Poly(aryl ether oxadiazoles)

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ABSTRACT: A general method for the preparation of poly(aryl ether oxadiazoles) has been developed based on an oxadiazole-activated halo or nitro displacement with phenoxides. The oxadiazole heterocycle was found to be sufficiently electron withdrawing to activate halo and nitro substituents toward nucleophilic aromatic substitution analogous to other heterocycles and conventional activating groups (i.e., sulfone, ketone, etc.). Model reactions demonstrated that the oxadiazole-activated displacement occurred with high selectively in near quantitative yield and was judged suitable as a polymer-forming reaction. Appropriately halo- or nitro-substituted 2,5-diphenyloxadiazoles were prepared and subjected to displacement polymerizations with bis(phenoxides) in an *N*-methyl-2-pyrrolidone (NMP)/*N*-cyclohexyl-2-pyrrolidone (CHP) solvent mixture. High molecular weight polymers with glass transition temperatures in the 200 °C range were obtained by each synthetic route. The thermal stability for the resulting polymers was good with decomposition temperatures in the 450 °C range, just below the temperature range of other heterocycle-containing polymers. The poly(aryl ether oxadiazoles) showed limited solubility in common organic solvents, but films could be readily fabricated from the melt.

Introduction

Aromatic poly(oxadiazoles) (POD) are a class of high-temperature polymers that show excellent thermal and hydrolytic stability and have received considerable attention as high modulus fibers due to their liquid crystalline morphology.[1] Among the synthetic routes available for the preparation of PODs, the cyclodehydration of a poly(diacylhydrazine), thermally or in the presence of a dehydrating agent (e.g., poly(phosphoric acid), phosphorus pentoxide, etc.), to produce poly(1,3,4-oxadiazole) has received the most attention.[1-3] However, it should be pointed out that the oxadiazole conversion by these routes is not always quantitative.[1] Alternatively, it has been demonstrated that milder conditions to oxadiazole formation may be employed by the cyclodehydration of disilyldiacylhydrazine in the presence of a nucleophilic catalyst.[4] Since the aromatic poly(oxadiazoles) have limited solubility in common organic solvents, they are generally processed from the soluble poly(hydrazine) precurser, somewhat analogous to polyimide formation from the poly(amic acid). Improved solubility and processability have been demonstrated by the incorporation of meta, aryl ether, and both pendent and main-chain alkyl substituents built into the monomers prior to polymerization.[1,5]

Another means of introducing aryl ether linkages is via a poly(ether) synthesis in which the generation of the aryl ether linkage is the polymer-forming reaction. Here the preformed oxadiazole heterocyclic linkage may be introduced in the bis(halide) or bis(phenol) monomer and purified prior to polymerization. The synthesis of poly(ether imide), a melt and solution processable engineering thermoplastic, by the nitro displacement polymerization of bis(nitrophthalimides) with bis(phenols) is a commercial example of such a polymerization.[6] Likewise, poly(aryl ether phenylquinoxalines) and poly(aryl ether benzoxazoles) have been prepared by the fluoro displacement polymerization of either appropriately substituted fluorophenylquinoxalines or difluorobis(benzoxazole) monomers with bis(phenols), respectively.[7,8] In these polymerizations, facile displacement of the aryl fluorides activated by the heterocyclic moieties was demonstrated with bis(phenols) generating high molecular weight poly(ethers) with significantly improved solubility and melt processability. Alternatively, Connell et al. have prepared bis(phenols) containing preformed heterocyclic linkages including phenylquinoxalines,[9] benzoxazoles,[10] triazoles,[11] and oxadiazoles[12] which were amenable toward nucleophilic aromatic substitution polymerizations. As in the previous examples, most of the heterocyclic poly(ethers) prepared by this route were soluble in common organic solvents and/or melt processable.

The application of this nucleophilic aromatic substitution synthetic approach toward the preparation of processable PODs should be possible. Farnham and coworkers have demonstrated in one case that the oxadiazole heterocycle is effective in activating halides toward nucleophilic aromatic substitution.[13] We have recently accomplished the synthesis of poly(aryl ether oxadiazoles) via a nucleophilic aromatic substitution with the objective of extending the scope of materials possible by this route.[14] The major advantage of this synthetic approach is the incorporation of greater structural variety in the polymer backbone. In this paper we will describe our further work on poly(aryl ether oxadiazoles), including details regarding the displacement reaction with different leaving groups by this polymerization as well as the results from the thermal and mechanical analysis. Furthermore, this represents another example of a poly(aryl ether) synthesis based on a heterocycle-activated halo (nitro) displacement which supports this general synthetic methodology as a means to high-temperature, high-T_g poly(ethers).

