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Synthesis and Chain-End Modification of a Novel Hyperbranched Polymer Containing Alternating Quinoxaline and Benzoxazole Repeat Units

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ABSTRACT: A new AB_2 monomer, 2,3-bis(3-amino-4-hydroxyphenyl)quinoxaline-6-carboxylic acid dihydrochloride, was synthesized in four steps starting from the double condensation of commercially available 3,4-diaminobenzoic acid and 4,4′-dimethoxybenzil. It underwent facile polycondensation in polyphosphoric acid to afford the corresponding hyperbranched quinoxaline−benzoxazole polymer (PPQ−BO **5**) with an intrinsic viscosity of 1.04 dL/g. It was end-capped with 2-thiophenecarboxylic acid, 3,5-dihydroxybenzoic acid, 3-sulfobenzoic acid, 4-sulfobenzoic acid, and 2,3-diphenylquinoxaline-6-carboxylic acid. These hyperbranched polymers displayed an unusual, nonlinear solution viscosity behavior at the concentrations below ∼0.25 g/dL. At these dilute concentrations, both reduced and inherent viscosities *decreased* precipitously ("inverse polyelectrolyte behavior"). The large numbers of *o*-aminophenol end groups were further chemically modified to afford hyperbranched PPQ−BO's with various functionalities. Similar to their linear analogues, the T_g's of all chain-end-modified polymers were not detected up to 450 °C by DSC. PPQ−BO's had UV absorption maxima near 377 nm in basic NMP and 448 nm in MSA. Its emission maxima were at 467 nm in NMP and 475.5 and 767 nm in MSA.

Introduction

Wholly aromatic poly(heterocyclics) such as polybenzoxazoles and polyquinoxalines continue to attract much attention because of their excellent heat resistance as well as their mechanical, optical, and electronic properties.[1] Polybenzoxazoles, especially rigid-rod polybenzobisoxazoles, have limited processability due to the nature of fused-ring systems and stiff-chain conformation, resulting in their insolubility, and their softening temperatures are generally above their degradation temperatures.[2] Chemical modification on these materials, for example, with the use of solubilizing pendants or flexible units in the main chain, has been quite successful to improve their processability, allowing the optimization of their properties as a function of processability.[3] Another viable approach to overcoming processing difficulty is to incorporate the elements of local rigidity and global randomness into the macromolecular architecture. The former is to preserve the thermal, electronic, and optical characteristics of the aromatic fused systems while the latter frustrates entanglement of the polymer chains, leading to greater solubility. Dendritic structures clearly embody these qualities with the understanding that there is a loss of polymer-chain entanglement in this macromolecular architecture.[4] Therefore, under an Air Force basic research program to explore and scope the applicability of the dendritic concept to stiff-chain aromatic and heteroaromatic polymers, we have been focusing on the design and synthesis of novel AB_2 monomers and their self-polymerization to form novel hyperbranched polymers as well as developing structure−property−processing relationships with respect to tailoring the end-group functionality.[5] To this end, we have chosen the hyperbranched over dendrimeric structure, chiefly because of the synthetic advantage that the former can offer.

Although numerous dendrimers and hyperbranched polymers have been described in the literature during the past decade or so, there are very few reported examples related to fused aromatic−heterocyclic dendritic polymers.[5a,6] Thus, this paper describes the results of the synthesis and some physical properties of a new class of hyperbranched poly(quinoxaline−benzoxazole)s.

Experimental Section

Materials. Polyphosphoric acid (assay ≥83%, Aldrich) was used as received as polymerization solvent after degassing with nitrogen purging for 10 h. All chemicals were purchased from Aldrich Chemical Inc. and used as received, unless otherwise mentioned. *N*-Methyl-2-pyrrolidinone (NMP) was distilled under reduced pressure over phosphorus pentoxide. Other solvents were used as received. 3-Sulfobenzoic acid (mp 357−359 °C) and 4-sulfobenzoic acid (mp > 385 °C) were obtained by recrystallization from water after acidification of commercially available sodium 3-sulfobenzoate and potassium 4-sulfobenzoate, respectively. Benzil (mp 94−95 °C) was recrystallized from ethanol.

Instrumentation. Proton and carbon nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra for intermediates, monomer, and polymers were measured at 270 and 50 MHz on a JEOL-ECX-270 NMR spectrometer. Infrared (IR) spectra were obtained with Beckman FT-2100 Fourier transform spectrophotometer. Elemental analysis and mass analysis were performed by Systems Support Materials Branch (MLSA) at Air Force Research Lab, Dayton, OH. All of the melting points (mp) of the compounds were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for methanesulfonic acid (MSA) solution and polymer concentrations of approximately 0.5−

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0.1 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) analyses were performed in nitrogen with a heating rate of 10 °C/min using a Perkin-Elmer model 2000 thermal analyzer equipped with a differential scanning calorimetry cell. Themogravimetric analyses (TGA) were obtained in helium and air atmospheres with a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 themogravimetric analyzer. Gel permeation chromatography (GPC) was carried out on a Waters 150-CV equipped with UV detector. Tetrahydrofuran (THF) was used as the elution solvent. UV−vis spectra were obtained with a Hewlett-Packard 8435 UV−vis spectrophotometer. Photoluminescence measurement was performed with a Shimadzu RF-5301PC spectrofluorophotometer. The excitation wavelength used was the UV absorption maximum of each sample. The energy-minimized space-filling structures and dihedral angle value of AB$_2$ monomer were obtained with the aid of a HyperChem molecular modeling package (Version 7.5, Hypercube Inc., Gainesville, FL).

2,3-Diphenylquinoxaline-6-carboxylic Acid. Into a 500 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, 3,4-diaminobenzoic acid (16.0 g, 105 mmol) was dissolved in deoxygenated acetic acid (250 mL). Benzil (21.0 g, 100 mmol) was then added in one portion. The mixture was heated under reflux for 12 h. During this time, an off-white precipitate formed. After the reaction mixture was allowed to cool to room temperature, the precipitate was collected to give 32.2 g (99% yield) of crude product; mp 290.5−292 °C. Recrystallization of the crude product from DMF afforded 29.6 g (91% yield) of pink crystals; mp 291−292.5 °C. Anal. Calcd for $C_{24}H_{14}N_2O_2$: C, 77.29%; H, 4.32%; N, 8.57%; O, 9.80%. Found: C, 76.93%; H, 4.77%; N, 8.57%; O, 9.63%. FT-IR (KBr, cm^{-1}): 1690 ν(CO). Mass spectrum (*m*/*e*): 326 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 7.35−7.43 (m, 6H, Ar), 7.48−7.51 (d, 4H, Ar), 8.18−8.21 (d, 1H, Ar), 8.28−8.32 (dd, 1H, Ar), 8.65 (s, 1H, Ar), 13.51 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6, δ in ppm): 128.00, 128.20, 128.95, 129.04, 129.15, 129.41, 129.67, 130.65, 132.01, 138.31, 139.61, 142.23, 153.98, 154.61, 166.50.

