Room-Temperature Free-Radical-Induced Polymerization of 1,1′-(Methylenedi-1,4-phenylene)bismaleimide via a Novel Diphenylquinoxaline-Containing Hyperbranched Aromatic Polyamide

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ABSTRACT: Two new diphenylquinoxaline-containing AB_2 monomers, 2,3-bis(4-aminophenyl)quinoxaline-6-carboxylic acid, **5**, and 2,3-bis[4-(4-aminophenoxy)phenyl]quinoxaline-6-carboxylic acid, **9**, were prepared and polymerized via the Yamazaki reaction to form the hyperbranched aromatic polyamides (designated as **II** and **III**, respectively) with $-NH_2$ as the reactive chain-end groups. Although these AB_2 monomers and their respective hyperbranched polymers are structurally similar except for the presence of a *p*-phenyloxy spacer between the quinoxaline and *p*-aminophenyl segments in **9** and **III**, the physical and chemical properties of both monomers and hyperbranched polymers are distinctly different. It is believed that the tautomerism in **5** and **II** is likely the basis for these differences. Since **III** was only marginally soluble in polar aprotic solvents in which **II** readily dissolved, a known, soluble hyperbranched polyamide (**I**) was prepared from 3,5-bis(4-aminophenyloxy)benzoic acid for comparison purposes in a subsequent blends study. The curing behaviors and thermal properties of the hyperbranched polyamides **I** and **II** blended in 0.75−3.75 wt % with a common bismaleimide [1,1′-(methylenedi-4,1-phenylene)bismaleimide, BMI] resin were studied with differential scanning calorimetry (DSC) and Fourier transform infrared (FT-IR) spectroscopy. Whereas the DSC results indicated that **I** reacted normally with BMI in a Michael-addition fashion, followed by homopolymerization of the excess BMI, **II** appeared to be able to initiate free radical polymerization of BMI at room temperature after co-dissolution with BMI in *N*-methyl-2-pyrrolidinone. The DSC results of the BMI/**II** blends indicated that, at ≥1.5 wt % of **II**, no exotherm attributable to the thermal curing of BMI was detected. Electron spin resonance (ESR) experiments confirmed that the parmagnetic species present in **II** were more reactive toward BMI in solution at room temperature than the radical detected in **I**. This unique property of **II** to initiate room-temperature radical polymerization of BMI makes it important as a prototype for the development of low-temperature, thermally curable thermosetting resin systems for high-temperature applications.

Introduction

Historically, fabrication of high performance, polymer matrix composite (PMC) structures for aircraft and space systems applications on a low volume basis is very costly. This is because the nonrecurring costs such as tooling and capital equipment are the major cost drivers for the low volume production. Since the autoclaves and hardened tooling, traditionally required for the fabrication of large composite-based structural components, have the lion's share in the fabrication cost, the affordability issue can be logically addressed by developing nonautoclave resins and processes. Toward this end, electron beam (E-beam) curing[1] is very attractive because of the following important advantages: (i) rapid curing (seconds to minutes as opposed to hours for thermal curing); (ii) good penetration depth up to an inch, where curing of a large and thick component can be performed on a "conveyor-belt" process with an overhead horn providing an adjustable e-beam coverage; (iii) low residual thermal stress. However, a high-energy electron-beam source (<250 keV to >1 MeV) is required, necessitating some measures of personnel protection. Another approach is to drastically lower the curing temperature and pressure for the composites so that tooling can be fabricated easily from relatively inexpensive materials such as wood, fiberglass, or foam. However, for these processing conditions, the material systems (prepreg, liquid resin, and adhesive) must possess characteristics that are conducive to be processed at low temperatures and pressures (e.g., ∼65 °C and 14 psi) and after post-cure in free-standing fashion should provide structural performance equivalent to current aerospace standards (e.g., epoxy-3501). This approach, nevertheless, is hampered by the lack of suitable material systems that can be cured at temperatures below 65 °C to form structures with high-temperature properties.

As a continued effort of our research program to explore and develop niche applications for aromatic hyperbranched polymers,[2] we describe herein the results on the synthesis and characterization of two new 2,3-diphenylquinoxaline-containing AB_2 monomers, where A = CO_2H and B = NH_2, and the respective hyperbranched aromatic polyamides with $-NH_2$ as the reactive chain-end groups. Also described are the unexpected and interesting results from a comparative study via thermal analysis, FT-IR, and ESR methods on the reactivity of one of the new quinoxaline-containing hyperbranched polyamides (with electron-deficient polymer backbone) and a known hyperbranched polyamide (with relatively electron-rich repeat units)[3] when blended in small amounts with a common bismaleimide resin. These results are relevant to the development of nonautoclave, thermally curable thermosetting systems.

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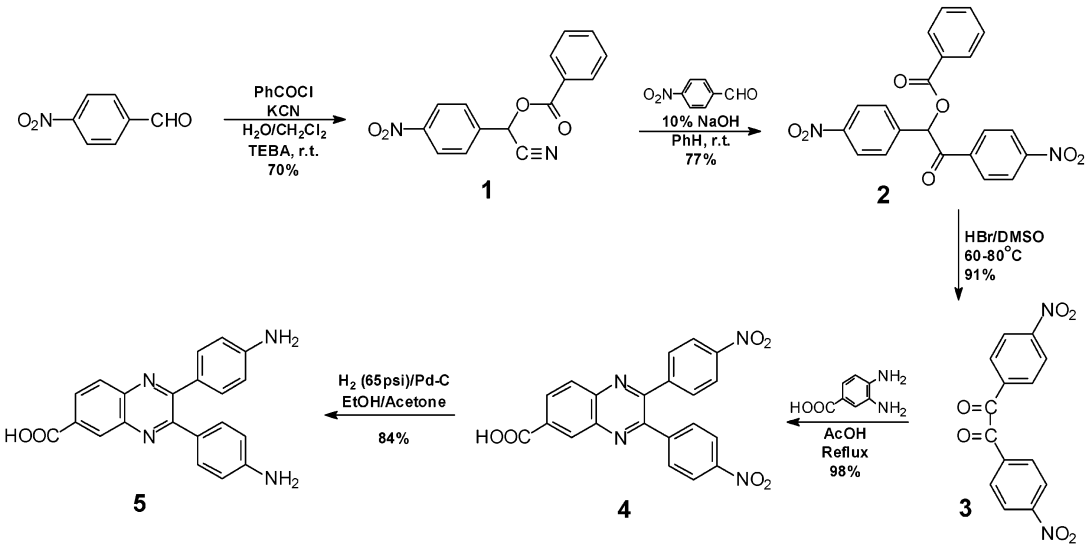
Scheme 1. Synthesis of 2,3-Bis(4-aminophenyl)quinoxaline-6-carboxylic Acid (5)



Results and Discussion

Poly(phenylquinoxalines) (PPQ's) and aromatic polyamides are important classes of high performance polymers.[4] Although PPQ's have several attractive features such as high glass-transition temperatures, heat-resistance, and amorphous character leading to excellent processability,[5] the utilization of PPQ's, in comparison with aromatic polyamides, is less widespread mainly because of the high cost associated with the preparations of their bis(dicarbonyl) and bis(*o*-diaminophenyl) monomers as well as the choice of *m*-cresol as the polymerization medium that is catalytic[6] but relatively corrosive and toxic. Thus, the preformed phenylquinoxaline monomers with suitable functions for step-growth polymerizations provide an attractive approach to circumvent this problem.[7,8,9] While there are several examples of linear aromatic polyamides containing main-chain phenylquinoxanine[10] or 2,3-bis(1,4-phenylene)quinoxaline[11] moieties described in the literature, to our knowledge, analogous hyperbranched polyamides have not been reported. However, a hyperbranched poly(phenylquinoxaline−arylene ether) was recently synthesized, and its chain ends were appropriately functionalized so as to control the morphological structures of organic−inorganic hybrids.[12]

Monomer Synthesis. Since we are interested in using an amide-forming reaction as the step-growth process in conjunction with the facts that 3,4-diaminobenzoic acid is commercially available and can easily react with suitable benzil derivatives to form the quinoxaline compounds, we designed our diphenylquinoxaline-containing AB_2 monomers accordingly.

