The synthesis of a catechol-based bis(ether anhydride) and poly(ether imide)s derived therefrom

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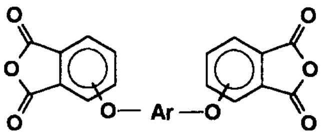
This work reports the development of nitrodisplacement reactions between catechol and nitrophthalodinitriles, thus providing a bis(ether anhydride) and high-molecular-weight, thermally stable poly(ether imide)s with *ortho*-linked units. These polymers are far more soluble and more readily processable than corresponding polymers with *para*- and *meta*-linked diol units.

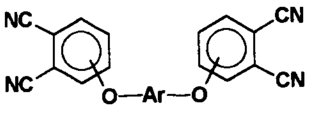
(Keywords: catechol; bis(ether anhydride); poly(ether imide))

Introduction

The development of nucleophilic displacement reactions, and nitrodisplacement reactions in particular, has led to the development of a large class of poly(ether imide)s derived from bis(ether anhydride)s (**I**) and various diamines. The bis(ether anhydride)s are usually formed by nitrodisplacement between either a diphenoxide and a nitrophthalimide, to form a bis(ether phthalimide) which is then converted to a bis(ether anhydride)[1-3] (route 1), or a diol and a nitrophthalodinitrile, in the presence of a catalyst, to form a tetranitrile (**II**) which is then converted to bis(ether anhydride)[4,5] (**I**) (route 2).



(**I**)



(**II**)

Both routes have been used to synthesize bis(ether anhydride)s from a variety of aromatic diols, including bisphenols, and from hydroquinone and resorcinol and their derivatives. We have recently reported that route 2 is preferred for displacements with many diols for which route 1 is unsuitable[6]. For example, only route 2 is suitable for reactions involving alkyl-substituted hydroquinones.

While displacement reactions with both hydroquinone and resorcinol derivatives have been reported, there are no reports in the literature, including the patent literature, of the synthesis of bis(ether anhydride)s from catechol or its derivatives and of polymers derived therefrom. There are recent reports of a chlorodisplacement reaction between 2,3-dihydroxynaphthalene and *p*-chloronitrobenzene leading to the synthesis of an *ortho*-linked bis(phenoxydiamine) and its use in polyimide synthesis[7,8].

Furthermore, there are relatively few reports of polymers containing *o*-substituted main-chain units. Existing reports are mainly of polyesters of low molecular weight based on *o*-hydroxybenzoic acid[9], copolyesters of *o*-hydroxybenzoic acid[10,11] or of catechol-based copolyesters[12], all of which have limited thermal stability to elimination of *o*-oxybenzoyl units.

In this preliminary communication we report the synthesis of a catechol-based tetranitrile (**III**), of type **II** (*Scheme 1*), its conversion into a catechol-based bis(ether anhydride) (**V**) and its incorporation into thermally stable poly(ether imide)s[13]. More extensive reports of the syntheses of bis(ether anhydride)s derived from catechol derivatives and of poly(ether imide)s derived therefrom will be published subsequently.

Experimental

4-Nitrophthalodinitrile (TCl, Tokyo, Japan), anhydrous dimethylacetamide (DMAC: Aldrich Chem. Co.) and dimethylsulfoxide (DMSO: Aldrich Chem. Co.) were used as supplied. Catechol (Aldrich Chem. Co.) was recrystallized from toluene. *m*-Phenylene diamine (MPD: Fluka) was purified by sublimation, 4,4′-diaminophenyl ether (ODA; ultra pure, ex BP), 3,4′-diaminophenyl ether (3,4-ODA: Kennedy and Klim Inc.), 1,4-bis[(1-(4-aminophenyl)-1-methyl)ethyl]benzene (BAP: Kennedy and Klim Inc.), 4,4′-bis(4-aminophenoxy)biphenyl (BAPB: Kennedy and Klim Inc.) and bis(4-amino-3,5-dimethylphenyl)methane (MBXD: Kennedy and Klim Inc.) were used as supplied. Acetic anhydride, glacial acetic acid, pyridine, acetonitrile, methanol, chloroform, potassium hydroxide and anhydrous potassium carbonate were all general laboratory reagents.

