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Poly(aryl ether oxadiazoles)

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Abstract

A general method for the preparation of poly(aryl ether oxadiazoles) has been developed where the generation of an aryl ether linkage was the polymer-forming reaction. Two synthetic approaches were investigated based on either an oxadiazole-activated halo displacement with phenoxides or a hydrazide-activated halo-displacement with phenoxides. The hydrazide may be subsequently thermally cyclodehydrated to the oxadiazole heterocyclic. In each case, the negative charge developed in the transition state could be stabilized through a Meisenheimer Complex, analogous to conventional activating groups (e.g., sulfone and ketone), and the electron affinity, as judged by ^{1}H NMR, was comparable to that of other activating groups. An appropriately substituted diarylfluoro oxadiazole was prepared and polymerized with various bisphenols in an NMP/CHP solvent mixture in the presence of K_2CO_3. High molecular weight poly(aryl ether oxadiazoles) were synthesized with viscosities ranging from 0.44 to 0.76 dL/g and Tg's in the 200 °C range. Conversely, the hydrazide activated halo-displacement as a means of preparing poly(aryl ether hydrazides) was not as successful, since it appears that the hydrazide was of sufficient acidity to form a salt with K_2CO_3 preventing solubility and polymerization.

Introduction

Aromatic poly(oxadiazoles) (POD) are a class of high temperature heterocyclic polymers that show excellent thermal stability and have received considerable attention as high melting fibers. There are numerous synthetic routes to the preparation of POD's, however, the thermal cyclodehydration of a 2,5-diacyl type of poly(hydrazine) to produce poly(1,3,4-oxadiazole) developed in the early sixties has received the most attention (1-3). The aromatic poly(hydrazide) precursors to the oxidiazoles are soluble in typical aprotic dipolar solvents, however, the subsequent aromatic poly(oxadiazoles) are not soluble in organic solvents and only the lower melting systems can be melt fabricated. Solubility and melt processibility has been demonstrated by the incorporation of eight to ten methylene units into the poly(oxadiazole) backbone (4). However, this is often at the sacrifice of the thermal stability.

Alternatively, the introduction of aryl ether linkages is known to improve the solubility of rigid high temperature polymers. An efficient means of introducing ether linkages in heterocyclic polymers is through a polyether synthesis, where the desired preformed heterocyclic ring is introduced in the bishalide or bisphenol monomer. An important example of this approach is poly(ether-imide) prepared via a nitro displacement polymerization of bis(nitrophthalimides) with bisphenols (5). These structures have moderate Tg's and can be effectively processed from either the melt or solution. We have recently demonstrated the synthesis of other heterocyclic containing poly(aryl ethers) via a nucleophilic aromatic substitution polymerization in which the generation of an aryl ether linkage was the polymer forming reaction. Polymerization of either bis(fluorophenylquinoxalines) or bis(fluorobibenzoxazoles) with bisphenols produced high molecular weight poly(aryl ether phenylquinoxalines) and poly(aryl ether benzoxazoles), respectively, which were processable from the melt or solution (6-7). These polymerizations were based on the activation of aryl fluoro-group towards nucleophilic aromatic substitution by either the pyrizine component of the quinoxaline heterocyclic or the oxazole heterocyclic. Alternatively, Connel and Hergenrother (8-10) have reported the synthesis of poly(aryl ethers) containing heterocyclics (including benzoxazoles, phenylquinoxalines, imidazoles and oxadiazoles) by the polymerization of bisphenols containing the preformed heterocyclics with conventional activated dihalides. The resulting polymers showed improved processibility and were amenable towards thermoplastic composite fabrication.

The heterocyclic activated poly(aryl ether) synthesis should be amenable towards other heterocyclic ring systems besides imides, phenylquinoxalines, benzothiazoles and benzoxazoles. The application of this synthetic approach towards the preparation of processible POD's should be possible. Farnham and coworkers (11) have previously demonstrated that the oxadiazole heterocyclic is effective in activating halides towards nucleophilic aromatic substitution. In this communication, the investigation of the oxadiazole-activated fluoro-displacement as a route in preparing POD's containing aryl ether linkages will be described, with the objective of extending the scope of materials possible by this route. In addition, the investigation of a hydrazide-activated halo-displacement will be discussed as a means of preparing poly(aryl ether hydrazide) precursors to the poly(aryl ether oxadiazoles). Since we have previously demonstrated that amides (12) can effectively activate halides towards nucleophilic aromatic substitution, we felt that the hydrazide moiety would also be an effective activating group.

