting precipitates were collected by suction filtration, washed with diluted ammonium hydroxide and then with large amounts of water, stirred in refluxing water for 100 h, and finally dried in the presence of phosphorus pentoxide under reduced pressure (1 mmHg) at 100 °C for 48 h. The yield was essentially quantitative (>99% yield). The intrinsic viscosity value of 1.46 dL/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd for $C_{15}H_{9.1}N_{0.2}O_{2.1}$: C, 79.54%; H, 4.08%; N, 0.24%; O, 16.13%. Found: C, 79.07%; H, 4.29%; N, 0.36%; O, 14.79%.

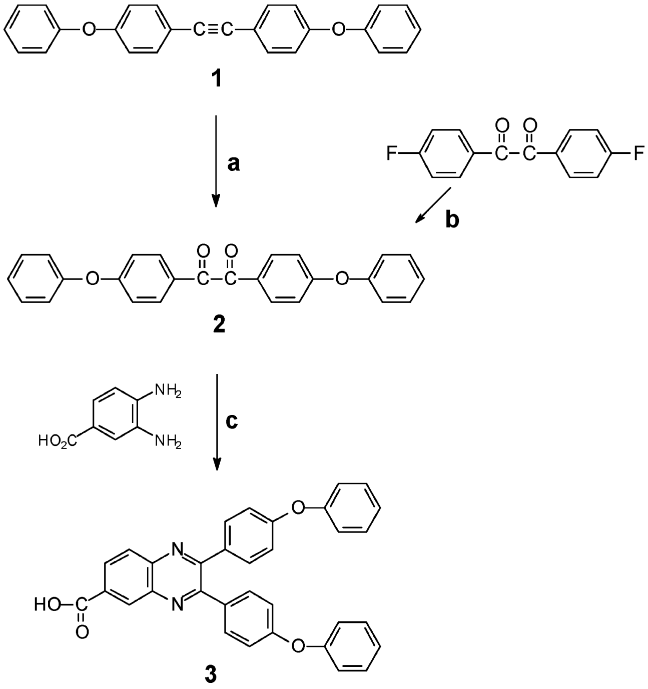
Preparation of 3,5-Dihydroxy-Terminated Poly(phenylquinoxaline−ether−ketone) (6a). Into a 250 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, and a pressure regulator, PPA (83% assay, 80 g) and P_2O_5 (25 wt % to PPA, 20.0 g) were placed and heated to 130 °C until it became homogeneous. After the reaction medium had been allowed to cool to 100 °C, the AB_2 monomer 2,3-bis(4-phenoxyphenyl)quinoxaline-6-carboxylic acid (4.0 g, 3.92 mmol) and the end-capper 3,5-dihydroxybenzoic acid (1.21 g, 7.84 mmol) were added at the same time. The color of mixture became deep purple. The mixture was heated to 130 °C for 2 h and 160 °C for 24 h. When the polymerization was terminated, the mixture was moderately viscous. It was allowed to cool to 100 °C (still fluid) to facilitate pouring into water. The resulting precipitates were collected by suction filtration, washed with diluted ammonium hydroxide and then with large amounts of water, Soxhlet-extracted with water for 50 h and then with methanol for 50 h, and finally dried in the presence of phosphorus pentoxide under reduced pressure (1 mmHg) at 100 °C for 48 h. The yield was essentially quantitative (>99% yield). The reduced viscosities at 0.5 g/dL were 0.09 dL/g (NMP, 30 ± 0.1 °C) and 0.21 dL/g (MSA, 30 ± 0.1 °C). Anal. Calcd for $C_{40}H_{24}N_2O_6$: C, 76.43%; H, 3.85%. Found: C, 76.05%; H, 4.28%.

Preparation of 3,5-Diallyl-Terminated Poly(quinoxaline−ether−ketone) (6b). Into a 100 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched polymer (example 5; 3.5 g, 5.57 mmol), potassium carbonate (4.0 g, 28.90 mmol), allyl bromide (3.37 g, 27.86 mmol), and DMAc (50 mL) were placed. The reaction mixture was then heated and maintained at 90−100 °C for 16 h. During this time period, the orange solution became light yellow in color and homogeneous. After it had been allowed to cool on its own, the mixture was filtered through a cake of Celite 545 to remove any insoluble salts. The filtrate was poured into a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60−70 °C for 2 h. The white powder was collected, air-dried, dissolved in dichloromethane, precipitated in methanol, collected, and dried under the reduced pressure in the presence of phosphorus pentoxide at 50 °C for 48 h. The yield was essentially quantitative. The reduced viscosities at 0.5 g/dL were 0.15 dL/g (NMP, 30 ± 0.1 °C) and 0.35 dL/g (MSA, 30 ± 0.1 °C). Anal. Calcd for $C_{46}H_{32}N_2O_6$: C, 77.95%; H, 4.55%; N, 3.95%; O, 13.54%. Found: C, 77.82%; H, 4.49%; N, 3.67%; O, 13.45%.