2,3-Bis(4-methoxyphenyl)quinoxaline-6-carboxylic Acid (1). Into a 500 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, and a condenser, 3,4-diaminobenzoic acid (14.21 g, 93.4 mmol) was dissolved in deoxygenated acetic acid (250 mL). 4,4′-Dimethoxybenzil (25,0 g, 92.5 mmol) was then added to brown clear mixture at room temperature. The reaction mixture was heated under reflux with vigorous stirring for 8 h. After having been allowed to cool to room temperature, the brown mixture was poured into distilled water. The resulting light brown precipitates were collected by suction filtration and then air-dried overnight. It was recrystallized from ethanol to give 34.8 g (97% yield) of yellow solid; mp 296−298 °C. Anal. Calcd for $C_{23}H_{18}N_2O_4$: C, 71.49%; H, 4.70%; N, 7.25%: Found: C, 71.51%; H, 4.55%; N, 7.11%. FT-IR (KBr, cm^{-1}): 1693 ν(CO), 2838 ν(CH$_3$). Mass spectrum (*m*/*e*): 386 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 3.80 (s, 6H, OCH$_3$), 6.92−6.96 (d, 4H, Ar), 7.44−7.48 (dd, 4H, Ar), 8.8.11−8.14 (d, 1H, Ar), 8.22−8.26 (dd, 1H, Ar), 8.58−8.59 (d, 1H, Ar), 13.49 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6, δ in ppm): 55.12, 113.52, 128.90, 128.98, 130.48, 130.74, 131.06, 131.17, 131.49, 139.38, 142.08, 153.46, 154.06, 159.85, 159.97, 166.59.

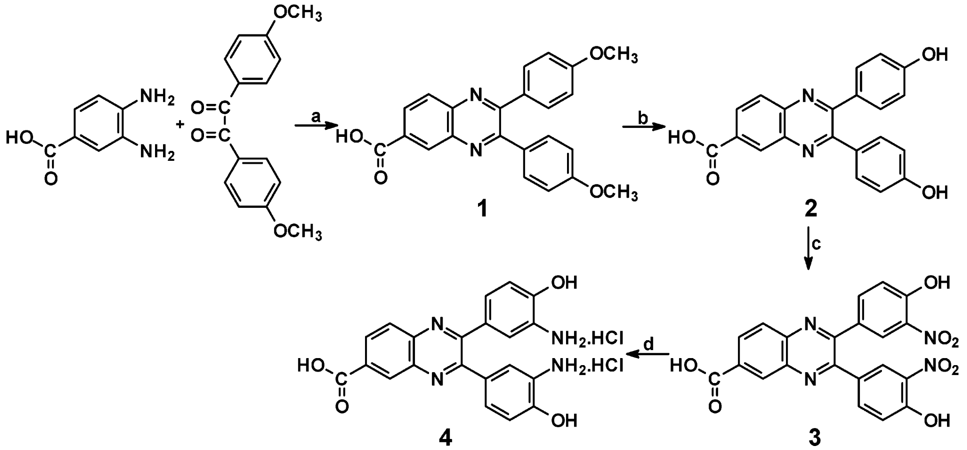
2,3-Bis(4-hydroxyphenyl)quinoxaline-6-carboxylic Acid (2). Into a 1000 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, and a condenser, 2,3-bis(4-methoxyphenyl)quinoxaline-6-carboxylic acid (34.7 g, 89.8 mmol) was dissolved in acetic acid (260 mL). Hydrobromic acid (48%, 500 mL) was then added to yellow clear mixture at room temperature. The reaction mixture was heated under reflux with vigorous stirring until the solution became homogeneous. It took about 6 h. After having been allowed to cool to room temperature, the red-brown mixture was poured into distilled water. The resulting light brown precipitate was collected by suction filtration and dried under the reduced pressure to give 31.9 g (99% crude yield) of yellow solid; mp 315−317 °C (dec). Anal. Calcd for $C_{21}H_{14}N_2O_4$: C, 70.39%; H, 3.94%; N, 7.82%. Found: C, 66.70%; H, 3.98%; N, 7.20%. FT-IR (KBr, cm^{-1}): 1698 ν(CO), 3396 ν(OH). Mass spectrum (*m*/*e*): 358 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 6.76−6.79 (d, 4H, Ar), 7.35−7.39 (d, 4H, Ar), 8.09−8.12 (d, 1H, Ar), 8.20−8.24 (d, 1H, Ar), 9.87−9.89 (d, 1H, OH), 13.50 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6, δ in ppm): 114.93, 128.78, 129.21, 129.27, 130.39, 131.11, 131.23, 139.29, 142.06, 153.78, 154.38, 158.30, 158.44, 166.62.

2,3-Bis(4-hydroxy-3-nitrophenyl)quinoxaline-6-carboxylic Acid (3). Into a 500 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, and a dropping funnel, 2,3-bis(4-hydroxyphenyl)quinoxaline-6-carboxylic acid (10.0 g, 27.9 mmol) was dissolved in acetic acid (200 mL). A solution of nitric acid (5 mL) in acetic acid (20 mL) was then added dropwise at room temperature for 20 min. The reaction mixture was stirred for an additional 12 h at room temperature. The light orange mixture was poured into distilled water. The resulting yellow precipitates were collected by suction filtration and then air-dried overnight. Recrystallization of the crude product from acetic acid gave 12.2 g (97.5% yield) of bright yellow solid; mp 263−267.5 °C. Anal. Calcd for $C_{21}H_{12}N_4O_8$: C, 56.26%; H, 2.70%; N, 12.50%; O, 28.55%. Found: C, 55.99%; H, 3.06%; N, 12.14%; O, 27.68%. FT-IR (KBr, cm^{-1}): 1347, 1540 ν(Ar−NO$_2$), 1628 ν(CO), 3421 ν(OH). Mass spectrum (*m*/*e*): 448 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 7.14−7.18 (dd, 2H, Ar), 7.61−7.65 (dd, 2H, Ar), 8.16−8.32 (m, 4H, Ar), 8.62−8.63 (d, 1H, Ar), 11.54 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6, δ in ppm): 118.87, 118.99, 126.82, 126.91, 128.84, 128.90, 129.10, 129.59, 129.70, 130.48, 132.15, 136.18, 136.27, 136.56, 139.61, 142.23, 151.65, 152,25, 152.85, 152.94, 166.45.