Experimental

Materials

N-Methyl-2-pyrrolidone (NMP) and N-cyclohexyl-2-pyrrolidone (CHP) were distilled from calcium hydride. m-Cresol, 4-fluorobenzoic acid, and oxalyl chloride (Aldrich) were used without further purification. 2,2'-Bis(4-hydroxyphenyl)propane **(3a)** was purchased from Aldrich and recrystallized from toluene. Bis[(4-hydroxyphenyl)-4-phenyl]methane **(3b)** (Applied Organic Silicones) was recrystallized from toluene. 2,2'-Bis(4-hydroxyphenyl)hexafluoropropane **(3c)** (Aldrich) was purified by recrystallization from a toluene/ethyl acetate (95:15) mixture. 9,9'-Bis(4-hydroxyphenyl)fluorene **(3d)** was kindly supplied by P. M. Hergenrother (NASA Langley). 4-Fluorobenzoyl chloride 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 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.

1,4-Bis(4-fluorophenyl)hydrazide (1). 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 then to a light yellow. Upon completion (6 h) the reaction mixture was isolated in excess water, filtered and subjected to both isopropanol and ethyl acetate rinses. The crude product was recrystallized (methanol/chloroform) to afford 1 and a white crystalline solid; m.p. = 244-246 °C. Anal. Calcd. for $C_{14}H_{10}N_20_2F_2$: C, 60.88; H, 3.65; N, 10.14. Found: C, 60.98; H, 3.63; N, 10.22.

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (2). A 50 mL round bottom flask equipped with a Dean-Stark trap and condenser was charged with 20 g of 1 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 1 was observed with the formation of a single product peak in most experiments. In several cases, another unidentified peak was observed which could be selectively removed with an isopropanol rinse. Upon cooling, the resulting monomer crystallized from the CHP, and the crystalline product was isolated in excess water to remove the CHP. The product was filtered and rinsed with isopropanol, and recrystallized (ethyl acetate/hexane) to afford 2 as a white crystalline solid; m.p. = 199-201 °C. Anal. Calcd. for $C_{14}H_8F_2N_20_1$: C, 65.12; H, 3.12; N, 10.85. Found: C, 65.00; H, 3.08; N, 10.97.

Polymer Synthesis

A typical synthesis of a poly(aryl ether-benzoxazole) was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap, and a condenser. A detailed synthetic procedure designed to prepare a poly(aryl ether-benzoxazole) based on **2** and **3c** is provided. The flask was charged with **2** (1.3120 g, 0.00508 mmol) and **3c** (1.17084 g, 0.00508 mmol) and carefully washed in 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 until the presence of water was no longer observed in the Dean-Stark trap. This usually took between 4 and 6 h, and, during this stage of the reaction, the solvent underwent several color changes. For example, during the initial formation of the phenoxide, a yellow-brown color was observed and as the refluxing proceeded, the color changed to dark brown. Upon dehydration, the polymerization was heated at 180 °C for approximately 20 h, and completion or near completion was qualitatively estimated by the point where the viscosity increased dramatically. The high molecular weight polymerization dope was diluted with 20 mL of NMP and filtered hot to remove the inorganic salts. The filtered solution was cooled, and several drops of weak acid (e.g., acetic acid) were added to neutralize the phenoxide end groups. The polymer solution was then coagulated in approximately 10× volume of methanol and then boiled in water to remove trapped salts. The polymer **(4c)** was then dried in a vacuum oven (80 °C) to a constant weight. In each case the yield was essentially quantitative.