Experimental Section

Materials. The *N*-methyl-2-pyrrolidone (NMP) and *N*-cyclohexyl-2-pyrrolidone (CHP) were distilled from calcium hydride. The *m*-cresol (**5**), 4-fluorobenzoic acid (**1a**), and oxalyl chloride (Aldrich) were used without further purification, while 2,2′-bis(4-hydroxyphenyl)propane (**7a**) (Aldrich) was recrystallized from toluene, bis[(4-hydroxyphenyl)-4-phenyl]methane (**7c**) (Applied Organic Silicones) was recrystallized from toluene, and 2,2′-bis(4-hydroxyphenyl)hexafluoropropane (**7b**) (Aldrich) was purified by recrystallization from a toluene/ethyl acetate (95:15) mixture. The 9,9′-bis(4-hydroxyphenyl)fluorene (**7d**) was kindly supplied by P. M. Hergenrother (NASA Langley). The 4-fluorobenzoyl chloride (**2**) was prepared by the reaction of 4-fluorobenzoic acid (98.00 g, 0.70 mol) with oxalyl chloride (100.00 g, 0.79 mol) in 250 mL of chloroform. The reaction was stirred

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until a clear solution was obtained, which usually took 24 h. The 4-fluorobenzoyl chloride was concentrated and purified by distillation (180 °C, N_2 atmosphere) to give 87 g of 4-fluorobenzoyl chloride as a clear liquid. The 4-fluorobenzoyl chloride is also commercially available (Aldrich).

Monomer Synthesis. a. 1,4-Bis(4-fluorophenyl)hydrazide (3a). A round-bottom flask equipped with a condenser was charged with 4-fluorobenzoyl chloride (14.0000 g, 0.0886 mol) and washed in with 80 mL of NMP. The reaction mixture was then cooled to −10 °C, and hydrazine (1.1000 g, 0.0443 mol) dissolved in NMP (10 mL) was added incrementally. The reaction mixture turned red and then light yellow. Upon completion (6 h, −10 °C), the reaction mixture was precipitated in excess water, filtered, and subjected to both 2-propanol and ethyl acetate rinses. The crude product was recrystallized (methanol/chloroform) to afford **3a** as a white crystalline solid: mp 244–246 °C; IR (KBr) 3053, 3160, 1493, 1471. Anal. Calcd for $C_{14}H_{10}N_2O_2F_2$: C, 60.88; H, 3.65; N, 10.14. Found: C, 60.98; H, 3.63; N, 10.22.

b. 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (4a). A 50-mL round-bottom flask equipped with a Dean-Stark trap and condenser was charged with 20 g of **3a** and ~25 mL of CHP. The reaction mixture was incrementally heated to 260 °C over a 3-h period. At temperatures above 80 °C, CHP is no longer miscible with water and serves as an effective dehydrating agent. The reaction was held at 260 °C (24 h), and TLC showed quantitative conversion of **3a** was observed with the formation of a single product by TLC in most experiments. In several cases, a second unidentified product was observed which could be selectively removed with an 2-propanol rinse. Upon cooling, the resulting monomer crystallized from the CHP, and the crystalline product was isolated in excess water to remove the CHP (~70% yield). The product was filtered and rinsed with 2-propanol and recrystallized (ethyl acetate/hexane) to afford **4a** as a white crystalline solid: mp 199–201 °C; IR (KBr) 1608, 1496, 1471, 1271, 1226, 1067. Anal. Calcd for $C_{14}H_8F_2N_2O_1$: C, 65.12; H, 3.12; N, 10.85. Found: C, 65.00; H, 3.08; N, 10.97.