2,3-Bis(3-amino-4-hydroxyphenyl)quinoxaline-6-carboxylic Acid Dihydrochloride (4). Into a 500 mL high-pressure bottle, 2,3-bis-(4-hydroxy-3-nitrophenyl)quinoxaline-6-carboxylic acid (10.0 g, 22.3 mmol), palladium on activated carbon (10%, 0.5 g), and 10% hydrochloric acid solution (150 mL) were introduced. The bottle was placed on a Parr hydrogenator, purged with hydrogen several times, and then agitated at 60−65 psi for 24 h. After the resulting mixture had been filtered through Celite 545 to remove catalyst, the solvent was removed by vacuum distillation. The off-white residue was recrystallized from deoxygenated 20% hydrochloric acid to give 6.7 g (65% yield) of white crystals; mp 260 °C (dec). Anal. Calcd for $C_{21}H_{18}Cl_2N_4O_4$: C, 54.68%; H, 3.93%; Cl, 15.37%; N, 12.15%: Found: C, 48.80%; H, 4.75%; Cl, 20.79%; N, 10.91%. FT-IR (KBr, cm^{-1}): 1293 ν(Ar−NH$_2$), 1628 ν(CO), 3421 ν(Ar−OH). Mass spectrum (*m*/*e*): 344 (M$^+$−CO$_2$−2HCl 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 7.13−7.16 (d, 2H, Ar), 7.30−7.31 (d, 2H, Ar), 7.78 (s, 2H, Ar), 8.17−8.21 (d, 1H, Ar), 8.27−8.28 (d, 2H, Ar), 8.6−8.61 (s, 1H, Ar), 10.11 (s, 4H, NH$_2$), 11.47 (s, 2H, −OH). ^{13}C NMR (DMSO-d_6, δ in ppm): 115.79, 118.99, 125.61, 128.95, 129.07, 129.13, 129.33, 130.36, 130.80, 131.83, 139.41, 142.08, 152.13, 152.51, 153.08, 166.42.

Polycondensation of AB$_2$ Monomer (5). Into a 100 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, and a pressure regulator, PPA (30 g) was placed and stirred a dry nitrogen purge for 10 h. The monomer, 2,3-bis(3-amino-4-hydroxyphenyl)quinoxaline-6-carboxylic acid dihydrochloride (3.0 g, 6.5 mmol), was added, and the resulting mixture was dehydrochlorinated under reduced pressure (1 mmHg) at 60 °C for 24 h and 100 °C for 6 h. Upon completion of the dehydrochlorination process, the mixture was gently heated to 130 °C. When the temperature was approaching 130 °C, the mixture had already become too viscous. Hence, it was allowed to stand for 30 min at this temperature and further heated to and kept at 160 °C without stirring for 2 h to ensure complete cyclization. The polymer dope was completely stuck onto the glass-rod stirrer, rendering any stirring ineffectual. At the end of the reaction, water was added into the flask and poured into a Warring blender and the bundles were chopped, collected by suction filtration, treated with ammonium hydroxide, Soxhlet-extracted with water for 48 h, collected, and finally dried under reduced pressure (1 mmHg) at 200 °C for 48 h. An intrinsic viscosity of 1.04 dL/g (MSA, 30

Scheme 1. AB$_2$ Monomer Synthesis[a]



[a] (a) acetic acid, reflux; (b) hydrobromic acid (48% concentrated), acetic acid, reflux; (c) nitric acid (70% concentrated), acetic acid, rt; (d) H_2 (65−70 psi), Pd−C, 10% hydrochloric acid, rt.

±0.1 °C) was determined. Anal. Calcd for $C_{21}H_{12}N_4O_2$: C, 71.58%; H, 3.43%; N, 15.90%. Found: C, 69.56%; H, 3.68%; N, 15.17%.

General Procedure of End-Capping Reaction (Method 1). Into a 100 mL resin flask equipped with a high-torque mechanical stirrer, a nitrogen inlet and outlet, and a pressure regulator, PPA (30 g) was placed and stirred with dried nitrogen purging for 10 h. The end-capper (90 mol % to AB$_2$ monomer) was added and heated to 100 °C until the mixture became homogeneous (2 h). The monomer, 2,3-bis(3-amino-4-hydroxyphenyl)quinoxaline-6-carboxylic acid dihydrochloride (3.0 g, 6.5 mmol), was added, and the resulting mixture was dehydrochlorinated under reduced pressure (1 mmHg) at 60 °C for 24 h and 100 °C for 6 h. Upon completion of the dehydrochlorination process, the mixture was gently heated to 130 °C for 24 h and 160 °C for 24 h. The workup was similar to that described above. The powdery product was finally dried under reduced pressure (1 mmHg) at 200 °C for 48 h. A range of intrinsic viscosity values of 0.18−0.22 dL/g (MSA, 30 ± 0.1 °C) was determined for the following end-cappers: 2-thiophenecarboxylic acid, 3,5-dihydroxybenzoic acid, 3-sulfobenzoic acid, 4-sulfobenzoic acid (all purchased from Aldrich), and 2,3-diphenylquinoxaline-6-carboxylic acid.

Representative Procedure of End-Capping: Postpolymerization (Method 2). Into a 100 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, and a pressure regulator, PPA (10 g) was placed and stirred under a dry nitrogen purge for 10 h. The hyperbranched polymer (1.0 g, 2.8 mmol, [η] 1.04 dL/g) was added and stirred at 100 °C until the mixture become homogeneous. It usually took about 2−4 h. The corresponding end-capper, 3-sulfobenzoic acid (5% excess amount), was then added at this temperature. The reaction mixture was stirred at 100 °C for 24 h and then at 160 °C for 48 h. The workup was followed as mentioned in the previous procedure. The powder product finally dried under reduced pressure (1 mmHg) at 200 °C for 48 h. An intrinsic viscosity of 0.35 dL/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd for $C_{28}H_{14}N_4O_5S$: C, 64.86%; H, 2.72%; N, 10.81%, 15.43%, 6.18%. Found: C, 63.36%; H, 3.43%; N, 10.42%, 13.97%. 5.33%.