Results and Discussion

Monomer Synthesis. The phenylquioxaline-containing AB_2 monomer (**3**) was synthesized from the double condensation of 4,4′-diphenoxybenzil (**2**) and commercially available 3,4-diaminobenzoic acid, as outlined in Scheme 1. While 4,4′-diphenoxybenzil (**2**) had been prepared from $AlCl_3$-catalyzed Friedel−Crafts reaction of oxalyl chloride in carbon disulfide[18] or in methylene chloride,[19] we explored two alternate synthetic routes to **2** via (i) $KMnO_4$ oxidation of 1,2-bis(4-phenoxyphenyl)acetylene[17] (**1**) and (ii) fluoride displacement reaction of commercially available 4,4′-difluorobenzil by phenolate anion. The main reason that we explored route (i) was because of the availability of **1** from an Air Force custom synthesis contract. It was prepared from the ethynylation of 4-bromophenyl ether with 4-phenoxyacetylene in triethylamine in the presence of copper(I) iodide, triphenylphosphine, and bis(triphenylphosphine)palladium(II) chloride. The similar Pd-catalyzed ethynylation of 4-bromophenyl ether with 2-methyl-3-butyn-2-ol was used to prepare 1-(2-methyl-3-butyn-2-ol)-2-(4-phenoxyphenyl)-acetylene, which was then deprotected in a toluene/KOH/MeOH mixture to afford 4-phenoxyphenylacetylene. The structure and purity of the AB_2 monomer were confirmed by conventional organic characterization methods, namely nuclear magnetic resonance spectroscopy (Figure 1), FT-IR, elemental analysis, and high-performance liquid chromatography (purity ∼100%).

Scheme 1. Synthesis of Self-Polymerizable AB_2 Monomer[a]



[a] (a) $KMnO_4$, Adogen 454, CH_2Cl_2, AcOH/water, reflux; (b) phenol, K_2CO_3, NMP, 140°C; (c) AcOH, reflux.

Thermal Properties and Space-Filling Model of AB_2 Monomer. The monomer **3** displayed an unusually slow crystallization behavior, as shown in Figure 2. It showed a sharp melting at 232 °C with heat of fusion of 80.22 J/g in the first heating DSC scan. Strangely, there was no recrystallization peak detected during cooling scan. During the second heating scan, however, this monomer did show a glass transition temperature at 87 °C, a recrystallization temperature at 141 °C, and a melting temperature at 231 °C with heat of fusion of 78.40 J/g. The observed slow crystallization could be rationalized by examining its molecular structure with a computer-generated (MM+ method; HyperChem, Release 6), energy-minimized space-filling model. As shown in Figure 3, the dihedral angle between 2- and 3-substituents on the quinoxaline ring is relatively large, ∼44°, and the two phenyl ether substituents are also relatively volume-demanding. Thus, we would expect that its crystal packing would be hampered, resulting in very a slow crystallization.

Polymerization. On the basis of our previous studies,[13] we carried out the aromatic electrophilic substitution polymerizations with the following conditions: (i) with/without additional amounts of P_2O_5 to PPA (83 wt % P_2O_5 content) and (ii) at the reaction temperatures of 130 and 160 °C. The first set of polymerization experiments was conducted with 5 wt % of monomer concentration in PPA at 160 °C and without addition of P_2O_5 (Scheme 2). It was observed that as soon as the

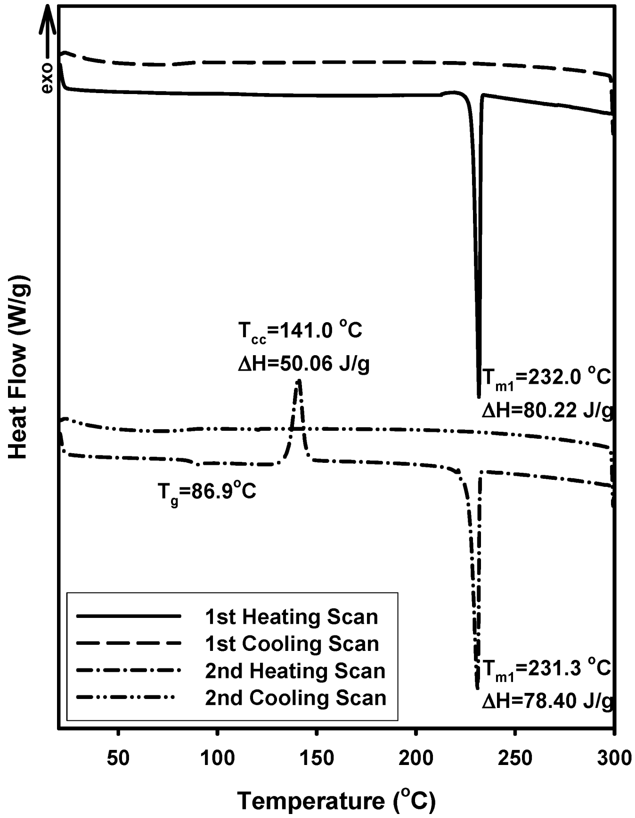


Figure 2. DSC thermograms of monomer **3**: first heating scan (solid); first cooling scan (long-dash); second heating scan (dash-dot-dash); second cooling scan (dash-dot-dot-dash).