c. 2,5-Bis(4-chlorophenyl)-1,3,4-oxadiazole (4b). A 250-mL round-bottom flask equipped with a condenser was charged with chlorobenzoic acid (14.025 g, 0.0899 mol), hydrazine (1.370 g, 0.0428 mol), and poly(phosphoric acid) (100 mL). The reaction mixture was heated to 250 °C (8 h) to effect the ring closure, and TLC (ethyl acetate/hexane) analysis showed the formation of a single product. The resulting product was isolated in water, extracted with chloroform, and rinsed three times with dilute base to remove excess chlorobenzoic acid. The solution was dried (magnesium sulfate), filtered, and concentrated to give the crude product (~80% yield) which was recrystallized from a chloroform/methanol solution yielding **4b** as a white crystalline solid: mp 249–251 °C; IR (KBr) 1531, 1480, 1462, 1400, 1091, 839. Anal. Calcd for $C_{14}H_8N_2O_1CL_2$: C, 57.75; H, 2.76; N, 9.62. Found: C, 57.96; H, 2.83; N, 9.66.

d. 2,5-Bis(4-nitrophenyl)-1,3,4-oxadiazole (4c). In a single-neck 1000-mL round-bottom flask fitted with stirbar, condenser, and nitrogen inlet was placed 4-nitrobenzoic acid (33.4 g, 200 mmol) and poly(phosphoric acid) (200 g). The resulting slurry was warmed to 120 °C, and hydrazine sulfate (13.0 g, 100 mmol) was added through the condenser in portions over the next 10 min. The temperature was then gradually raised to 150 °C and maintained for 6 h with stirring. The resulting slurry was cooled and the reaction mixture brought up to about 800 mL by gradual addition of water; the resulting suspension was broken up and stirred. The crude solid product was isolated by suction filtration, washed well with water, and air-dried. It was recrystallized from methyl sulfoxide (500 mL) to give 27.5 g (88%) of pure product: mp 312–314 °C; IR (KBr) 1606, 1533, 1481, 1347, 1072. Anal. Calcd for $C_{14}H_8N_4O_5$: C, 53.85; H, 2.58; N, 17.93. Found: C, 53.66; H, 2.63; N, 17.92.

e. 2,5-Bis[4-(3-methylphenoxy)phenyl]-1,3,4-oxadiazole (6). A three-neck 15-mL flask fitted with a nitrogen inlet and Dean-Stark trap with condenser was charged with **4a**, **5**, and K_2CO_3 and carefully rinsed into the flask with 8 mL of a NMP/CHP (50/50) solvent mixture. The reaction mixture was heated to 150–160 °C to effect the dehydration of the system, and the water generated by phenoxide formation was collected in the Dean-Stark trap. After complete dehydration of the system (4–6 h), the reaction was heated to 180 °C for 18 h, at which time TLC analysis (ethyl acetate/hexane (1/3)) showed complete conversion of **4a** and the formation of a single product. The reaction mixture was partitioned between chloroform and water, and the chloroform layer was washed five times with water, dried ($MgSO_4$), and concentrated on a rotary evaporator (~95% yield). The crude product was purified by flash chromatography (10% ethyl acetate/hexane, silica gel) and recrystallized (methanol) to afford **6** as a light brown crystalline powder. Likewise, compounds **4b** and **4c** were subjected to either chloro or nitro displacement, respectively, with **5** in the presence of K_2CO_3 in a procedure analogous to that described above. In each case, conversion of either **4b** or **4c** to **6** was observed (TLC) with the formation of a single product in high yield, identical to that prepared by the fluoro displacement described above: mp 118–124 °C; IR (KBr) 1587, 1492, 1256, 1223, 1145, 1083, 1022. Anal. Calcd for $C_{28}H_{22}O_3N_2$: C, 77.39; H, 5.10; N, 6.45. Found: C, 77.54; H, 5.21; N, 6.16.

Polymer Synthesis. A detailed synthetic procedure designed to prepare the poly(aryl ether benzoxazole) **9a** from **4a** and **7b** is provided. A typical synthesis of a poly(aryl ether oxadiazole) was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap, and condenser. The flask was charged with **4a** (1.3120 g, 0.00508 mol) and **7b** (1.17084 g, 0.00508 mol) and carefully washed into the flask with 25 mL of a NMP/CHP solvent mixture. An excess of K_2CO_3 (1.25 g, 9.06 mmol) was then added. The reaction mixture was then heated to ~150 °C to dehydrate the system. The reaction mixture was maintained at 150 °C usually for 4–6 h until the presence of water was no longer observed in the Dean-Stark trap. Upon dehydration, the polymerization was heated at 180 °C for approximately 20 h, and the reaction was terminated about the point where the viscosity increased dramatically. The high molecular weight polymerization dope was diluted with about an equimolar volume of NMP and filtered hot to remove the inorganic salts. The polymer solution was then coagulated in approximately 10× volume of methanol and then boiled in water to remove trapped salts. The polymer (**9a**) was then dried in a vacuum oven (80 °C) to a constant weight. In each case the yield was essentially quantitative.