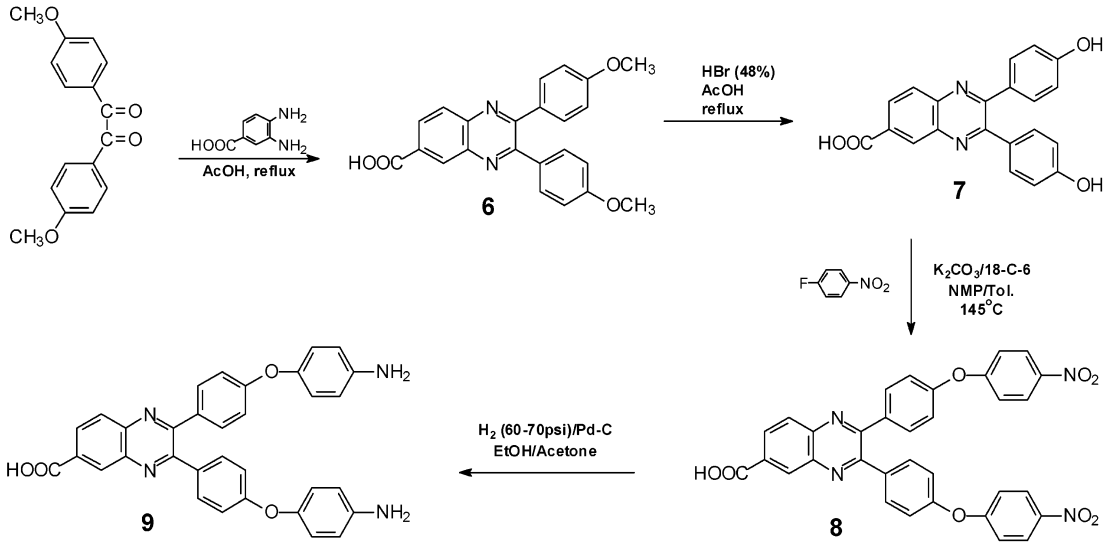
Thus, the AB_2 monomer, 2,3-bis(4-aminophenyl)-quinoxaline-6-carboxylic acid, was synthesized according to Scheme 1. Initially, we attempted the synthesis of an α-hydroxyketone dinitro compound, a key intermediate to 4,4′-dinitrobenzil from the benzoin condensation of 4-nitrobenzaldehyde in the presence of KCN. Unfortunately, the effort resulted in poor yield of the corresponding α-hydroxyketone. Thus, the synthesis of 4,4′-dinitrobenzil was prepared in three steps. The first two are (i) in situ benzoylation of the nitrobenzaldehyde cyanohydrin anion[13] and isolation of 2-benzoyloxy-2-(4-nitrophenyl)acetonitrile, **1**, (ii) condensation of **1** and 4-nitrobenzaldehyde in a 10% NaOH(aq)/benzene mixture to form the benzoylated α-hydroxyketone, **2**, which under the strongly acidic, aqueous conditions of HBr/DMSO oxidation[14] was first converted to an α-hydroxyketone and oxidized to the target benzil compound, **3**. Subsequently, (iii) tandem condensation−cyclodehydration reactions of 4,4′-dinitrobenzil with 3,4-diaminobenzoic acid in refluxing acetic acid resulted in excellent yield of 2,3-bis(4-nitrophenyl)quinoxaline-6-carboxylic acid, **4**. Finally, catalytic hydrogenation of the dinitro intermediate led to the formation of the desired AB_2 monomer, 2,3-bis(4-aminophenyl)quinoxaline-6-carboxylic acid, **5**.

The AB_2 monomer, 2,3-bis[4-(4-aminophenoxy)phenyl]-quinoxaline-6-carboxylic acid, was synthesized according to Scheme 2. Double condensation reaction of commercially available 4,4′-dimethoxybenzil with 3,4-diaminobenzoic acid in refluxing acetic acid resulted in excellent yield of 2,3-bis(4-dimethoxyphenyl)quinoxaline-6-carboxylic acid, **6**. Demethylation of **6** in refluxing 48% hydrobromic acid−acetic acid mixture afforded 2,3-bis(4-hydroxyphenyl)quinoxaline-6-carboxylic acid, **7**, which was subsequently subjected to an aromatic nulceophilic substitution reaction with 4-fluoronitrobenzene in the presence of potassium carbonate and 18-crown-6 under Dean−Stark conditions to result in the isolation of 2,3-bis(4-nitrophenyloxyphenyl)quinoxaline-6-carboxylic acid, **8**. Finally, catalytic hydrogenation of the dinitro intermediate led to the formation of the desired AB_2 monomer, 2,3-bis[4-(4-aminophenoxy)phenyl]quinoxaline-6-carboxylic acid, **9**.

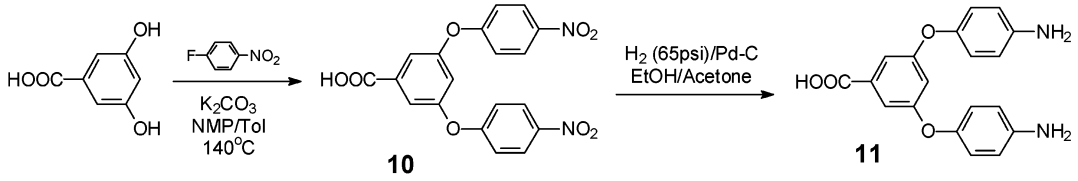
The AB_2 monomer (**11**) for hyperbranched polymers **I** was prepared according to the reported procedures (Scheme 3).[3]

^{1}H NMR and Tautomerism of Monomer 5. Surprisingly, monomer **9** turned out to be less soluble in the solvents that easily dissolved monomer **5** even though the presence of two extra phenyl ether groups should render **9** structurally more flexible and in turn, more soluble. Furthermore, when monomer **5** (orange solid) dissolved in NMP, a red solution resulted whereas the NMP solution of monomer **9** (light yellow solid) was yellow, suggesting greater conjugation length in the molecular structure of **5**. The tautomerism of monomer **5** in polar aprotic solvent would be a plausible explanation for the observed disparity in solubility because

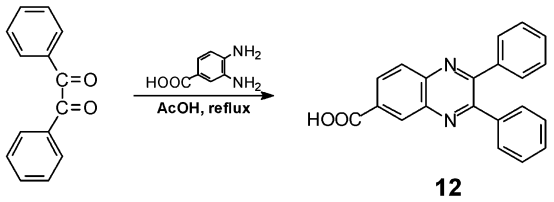
Scheme 2. Synthesis of 2,3-Bis[4-(4-aminophenoxy)phenyl]quinoxaline-6-carboxylic Acid (9)



Scheme 3. Synthesis of 3,5-Bis(4-aminophenoxy)benzoic Acid (11)



Scheme 4. Synthesis of 2,3-Diphenylquinoxaline-6-carboxylic Acid (12)



there are more intermolecular hydrogen-bonding possibilities with polar aprotic solvents in **9** than **5**. To support the hypothesis, we examined closely the proton nuclear magnetic resonance (^{1}H NMR) spectra of the diphenylquinoxaline compounds prepared in our laboratory and the ^{1}H NMR spectral data reported for a number of similar 6-substituted 2,3-diarylquinoxaline compounds (where 6-substituents are H, Cl, F, CF_3, and 3-aminophenoxy).[15,16] It appears that H_a, H_b, and H_c of the benzene component of quinoxaline ring have characteristically their chemical shift (δ) values in the range of 7.6−8.5 ppm. The predominant deshielding effect (downfield shift) on these protons is due to the strongly electron-withdrawing nature of the pyrazine component. For 2,3-diphenylquinoxaline-6-carboxylic acid, **12** (see Scheme 4), the range is 8.2−8.6 ppm, and for monomer **9**, 8.3−8.6 ppm. As depicted in Figure 1, the chemical shifts of H_a, H_b, and H_c of monomer **5** are in the range of 6.6−7.2 ppm, which is shifted *upfield* in comparison with the aforementioned 6-substituted 2,3-diarylquinoxaline compounds ($\Delta \sim 1.0-1.3$ ppm), diphenylquinoxaline-6-carboxylic acid ($\Delta \sim 1.6$ ppm) and monomer **9** ($\Delta \sim 1.4-1.7$ ppm). Such large upfield shifts can only be effected by the dramatic change in the electronic character of the C_4N_2 fused ring from strongly electron-withdrawing (pyrazine ring) to strongly electron-donating (piperazine ring).[17] In addition, a comparison between the ^{1}H NMR spectra of monomer **5** and its nitro precursor to those of monomer **9** and its nitro precursor reveals that changing the distal nitro group to amino group only slightly shifted H_a, H_b, and H_c signals upfield, consistent with the inductive effect exerted by *p*-aminophenoxy group. However, this is not the case for monomer **5** and its nitro precursor; a much larger upfield shift was observed (e.g., ~1.5 ppm for H_a; see Figure 1).