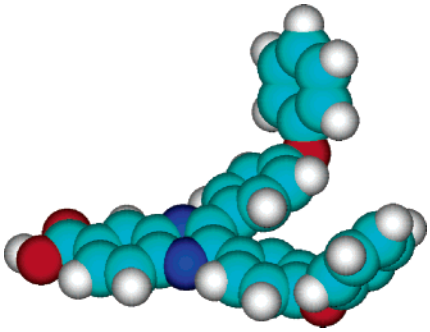
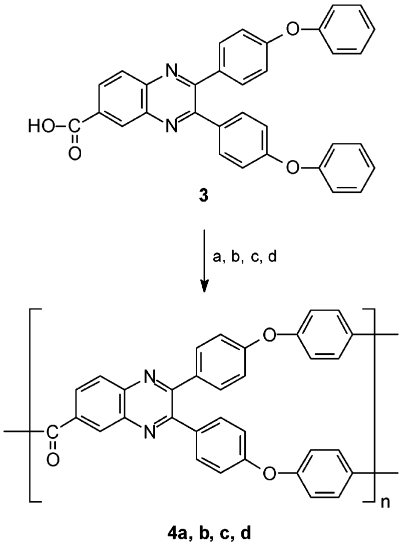


Figure 3. Space-filling model of monomer **3** (Hyperchem Release 6.0).

monomer was added to PPA at room temperature, the mixture became deep purple, indicating the formation of a positively charged, reactive intermediate (acylonium). However, the reaction did not result in a high-molecular-weight polymer as revealed by GPC analysis and solution viscosity determination (Figure 4a and Table 1). Despite a prolonged heating at 160 °C for 48 h, there were still traces of monomers and oligomeric products ranging from dimers to heptamers.

In the second set of polymerization experiments, the P_2O_5 content of polymerization medium was optimized with PPA/P_2O_5 weight ratio at 4/1, and the reaction was monitored with GPC[20] (Figure 4b and Table 2). We observed that until the reaction temperature had approached 100 °C the polycondensation process did not progress well and produced only small amounts of dimers and trimers. When the reaction temperature approached 130 °C, polymerization reaction proceeded rapidly, as evidenced by a drastic increase in the bulk viscosity. As shown in Figure 5a,b, the molecular weight and molecular weight distribution gradually increased during the first 10 h at 130 °C, and then both slowly leveled off during the next 20 h.

Scheme 2. Polymerization in Various Conditions[a]



[a] (a) PPA at 160 °C; (b) PPA/P_2O_5 at 130 °C; (c) PPA/P_2O_5 at 160 °C; (d) PPMA (MSA/P_2O_5) at 110 °C.

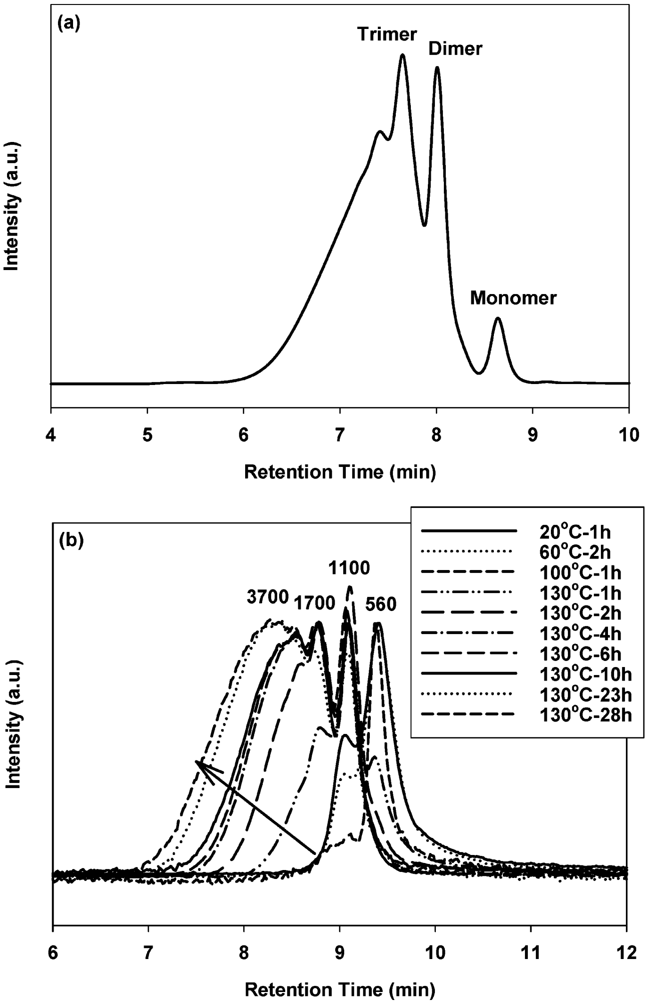


Figure 4. GPC traces of hyperbranched polymers: (a) **4a** prepared from PPA (83% P_2O_5 content) at 160 °C; (b) **9b** prepared from PPA (83%)/P_2O_5 (4/1, w/w) as functions of temperature and time.