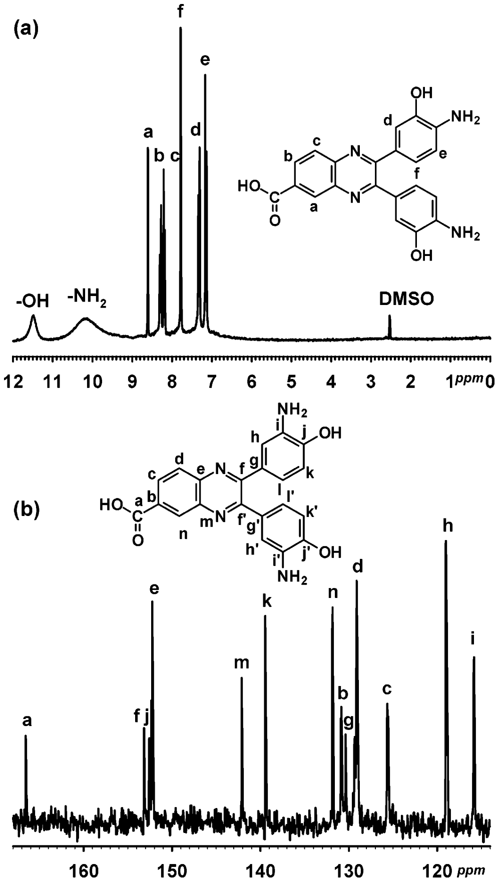


Figure 1. NMR (DMSO-d_6) spectra of AB$_2$ monomer **4**: (a) proton; (b) carbon.

Results and Discussion

Self-Polymerizable AB$_2$ Monomer. The synthesis of the monomer, 2,3-bis(3-amino-4-hydroxyphenyl)quinoxaline-6-carboxylic acid dihydrochloride (**4**), started with the condensation of 3,4-diaminobenzoic acid and 4,4′-dimethoxybenzil to afford 2,3-bis(4-methoxyphenyl) quinoxaline-6-carboxylic acid (**1**) (Scheme 1). Compound **1** was then hydrolyzed in hydrobromic acid in acetic acid to 2,3-bis(4-hydroxyphenyl)quinoxaline-6-carboxylic acid (**2**), and then it was nitrated by using nitric acid (70% concentrated) in acetic acid at room temperature to 2,3-bis(3-nitro-4-hydroxyphenyl)quinoxaline-6-carboxylic acid (**3**). Finally, the monomer (**4**) was obtained after the catalytic reduction of **3** in the presence of a palladium catalyst in 10% hydrochloric acid. All intermediates and monomers were characterized with routine techniques such as melting point, proton and carbon nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR, Figure 1), FT-IR (KBr pellet), mass spectroscopy, and elemental analysis. It should be mentioned that the presence of carboxylic acid, hydroxyl, and ammonium hydrochloride groups renders the AB$_2$ monomers very hygroscopic, and because of the moisture in the samples, the experimental percentages of carbon from elemental analysis were always less than the theoretical values.

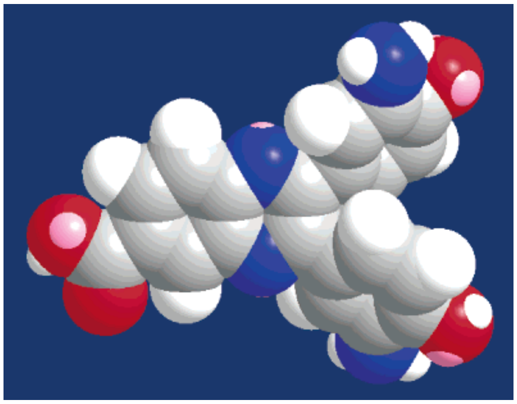


Figure 2. Energy-minimized space-filling structure of AB$_2$ monomer (HyperChem V7.5 Professional).

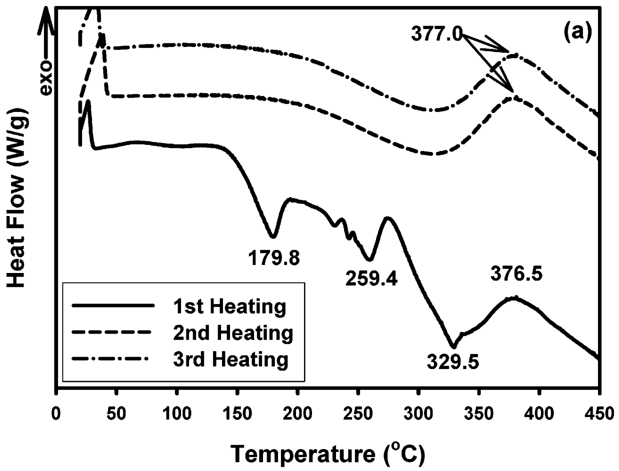
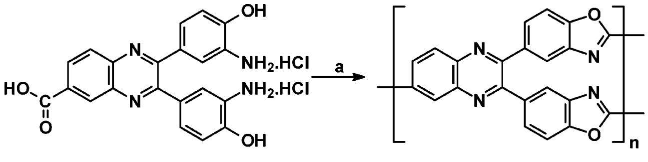


Figure 3. DSC thermograms of AB$_2$ monomer with a heating rate of 10 °C/min.

Energy minimization (HyperChem 7.5) of a space-filling molecular model showed that the 2- and 3-phenyl groups of the AB$_2$ monomer are twisted with respect to each other so that they are ~40° out of the plane defined by the quinoxaline ring (Figure 2). This relatively large dihedral angle could have enhanced the solubility for 2,3-diphenylquinoxaline derivatives as well as their polymers due to the difficulty in molecular packing.[5b]

Thermal Properties of AB$_2$ Monomer. The DSC thermograms of the AB$_2$ monomer were obtained from powder sample with a common heating rate of 10 °C/min (Figure 3). From the first heating run, the AB$_2$ monomer exhibited multiple melting endotherms at 180, 259, and 330 °C. Even though there is no structural isomerism in AB$_2$ monomer, the first melting at 180 °C is ascribable to an ordinary isotropic crystal melting while the latter two major melting peaks are believed to be stemming from the dissociation of hydrogen bonding, which were formed after crystal melting. Polymorphism in phenylquinoxiline derivatives has been well discussed in the literature.[7] The exothermic peak maximum at 376.5 °C would be originated from thermal cyclization between carboxylic acid and *o*-aminophenol on AB$_2$ monomer. The exothermic peak maximum at 376.5 °C is attributed to the enthalpy generated from the intermolecular, thermal cyclization and dehydration between carboxylic acid and *o*-aminophenol of AB$_2$ molecules. This exothermic peak is reproducible in the second and third runs (377 °C).