Since there are theoretically three tautomers for monomer **5**, namely the bis(4-aminophenyl)quinoxaline form (**5**), the bis(quinoneimine)piperazine form (**5b**), and the intermediate form, **5a**, we used a ^{1}H NMR prediction/simulation software program[18] to generate the simulated proton NMR spectra in the aromatic proton region (δ range = 6.00−9.00 ppm) for the these tautomers. The results are shown in Figure 2. In comparison with the experimental ^{1}H NMR spectrum for monomer **5** (Figure 1a), it is quite clear that the experimental spectrum is more closely matched with the simulated spectrum corresponding to the bis(quinoneimine)piperazine form (Figure 2, bottom) than the other two spectra. Thus, we tentatively conclude that only bis(quinoneimine)piperazine form (**5b)** was present in solution. This is very surprising because from the enthalpy consideration, the bis(4-aminophenyl)quinoxaline form (**5**) should be more stable than the other two tautomers since there is a loss of the resonance energies in benzene ring and to lesser extent, piperazine ring in going from the **5** form to the **5a** and **5b** forms. As there are more intermolecular hydrogen bonding sites in **5b** than **5** and **5a**[19] for the interactions with polar aprotic solvents (H-bonding acceptors), the heat of solvation may be able to compensate for the loss in resonance energy and drive the tautomerization process. However, the existence of **5** and **5a** in solution cannot be ruled out completely because tautomerization processes[20] can also be influenced by the nature of the solvent.[21]

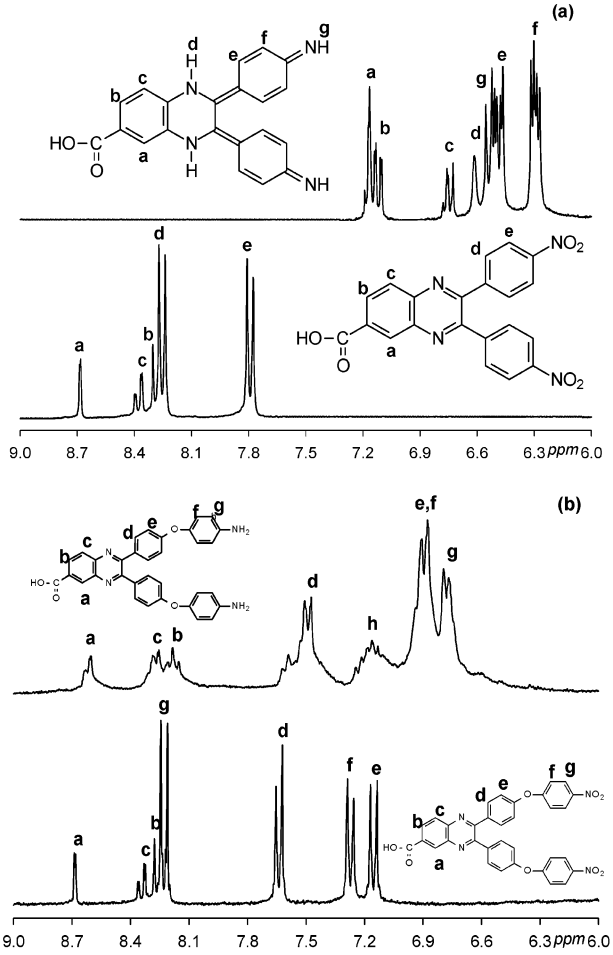


Figure 1. ^{1}H NMR spectra: (a) monomer **5** and its nitro precursor; (b) monomer **9** and its nitro precursor.

Aromatic Hyperbranched Polymers, I, II, and III. The direct polycondensation of the three monomers via the Yamazaki reaction[22] was conducted following literature procedures.[3,23] The hyperbranched aromatic polyamides with the structures for the repeat units of **I**−**III** as shown in Scheme 5, were obtained as white (**I**) or light brown (**II** and **III**) powders from monomers **11**, **5**, and **9**, in that order. It is noteworthy that only polymers **I** and **II** are soluble in polar aprotic solvents, such as DMF, DMAc, NMP, and DMSO, and polymer **III** is not. This precludes the use of **III** in the BMI blends study *(vide infra)*. Therefore, hyperbranched polymer **I,** a known polymer,[3] was prepared for comparison purposes.

As expected (see Table 1), the intrinsic viscosity values for both hyperbranched polymers **I** and **II** are low and fortuitously the same (0.19 dL/g). From differential scanning calorimetry (DSC) experiments, the glass-transition temperature (T_g) of **II** (252 °C) is found to be 35 °C higher than that of **I**. However, no T_g was detected for **III** *from room temperature to 450 °C via either DSC or thermomechnical analysis (TMA)*. The thermal and thermooxidative stabilities of both heteroaromatic hyperbranched polymers (powder samples) were considerably higher (∼142−174 °C in air, and ∼174 °C in helium) than **I** as indicated by temperatures at which a 5% weight losses from thermogravimetric analysis (TGA) experiments. This is consistent with the high thermal stability observed for linear aromatic poly(quinoxaline−amides).[10]

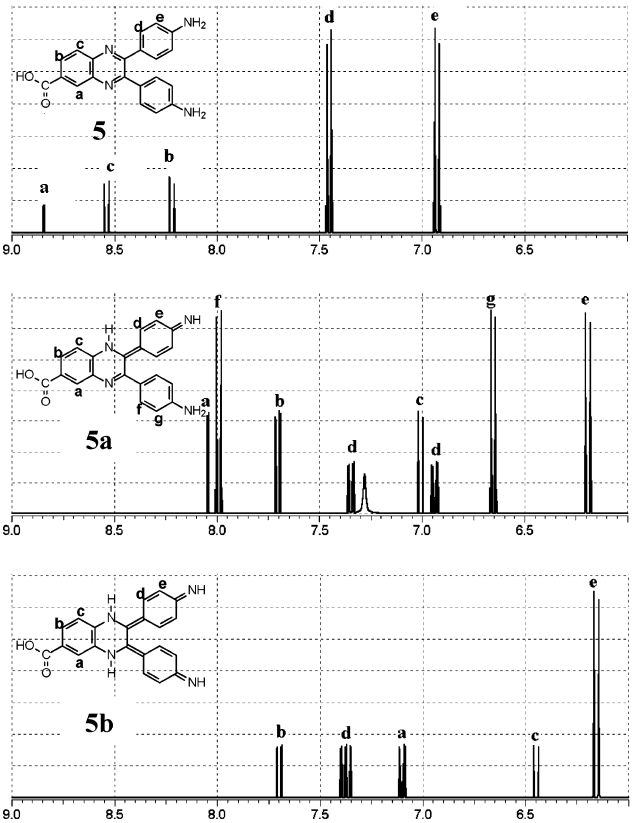
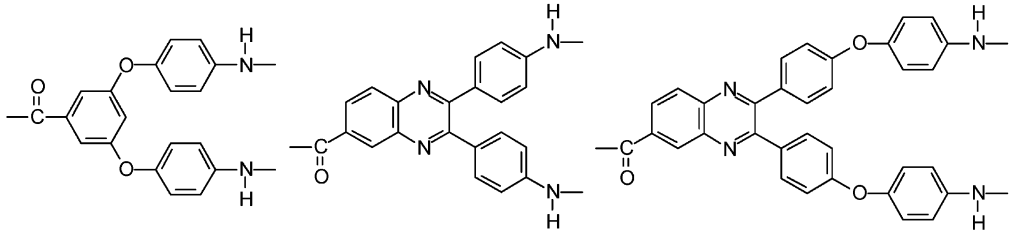


Figure 2. Computer-simulated ^{1}H NMR spectra for the three tautomers for monomer 5: the bis(4-aminophenyl)quinoxaline form, **5** (top), the intermediate form, **5a** (middle), and the bis(quinoneimine)piperazine form, **5b** (bottom). Note that the ACD software program was unable to distinguish the labile protons such as OH and NH.

Hyperbranched Polyamide/BMI Blends. Our initial objective of preparing the hyperbranched polyamides was to investigate their use as reactive additives for high performance thermoset resins such as bismaleimides (BMI) to improve the fracture toughness properties based on the work by Månson et al. that the addition of aliphatic hyperbranched polyesters increased significantly the toughness of epoxy resins.[24] Since the end groups in the ether−amide (**I**) and diphenylquinoxaline−amide (**II**) hyperbranched polymers are amine functions, which can thermally react with maleimide via Michael addition without the generation of volatile byproducts, they were ideal for blends studies. This effort was carried out in parallel with our recently reported work on the blends of a BMI resin with an allyl-terminated hyperbranched poly(arylene−ether−ketone−imide) (**AT-PAEKI**).[25]

We selected 1,1′-(methylenedi-4,1-phenylene)bismaleimide as the BMI component in this study mainly because it is the most common component used in commercially available BMI formulations. Although both hyperbranched polymers **I** and **II** were found to be able to form homogeneous and transparent melts with this BMI at temperatures 160−165 °C, it was more convenient to prepare the blends via solution mixing. Thus, the mixtures of BMI and **I** or **II** were first completely dissolved in NMP and the solvent was then removed under the reduced pressure (1 mmHg) at 100 °C for 200 h. The DSC thermograms were run on powder samples after they had been heated to 200 °C, cooled to 20 °C, heated to 320 °C, cooled to 20 °C, and heated to 320 °C again with heating and cooling rates of 10

Scheme 5. Repeating Units of Amine-Terminated Hyperbranched Polymers



I **II** **III**

Table 1. Intrinsic Viscosities and Thermal Properties of Amine-Terminated Hyperbranched Polymers]

			$T_{d5\%}$ (°C)[c]	
entry	$[\eta]$ (dL/g)[a]	T_g (°C)[b]	in air	in helium
I	0.19	217	360	359
II	0.19	252	502	532
III	insol.[d]	*e*	523	532

[a] Intrinsic viscosity determined in NMP at 30 ± 0.1 °C. [b] Glass transition temperature (T_g) determined by DSC with a heating rate of 10 °C/min. [c] The temperature at which 5% weight loss occurred on TGA thermogram obtained with a heating rate of 10 °C/min. [d] Insoluble in NMP. [e] Not observed.