This might be because after all the AB_2 monomers had been consumed, the focal point (A or the CO_2H group), which was critical in the subsequent stage of molecular weight buildup, became kinetically inaccessible as a result of being "buried by

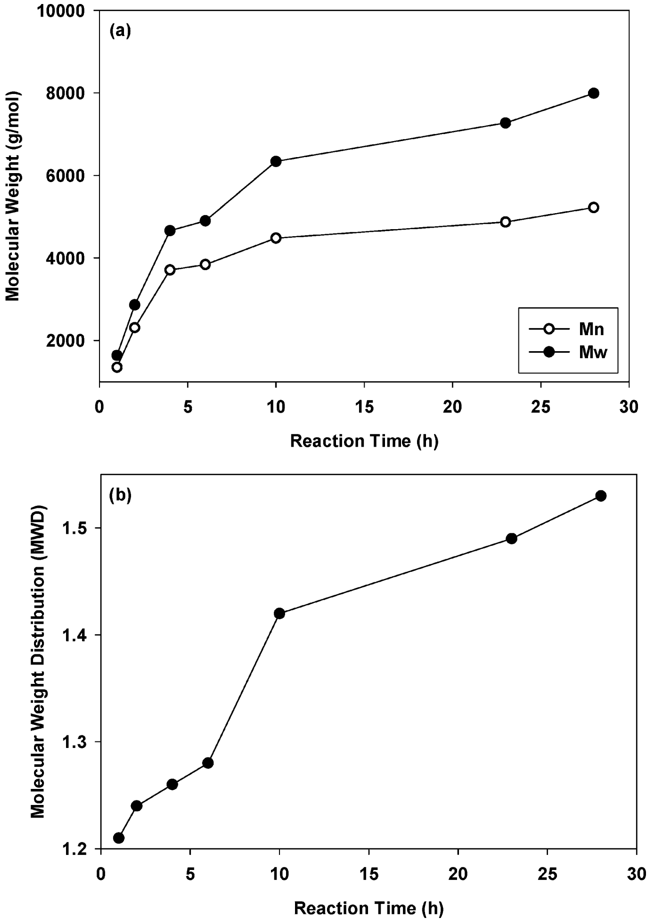


Figure 5. Plots of (a) molecular weight and (b) molecular weight distribution (MWD) as a function of reaction time at 130 °C.

Table 1. Polymerization Conditions and Isolated Yields

entry	medium	P_2O_5 (wt %)	temp (°C)	time (h)	[η] (dL/g)[a]	yield (%)
4a	PPA	0	160	48	0.07	∼97
4b	PPA	25	130	24	0.56	>99
4c	PPA	25	160	3	gel	>99
4d	MSA	10	110	8	0.50	>99

[a] Intrinsic viscosity measured in MSA at 30 ± 0.1 °C.

Table 2. GPC Results of Hyperbranched Polymer 4b in a PPA/P_2O_5 (4/1, w/w) Mixture

entry	temp (°C)	time (h)	M_n (g/mol)	M_w (g/mol)	MWD
1	20	1	570	630	1.11
2	60	2	570	630	1.11
3	100	1	1150	1310	1.14
4	130	1	1350	1640	1.21
5	130	2	2310	2860	1.24
6	130	4	3710	4660	1.26
7	130	6	3840	4900	1.28
8	130	10	4480	6340	1.42
9	130	23	4870	7270	1.49
10	130	28	5220	7990	1.53

the branches” or was destroyed by intramolecular cyclization. The final polymer had an intrinsic viscosity ([η]) of 0.56 dL/g (MSA, at 30 ± 0.1 °C). In a separate polymerization experiment, when the reaction temperature was allowed to approach 160 °C, the polymer became an insoluble gel (Table 1). Thus, these results confirmed the optimal conditions, which we had reported previously,[13] with respect to the reaction temperature and the requirement for a “booster” amount of P_2O_5 to accelerate the electrophilic substitution reaction and polymerization in PPA/P_2O_5. For comparison purposes, a similar polymerization in a superacid medium containing 10 wt % phosphorus pentoxide in methanesulfonic acid (PPMA, also known as Eaton’s reagent)[21] was also carried out at 110 °C for 10 h. The resulting polymer had a comparable intrinsic viscosity of 0.50 dL/g (MSA, at 30 ± 0.1 °C).

To monitor the polymerization process, FT-IR measurements were conducted for all samples used in the GPC analysis, and the composite FT-IR spectra are provided as part of the Supporting Information. As the polymer-forming process was progressing, the intensity of the characteristic carboxylic acid CO stretch at 1699 cm^{-1} and an associated band at 1645 cm^{-1} diminished until the reaction temperature approached 130 °C. After an hour at 130 °C, FT-IR indicated that most of carboxylic acids had disappeared with the emergence of product keto-CO band at 1653 cm^{-1}. This result was in a good agreement with GPC analysis and also supported that the optimum reaction temperature was 130 °C.

Qualitative Profile on the Evolution of Polymer Density during AB_2 Polymerization. An important difference between the step-growth process of a linear polymer and that of a hyperbranched polymer is that in the former case the number of end groups per macromolecule is independent of the degree of polymerization (DP) (i.e., it is always 2), whereas during the course of generating a hyperbranched polymer from an AB_2 monomer, the number of B groups at the chain ends of the hyperbranched molecule at any given time is DP + 1. It is expected that when the DP increases, the macromolecular shape of the hyperbranched polymer should be correspondingly