To synthesize 1,2-bis(3,4-dicyanophenoxy)benzene (**III**), 0.3 mol of 4-nitrophthalodinitrile was dissolved in 200 ml anhydrous DMSO in a flask fitted with a stirrer, nitrogen-gas inlet and thermometer. Catechol (0.15 mol) was added to the mixture, followed by 23 g of anhydrous potassium carbonate. The mixture was stirred at room temperature with a stream of dry, oxygen-free nitrogen passing through for 20 h. After that time an additional 0.011 mol of 4-nitrophthalodinitrile was added, followed by 16 g potassium carbonate and the mixture stirred for an additional 6 h. The reaction mixture was then poured into 3 dm^3 of water to produce a solid product which was washed five times with water and three times with

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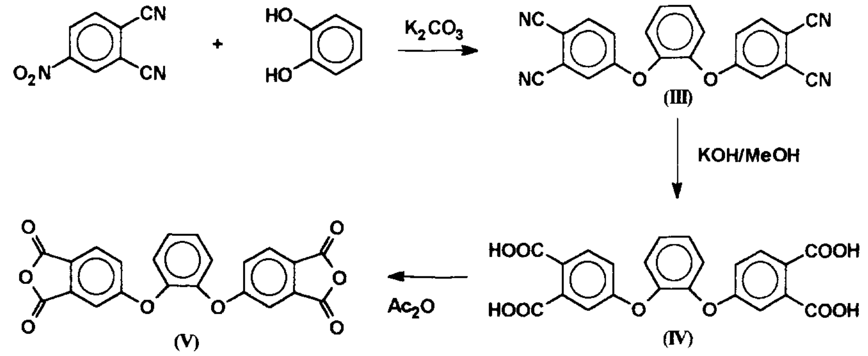


Scheme 1

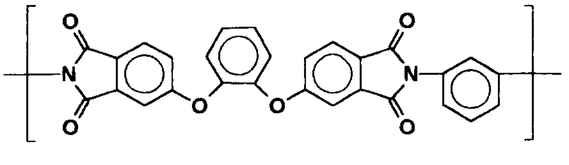
methanol. The product (50 g, 92.1% yield), in the form of a white powder, was recrystallized from acetonitrile to yield white crystals of 1,2-bis(3,4-dicyanophenoxy)benzene (**III**). The melting point of this product was 190.1–190.6°C. Elemental analysis of $C_{22}H_{10}N_4O_2$: calculated C, 72.92%, H, 2.76%, N, 15.67%; found C, 72.83%, H, 2.76%, N, 15.57%.

To prepare 1,2-bis(3,4-carboxyphenoxy)benzene (**IV**), 0.1 mol of **III** was suspended in 100 g of a 50 wt% aqueous solution of potassium hydroxide. Then 100 ml of methanol was added. The mixture was boiled under reflux. Within 2–4 h the solid tetranitrile dissolved. Reflux was continued until the evolution of ammonia had ceased. The solution was diluted with deionized water to 1.5–2 l and acidified with concentrated hydrochloric acid to pH 1.5–2. The solid tetra-acid (**IV**) was filtered off and washed with deionized water until it was neutral and no chloride ions could be detected. Then the product tetra-acid (**IV**) was dried. The yield of acid was 98% of theoretical; the acid was not characterized in detail.

To synthesize 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride (CBA) (**V**), 0.123 mol of **IV** was suspended in 300 ml of warm glacial acetic acid and 300 ml of acetic anhydride was added. The mixture was boiled under reflux for 30 min and left to crystallize overnight. The recovered needles of crystalline bisanhydride (**V**) were recrystallized from 200 ml of acetic anhydride to yield 41 g of off-white long needles of CBA (**V**), which had a melting point of 187.1–187.6°C. Elemental analysis of $C_{22}H_{10}O_8$: calculated C, 65.67%, H, 2.48%; found C, 65.69%, H, 2.45%.