Table 2. Thermal Properties of BMI and I Blends[a]

I content (wt %)	mp (°C)	ΔH_f (J/g)	T_{exo} (°C)	ΔH_{exo} (J/g)
0.00	161.7	105.1	252.7	−130
0.75	154.0	78.1	261.9	−160
1.50	152.7	83.9	260.4	−205
2.25	150.4	69.6	253.6	−241
3.00	151.7	64.7	248.0	−185
3.75	152.7	64.1	247.3	−157

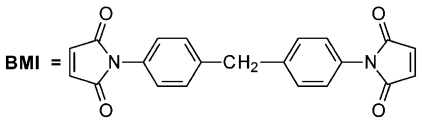
[a] BMI = 

Table 3. Thermal Properties of BMI and II Blends

II content (wt %)	mp (°C)	ΔH_f (J/g)	T_{exo} (°C)	ΔH_{exo} (J/g)
0.00	161.7	105.1	252.7	−130
0.75	139.4	34.0	224.0	−42
1.50	138.4	2.4	*a*	*a*
2.25	133.0	1.3	*a*	*a*
3.00	128.4	1.3	*a*	*a*
3.75	*a*	*a*	*a*	*a*

[a] Not observed.

°C/min. The thermal analysis data are summarized in Tables 2 and 3. In the case of **I**/BMI blends (Table 2 and Figure 3), the melting points (mp) of BMI component decreased approximately 10−12 °C as compared to pure BMI. The heat of fusion (ΔH_f) decreased as content of **I** increased. We observed that the peak temperature (T_{exo}) during curing increased to 262 °C (∼9 °C > pure BMI) and then decreased to 247 °C (∼5 °C < pure BMI) as the hyperbranched polymer **I** content varied from 0.75% to 3.75%. The heats of curing (ΔH_{exo}) were higher at all compositions, indicating that the large numbers of free amine at chain ends indeed reacted with BMI. However, the amount of enthalpy detected during curing also showed a maximum value at relatively low polymer **I** content, 2.25 wt %.

In the case of **II**/BMI blends, both melting points and heat of fusion (ΔH_f) of BMI decreased as hyperbranched polymer **II** content increased (Table 3 and Figure 4). We were surprised to observe that there was a dramatic reduction in the intensity of the cure exotherm (∼31% of ΔH_{exo} BMI) when only 0.75 wt % **II** was present in the blend. Furthermore, at all other compositions, no cure exotherm was detected by DSC as the curing had already taken placed prior to DSC runs. The results were intriguing, as we had expected that the amine functions of **II** to be much less nucleophilic than those of **II** because of the π-accepting nature of quinoxaline. The greatly reduced nucleophilicities of the amino functions of the quinoxaline derivatives, 2,3-bis(4-aminophenyl)quinoxaline and 2,3-bis(4-aminophenyl)-6-methylquinoxaline, were noted when they were investigated as curing agents of epoxy resins. The exotherms on DSC thermograms of the mixtures of the diglycidyl ether of bisphenol A (DGEBA) with them were observed at higher temperatures than that of the mixture of DGEBA with a common aromatic diamine such as 4,4-diaminodiphenyl sulfone.[26]

The aforementioned DSC samples were also subjected to an FT-IR study. The representative infrared spectra are shown in Figure 5. Three important deductions can be drawn from the comparison of these spectra: (i) the spectra of the BMI/**II** (3 wt %) blend taken before and after DSC curing (Figure 5, parts e and f, respectively) are practically identical, confirming the DSC result that this blend sample contained cured BMI without any prior heat treatment; (ii) the spectra of BMI (Figure 5a) and the BMI/**I**(3 wt %) blend (Figure 5c) *before thermal cure* are practically identical, revealing the absence of any chemical reactions (Michael addition and/or radical polymerization) between BMI and **II** at room temperature; (iii) the spectra of BMI and the BMI/**I** blend that were similarly cured under DSC conditions (Figure 5, parts b and d, respectively) as well as the spectra of the BMI/**II** blend (Figure 5, parts e and f) are basically the same, implicating that the chemical structures of the cured BMI in all three samples should resemble one another and have arisen from the same curing mechanism. All these four spectra depicted a characteristic strong broad band centered at 1167−1168 cm^{-1}. This band was assigned to the C−N−C (succinimide ring) stretch; the corresponding C−N−C (maleimide ring) stretch is present as a strong band at 1149 cm^{-1} in the spectrum of uncured BMI.[27] To sum up, the IR results clearly pointed out that (a) the diametrically opposite reactivities of **I** and **II** toward BMI at room temperature, and (b) Michael addition reaction did not occur in both BMI/**I** and BMI/**II** blends at room temperature, strongly implicating the radical polymerization of BMI at room temperature in the presence of **II**.

Finally, for the sake of reproducibility, three vial samples of NMP (1 mL) solutions were prepared con-

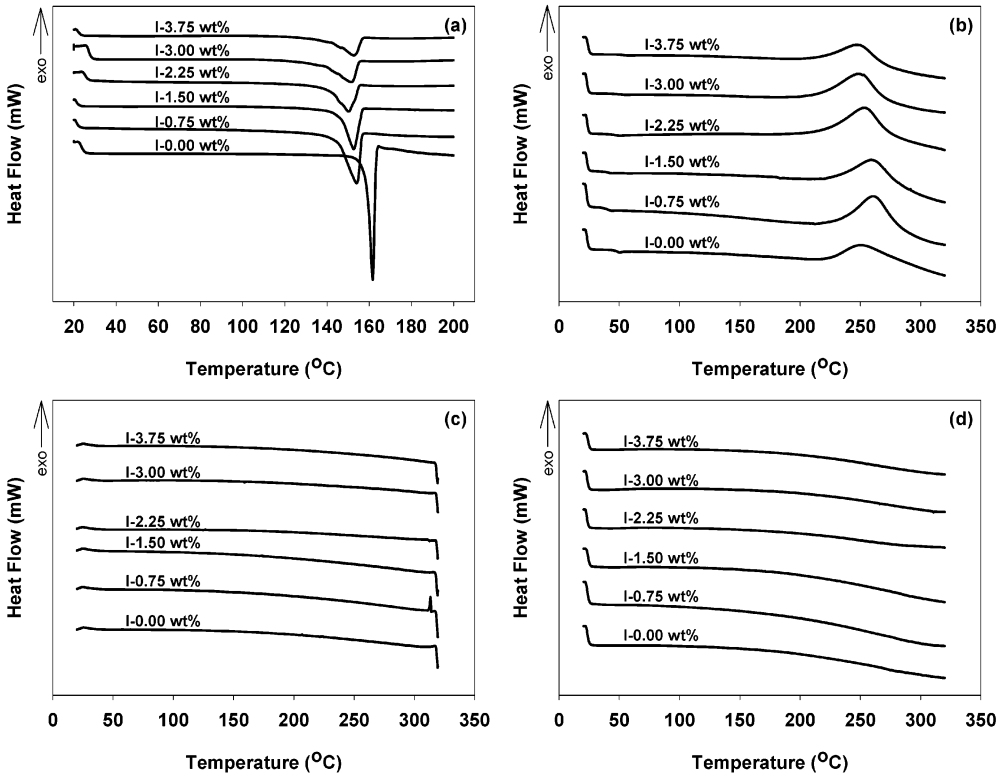


Figure 3. DSC thermograms of a I/BMI blend with heating and cooling rate of 10 °C/min: (a) first heating scan, (b) second heating scan, (c) second cooling scan, and (d) third heating scan.

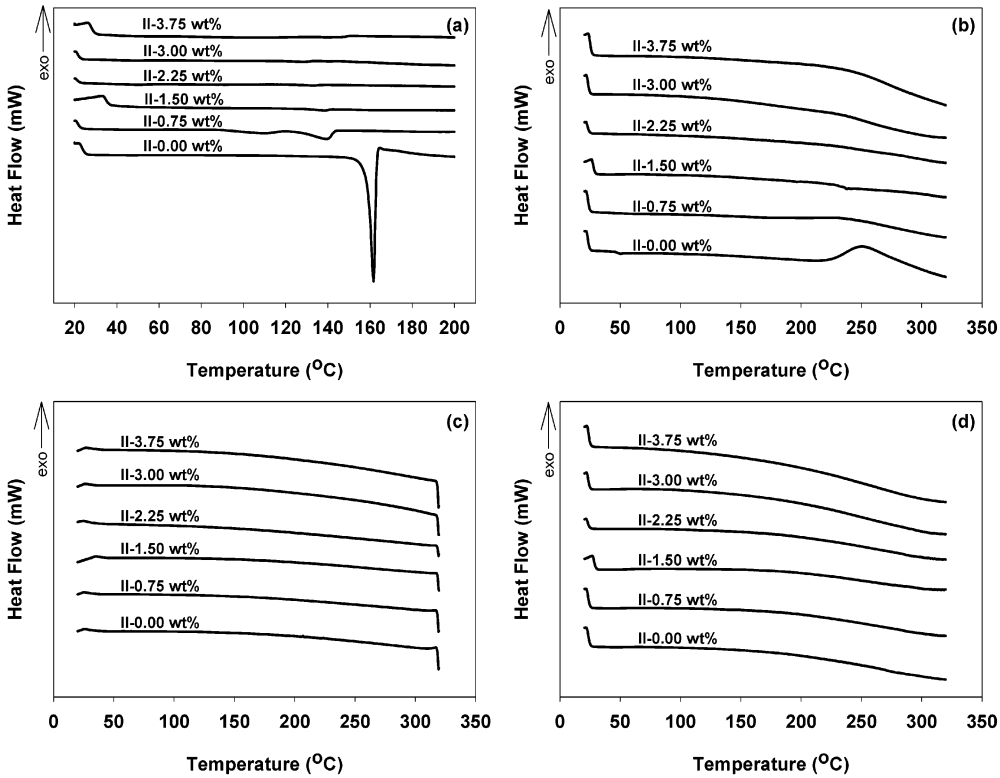


Figure 4. DSC thermograms of a II/BMI blend with heating and cooling rate of 10 °C/min: (a) first heating scan, (b) second heating scan, (c) second cooling scan, and (d) third heating scan.