Scheme 2. Self-Polymerization of AB$_2$ Monomer (a: PPA, 60, 100, 130, 160 °C)



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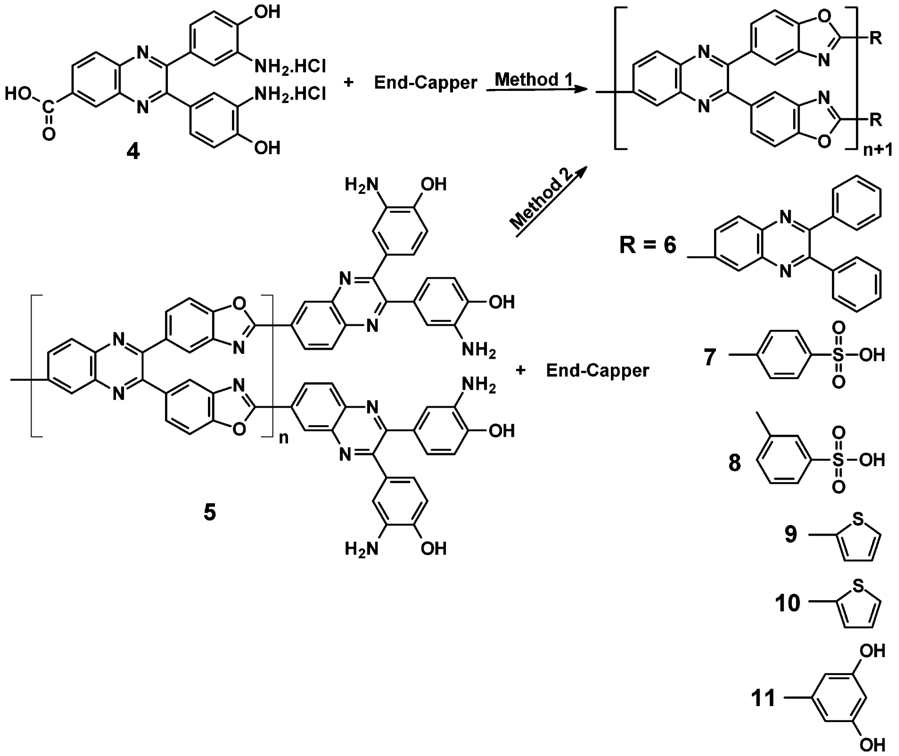
Self-Polymerization of AB$_2$ Monomer 4. Polycondensation to prepare the hyperbranched PPQ−BO **5** was conducted at monomer concentration of 6% in PPA (83% assay), and the reaction temperature step increased up to 160 °C. Soon after the mixture temperature had approached 130 °C, the mixture became very viscous, indicating that high molecular weight polymer was being generated. Approximately 30 min later, the mixture stuck to the stirring rod, rendering further stirring ineffectual. To ensure complete cyclization, the mixture was further heated to and kept at 160 °C for 2 h. The resulting polymer has an intrinsic viscosity of 1.04 dL/g (MSA at 30 ± 0.1 °C), and no glass transition temperature (T_g) was detected at and below 450 °C (Scheme 2).

End-Capped Hyperbranched Polymers. Because of the large number of end groups, the end-functionalization of hyperbranched polymers generated from an AB$_2$ monomer can possibly be tailored chemically to meet the property and/or processing requirements of a specific application. The available B functional groups should be equal to average degree of polymerization plus one (DP + 1), and an A functional (focal) group should also be present, assuming that there were no intramolecular cyclization, forming a loop between A and B. If there was a loop formation, the average number should be DP without focal A functionality. As shown in Scheme 3, hyperbranched PPQ−BO's (**6**, **7**, **8**, **9**, **10**, and **11**) with a variety of different end-cappers could be synthesized in two different ways. In method 1, the end-capper (90 mol % to AB$_2$ monomer) was placed in PPA and completely dissolved. The monomer was then added, followed by the same procedure used for PPQ−BO **5**. Finally, the mixture was heated to 160 °C for 24 h to make complete ring closure at the chain ends (Scheme 3, method 1). In method 2, the hyperbranched polymer PPQ−BO **5** ($[\eta]$ 1.04 dL/g) was completely dissolved in PPA at 100 °C, an end-capping agent (5 mol % excess to the repeating unit) was then added, and the solution was heated to 160 °C for 48 h (Scheme 3, method 2). PPQ−BO **6** was prepared by the reaction of AB$_2$ monomer and 2,3-diphenylquinoxaline-6-carboxylic acid (method 1). PPQ−BO **7** was prepared by the reaction of AB$_2$ monomer and 4-sulfobenzoic acid (method 1). PPQ−BO **8** was prepared by the reaction of PPQ−BO **5** and 3-sulfobenzoic acid (method 2). There were two attempts to prepare 2-thiophene-terminated PPQ−BO. The attempt on the reaction of PPQ−BO **5** and 2-thiophenecarbonyl chloride (method 2) was unsuccessful, producing only an insoluble gel (PPQ−BO **9**). On the other hand, soluble PPQ−BO **10** was obtained from the reaction of AB$_2$ monomer and 2-thiophenecarboxylic acid (method 1). PPQ−BO **11** was prepared by the reaction of AB$_2$ monomer and 3,5-dihydroxybenzoic acid (method 1). All polymers were isolated by precipitation of the polymer dopes in water, filtration, washing the polymers with ammonium hydroxide, Soxhlet-extraction with water for 48 h, filtration, and drying at reduced pressure at 200 °C for another 48 h. They were soluble in MSA, and the intrinsic viscosities were measured in MSA with the exception of 2-thiophenecarbonyl end-capped PPQ−BO **5**. Properties of hyperbranched polymers are summarized in Table 1.

Scheme 3. End-Functionalization of Hyperbranched PPQ−BO[a]



[a] Method 1: PPA, 60, 100, 130, 160 °C; method 2: PPA, 100, 160 °C.

