Heterocycle-Activated Aromatic Nucleophilic Substitution of AB_2 Poly(aryl ether phenylquinoxaline) Monomers. 3

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Poly(aryl ether)s and related polymers comprise a class of materials known as engineering thermoplastics which possess desirable properties including melt and solution processability, high T_g (glass transition temperature), and good mechanical properties. It has been demonstrated that nucleophilic aromatic substitution reactions between activated bishaloaromatic and bisphenol monomers can lead to such (A_2B_2) aryl ether polymers, and commercial examples include polysulfone (UDEL, Amoco) and poly(ether ether ketone) (PEEK, ICI). In these polymerizations the aryl halide is activated toward substitution by an electron-withdrawing group (i.e., sulfone or ketone) which lowers the electron density at the site of substitution and also stabilizes the transition state once substitution has occurred.[1,2] Certain heterocycles function similarly, and reports of the use of these nonconventional activating groups in polymer-forming reactions have appeared recently.[3]

Miller and co-workers,[4] as well as Chu and Hawker,[5] have described the synthesis of hyperbranched analogues of poly(aryl ether)s. A variety of AB_2 monomers were prepared which contain a single phenol group and a pair of aryl fluorides which are activated toward displacement by either a carbonyl or sulfone group. The polymerizations of these AB_2 monomers were carried out in aprotic dipolar solvents containing base, and high molecular weight polymers with low dispersities and T_g's ranging from 135 to 231 °C were obtained.

It is of obvious interest to extend this synthesis of hyperbranched poly(aryl ethers) to heterocycle-activated systems. The quinoxaline heterocycle is particularly well-suited for this application since the appropriately substituted monomers are readily prepared and the quinoxaline possesses significant activation capability. It has been demonstrated in earlier polymerizations with AA and BB monomer pairs that the 6- and 7-positions of a quinoxaline heterocycle as well as the para positions of both the 2-phenyl and 3-phenyl groups of 2,3-diphenylquinoxaline are activated.[6,7] Furthermore, the quinoxaline-activated polyether synthesis has been extended to the self-polymerization of an AB monomer.[8,9] High molecular weight linear poly(aryl ether phenylquinoxaline)s have been prepared by each synthetic pathway by the polymerization of appropriately substituted aryl fluorides containing preformed quinoxaline heterocycles with a variety of bisphenols. The AB_2 quinoxaline monomer synthesis involves condensation of a bisphenol-substituted benzil and a fluoro-substituted o-phenylenediamine (Scheme 1).[10,11] The requisite bisphenolic benzil is itself easily prepared by aromatic nucleophilic substitution on 4,4′-difluorobenzil. For this study, AB_2 monomers (**1** and **2**) containing a single aryl fluoride and two phenolic hydroxyl groups were prepared and polymerized to give hyperbranched quinoxaline containing poly(aryl ether)s.

The self-polymerization of the quinoxaline AB_2 monomers (**1** and **2**) was carried out in *N*-methylpyrrolidinone (NMP) containing potassium carbonate (Scheme 2).[12] The potassium carbonate was used to convert the bisphenol into the more reactive bisphenoxide, and since potassium carbonate is a relatively weak and non-nucleophilic base, no hydrolytic side reactions with the 2,3-bis(4-fluorophenyl)quinoxalines were observed. As for the case of almost all poly(aryl ether) syntheses, dipolar aprotic solvents were used since they effectively solvate the monomers, polar intermediates, and, in most cases, the subsequent polymer. For this investigation, we examined several solvent systems: NMP, NMP/CHP (*N*-cyclohexyl-2-pyrrolidone) (50/50) mixture, and DMPU (*N*,*N*′-dimethylpropyleneurea).[13] Although NMP tends to be a better solvent and easier to handle, NMP/CHP solvent mixtures are often used since CHP is not miscible with water at temperature above 100 °C. Thus, nonpolar cosolvents used to azeotrope the water generated during the polymerization are not required. On the other hand, DMPU has been shown to be an excellent solvent for polyether syntheses and, in particular, for those polymers which are only marginally soluble in other aprotic dipolar solvents.[13] Furthermore, DMPU allows high reaction temperatures (260 °C). As in the case for most poly(aryl ether) syntheses, the solid compositions were maintained at 20% to avoid side reactions with fluoride ion.[14] Irrespective of the polymerization solvent(s), toluene was used during the initial stages of the polymerizations to remove water generated by bisphenoxide formation. This solvent mixture gave a reflux temperature between 150 and 165 °C. In an effort to maintain a dry system, the toluene was periodically removed through the Dean−Stark trap and replaced with deoxygenated dry toluene. Upon completion of bisphenoxide formation and dehydration, the polymerization mixtures were heated to 180−220 °C to effect the displacement reaction. In each case, high molecular weight polymer was attained within 48 h as judged by the dramatic increase in viscosity. The polymers were isolated by precipitation into a 10-fold excess of methanol and boiled in water to remove the remaining salts.