Characterization

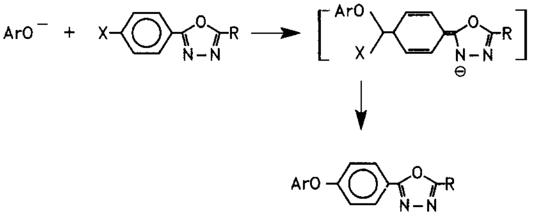
Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) on the polymer films was conducted with a heating rate of 5 °C/min for the ramped-temperature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

Results and Discussion

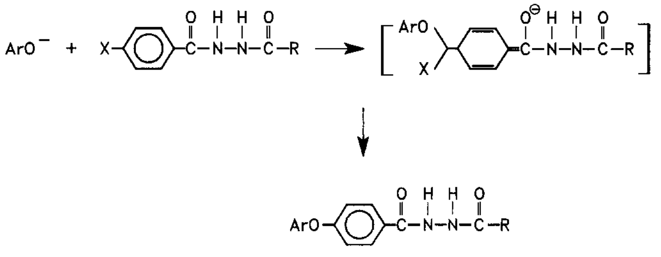
The synthesis of poly(aryl ethers) is based on the nucleophilic aromatic displacement of an aryl halide with a phenoxide in polar aprotic solvents, where the aryl halide is activated by an electron withdrawing group (e.g., sulfone or carbonyl) (13-14). These activating groups can also accept a negative charge lowering the activation energy for the displacement through a Meisenheimer complex. Recently, we have demonstrated the use of both heterocyclic rings (e.g., quinoxaline, benzoxazole and benzothiazole heterocycles) (5,6,15) and an amide (12) moiety to activate halides towards nucleophilic aromatic substitution polymerization.

It seemed plausible that these new activating groups and synthetic methodology could be extended to for the preparation of poly(aryl ether oxadiazoles). Two synthetic approaches to poly(aryl ether oxadiazoles) were investigated: (1) An oxadiazole-activated halo-displacement by phenoxides and (2) a hydrazide activated halo-displacement by phenoxides. Facile nucleophilic aromatic substitution should occur as a result of the oxadiazole-or hydrazide-activation, since both of these groups can stabilize the negative charge developed in the transition state through a Meisenheimer complex, analogous to other activating groups (e.g., sulfone, amide, oxazole) as shown in Scheme 1. The effectiveness of these substituents as electron withdrawing groups can be estimated by the chemical shift of the aromatic protons ortho to the hydrazide or oxadiazole substituent, as previously published for other new activating groups (67,101,154,16). Comparison of the ^{1}H NMR spectra shows the deshielding of the aromatic protons ortho to both the oxadiazole group (δ = 8.0) of **2** and the hydrazide group (δ = 8.0) of **1** versus the aromatic protons ortho to a ketone group (δ = 7.9) to be greater with respect to electron affinity and further indicates the likelihood of displacement.