Table 1. Properties of End-Capped Hyperbranched PPQ−BO's

					$T_{d5\%}$ (°C)[e]			
no.	method	η^* (dL/g)[a]	η^* (dL/g)[b]	T_g (°C)[c]	in air (onset)	char (%) at 900 °C	in helium (onset)	char (%) at 900 °C
5		1.16 (1.04)[f]	0.43 (0.40)[g]	ND[d]	430	0.43	482	69
6	1	0.19	0.16	ND	388	0.65	438	59
7	1	0.18	0.15	ND	404	3.87	353	59
8	2	0.66 (0.35)[f]	0.26 (0.33)[g]	ND	368[h]	3.15	337[h]	60
9	1	0.22	0.13	ND	408	0.76	405	46
10	2	insol	insol	ND	413	4.43	429	52
11	1	0.23	0.14	ND	350	2.38	359	48

[a] Reduced viscosity determined with 0.5% solution in MSA at 30 ± 0.1 °C. [b] Reduced viscosity determined with 0.5% solution in NMP at 30 ± 0.1 °C. [c] Glass transition temperature (T_g) determined by DSC with heating rate of 10 °C/min. [d] ND = not detectable up to 450 °C. Calculated T_g of rigid rod PBO is 900 °C. [e] The temperature at which 5% weight loss occurred on TGA thermogram obtained with a heating rate of 10 °C/min. [f] Intrinsic viscosity determined by two points extrapolation to the origin in MSA at 30 ± 0.1 °C. [g] Intrinsic viscosity determined by two points extrapolation to the origin in NMP at 30 ± 0.1 °C. [h] Desulfonylation temperature.

Thermal Properties. As-worked-up PPQ−BO **5** displayed an exothermic peak maximum at 381 °C during the first heating scan (Figure 4a). The location was very close to the exothermic peak from AB_2 monomer. During the second and third runs, the heat of exothermic reaction decreased, since the number of residual carboxylic acid groups had diminished. To provide evidence to the assumption that further thermal cyclization reaction would be the main reason, the PPQ−BO **5** was heat treated at 350 °C under nitrogen for 24 h. There was no noticeable thermal transition detected by DSC (Figure 4b). Similar to most of fused linear heterocyclic polymer, the glass transition temperature (T_g) of the hyperbranched polymers was not able to detect as high as 450 °C by DSC.[2]

The temperatures at which 5% weight losses ($T_{d5\%}$) of PPQ−BO **5** occurred during TGA runs in air (Figure 5a) and in helium (Figure 5b) were 430 and 482 °C, respectively. Weight loss occurring at lower temperature in comparison with their linear analogues could be rationalized in terms of the loss of water of reaction from the further chain extension process in solid state during benzoxazole ring formation and/or degradation of certain thermally unstable terminal moieties above 300 °C. Noteworthy is that all PPQ−BO's had 5% weight loss in helium above 350 °C, except PPQ−BO **7**, PPQ−BO **8**, and PPQ−BO **11**, whose sulfonic acid and hydroxyl substituents are prone to decompose as SO_3, SO_2, and H_2O in this temperature range.

Dilute Solution Behaviors. All polymers were soluble in most of polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), methyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP). Some polymers containing polar surface groups such as PPQ−BO **5**, PPQ−BO **7**, PPQ−BO **8**, and PPQ−BO **11** were not completely soluble upon complete dryness due to inter- and intramolecular interactions. In these cases, when residual water content was more than 5 wt % by TGA, the polymers were soluble, and there were no insoluble gels monitored in the solutions. Once the samples were upon complete dryness, they were not completely dissolved in common polar aprotic solvents but well soluble in strong acids such as trifluoroacetic acid (TFAA),

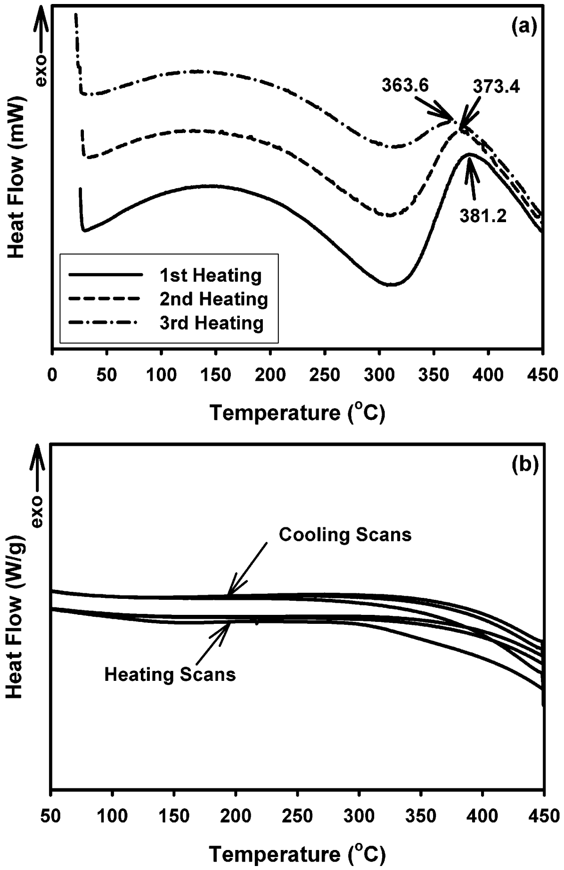


Figure 4. DSC thermograms of hyperbranched PPQ−BO **5** with a heating rate of 10 °C/min: (a) before heat treatment; (b) after heat treatment at 350 °C for 24 h.

sulfuric acid, methanesulfonic acid (MSA), and trifluoromethanesulfonic acid (TFMSA).

Noteworthy is the unusual solution behavior of these hyperbranched polymers as a function of their concentrations. In all cases but PPQ−BO **11**, as the concentration decreased, both reduced and inherent viscosities also decreased but plummeted at ∼0.25 g/dL (see Figure 6a,b). Thus, the intrinsic viscosities were approximately determined from the two-point extrapolation of reduced viscosity and inherent viscosity to the origin (Table 1). In contemplating the observation, we can reasonably assume that in a strong acid such as methanesulfonic acid (MSA) all PPQ−BO's except PPQ−BO **11** are polyelectrolytes due to the protonation of the basic functions (OH, NH_2, and nitrogen of quinoxaline or benzoxazole units). In diluting the solution, we would also expect these hyperbranched polyelectrolytes to be opening up as more free volumes become available in response to normal polyelectrolye effect with the drastic increase in viscosities. However, unlike linear (coil and rigid-rod) polyelectrolytes in MSA, the dilute solution behaviors of PPQ−BO's were just the opposite, suggesting the overall contraction of the macromolecular sizes and reduction in the hydrodynamic volumes. We have previously termed this observation as an "inverse" or negative polyelectrolyte effect for the similar dilute solution behavior of a hyperbranched poly(quinoxaline−ether−kotone).[5a] While the exact origin of this effect is not known, we suspect that it is possibly related to the dynamics of inter- and intramolecular interactions, e.g., hydrogen-bonding and electrostatic interactions, as a function of concentrations. Thus, when intermolecular interactions leading to aggregation are dominant at higher concentrations and intramolecular interactions (possible chain folding into the bulk) prevail at lower concentrations, similar inverse polyelectrolyte behavior would be expected.