This general procedure was applied to each of the AB_2 monomers (**1** and **2**), yielding polymers **3** and **4**, respectively. It appears that moderately high molecular weight polymer was achieved in each case as indicated by the intrinsic viscosity measurements (Chart 1). Monomer **1** was polymerized in a NMP/CHP solvent mixture or in NMP containing potassium carbonate. The polymer remained soluble throughout the polymerization, affording moderately high viscosity. The T_g of the resulting branched poly(aryl ether phenylquinoxaline) was comparable to those of its linear analogues (190 °C). In contrast to many heterocycle-containing polymers, poly(aryl ether phenylquinoxaline) was soluble in NMP, a solvent commonly used for polymer processing in the microelectronics industry. The resulting polymer was capable of film formation; however, the film was somewhat brittle. Polymerization of monomer **2** in NMP/CHP appeared to have limited solubility for the desired solids composition at 190 °C, whereas polymerization in DMPU proceeded readily to afford polymer **4**. There is a considerable difference in the molecular weight of the polymers, as judged by intrinsic viscosity measurements, as a result of the polymerization being performed in different solvents, and this presumably results from the improved polymer solubility in DMPU.

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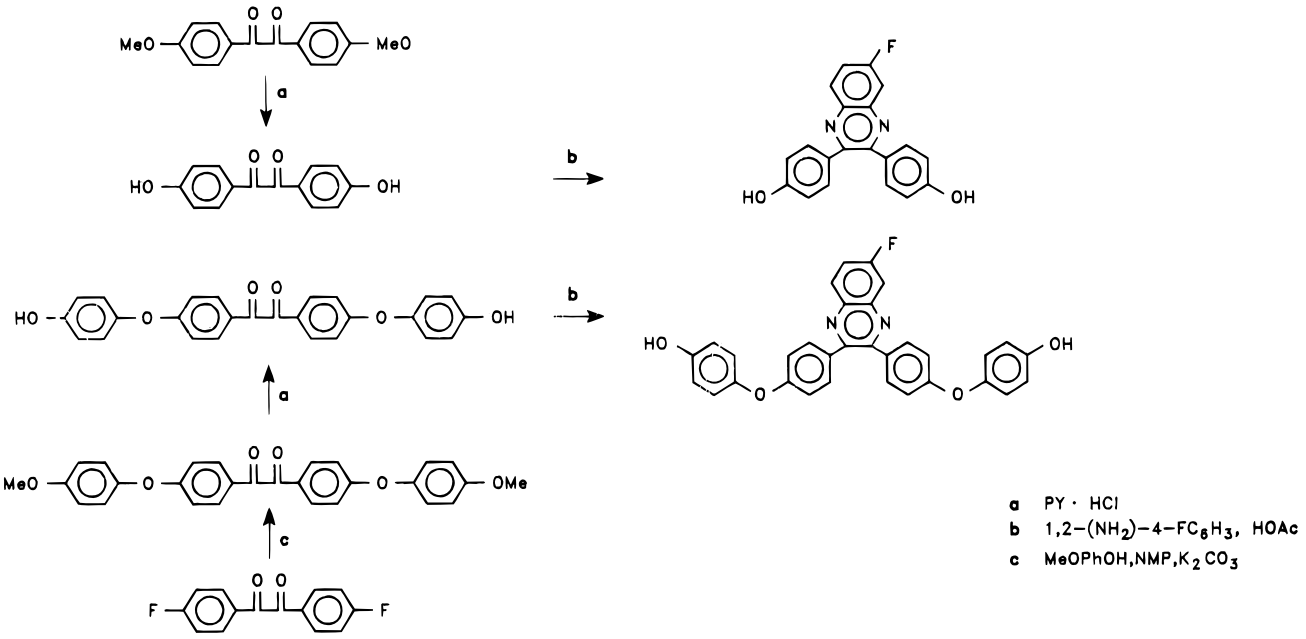
Scheme 1