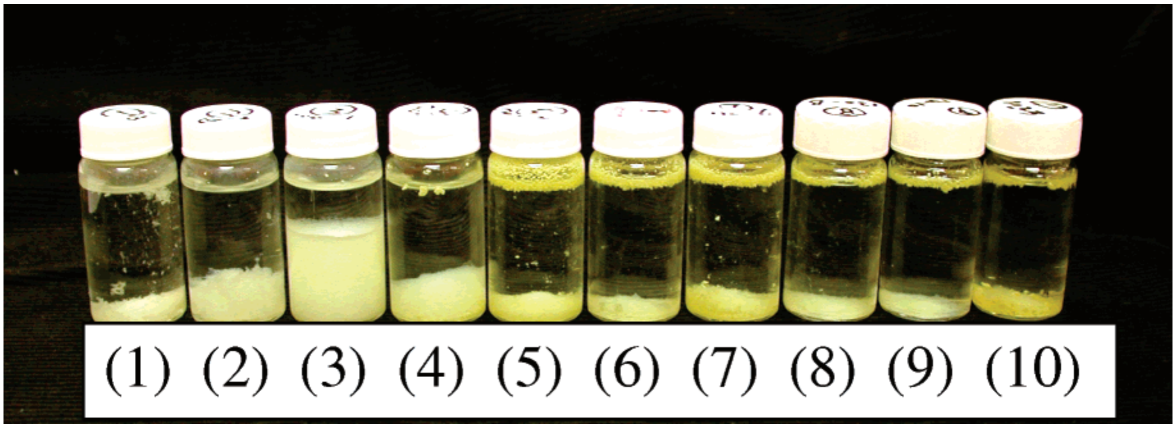


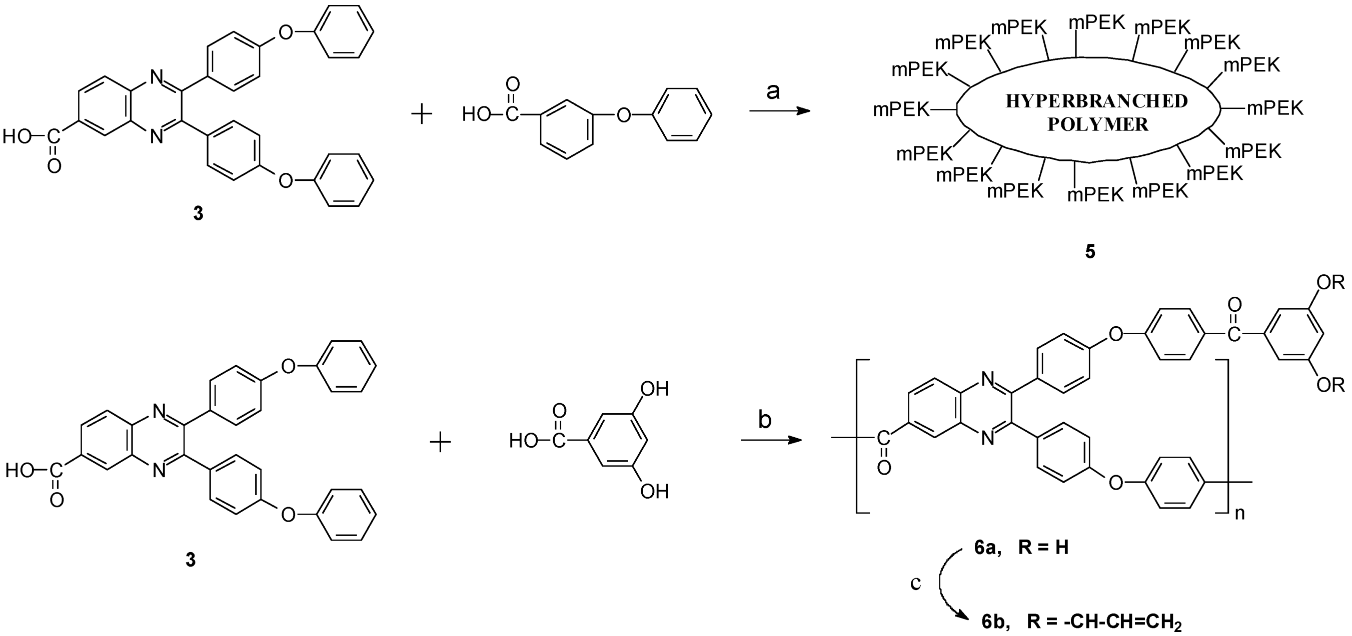
Figure 6. Photograph of hyperbranched polymer **4b** samples from aliquots of equal weight taken at various time and temperature and precipitated in water and stored a month: (1) 20 °C−1 h; (2) 60 °C−2 h; (3) 100 °C−1 h; (4) 130 °C−1 h; (5) 130 °C−2 h; (6) 130 °C−4 h; (7) 130 °C−6 h; (8) 130 °C−10 h; (9) 130 °C−23 h; (10) 130 °C−28 h.