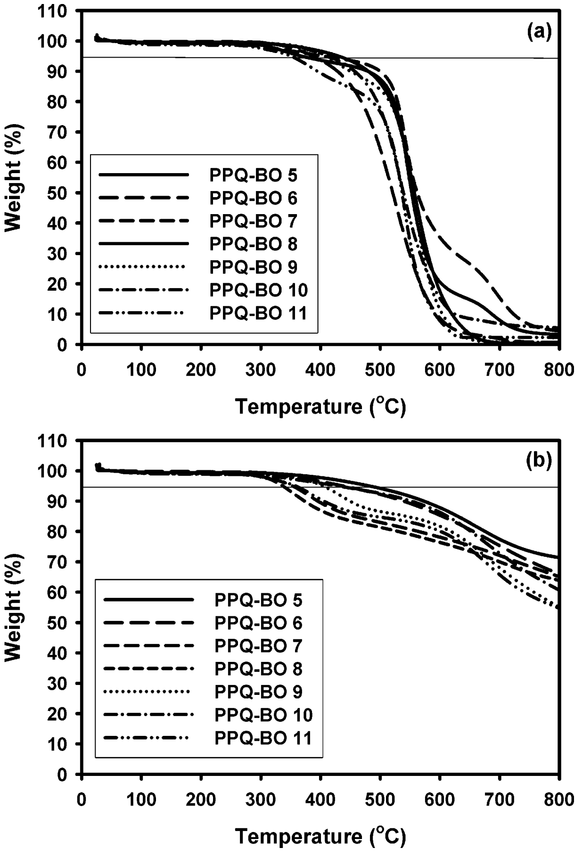


Figure 5. TGA thermograms of PPQ−BO's: (a) in air; (b) in helium.

To further probe this effect, the parent hyperbranched polymer ([η] = 1.04 dL/g) was end-capped with 3-sulfobenzoic acid, resulted in the hyperbranched PPQ−BO **8** with benzenesulfonic acid at the ends. The sulfonic acid groups are capable to form stronger interactions than any other groups we have introduced at the termini. The polymer PPQ−BO **8** has much less intrinsic viscosity as compared to polymer PPQ−BO **5** (Figure 6c). This can be probably explained by that the intramolecular interactions are dominant over intermolecular interactions in the polymer PPQ−BO **8**. On the other hand, PPQ−BO **5** did not show any polyelectrolyte behavior in a basic solvent, viz. NMP (Figure 6b), whereas PPQ−BO **8**, which has stronger acid surface groups, did display a positive polyelectrolyte effect (Figure 6d). PPQ−BO's **6**, **7**, and **9** show the same trends of solution viscosities in both acidic and basic solvents as PPQ−BO **8** (Figure S1). However, the dilute solution behavior of PPQ−BO **11** shows linear dependence in acidic solvent for both reduced and inherent viscosities as the concentrations were decreased (Figure 6e), and it displays the same positive polyelectrolyte effect as the others in basic solvent (Figure 6f).

On the basis of previous[5a] and current observations on dilute solution behaviors, some interesting points could be drawn depending upon the dynamics of intra- and intermolecular interactions. For the case of hyperbranched polymers, they could be closely related to the combination of surface group natures, interior structures, and molecular flexibilities. If the system is dominated by the intramolecular interaction as concentration lowered, it displays a negative electrolyte. When the system is governed by the intermolecular interaction, it shows a positive electrolyte. When the interactions are in the equilibrium state, the system shows a linear solution behavior.