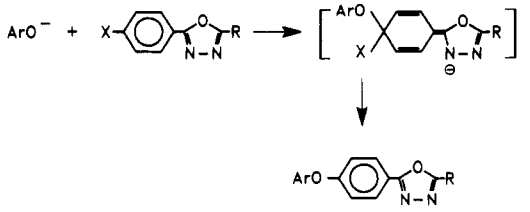
Characterization. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) on the polymer films was conducted with a heating rate of 5 °C/min for the ramped-temperature scans. Intrinsic viscosity measurements were determined using a Cannon-Ubbelodhe dilution viscometer in NMP (25 °C).

Results and Discussion

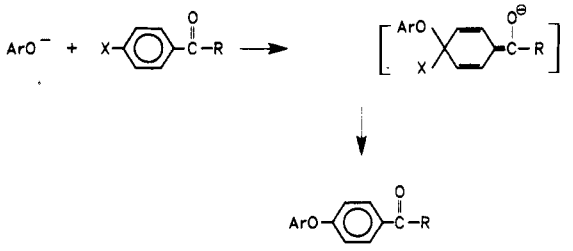
Among the synthetic routes to poly(aryl ethers) including electrophilic aromatic substitution,[15] oxidative coupling,[16] and others,[17] the nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to high-performance, high-temperature poly(aryl ethers).[13,18] Aryl halides, when activated by an electron-withdrawing substituent (i.e., sulfone, ketone, etc.) which can also accept the negative charge developed through the formation of a Meisenheimer complex, become more susceptible toward nucleophilic aromatic substitution polymerizations. Recently, it has been demonstrated that heterocycles can activate aryl halides and aryl nitro compounds toward nucleophilic aromatic substitution polymerizations generating high molecular weight poly(aryl ethers) containing preformed heterocyclic linkages.[7,8,14,19] Halo displacement from the 6- or 7-position of the quinoxaline ring system and from the 4-position of a benzoxazole- and benzothiazole-substituted benzene ring was reported and used to prepare the respective poly(aryl ethers). Proton NMR was used to assess the electron-withdrawing effects of the heterocycles on both the fused benzo aromatic ring and the 2-phenyl group to design the appropriately halo-substituted monomers.

Scheme I

Oxadiazole Activation



Ketone Activation



We sought to extend the heterocycle-activated halo displacement polymerization toward other heterocyclic ring systems such as an oxadiazole to prepare poly(aryl ether oxadiazoles). The rationale for facile nucleophilic aromatic substitution from an oxadiazole-substituted benzene ring was similar to that previously described for other heterocyclic systems. First, the electron-poor oxadiazole ring would act as an electron-withdrawing substituent, and second, the oxadiazole heterocycle can stabilize the negative charge developed through a stabilized transition state (Meisenheimer complex) during the transformation to lower the activation energy for the process, analogous to a conventional activating group (Scheme I). The electronic effect of an oxadiazole heterocycle on the 2-phenyl group can be evaluated by ^{1}H NMR, as the deshielding of the protons ortho to the substituent is indicative of an electron-withdrawing group analogous to a published procedure.[7,8,19] Comparison of the ^{1}H NMR spectra shows the deshielding of the aromatic protons ortho to the oxadiazole heterocycle (δ = 8.0) of **4a** vs the aromatic protons ortho to a ketone group (δ = 7.9), a more conventional activating group, to be greater with respect to electron affinity (Figure 1). The electronic effect of the oxadiazole on the 2-phenyl substituent is similar to that of both the oxazole and thiazole heterocycles, while the pyrazine component in phenylquinoxalines was found to have a greater effect on the benzo ring.[7] This demonstrates that the electron-withdrawing effect of the oxadiazole group on a benzene ring may be comparable to that of a ketone group and further indicates the possibility of facile nucleophilic aromatic substitution at the para position of the 2-phenyl ring.