taining (a) BMI/**II** (200 mg/1.5 mg), (b) BMI/**II** (200 mg/3.0 mg), and (c) **II** (200 mg). The resulting solutions were all clear and (a) orange, (b) yellow-orange, and (c) pink, in that order. They were allowed to stand at room temperature, and several hours later, the solutions a and b were cloudy and insoluble gels started to precipitate from the mixture, indicative of some polymerization reaction under ambient conditions. After 24 h, at the bottom of the vials, both samples a and b formed clear, red gels that remained immobile when the vials were

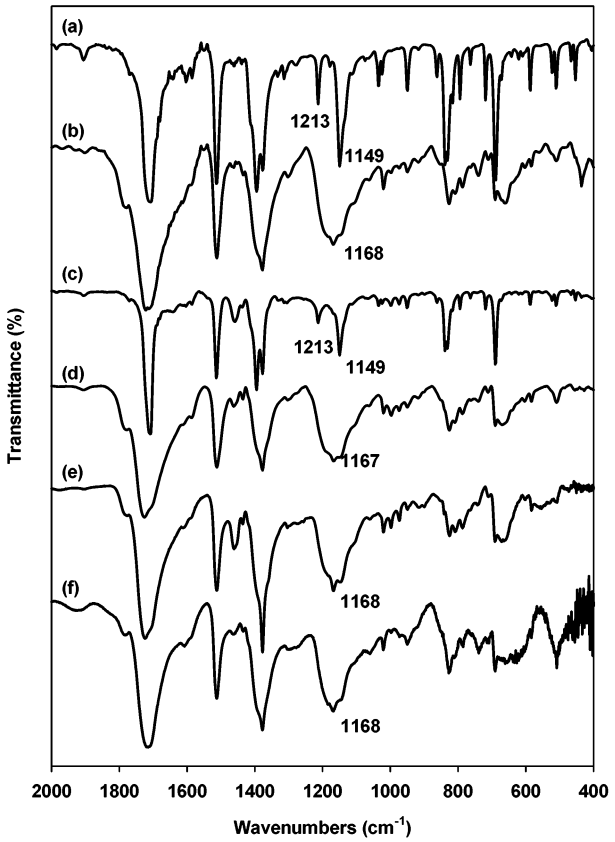


Figure 5. FT-IR (KBr pellet) spectra: (a) pure BMI before thermal cure, (b) BMI after thermal cure, (c) BMI/I (3 wt %) before thermal cure, (d) BMI/I (3 wt %) after thermal cure, (e) BMI/II (3 wt %) before thermal cure, and (f) BMI/II (3 wt %) after thermal cure.

inverted. Sample c, however, was still a pink and clear solution.[28] These observations in conjunction with the results from the DSC and FT-IR studies clearly ruled out Michael addition reaction at room temperature,[29] reaffirming the possibility of free-radical polymerization of BMI promoted by **II**. Indeed, the electron spin resonance (ESR) experiments of **II** and a BMI/**II** blend indicated that active paramagnetic species did appear in **II** and reacted with BMI in solution at room temperature.

To probe the active species that were responsible for initiating the curing of a BMI under ambient conditions, we prepared the following four samples for an electron spin resonance (ESR) study: **I**, **II**, BMI/**I** (3.75 wt %) blend, and BMI/**II** (3.75 wt %) blend. As shown in Figure 6, parts b and d, the sample containing only hyperbranched polymer **I** and the BMI/**I** (3.75 wt %) blend showed almost identical ESR behavior. Since pure BMI is diamagnetic and shows no ESR signal, the signal for both samples must be due to some radical species associated with the hyperbranched polymer **I**. As there are numerous aromatic amine groups present as the end groups of the hyperbranched polymer, the ESR signal is most likely due to the oxidized amines that formed radical cations as in the case of aromatic amine serving as antioxidants. Ostensibly, these radical species are not reactive enough to initiate room-temperature polymerization of BMI. On the other hand, the ESR spectrum for hyperbranched polymer **II** (Figure 6a) suggests the presence of a structurally different radical species in the sample. For the sample BMI/**II** (3.75 wt %) blend, the resulting ESR spectrum (Figure 6c) is distinctly different from that of **II** alone. The existence of a multiplet in the ESR spectrum for **II** is an indication that the radical species in **II** is more mobile than **I** and, therefore, also has a greater probability to hop from **II** to BMI monomer and initiate the polymerization. Unfortunately, the overlap of individual structure elements is too great to allow an exact determination of multiplet detail.[30] A number of possible paramagnetic species present in **II** are shown in Scheme 6.

Conclusion

In summary, we have prepared two new diphenylquinoxaline-containing AB_2 monomers, **5** and **9** and their hyperbranched polyamides, **II** and **III**. Although these AB_2 monomers and their respective hyperbranched polymers are structurally similar except for the presence of a *p*-phenyloxy spacer between the quinoxaline and *p*-aminophenyl groups in **9** and **III**, the physical and chemical properties of both monomers and hyperbranched polymers are noticeably different. In the case of the AB_2 monomers, the observations on their solution behaviors in polar aprotic solvents; i.e., their relative solubilities, colors and ^{1}H NMR spectra suggested that their molecular structures must be distinctly different. Thus, we believe that the tautomerism that exists only for the AB_2 monomer **9** (without the *p*-phenyloxy spacers) is a reasonable explanation. Whereas hyperbranched polymer **II** remained in solution (NMP) throughout the polymerization process, **III** precipitated out of the solution after substantial viscosity buildup and would not redissolve in polar aprotic solvents after the usual workup. This is contrary to our expectation since the presence of *p*-phenyloxy units should make **III** more flexible and soluble than **II**. With the understanding that the nature of myriad end groups collectively control the solubility of the hyperbranched polymer, among other physical properties, it is possible that the intermolecular hydrogen-bonding between the terminal amino group and the quinoxaline units (see Scheme 7) provides the driving force for a large-scale aggregation, which eventually led to the observed precipitation during the polymerization process of **III**. The inability of polar aprotic solvents to penetrate such deeply imbeded H-bonded structures resulted in the observed marginal solubility of **III**[31] In the case of **II**, the predominant bis(iminophenyl)piperazine form of the end groups can interact with polar aprotic solvents which are strong H-bond acceptors. Finally, the results from the blends study indicate that the amine function in conjugation with a phenyloxy group behaves like normal nucleophile and reacts with maleimide via a Michael addition reaction whereas the amine in conjugation with a quinoxaline ring is more prone to be engaged in radical processes. Since tautomerization is an equilibrium process that not only involves the rapid hopping of a proton from one heteroatom to another, the electrons are also moving back and forth. Therefore, we believe that the electrons in the tautomeric segments of hyperbranched polymer **II** is more mobile and susceptible to facile air oxidation to generate stable nitrogen-centered radical-cations. We propose that such radical species are likely to be responsible for the observed room-temperature reactivity toward BMI. Since it is known that quinoxaline derivatives in conjunction with UV light and a tertiary amine could initiate free-radical polymerization of methyl methacrylate,[32] we have yet to consider the photochemical effect in our future work in addition to the unequivocal identification of the respon-