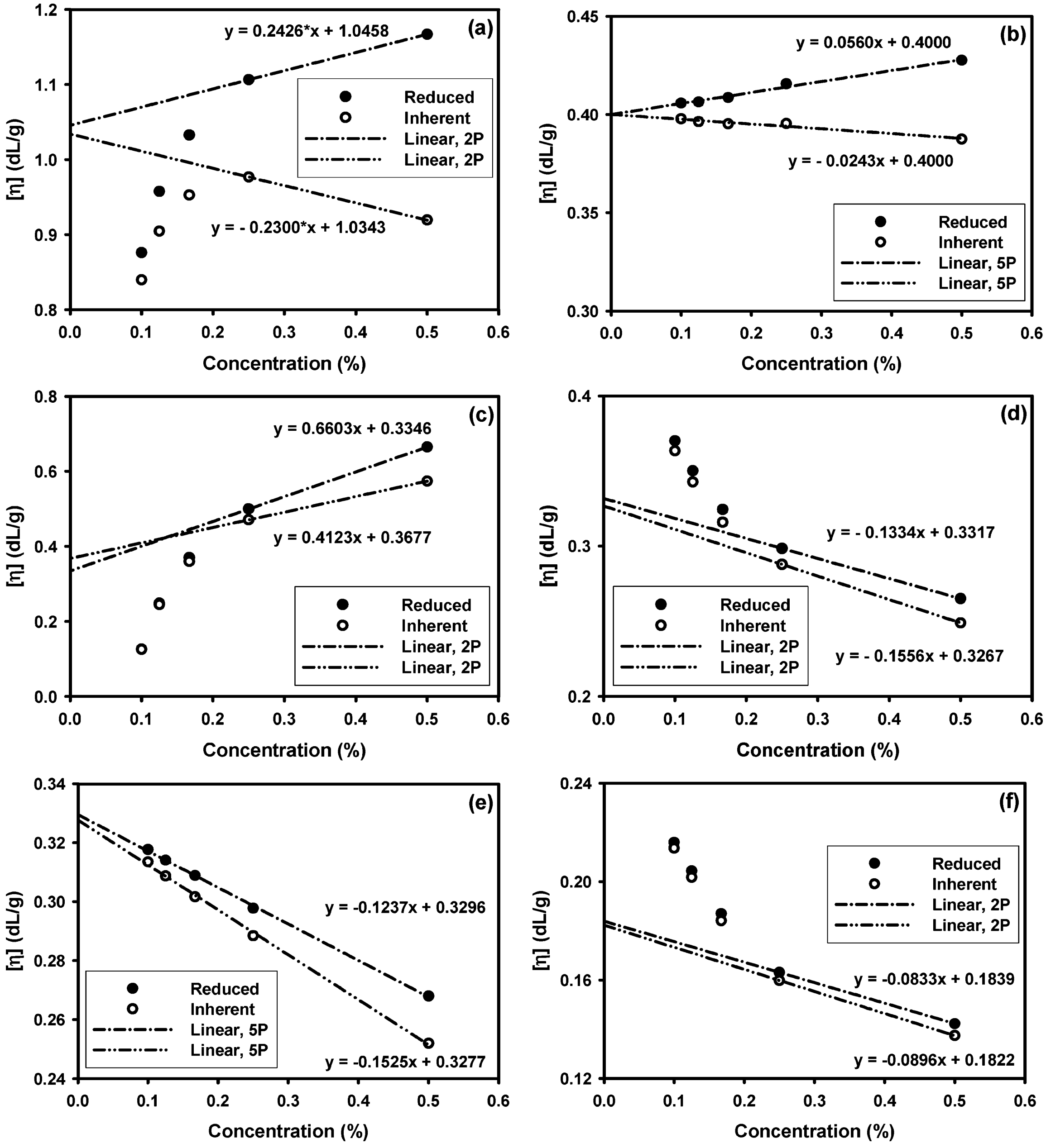


Figure 6. Solution viscosity behaviors of hyperbranched PPQ−BO's as a function of concentration and solvent: (a) PPQ−BO **5** in MSA; (b) PPQ−BO **5** in NMP; (c) PPQ−BO **8** in MSA; (d) PPQ−BO **8** in NMP; (e) PPQ−BO **11** in MSA; (f) PPQ−BO **11** in NMP.

UV Absorption and Emission Properties. Polymers containing diphenylquinoxaline moieties are well-known photoluminescent (PL) and electroluminescent (EL) materials. They displayed surprisingly unaltered from luminescent properties without electron-transporting layer and long-term stability.[8] In practice, 2,3-diphenylquinoxaline compounds have excellent solubility, since the 2- and 3-position phenyl rings are 44° out of plane to quinoxaline ring, which are consisted of fused aromatic heterocyclic ring and two additional aromatic rings; they are disrupting molecular packing, and still conjugated enough to be optically active.[6b]

Stock solutions (1.0×10^{-4} mol/L) of each sample were prepared in NMP, and MSA and UV absorption and emission were obtained. The absorption maxima of PPQ−BO **5** are 377 nm in NMP and 448 nm in MSA (Figure 7a). Interestingly, the sample in NMP solution displays a second minor peak at 767 nm. Ionic interaction of protonated *o*-aminophenol groups at the surface region and benzoxazole and quinoxaline moieties at the inner region of PPQ−BO **5** in MSA solution compared to the sample in basic NMP solution without ionic interaction causes a 71 nm red-shifted absorption maximum. Thus, the effective conjugation length at the ground state of PPQ−BO **5** is longer in an acidic than a basic solvent.

For the comparison of UV absorption behaviors, slightly longer conjugation length of PPQ−BO **5** due to oxazole moiety contributed an ∼7 nm longer absorption peak maximum than polyphenylquinoxaline (PPQ), which has an absorption maximum at 370 nm in NMP solution.[5a]

When the samples excited at their absorption maxima, PPQ−BO **5** in NMP and MSA solutions emit light, and peak maxima were at 475.5 and 467 nm, respectively (Figure 7b). The value obtained from NMP solution was also ∼30 nm red-shifted due to longer conjugation length than PPQ itself.[5a] Surprisingly, PPQ−BO **5** in an acidic solvent displays a much lower Stokes' shift (19 nm) than in a basic solvent (∼98 nm). This would also be related to ionic interactions in protonated species in outer and inner regions in MSA solution.

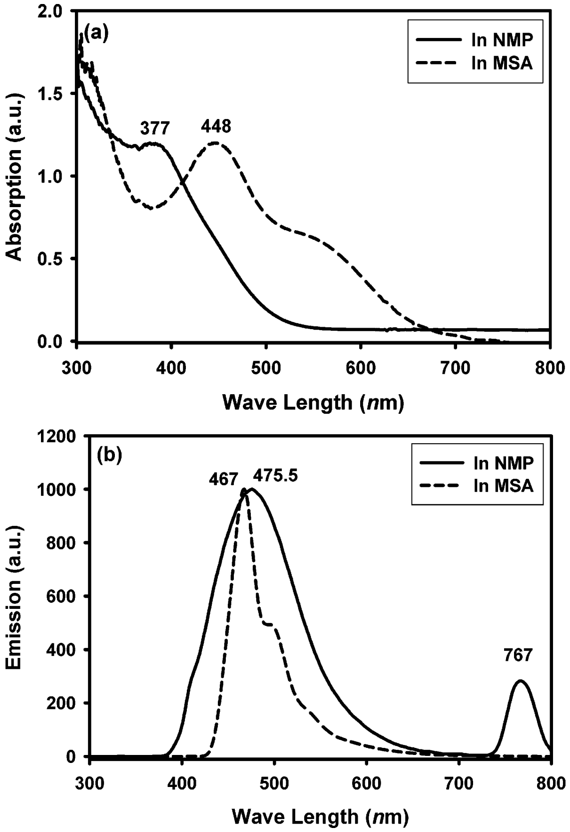


Figure 7. (a) UV absorption and (b) emission spectra obtained from hyperbranched PPQ−BO **5** depending upon basic and acidic solvents.

Conclusion

We have prepared a new self-polymerizable AB_2 monomer containing a preformed quioxaline ring and the requisite functional groups that can react to generate a novel example of hyperbranched polybenzoxazole. Unlike its rigid-rod benzazole analogues, it is soluble in most polar aprotic solvent such as NMP, DMF, DMAc, and DMSO as well as acidic solvents such as MSA and sulfonic acid. In addition, it has higher intrinsic viscosity in a strongly acidic solvent (MSA) than the basic amide solvent (NMP) due to the ionic interactions between polymer and acid solvent and shows a nonlinear solution viscosity behavior at very dilute concentration. Thus, it provides an additional example to illustrate the so-called “inverse or negative” polyelectrolyte effect. The chain-end modification could also be accomplished in a one- or two-stage fashion, showing the possibility to modify the polymer properties. In addition to being heat-resistant showing no T_g’s up to 450 °C during DSC scans, these polymers are highly fluorescent.

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Supporting Information Available: Dilute solution behaviors of PPQ−BO’s **6**, **7**, and **9** as a function of concentration and solvent. This material is available free of charge via the Internet at http://pubs.acs.org.

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