The synthesis of the poly(aryl ether oxadiazoles) required the synthesis of the appropriate difluoro, dichloro, and dinitro monomers containing a preformed oxadiazole heterocycle. The synthetic routes employed for the synthesis of these monomers were based on either the cyclohydration of an appropriately substituted diacyl hydrazine or a one-step synthesis from hydrazine and a substituted benzoic acid (**1**) in poly(phosphoric acid). The preparation of 1,4-bis(4-fluorophenyl)hydrazine (**3a**), the precurser to the oxadiazole, involved the reaction of 4-fluorobenzoyl chloride with hydrazine (−10 °C) (Scheme II). Quantitative conversion of hydrazine was observed (TLC, chloroform/methanol) with the formation of a single product peak. The crude product was isolated in water

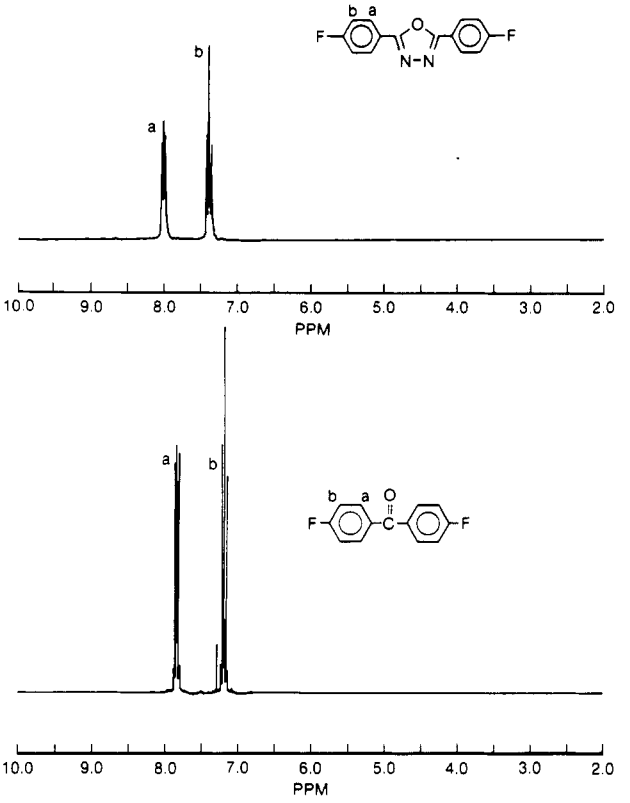
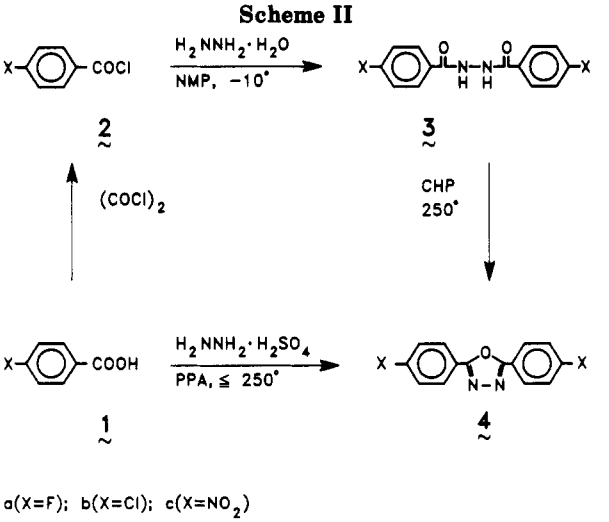


Figure 1. ^{1}H NMR spectra of **4a** (top) and 4,4′-difluorobenzophenone (bottom).

Scheme II

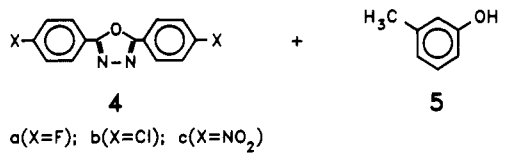


a(X=F); b(X=Cl); c(X=NO_2)

and recrystallized (methanol/chloroform) to afford **3a** as a white crystalline powder. The oxadiazole-containing monomer, 2,5-bis(fluorophenyl)-1,3,4-oxadiazole (**4a**), was prepared by the thermal cyclodehydration of **3a** in CHP (260 °C). Alternatively, the appropriately substituted benzoic acid could be reacted with hydrazine in poly(phosphoric acid) at 265 °C in a single-step direct method to the oxadiazole heterocycle. The 2,5-bis(chlorophenyl)-1,3,4-oxadiazole (**4b**) and 2,5-bis(nitrophenyl)-1,3,4-oxadiazole (**4c**) were prepared in this manner and recrystallized from a chloroform/methanol solvent mixture and DMSO, respectively.