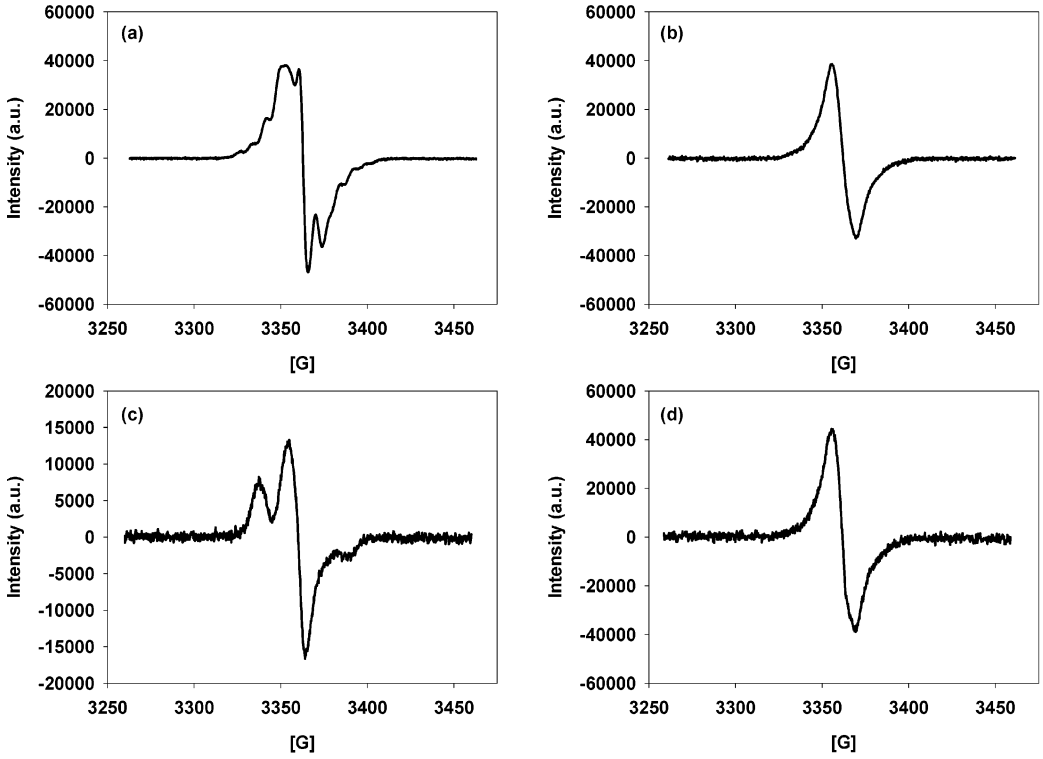
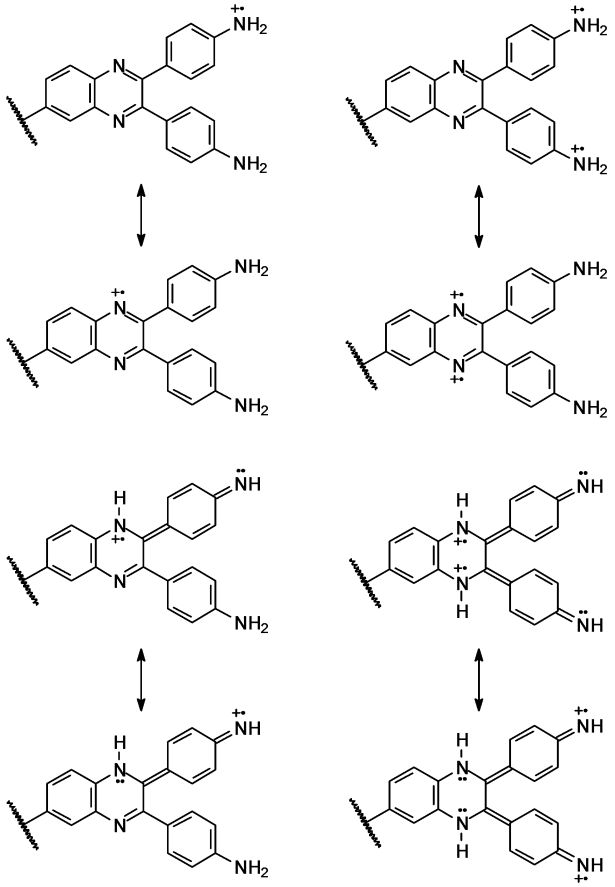
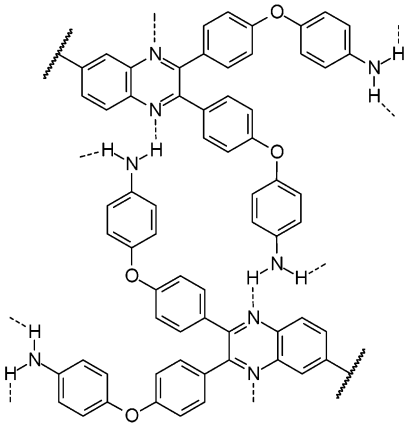


Figure 6. ESR spectra: (a) **II**, (b) **I**, (c) **II** (3.75 wt %)/BMI, and (d) **I** (3.75 wt %)/BMI.

Scheme 6. Molecular Structures of Proposed Cation-Radical (Left Column) and Dication-Radicals (Right Column) and Their Resonance Structures



Scheme 7. Idealized Structure Showing the Interdigitation of Hyperbranched Macromolecules of III via Hydrogen Bonding



sible paramagnetic species. Nonetheless, the unique property of hyperbranched polymer **II** to initiate radical polymerization of BMI[33] has never been observed before and provides an important step in the design and development of nonautoclave, thermally curable thermosetting systems.

Experimental Section

Materials. All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise specified. *N*-Methyl-2-pyrrolidinone (NMP) was distilled under reduced pressure over phosphorus pentoxide. The commercially available AB_2 monomers and 3,5-diaminobenzoic acid (Aldrich Chemical Inc.) were recrystallized from deoxygenated water after treating with charcoal to give white needles for the first two and white flakes for the latter, respectively (mp 238 °C, dec, mp >300 °C, respectively). 1,1′-(Methylenedi-4,1-phenylene)bismaleimide (BMI, Aldrich Chemical Co.) was first purified via column chromatography as described before,[34] followed by recrystallization from ethanol to give yellow crystals (mp 161.7 °C and T_{exo} 252.7 °C, from DSC).

Instrumentations. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR, 270 and 50 MHz, respec-

tively) spectra for the intermediates, monomers, and polymers were obtained on a JEOL-270 spectrometer. Electron spinning resonance (ESR) spectra were obtained from a Bruker EMX instrument. Infrared (FT-IR) spectra were recorded on a Bruker IFS 28 Equinox Fourier transform spectrophotometer. Elemental analysis and mass spectral analysis were performed by the System Supports Branch, Air Force Research Lab, Dayton, OH. The melting points (mp) of all the compounds were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 150 viscometers. Flow times were recorded for *N*-methyl-2-pyrrolidinone (NMP) solution containing 1% lithium bromide and polymer solutions with concentrations of approximately 0.5−0.10 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) analyses were performed in nitrogen at a heating rate of 10 °C/min using a Perkin-Elmer model 2000 thermal analyzer equipped with 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. Thermomechamical analysis (TMA) was conducted in helium with heating rate of 4 °C/min in nitrogen. Sample **III,** which was not consolidated at oven temperatures up to 240 °C, was compressed with a hydraulic press at a ram force of 40 000 lbs.

2-Benzoyloxy-2-(4-nitrophenyl)acetonitrile (Cyano(4-nitrophenyl)methyl benzoate, 1). In a 500 mL three-necked round-bottomed flask equipped with a magnetic stirbar and nitrogen inlet were dissolved 4-nitrobenzaldehyde (50.0 g, 331 mmol) and benzoyl chloride (50 mL) in dichloromethane (50 mL). Potassium cyanide (33.0 g, 507 mmol) in water (100 mL) was added dropwise at an ice-bath temperature. Triethylbenzylammonium chloride (**TEBA**, 2.5 g) was added, and this two-phase system was stirred for 24 h at room temperature. The organic layer was diluted with dichloromethane (100 mL), separated, washed with aqueous sodium bicarbonate, and dried over magnesium sulfate. Solvent was completely removed from the CH_2Cl_2 extract, and the resulting light orange residue was dissolved in warm ethanol and cooled to room temperature to give 65.4 g (70% yield) of off-white crystals: mp 114−116 °C (lit. mp 116−117.5 °C). Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.92; O, 22.67. Found: C, 63.96; H, 3.62; N, 9.42; O, 23.71: FT-IR (KBr, cm^{-1}): 1733, 2923. Mass spectrum (*m*/*e*): 282 (M^+, 100% relative abundance), 255, 225, 105. ^{1}H NMR ($CDCl_3$, ppm): δ 6.79 (s, 1H, CH), 7.47−7.53 (t, 2H, Ar), 7.63−7.66 (t, 1H, Ar), 7.82−7.75 (dd, 2H, Ar), 8.06−8.09 (dd, 2H, Ar), 8.33−8.36 (dd, 2H, Ar). ^{13}C NMR ($CDCl_3$, ppm): δ 62.23, 115.25, 124.12, 127.46, 128.87, 130.16, 134.57, 138.28, 149.03, 164.32.

2-Benzoyloxy-1,2-bis(4-nitrophenyl)ethanone (2). In a 1000 mL three-necked, round-bottomed flask equipped with a magnetic stirbar and nitrogen inlet, 2-benzoyloxy-2-(4-nitrophenyl)acetonitrile (42.0 g, 149 mmol) in benzene (450 mL) were stirred 10% sodium hydroxide (30 mL) and TEBA (2.2 mg) for 10 min under the nitrogen. Then, 4-nitrobenzaldehyde (22.52 g, 149 mmol) in benzene (100 mL) was added at ice-bath temperature and the resulting mixture was stirred for 4 h at room temperature. The organic layer was separated, washed with water, and dried over magnesium sulfate. Solvent was removed to dryness and the residue dissolved in ethanol and cooled to room temperature to give 69.6 g (77% yield) of off-white crystals: mp 131−133 °C (lit. mp 132−134 °C). Anal. Calcd for $C_{21}H_{14}N_2O_7$: C, 62.07; H, 3.47; N, 6.89. Found: C, 62.26; H, 3.36; N, 6.77. FT-IR (KBr, cm^{-1}): 1701, 1720. Mass spectrum (*m*/*e*): 406, 150 (M^+, 1% relative abundance).