Scheme 2

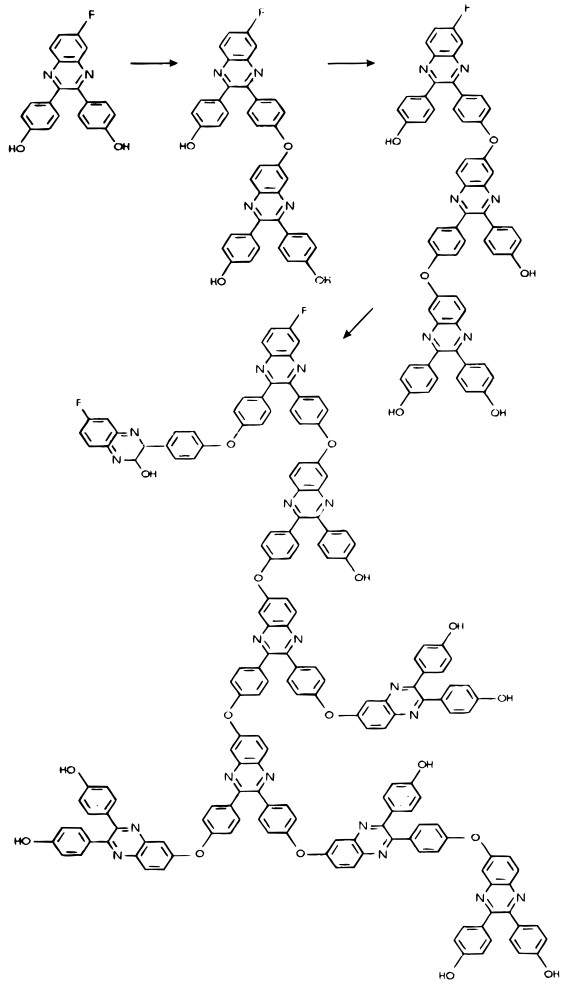
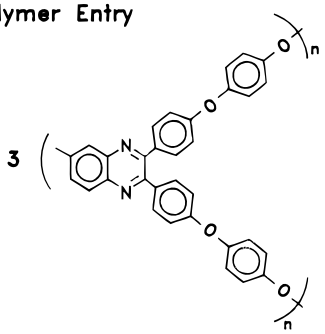
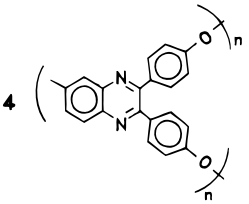


Chart 1

Polymer	Entry	$[\eta]$ NMP 25 °C dL/g	Tg, °C
	3	0.47	190
	4	0.55	255

The presence, or absence, of the unique focal point group in hyperbranched macromolecules has recently been investigated by several authors.[15,16] In the above systems, a single fluoro group at the focal point of the hyperbranched macromolecule should be present if no intramolecular cyclization occurs. To investigate this point, the MALDI-TOF mass spectrum of the hyperbranched macromolecule **4** was examined. As shown in Figure 1, a sequence of peaks separated by 516 amu (which correlates with the repeat unit molecular weight) was observed. However, the mass value of each peak is 20 amu lower than that expected; this value of 20 amu correlated with loss of HF, which would occur if intramolecular ring closure is occurring, leading to loss of the unique fluoro group at the focal point group. This absence of a focal point group was supported by examination of the ^{1}H NMR spectra, which revealed no resonance in the expected region for the proton ortho (PTO) to the fluoro group at the focal point. From these results, it can be concluded that intramolecular ring closure, leading to loss of the focal point group, is a dominant process in the synthesis of these hyperbranched poly(aryl ether phenylquinoxaline)s.

These results represent one of the first examples of a hyperbranched heterocycle containing poly(aryl ether)s. The quinoxaline-based poly(aryl ether)s were synthesized from AB_2 monomers via a fluoro-displacement polymerization, where the fused pyrazine ring was the activating group. The polymerization provides a general

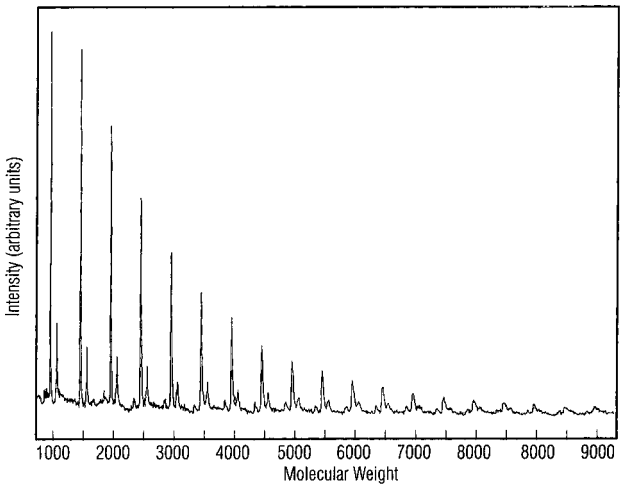


Figure 1. The MALDI-TOF mass spectra of poly(aryl ether phenylquinoxalines).

method for the preparation of poly(aryl ether phenylquinoxaline)s, where the polymer structure can be varied with the AB_2 monomer used. Furthermore, the heterocycle-activated nucleophilic substitution reaction should be effective with AB_2 monomers derived from other ring systems (i.e., benzoxazoles, benzothiazoles, triazoles). Future work will focus on demonstrating the range of possible materials generated by this approach as well as the utilization of the abundant end groups for subsequent transformations.