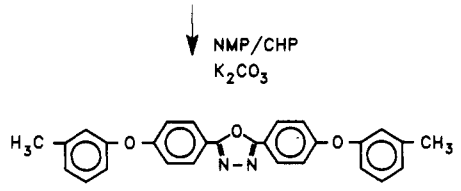
To demonstrate the feasibility of the oxadiazole-activated aryl ether synthesis, the model reaction of a monophenoxide with bis(halophenyl)oxadiazole and bis(nitrophenyl)oxadiazole was investigated (Scheme III). Our first example involved the oxadiazole-activated fluoro displacement of **4a** with *m*-cresol in the presence of

Scheme III



4 5

a(X=F); b(X=Cl); c(X=NO_2)



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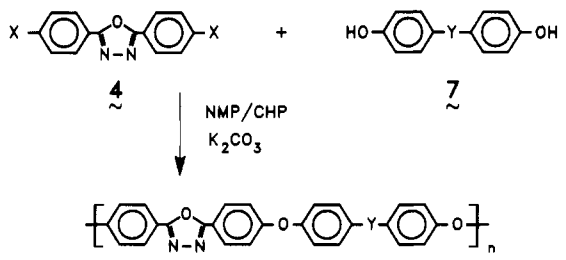
Scheme IV



Polymer	Oxadiazole Monomer		Bisphenol	
8a	4a	X=F	7a	$Y=C(CH_3)_2$
8c	4c	X=NO_2	7a	
9a	4a	X=F	7b	$Y=C(CF_3)_2$
9c	4c	X=NO_2	7b	
10a	4a	X=F	7c	$Y=CPh_2$
10c	4c	X=NO_2	7c	
11a	4a	X=F	7d	Y=C
11c	4c	X=NO_2	7d	

K_2CO_3 in a NMP/CHP solvent mixture. Since CHP is not miscible with water at elevated temperatures, water generated by phenoxide formation (140–150 °C) was effectively removed through the Dean-Stark trap.[7,8] Upon dehydration (4–6 h), the reaction mixture was heated to 185 °C to effect the displacement reaction. TLC analysis (ethyl acetate/hexane) showed that quantitative conversion of **4a** had occurred with the formation of a single product peak. The expected product, **6**, was isolated as a single homogeneous product in high yield (>90%). The analogous reaction of both the chloro-substituted (**4b**) and nitro-substituted (**4c**) oxadiazoles also occurred in high yield and quantitative conversion. Interestingly, side reactions associated with the generation of nitrite ion were not observed as in the case for poly(aryl ether phenylquinoxaline)[7] and poly(ether imide)[6] syntheses. The model reactions demonstrated that the fluoride, chloride, and nitro substituents para to the oxadiazole group were cleanly displaced by phenoxides. The high selectively and yield observed in each of the displacements demonstrated that these transformations are suitable as polymer-forming reactions.

Table I
Characteristics of Poly(aryl ether oxadiazoles)

polymer entry	$[\eta]^{NMP}_{25\,°C}$, dL/g	T_g, °C
8a	0.45	201
8c	0.48	200
9a	0.50	210
9c	1.39	210
10a	0.44	190
10c	0.40	191
11a	0.76	
11c	0.55	220

To demonstrate the utility of the oxadiazole-activated halo (nitro) displacement to prepare high molecular weight poly(aryl ether oxadiazoles), polymerization of **4a** or **4c** was carried out with various bis(phenols) (**7a–d**) in the presence of K_2CO_3 in a NMP/CHP solvent mixture according to literature procedures[7-12] (Scheme IV). As in the case for most polyether syntheses, the solids composition was maintained between 20 and 25 wt %. The water generated by bis(phenoxide) formation in the initial stages of the polymerizations was effectively removed through the Dean-Stark trap due to the immiscibility with the CHP solvent mixture (150–155 °C). Upon completion of bis(phenoxide) formation and dehydration, the polymerization mixtures were heated to 185–195 °C to effect the displacement reaction. In each case high polymer was attained within 4–8 h as judged by the dramatic increase in viscosity. In fact, many of the polymerizations were observed rod climbing and required dilution with additional CHP and higher polymerization temperatures (230 °C) to maintain solubility. Alternatively, diphenyl sulfone, a high temperature solvent used to prepare semicrystalline poly(aryl ether ether ketones), was also investigated as a solvent medium for the polymerizations. However, no significant advantages in polymer solubility or molecular weight were observed over the use of the CHP/NMP solvent mixture. The resulting polymerization dopes were diluted, coagulated in excess methanol, washed with water to remove remaining salts, and dried in a vacuum oven at 80 °C for 24 h.