4,4′-Dinitrobenzil (1,2-Bis(4-dinitrophenyl)ethane-1,2-dione, 3). In a 500 mL three-necked, round-bottomed flask equipped with a magnetic stirbar, dropping funnel, and nitrogen inlet was dissolved 2-benzoyloxy-1,2-bis(4-nitrophenyl)-ethanone (15.0 g, 36.9 mmol) in DMSO (150 mL) and stirred until the solution become homogeneous. Then, hydrobromic acid (48%, 50 mL) was added through dropping funnel and the reaction stirred at 60 °C. During this process the light yellow crystals were isolated. After cooled, the crystals were collected by suction filtration to give 10.1 g (91% yield) of yellow crystals: mp 211−212 °C. Anal. Calcd for $C_{21}H_{12}N_4O_6$: C, 56.01; H, 2.69; N, 9.33; O, 31.97. Found: C, 55.75; H, 2.50; N, 9.30; O, 33.98. FT-IR (KBr, cm^{-1}): 1347, 1527, 1682. Mass spectrum (*m*/*e*): 282 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 8.27−8.30 (dd, 4H, Ar), 8.41−8.44 (dd, 4H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 123.94, 131.66, 136.81, 150.75, 190.06.

2,3-Bis(4-nitrophenyl)quinoxaline-6-carboxylic acid (4). In a 250 mL three-necked round-bottomed flask equipped with a magnetic stirbar, a condenser, and nitrogen inlet were dissolved 4,4′-dinitrobenzil (8.2 g, 27,3 mmol) and 3,4-diaminobenzoic acid (4.4 g, 28.9 mmol) in acetic acid (100 mL) and heated under reflux for 12 h. After being cooled to room temperature, the dark red solution was filtered, and the filtrate was poured into 5% hydrochloric acid. The resulting precipitate was collected by suction filtration and then air-dried overnight to give 11.1 g (98% yield) of an off-white powder: mp 287−289 °C. Anal. Calcd for $C_{21}H_{12}N4O_6$: C, 60.58; H, 2.91; N, 13.46; O, 23.06. Found: C, 60.25; H, 3.10; N, 13.12; O, 24.84. FT-IR (KBr, cm^{-1}): 1521, 1670. Mass spectrum (*m*/*e*): 419 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 7.78−7.81 (d, 4H, Ar), 8.24−8.27 (d, 4H, Ar), 8.30 (s, 1H, Ar), 8.36−8.37 (d, 1H, Ar), 8.39−8.40 (d, 1H, Ar), 8.68−8.69 (d, 1H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 123.34, 129.44, 130.31, 130.74, 131.29, 139.81, 142.31, 144.04, 147.61, 147.67, 152.16, 152.80, 166.27, 171.89.

2,3-Bis(4-aminophenyl)quinoxaline-6-carboxylic acid (5). Into a 500 mL high-pressure bottle were charged 2,3-bis-(4-nitrophenyl)quinoxaline-6-carboxylic acid (8.0 g, 19 mmol), palladium on activated carbon (10%, 0.5 g), and mixture of ethanol (100 mL) and acetone (50 mL). The bottle was placed on a hydrogenator. It was then subjected to five cycles of charging and discharging hydrogen gas and agitated at 60−65 psi for 24 h. After the resulting mixture had been filtered through Celite 545 to remove the catalyst, the solvent was removed on a rotary evaporator. The gray solid was slurred in deoxygenated 2-propanol and collected by suction filtration to give 5.2 g (76.5% yield) of orange powder: mp = 187−195 °C. DSC showed three broad melting endotherms centered at 181, 199, and 216 °C and a strong endotherm centered at 240 °C). The polymorphoism of quinoxaline derivatives with multiple substitutents is not uncommon.[8b] Anal. Calcd for $C_{21}H_{16}N_4O_2$: C, 70.78; H, 4.53; N, 15.72; O, 8.98. Found: C, 69.26; H, 5.78; N, 13.86; O, 10.50. FT-IR (KBr, cm^{-1}): 1670, 3356. Mass spectrum (*m*/*e*): 358, 360 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 6.29−6.33 (dd, 4H, Ar), 6.48−6.56 (m, 4H, Ar), 6.62−6.76 (m, 1H, Ar), 7.10−7.18 (m, 2H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 57.19, 58.23, 110.87, 112.83, 112.97, 113.78, 115.10, 117.41, 118.67, 120.20, 128.20, 128.38, 128.72, 129.24, 132.70, 138.51, 146.72, 146.81, 157.17, 167.92.

2,3-Bis(4-methoxyphenyl)quinoxaline-6-carboxylic acid (6). In a 500 mL three-necked, round-bottomed flask equipped with a magnetic stirbar, nitrogen inlet, and a condenser was completely dissolved 3,4-diaminobenzoic acid (14.2 g, 93.4 mmol) in acetic acid (300 mL). 4,4′-Dimethoxybenzol (25.0 g, 92. mmol) was then added, and the reaction mixture was heated under reflux for 8 h. While the red-brown mixture was allowed to cool on its own, light orange needles separated from the mother liquid; 34.8 g (97% crude yield, mp 295−297 °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, 4.45; N, 6.96. FT-IR (KBr, cm^{-1}): 1693. Mass spectrum (*m*/*e*): 386 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 3.80 (s, 6H, CH_3), 6.93−6.96 (d, 4H, Ar), 7.45−7.49 (dd, 4H, Ar), 8.12−8.15 (d, 1H, Ar), 8.22−8.26 (dd, 1H, Ar), 8.58−8.59 (d, 1H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 55.12, 113.55, 128.92, 130.48, 130.74, 131.08, 131.17, 131.52, 139.41, 142.11, 153.49, 154.09, 159.88, 159.97, 166.59.

2,3-Bis(4-hydroxyphenyl)quinoxaline-6-carboxylic acid (7). In a 1000 mL three-necked round-bottomed flask equipped with a magnetic stirbar, nitrogen inlet, and a condenser, was dissolved 2,3-bis(4-methoxyphenyl)quinoxaline-6-carboxylic acid (34.7 g, 89.8 mmol) in acetic acid (260 mL). Hydrobromic acid (500 mL) was then added to the clear, yellow mixture at room temperature. The reaction mixture was heated under reflux

with vigorous stirring until the solution become homogeneous. It took about 6 h. After the red-brown mixture was allowed to cool on its own, it was poured into distilled water. The resulting light brown precipitate was collected by suction filtration and dried under reduced pressure to give 31.9 g (99% crude yield) of yellow solid: mp 319−320 °C dec. Anal. Calcd for $C_{21}H_{14}N_2O_4$: C, 70.38; H, 3.94; N, 7.82. Found: C, 66.70; H, 3.98; N, 7.20. FT-IR (KBr, cm^{-1}): 1698, 3396. Mass spectrum (*m*/*e*): 358 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 6.76−6.79 (d, 4H, Ar), 7.36−7.40 (dd, 4H, Ar), 8.09−8.12 (d, 1H, Ar), 8.21−8.25 (dd, 1H, Ar), 8.57 (d, 1H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 114.93, 128.84, 129.21, 130.34, 131.11, 131.52, 139.32, 142.03, 153.75, 154.35, 158.44, 166.68.

2,3-Bis(4-nitrophenyloxyphenyl)quinoxaline-6-carboxylic acid (8). Into a 250 mL three-necked round-bottomed flask equipped with a magnetic stirbar, nitrogen inlet, and a condenser were placed 4-fluoronitrobenzene (8.3 g, 57 mmol), 2,3-bis(4-hydroxyphenyl)quinoxaline-6-carboxylic acid (10.0 g, 28 mmol), potassium carbonate (14.0 g, 100 mmol), and a mixture of NMP (110 mL) and toluene (60 mL). The reaction mixture was then heated and maintained around 140 °C for 8 h with vigorous nitrogen flow. The dark solution was filtered while it was warm, and the filtrate was poured into distilled water containing 5% hydrochloric acid. The resulting precipitates were collected by suction filtration and then air-dried overnight. Bright yellow crude product was boiled in acetic acid and filtered while hot to afford 16.4 g (98% yield) of light yellow powder: mp 252−254 °C. Anal. Calcd for $C_{33}H_{20}N_4O_8$: C, 66.00; H, 3.36; N, 9.33; O, 21.31. Found: C, 65.72; H, 3.55; N, 9.24; O, 21.37. FT-IR (KBr, cm^{-1}): 1586, 1701. Mass spectrum (*m*/*e*): 600 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 7.13−7.18 (d, 4H, Ar), 7.26−7.29 (d, 4H, Ar), 7.62−7.65 (d, 4H, Ar), 8.21−8.24 (dd, 4H, Ar), 8.28 (s, 1H, Ar), 8.32−8.36 (dd, 1H, Ar), 8.68−8.69 (d, 1H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 117.58, 120.11, 126.13, 129.21, 132.12, 132.24, 135.29, 142.34, 153.40, 154.04, 154.96, 155.04, 162.39, 166.45.