References and Notes

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(10) **2,3-Bis(4′-hydroxyphenyl)-5-fluoroquinoxaline, 1:** In a round-bottom flask equipped with a stir bar, reflux condenser, and nitrogen inlet was placed 4,4′-dihydroxybenzil (24.80 g, 0.092 mol), 4-fluoro-1,2-phenylenediamine (11.60 g, 0.092 mol), and 300 mL of chloroform. The reaction mixture was heated to 50 °C and trifluoroacetic acid (0.2 mL) was added. The resulting dark solution was maintained at 50 °C for 24 h. The crude product was diluted with excess chloroform (300 mL), rinsed three times with dilute aqueous HCl to remove excess amine, dried (magnesium sulfate), and concentrated. The crude product was recrystallized from ethyl acetate/hexane to afford a yellow powder: ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 6H, OMe), 6.75 and 7.33 (AB q, J = 6 Hz, 8H, ArH), 7.30, 7.65 and 8.10 (each d of d, 1H, ArH); ^{13}C NMR (acetone-d_6) δ 55.23, 112.27, 112.61, 113.79, 119.54, 119.96, 130.90, 131.07, 131.20, 138.22, 141.65, 141.86, 152.36, 153.71, 160.23, 160.39, 160.64, and 164.63; MS *m/z* (FAB) 360.
(11) **4,4′-Bis(4-methoxyphenoxy)benzil:** To a 200 mL round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a Dean−Stark trap fitted with a condenser and a nitrogen outlet were added 4,4′-difluorobenzil (50 mmol, 12.3 g), 4-methoxyphenol (110 mmol, 13.6 g), and anhydrous K_2CO_3 (70 mmol, 9.7 g). This was followed by the addition of 100 mL of *N,N*-dimethylacetamide (DMAC) and 30 mL of toluene as an azeotroping agent. The contents of the flask were maintained at 140−150 °C for 2−4 h to allow for the complete removal of water from the system. The reaction temperature was further raised to 160 °C and allowed to proceed for a further 12−14 h. The solution was subsequently cooled and filtered. Water was added dropwise to the filtrate with stirring and the precipitate was collected by suction filtration, washed well with water, and air-dried. The pure product (22 g, 93%) was obtained by recrystallization from isopropyl alcohol (mp = 121−122 °C): ^{1}H NMR (DMSO, 250 MHz) δ 7.84−7.9 (m, 4H), 6.97−7.13 (m, 12H), 3.76 (s, 6H); ^{13}C NMR (DMSO, 250 MHz) δ 55.45, 115.38, 116.77, 121.92, 126.51, 132.34, 147.26, 156.67, 164.06, 193.31. **4,4′-Bis(4-hydroxyphenoxy)benzil:** In a 250 mL round-bottom flask with a stir bar were placed 4,4′-bis(4-methoxyphenoxy)benzil (7.81 g, 20 mmol) and pyridine hydrochloride (13.87 g, 120 mmol). The mixture was heated under nitrogen in a 220 °C oil bath for 45 min, after which time deprotection was complete. The mixture was cooled to 80 °C and diluted to a volume of 250 mL by dropwise addition of water. The crude product was isolated by suction filtration, washed with water, and then recrystallized from acetic acid to give the product (6.91 g, 81%) (mp = 220−221 °C): ^{1}H NMR (DMSO, 250 MHz) δ 9.7 (s, 2H), 7.82−7.87 (d, 4H), 6.59−7.02 (m, 8H); ^{13}C NMR (DMSO, 250 MHz) 116.55, 121.89, 126.34, 132.29, 145.9, 154.94, 164.32, 193.36. **2,3-Bis(4-hydroxyphenoxyphenyl)-5-fluoroquinoxaline, 2:** In a 250 mL round-bottom flask equipped with a stir bar, reflux condenser, and a nitrogen inlet were placed 4,4′-bis(4-hydroxyphenoxy)benzil (4.26 g, 10 mmol), 4-fluoro-1,2-phenylenediamine (1.36 g, 10 mmol), and acetic acid (75 mL). The resulting slurry was boiled for 2 h and then cooled, and the solid was isolated by suction filtration, washed with acetic acid, and air-dried. The product was recrystallized from ethyl acetate to give a light yellow powder (80% yield) (mp = 263−264.5 °C): ^{1}H NMR (DMSO, 250 MHz) δ 9.41 (s, 2H), 8.11−8.18 (m, 1H), 7.73−7.88 (m, 2H), 7.41−7.45 (m, 4H), 6.77−6.93 (m, 8H); ^{13}C NMR (DMSO, 250 MHz) δ 55.46, 115.38, 116.77, 121.92, 126.51, 132.33, 147.26, 156.68, 164.05, 193.31.
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