Oxadiazole Activation

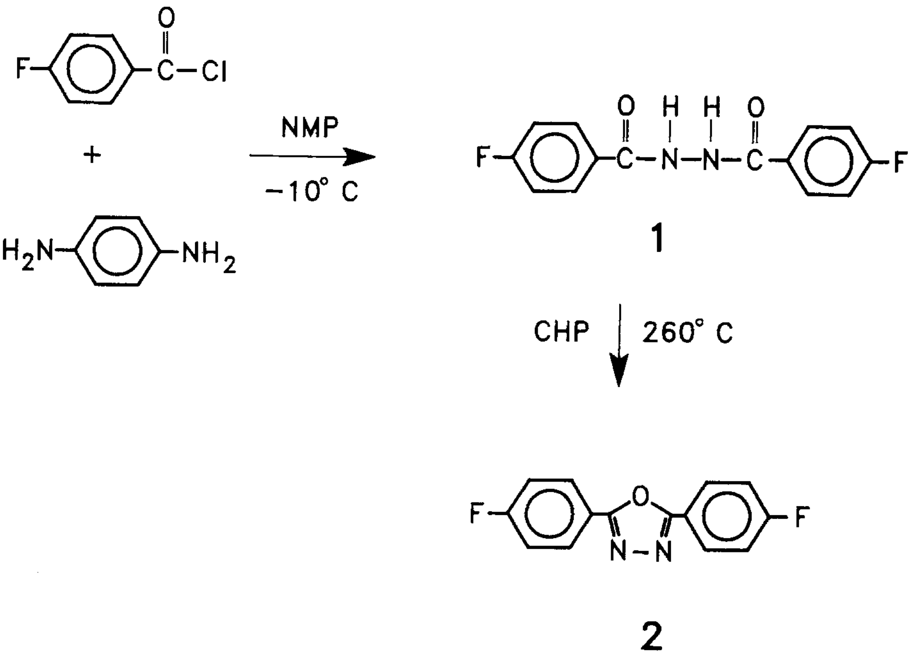


Hydrazide Activation



Scheme 1

The synthesis of the poly(aryl ether oxadiazoles) required the synthesis of the appropriate difluoro-monomers containing a preformed hydrazide or oxadiazole group. The synthesis of 1,4-bis(4-fluorophenyl)hydrazide **1**, involved the reaction of 4-fluorobenzoyl chloride with hydrazine in NMP (− 10) (Scheme 2). Quantitative conversion of the hydrazine was observed (TLC) with the formation of a single product peak with no evidence of side reactions. The crude product was isolated in water and recrystallized (methanol/chloroform) to afford **1** as a white crystalline powder. The oxadiazole containing monomer, 2,5-bis(fluorophenyl)-1,3,4-oxadiazole, **2**, was prepared by the thermal cyclodehydration of **1** in CHP (260 °C). Since CHP is not miscible with water at temperatures above 80 °C, the water generated from ring closure is effectively removed (8-10 h). In most cases, quantitative conversion of **1** was observed with the formation of a single product peak (TLC). However, in several experiments an unidentified side-product was observed which prevented the formation of high molecular weight polymer. After isolation (water), a selective isopropanol rinse could quantitatively remove the side-product. Recrystallization (ethyl acetate/hexane) of the crude product afforded **2** as a white crystalline solid suitable for step-growth polymerization requirements.

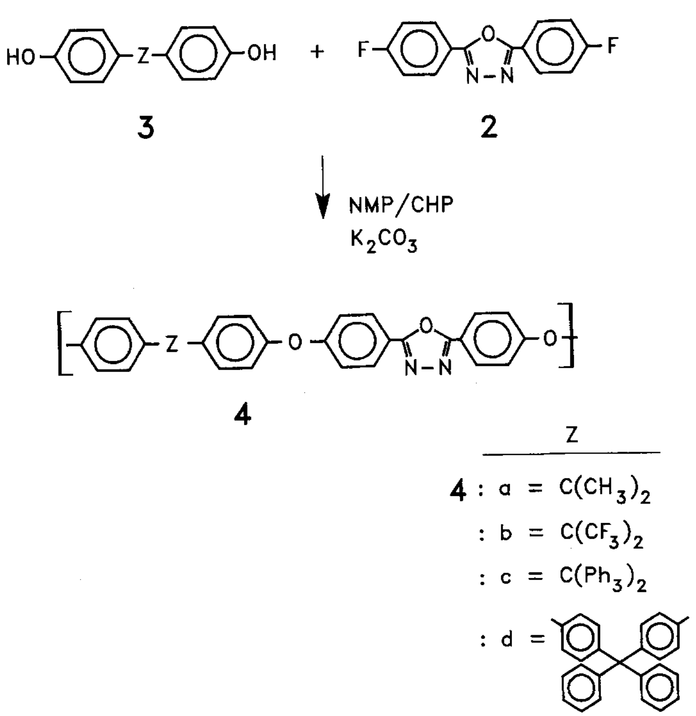


Scheme 2

The synthesis of poly(aryl ethers) is generally carried out in aprotic dipolar solvents such as NMP, CHP, or dimethyl sulfoxide (DMSO). These solvents effectively solvate the monomers, polar intermediates, and in most cases the subsequent polymer. Furthermore, the formation of the Meisenheimer complex is strongly influenced by the solvent, and polar solvents stabilize this complex assisting the displacement reaction. The choice of the solvent depends on the solubility of the polymer and the polymerization temperatures required to produce high molecular weight. NMP and CHP allow the highest reaction temperatures, 200 and 260 °C, respectively, and these high polymerization temperatures are required in the preparation of rigid or stiff chain poly(aryl ethers) to maintain solubility. Furthermore, since CHP is not miscible with water at temperatures above