Table 3. Properties of Hyperbranched Polymer Samples

				TGA^c				elemental analysis			
				air		helium		calcd		found	
entry	$[\eta]^a$ (dL/g)	$T_{gh}{}^b$ (°C)	$T_{gc}{}^b$ (°C)	$T_{d5\%}{}^c$ (°C)	char (%)	$T_{d5\%}{}^c$ (°C)	char (%)	C	H	C	H
4a	0.07	149	147	505	2	516	36	80.31	4.29	78.69	4.34
4b	0.56	113	144	520	3	533	51	80.31	4.29	80.08	4.57
4c	gel	ND	ND	525	2	536	53	80.31	4.29	78.34	4.34
4d	0.50	91	90	513	3	517	45	80.31	4.29	78.12	4.33

[a] Intrinsic viscosity measured in MSA at 30 ± 0.1 °C. [b] Glass transition temperature (T_g) determined by DSC with heating rate of 10 °C/min. [c] The temperature at which 5% weight loss occurred on TGA thermogram obtained with heating rate of 10 °C/min.

Scheme 3. Functionalization of Hyperbranched Polymer[a]



[a] (a) PPA/P_2O_5 at 130 °C; (b) PPA/P_2O_5 at 160 °C; (c) $CH_2{=}CH{-}CH_2{-}Br$, K_2CO_3, DMAc, room temperature to 90°C.

changing from a two-dimensional fan (dendron-like) to a three-dimensional sphere (dendrimer-like). We theorize that such a transition in the macromolecular architecture should be observable by following the density profile of the growing hyperbranched polymer during the polymerization process. To monitor and visualize qualitatively this dynamic density change during the chain-growth process of hyperbranched poly(phenylquinoxaline−ether−ketone), in a separate experiment, sampling the polymerization mixture at various temperature and time intervals was conducted (see Table 2). Thus, 10 aliquots were taken and precipitated into distilled water in separate vials which were allowed to stand for a month at room temperature (Figure 6) before GPC analysis. The related GPC results that tracked the progressive change are summarized in Table 2 and Figure 4b. As expected, it was observed that the polymer density decreased at the early stage (Figure 6, 100 °C, 1 h, vials 1−3) as evidenced by qualitatively the swelling and apparent fluffiness of the polymer samples. When the polymerization temperature approached 130 °C (Figure 6, vial 4), the polymer density started to increase and apparently continued the upward trend (vials 5−10). Therefore, these qualitative results not only correlate well with the observation that the drastic rise in the bulk viscosity at polymerization temperature approaching 130 °C but also provide experimental evidence for the existence of the conformational (density) changes in the chain-growth process of hyperbranched polymers.

Optical Properties. The UV−vis absorption spectra of the AB_2 monomer and the polymer samples (**4a**, **4b**, **4d**) in THF solutions were almost identical at 369, 370, 371, and 365 nm, in that order, indicating that with the ketone linkages between the chromophoric units, hyperbranched polymer can retain practically the same linear absorption properties of the monomer (Figure 7) since keto linkages do not normally increase conjugation length. The emission peak values of the monomer and polymer samples **4a** and **4d** in THF solutions were also identical. It is interesting to note that **4b**, which was prepared in PPA/P_2O_5 medium, is about 13 nm red-shifted in reference to the emission peak of **4d**, which was prepared in PPMA/P_2O_5 and has a comparable molecular weight (based on $[\eta]$ values).

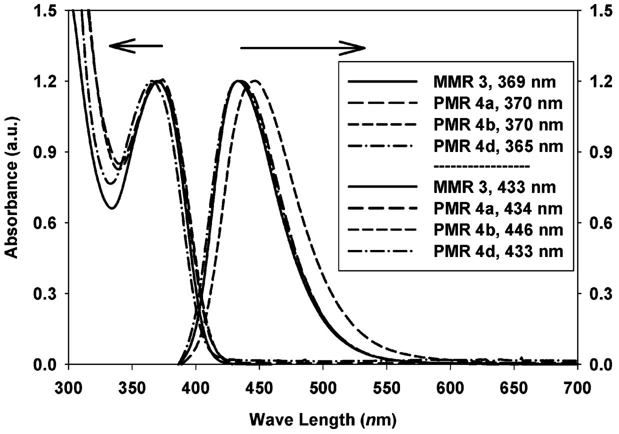


Figure 7. UV−vis absorption and emission spectra of monomer and polymers: monomer **3** (solid); polymer **4a** (medium-dash); polymer **4b** (short-dash); polymer **4d** (dash-dot-dash).

Table 4. Polymerization Conditions, Viscosity Data, and Isolated Yields of Functionalized Hyperbranched Polymers

entry	PPA (wt %)	P_2O_5 (wt %)	temp (°C)	time (h)	[η] or η* (dL/g)	yield (%)
5	100	25	130	(6) (18)	1.46[a]	>99
6a	100	25	160	24	0.21[b] (0.09)[c]	>99
6b	DMAc	K_2CO_3	90−100	16	0.35[b] (0.15)[c]	>98

[a] Intrinsic viscosity measured in MSA at 30 ± 0.1 °C. [b] Reduced viscosity at 0.5 g/dL measured in MSA at 30 ± 0.1 °C. [c] The values in parentheses are reduced viscosities at 0.5 g/dL in NMP at 30 ± 0.1 °C.