This general procedure was applied to a number of bis(phenols) (**7a–d**) for both the activated difluoride (**4a**) and dinitro (**4c**) monomers yielding polymers **8a–11a** and **8c–11c**, respectively (Scheme IV). High molecular weight polymer was achieved in each case as indicated by the intrinsic viscosity measurements. For comparison, the commercially available poly(aryl ether sulfone) (UDEL) with an intrinsic viscosity value of 0.48 dL/g in NMP was used. Interestingly, high molecular weight poly(aryl ether oxadiazoles) were prepared by the use of both the difluoro and dinitro monomers using conventional polymerization conditions, whereas poly(ether imide) synthesis requires milder conditions to avoid side reactions associated with nitrite ion generation in the polymerization. Although the polymers could be prepared in an NMP/CHP solvent mixture at elevated temperatures, at ambient temperatures the polymers had limited solubility, consistent with the reports by Hergenrother and co-workers on similar structures.[11,12]

The T_g's of the poly(aryl ether oxadiazoles) ranged from 190 to 230 °C depending on the bis(phenol) used in the synthesis (Table I), and no evidence of crystallinity was observed by the calorimetry measurements in any case. The thermal stability of the poly(aryl ether oxadiazoles) was assessed by the weight loss in a variable-temperature thermogram. The onset of weight loss or polymer decomposition temperature for each of the polymers was in

the 450–460 °C range. These values are in the range of decomposition temperatures reported for the poly(aryl ether phenylquinoxaline) analogues. The excellent thermal stability of these materials allowed them to be melt processed in spite of their high T_g's. Clear and fingernail creasable films could be fabricated by compression molding. WAXS measurements on the molded films showed no evidence of structure either crystallinity or liquid crystallinity consistent with the calorimetry measurements.

Summary

Poly(aryl ether oxadiazoles) have been prepared by nucleophilic aromatic substitution generating aryl ether linkages as the polymer-forming reaction. We have demonstrated that the electron-deficient oxadiazole heterocyclic activated fluoro, chloro, and nitro para substituents of a 2-phenyl group toward displacement by a variety of nucleophiles. The appropriately substituted oxadiazole monomers were prepared and subjected to the displacement polymerization with various bis(phenols) in the presence of potassium carbonate in an NMP/CHP solvent mixture. High molecular weight polymer was readily achieved, and structural variety could be introduced through the use of different bis(phenols). The resulting polymers showed T_g's in the 190–230 °C range, depending on the monomers used in the synthesis, and polymer decomposition temperatures in the 450 °C range. The high thermal stability of the poly(aryl ether oxadiazoles) allowed for the melt fabrication of polymer films. This represents another example of the synthesis of poly(aryl ethers) based on a heterocyclic activated halo (nitro) displacement, and this synthesis can be considered the oxadiazole analogue of the poly(ether imide) synthesis. Moreover, the heterocyclic activated nucleophilic displacement chemistry provides a general methodology to high-temperature, high-T_g poly(aryl ethers).

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Registry No. **3a**, 582-91-2; **4a**, 324-81-2; **4b**, 2491-90-9; **4c**, 1044-49-1; **5**, 108-39-4; **6**, 139277-49-9; **8** (SRU), 31694-04-9; **8a** (copolymer), 134438-35-0; **8c** (copolymer), 139277-50-2; **9** (SRU), 134436-85-4; **9a** (copolymer), 134438-36-1; **9c** (copolymer), 139277-51-3; **10** (SRU), 134415-78-4; **10a** (copolymer), 134438-37-2; **10c** (copolymer), 139277-52-4; **11** (SRU), 139277-55-7; **11a** (copolymer), 139277-53-5; **11c** (copolymer), 139277-54-6; 4-fluorobenzoyl chloride, 403-43-0; hydrazine, 302-01-2; chlorobenzoic acid, 26264-09-5; 4-nitrobenzoic acid, 62-23-7; hydrazine sulfate, 10034-93-2.