2,3-Bis(4-aminophenyloxyphenyl)quinoxaline-6-carboxylic acid (9). Into a 500 mL high-pressure bottle were added 2,3-bis(4-nitrophenoxyphenyl)quinoxaline-6-carboxylic acid (13.3 g, 22.1 mmol), 10% palladium on activated carbon (0.5 g), and a mixture of ethanol (150 mL) and acetone (150 mL). The bottle was placed on a hydrogenator. It was subjected to five cycles of charging and discharging with hydrogen gas. The reaction mixture was then agitated mechanically at 60−65 psi for 24 h. After the resulting mixture had been filtered through Celite 545 to remove the catalyst, the solvent was removed on a rotary evaporator. The yellow solid was poured into deoxygenated water. The resulting precipitate was collected to give 10.65 g (83.7% yield) of light yellow solids: mp 184.5 °C dec. Anal. Calcd for $C_{33}H_{24}N_4O_4$: C, 73.32; H, 4.47; N, 10.36; O, 11.84. Found: C, 72.98; H, 4.60; N, 9.52; O, 12.05. FT-IR (KBr, cm^{-1}): 1705, 3373. Mass spectrum (*m*/*e*): 540 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 6.77−6.80 (d, 4H, Ar), 6.88−6.91 (d, 8H, Ar), 7.48−7.51 (d, 4H, Ar), 8.25−8.28 (d, 1H, Ar), 8.29 (s, 1H, Ar), 8.60 (s, 1H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 48.38, 116.11, 116.22, 116.60, 116.71, 116.86, 116.94, 118.85, 120.80, 120.89, 121.03, 129.24, 131.43, 131.75, 131.92, 142.14, 166.50.

3,5-Bis(4-nitrophenyloxy)benzoic acid (10). Into a 500 mL three-necked round-bottomed flask equipped with a magnetic stirbar, nitrogen inlet, and a condenser were placed 4-fluoronitrobenzene (30.0 g, 0.21 mol), 3,5-dihydroxybenzoic acid (15.4 g, 0.10 mol), potassium carbonate (50.0 g, 0.36 mol), and NMP (250 mL). The reaction mixture was then heated and maintained between 120 and 140 °C for 8 h. The dark solution was filtered while it was still warm, and the filtrate was poured into distilled water containing 5% hydrochloric acid. The resulting precipitate was collected by suction filtration and then air-dried overnight. The crude product was recrystallized from hot acetic acid to afford 39.6 g (91% yield) of brown crystals: mp 228−229 °C. Anal. Calcd for $C_{19}H_{12}N_2O_8$: C, 57.58; H, 3.05; N, 7.07; O, 32.30. Found: C, 57.45; H, 2.74; N, 6.96; O, 33.46. FT-IR (KBr, cm^{-1}): 1105, 1350, 1454, 1625. Mass spectrum (*m*/*e*): 396 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 7.29−7.34 (d, 4H, Ar), 7.38−7.40 (t, 1H, Ar), 7.50−7.51 (s, 2H, Ar), and 8.26−8.32 (d, 4H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 116.67, 118.38, 126.19, 134.77, 142.98, 156.22, 161.67, 165.58.

3,5-Bis(4-aminophenyloxy)benzoic acid (11). Into a 500 mL high-pressure bottle were added 3,5-bis(4-nitrophenyloxy)-benzoic acid (15.0 g, 38 mmol), 10% palladium on activated carbon (0.5 g), and a mixture of ethanol (150 mL) and acetone (50 mL). The bottle was placed on the hydrogenation vessel. It was then subjected to five cycles of charging and discharging hydrogen gas and agitated at 60−65 psi for 24 h. After the resulting mixture had been filtered through Celite 545 to remove the catalyst, the solvent was removed on a rotary evaporator. The orange residue was recrystallized from deoxygenated 90% 2-propanol to give 10.65 g (83.7% yield) of brown crystals: mp 228−230 °C (free amine, dec), 245 °C (dihydrochloric acid salt, dec). Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33; O, 19.03. Found: C, 66.44; H, 6.25; N, 6.97; O, 19.70. FT-IR (KBr, cm^{-1}): 1594, 3412. Mass spectrum (*m*/*e*): 336 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 6.63−6.67 (d, 4H, Ar), 6.69−6.71 (t, 1H, Ar), 6.81−6.87 (d, 4H, Ar), 6.97−6.98 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6, ppm): δ 108.88, 109.54, 114.90, 121.29, 133.04, 144.59, 145.91, 160.43, 166.45.

2,3-Diphenylquinoxaline-6-carboxylic acid (12). In a 500 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet was dissolved 3,4-diaminobenzoic acid (16.0 g, 105 mmol) 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 fell out of the solution. After the reaction mixture had been allowed to cool, the precipitate was collected to give 32.2 g (99% yield) of the 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, 8.52; O, 9.63. FT-IR (KBr, cm^{-1}): 696, 1691, 2922, 2958, 3400. Mass spectrum (*m*/*e*): 326 (M^+, 100% relative abundance). ^{1}H NMR (DMSO-d_6, ppm): δ 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, ppm): δ 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.

Hyperbranched Polyamide Derived from 3,5-Bis(4-aminophenyloxy)benzoic Acid (I). Into a 100 mL three-necked round-bottomed flask equipped with a magnetic stirbar, nitrogen inlet, and a reflux condenser were placed 3,5-bis(4-aminophenyloxy)benzoic acid (3.0 g., 8.9 mmol), triphenyl phosphite (7 mL), pyridine (5 mL), and freshly distilled *N*-methyl-2-pyrrolidinone (40 mL), and the reaction mixture was heated to 80 °C and maintained at this temperature for 12 h. After the dark brown, homogeneous mixture had been allowed to cool to room temperature, it was poured into a deoxygenated mixture of methanol and acetic acid (1/1, v/v). The resulting white precipitate was collected by suction filtration and dried under reduced pressure (1 mmHg) at 100 °C for 200 h.

Hyperbranched Polyamide Derived from 2,3-Bis(4-aminophenyl)quinoxaline-6-carboxylic Acid (II). This was prepared and worked up similarly as above from a mixture of 2,3-bis(4-aminophenyl)quinoxaline-6-carboxylic acid (3.0 g, 8.4 mmol), triphenyl phosphite (7 mL), pyridine (5 mL), and freshly distilled *N*-methyl-2-pyrrolidinone (40 mL).

Hyperbranched Polyamide derived from 2,3-Bis(4-aminophenyloxyphenyl)quinoxaline-6-carboxylic Acid (III). This was prepared and worked up similarly as above from a mixture of 2,3-bis(4-aminophenyloxyphenyl)quinoxaline-6-carboxylic acid (4.5 g, 8.3 mmol), triphenyl phosphite (7 mL), pyridine (5 mL), and freshly distilled *N*-methyl-2-pyrrolidinone (40 mL). However, 2.5 h after the reaction mixture was heated at 80 °C, the solution viscosity built up drastically, and the mixture became heterogeneous due to some precipitation. Although stirring such a viscous reaction

mixture had become inefficient, the heterogeneous mixture was maintained at 80 °C overnight (~12 h). After the very viscous mixture had been allowed to cool to room temperature, it was poured into a deoxygenated mixture of methanol and acetic acid (1/1, v/v). The resulting white precipitate was collected by suction filtration and dried under reduced pressure (1 mmHg) at 100 °C for 200 h. The insolubility of this hyperbranched polymer in common organic solvents and strong acid such as methanesulfonic acid (MSA) precluded the viscosity determination.

General Procedure for the Preparation of BMI Blends. The hyperbranched polyamides (**I** or **II**) was dissolved in NMP (1 wt %) and filtered. Exact weight of the filtrate (stock solution) was added into sample vials containing preweighted BMI, and the resulting mixtures were agitated until the solutions became homogeneous. The content of **I** or **II** in the blends were varied from 0 to 3.75 wt % in both series of the blends. The solvent from each of the blend/NMP solutions was removed under reduced pressure (1 mmHg) for 1 week at 100 °C. The solvent residue was monitored by FT-IR to ensure that none was present in the samples before thermal characterization (see Tables 2 and 3). This was confirmed by thermogravemetric analysis results.

Preparation of ESR Samples. The blend samples (from the above preparation) were ball-milled as fine mesh as possible and packed into ESR glass sample tubes and dried under reduced pressure (1 mmHg) at 100 °C for 24 h. The tubes were filled with nitrogen and then sealed with a torch.

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Supporting Information Available: A color photograph showing the three sample vials containing NMP (1 mL) solutions, (a) **II**/BMI (1.5 mg/200 mg), (b) **II**/BMI (3.0 mg/200 mg), and (c) **II** (200 mg), after they had been allowed to stand under room conditions for 24 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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