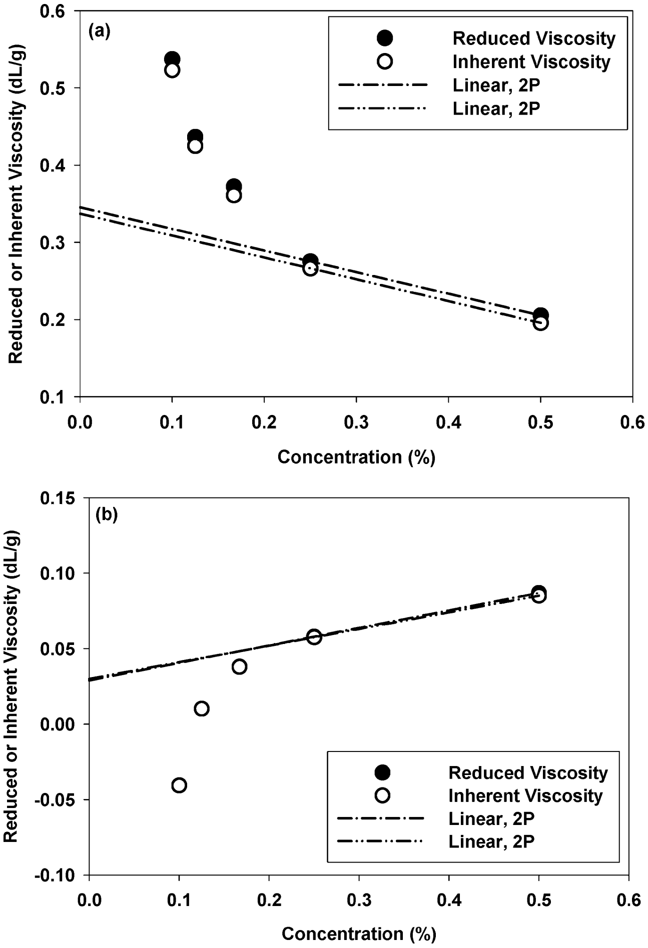


Figure 8. Solution viscosity behaviors of **6a** as a function of concentration: (a) in MSA; (b) in NMP. Note that in (b) the data points for both reduced and inherent viscosities are practically identical.

However, the differences (8−12 nm) in Stokes' shift of **4b** (76 nm) and those of **4a** (64 nm) and **4d** (68 nm) are not large enough for speculation.

Thermal Properties. The glass-transition temperatures (T_g's) of the polymers were determined by differential scanning calorimetry (DSC). The thermograms were obtained on powder samples after they had been heated to 400 °C and cooled to 20 °C with heating and cooling rate of 10 °C/min. Each glass transition temperature (T_g) was taken as the midpoint of the maximum baseline shift from the second run. The polymer samples **4a** ([η] = 0.07 dL/g), **4b** ([η] = 0.56 dL/g), **4c** ([η] = gel), and **4d** ([η] = 0.50 dL/g), which were prepared under different reaction conditions, displayed T_g's at 149 °C, 113 °C, not detectable, and 91 °C, in that order. The vast differences among the T_g values for the supposedly same polymer structure underscore the dependence of thermal properties on the history of the samples. To explain the data, we offer the following interpretations from considering the roles of molecular weight and free volumes: (i) **4a** has the highest T_g value, even though it has the lowest MW (oligomers). We suspect that it has the least amount of free volumes because of the more compact, fanlike morphology associated the low molecular weights. (ii) **4b** has a globular (core−shell) morphology with much greater amount of free volumes, which was initially occupied by the viscous PPA. During the aqueous workup, PPA was dissolved away, leaving many inter- and intramolecular voids in **4b** until it was thermally consolidated during heating to 360 °C. Thus, during the cooling scan (10 °C/min), the T_g reverted to its original value around 144 °C (see Table 3). (iii) In the case of **4d**, we suspect that the residual MSA, that was more difficult to completely remove because of its stronger binding with **4d** via organic salt formation, might have acted as a plasticizer to greatly lower the glass transition.

Thermogravimetric analysis (TGA) of these polymers showed that they were highly heat-resistant. The temperatures at which a 5% weight loss was observed were in the range of 505−525 °C in air and 515−536 °C in helium.

Chain-End Functionalization. Because of the large number (DP +1) of phenyl ether end groups, various chain-end functionalizations of the phenyquinoxaline hyperbranched polymer are possible to modify or tailor its properties. To illustrate these possibilities, we conducted the one-pot synthesis experiments to generate the derivative polymers **5** and **6** from the in-situ polymerization of the AB_2 monomer **3** with (i) an AB monomer and (ii) a carboxylic acid-based end-capper that can engage in Friedel−Crafts acylation (Scheme 3). In case (i), the star-branched polymer **5** was generated from monomer **3** and 3-phenoxybenzoic acid, an AB monomer for a meta-poly(ether−ketone). It had an intrinsic viscosity of 1.46 dL/g (MSA, at 30 ± 0.1 °C) (Table 4). In case (ii), the dihydroxyl-terminated hyperbranched polymer **6a** was prepared from monomer **3** and 3,5-dihydroxybenzoic acid and had a reduced viscosity of 0.21 dL/g at 0.50 g/dL. The hyperbranched polymer **6a** was further reacted with allyl bromide in DMAc in the presence of potassium carbonate to afford corresponding allyl-terminated hyperbranched polymer **6b** (Scheme 3). Because of the anomalous dilute solution behaviors of both polymers **6a** and **6b**, only reduced viscosity values are given in Table 4.