100 °C, nonpolar cosolvents used to azeotrope the water generated during the polymerization are not required. Mixtures of NMP and CHP also show a similar behavior with water, with CHP compositions as low as 20%. We have found that a CHP/NMP (50/50) solvent mixture is the prefered reaction medium for the polymerizations.

Polymerization of **1** with various bisphenols (**3a-d**) in a NMP/CHP (1/1) solvent mixture in the presence of K_2CO_3 was found to be unsuccessful. Likewise, model reactions between m-cresol and **1** under the same reaction conditions were also unsuccessful, presumably due to salt formation between **1** and K_2CO_3. **1** was treated with K_2CO_3 in NMP (~150 °C) and a brightly colored green precipitate formed. Similarly, **1** treated with sodium hydride also formed a green precipitate. Methanol added to either of these mixtures, afforded starting material, suggesting that **1** readily forms a salt with the bases. Unlike the weakly acidic amide moiety used as an activating group for the preparation of poly(aryl ether imides), it appears that the hydrazide is of sufficient acidity to form a salt with K_2CO_3, preventing solubility and polymerization.

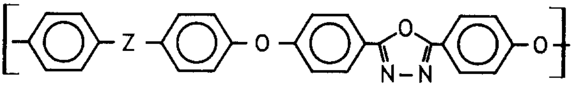


Scheme 3

Conversely, the polymerization of **2** with various bisphenols (**3a-d**) in a CHP/NMP (1/1) solvent mixture in the presence of K_2CO_3 was found to be a successful route for preparing high molecular weight poly(aryl ether oxadiazoles) (**4a-d**) (Scheme 3) (6,7). During the initial stage of the polymerizations, the reaction temperatures were maintained at approximately 150 °C and the water generated by phenoxide formation was removed through the Dean-Stark trap. Upon dehydration (4-6 h), the polymerization temperatures were increased to 185-195 °C to effect the displacement reactions. High polymer was obtained within 6 h as judged by the viscosity increase and in some cases, the viscosity increase was so dramatic the polymers were observed climbing the stirring rod. The resulting polymers **(4a-d)** were isolated in an excess methanol/water mixture, subjected to the appropriate solvent rinses, and dried in a vacuum oven (80 °C) for 24 h.

Table 1 contains the results of the intrinsic viscosity and thermal analysis measurements. The viscosity values, measured in NMP (25 °C), ranged from 0.44 to 0.76 dL/g, typical values for a high molecular weight poly(aryl ether). For comparison, the commercially available poly(aryl ether sulfone) (UDEL®) has an intrinsic viscosity of 0.48 dL/g in NMP and the previously reported poly(aryl ether oxidiazole) had an intrinsic viscosity of 0.54 dL/g in chloroform (11). Although the polymers could be prepared in an NMP/CHP solvent mixture at elevated temperatures, at ambient temperature the polymers had limited solubility, consistent with the reports by Hergenrother and coworkers on similar structures (8-10). The Tg's of the poly(aryl ether oxadiazoles) ranged from 190-220 °C depending on the bisphenol used in the synthesis (Table 1), and no evidence of a melting point or crystallization was observed in any case. The excellent thermal stability of these materials (polymer decomposition temperatures in excess of 450 °C) allowed them to be melt processed in spite of their high Tg. Clear and fingernail creasable films could be fabricated by compression molding.

Characteristics of Poly(aryl ether oxadiazoles)



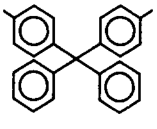
Sample	Z	[η] NMP 25° t dL/g	Tg, °C
4a	$C(CH_3)_2$	0.45	201
4b	$C(CF_3)_2$	0.50	210
4c	$C(Ph)_2$	0.44	190
4d		0.76	--

Table 1

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