Dilute Solution Behaviors of Hyperbranched Polymers 6a and 6b. We are perplexed by the observation that the dihydroxyl-terminated hyperbranched polymer **6a** displayed two distinctly opposite solution-viscosity behaviors in acidic (MSA) and basic (NMP) solvents as a function of concentration. In a strongly acidic solution, the polymer displayed a typical (positive) polyelectrolyte effect (Figure 8a), whereas in a weakly basic solution it showed an inverse (negative) polyelectrolyte effect (Figure 8b); namely, its inherent viscosity were getting smaller and approaching negative values as the concentration decreased, seemingly suggesting a great reduction in the hydrodynamic volume. In contrast, the allyl-terminated hyperbranched polymer **6b** in NMP behaved normally (Figure 9b), while in MSA it displayed a positive polyelectrolyte behavior (Figure 9a). Thus, it appears that protonation of the quinoxaline groups in the bulk of the hyperbranched polymers **6a** and **6b** are important in inducing the polyelectrolyte effect observed for both polymers in MSA. For the observed inverse polyelectrolyte effect, we speculate that the polar hydroxyl groups with their capabilities to accept protons from MSA and engage in

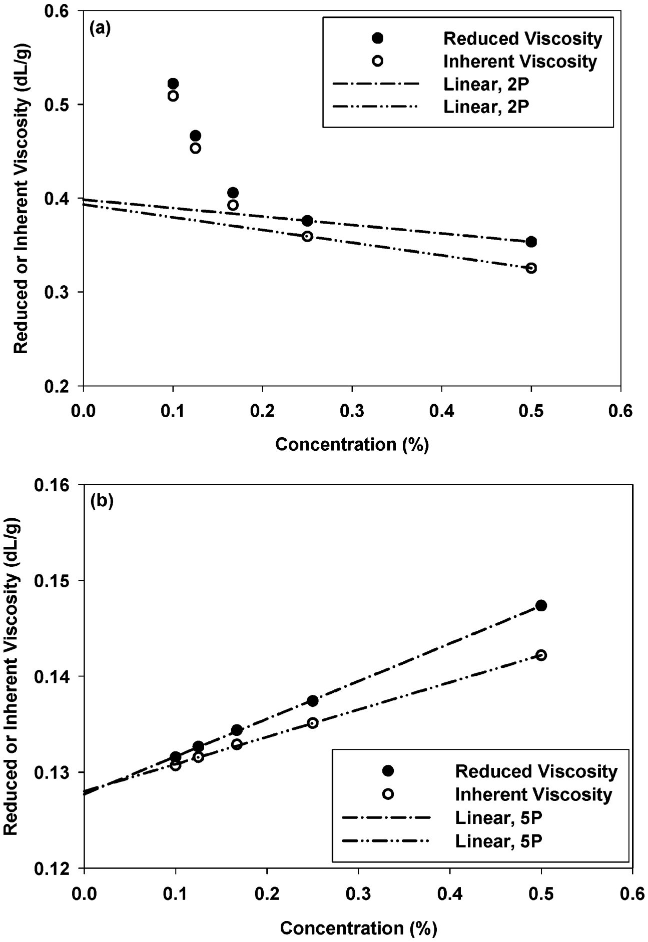


Figure 9. Solution viscosity behavior of **6b** as a function of concentration: (a) in MSA; (b) in NMP.

hydrogen bonding with NMP are likely a determinant responsible for the observed viscosity properties.

Conclusion

A new phenylquinoxaline-containing AB_2 monomer was designed and synthesized as a further example to demonstrate the scope of utility for the efficient synthesis of aromatic ether−ketone-based polymers using our optimized PPA/P_2O_5 method. At the optimal temperature (∼130 °C) and PPA/P_2O_5 (4:1) composition, the corresponding hyperbranched polymer was successfully synthesized and thus explicated that the presence of electron-withdrawing quinoxaline structure did not adversely affect the reactivity of the AB_2 monomer in the Friedel−Crafts polycondensation with respect to the formation of the reactive acylonium from the carboxylic acid group. During the optimization study, we also followed qualitatively the evolution of polymer density as a simple way of visualizing the existence of a changeover in the macromolecular architecture. These qualitative results not only correlate well with the observation that the drastic rise in the bulk viscosity at polymerization temperature approaching 130 °C and the corresponding GPC data but also provide an experimental evidence for the existence of the conformational transition in the chain-growth process of hyperbranched polymers. As an extension of our effort in new polymer synthesis, we showed that the subsequent chain-end functionality transformation for the resulting hyperbranched polymer could be performed either in a one-pot fashion or a batch process. Finally, we also observed some anomaly in the context of polyelectrolyte effect in a preliminary dilute-solution study of the hyperbranched derivatives that were end-group-functionalized with 3,5-dihydroxyphenylcarbonyl and 3,5-diallyloxyphenylcarbonyl groups. Because of our lack of expertise to further the dilute-solution study of these hyperbranched heterocyclic polymers, it is hoped that our report will stimulate some great insights from the polymer science community to better explain the observation.

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Supporting Information Available: FT-IR (KBr pellet) spectra of hyperbranched polymer **4b** as a function of reaction temperature and reaction time; proton and C-13 NMR spectra (raw data) for a sample of compound **2** (1,2-bis(4-phenoxyphenyl)benzyl). This material is available free of charge via the Internet at http://pubs.acs.org.

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