Polymer syntheses

To prepare a polymer from CBA and MPD, 0.025 mol of sublimed MPD was dissolved in 100 ml of anhydrous DMAC in a flask fitted with a magnetic stirrer bar. CBA (0.025 mol) was added, in one portion, with stirring at room temperature. After 20 h the viscous solution was imidized with 40 ml of a 50:50 mixture of acetic anhydride and pyridine. Imidization was allowed to continue, with stirring, for 6 h. The mixture was then precipitated into 4 l of methanol and was boiled in methanol to remove residual solvent. The polymer was filtered off and dried, redissolved in 100 ml of chloroform and reprecipitated. The final yield was 11.9 g of a white polymer with formula:



The molecular weights of the polymer were determined by gel permeation chromatography using *N,N*-dimethylformamide containing 1 M lithium chloride as eluent, with a flow rate of 1 $cm^3\,min^{-1}$ and a polystyrene calibration. The polymer had molecular weights $\bar{M}_n = 11\,700$, $\bar{M}_w = 44\,000$ and $M_{peak} = 62\,000\,g\,mol^{-1}$ (*Table 1*); M_{peak} was the molecular weight at the peak of the gel permeation chromatogram for the polymer.

A series of polymers was synthesized from CBA and other aromatic diamines by the same procedure; structures of the diamines are shown in *Table 2*. Diamines included ODA, 3,4-ODA, BAP, BAPB and MBXD. In all cases the polymers remained in solution on imidization. The properties of several polymers are collected in *Table 1*.

For comparative purposes, bis(ether anhydride)s HBA and RBA of type **I** were prepared from hydroquinone and resorcinol, respectively, where Ar are *para*- and *meta*-linked units, according to *Scheme 1*, and polymers were prepared from them with MPD. These anhydrides and polymers have previously been reported by Takekoshi[14]. Owing to lack of solubility, the molecular weights of these polymers were not determined.

Polymer properties

Glass transition temperatures (T_g) of the polymers were determined on a Perkin–Elmer DSC2. Transition temperatures determined in this work were onset temperatures. T_gs of the catechol-based polymer and the comparative polymers are reported in *Table 1*.

The solubilities of the polymers were tested in chlorinated hydrocarbons (CH_2Cl_2, $CHCl_3$), DMAC, *N*-methylpyrrolidone (NMP) and cresol; the solvent power for these and other polyimides increases in this order. Room-temperature solubilities are quoted in *Table 1*.

Thermal stabilities of some polymers were determined by thermogravimetric analysis (t.g.a.). Measurements were made with the aid of a Perkin–Elmer TGA7; the results are quoted in *Table 1*.

When the polymer derived from catechol-based anhydride was heated to 360°C, long fibres could be pulled from the melt. Fibres could not be pulled from the corresponding polymers prepared from HBA or RBA.

Conclusions

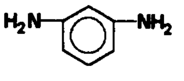
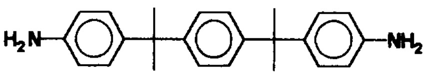
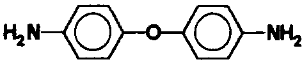
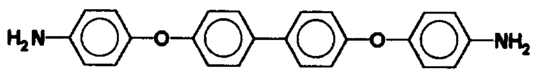
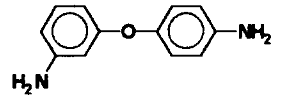
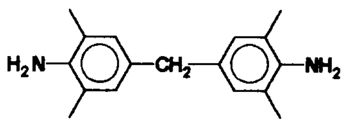
Although nitrodisplacement reactions with catechol have not previously been referred to in patents or in the open literature, we have now demonstrated that nitrodisplacement reactions between catechol and 4-nitrophthalodinitrile can be performed successfully to yield a tetranitrile in high yield. The tetranitrile can be

Table 1 Characteristics of polymers derived from anhydrides based on dihydroxybenzenes

					Weight loss		Temperature for 5% weight loss (°C)
Anhydride	Amine	M_{peak}[a] (kg mol^{-1})	T_g (°C)	Solubility[b]	(%)	Temperature range (°C)	
CBA	MPD	112	220	s	98.5	477–670	
CBA	ODA	287	208	s			
CBA	3,4-ODA	151	190	s			
CBA	BAP	422	211	s			
CBA	BAPB	476	204	s	95	520–676	
CBA	MBXD	214	243	s			
HBA	MPD		244[c] 255[d] 242[e]	NMP	97	527–682[c]	526[d]
RBA	MPD		224[d]	NMP			

[a] Highest value from multiple syntheses and of samples used to determine T_g
[b] s, Soluble in all solvents used; NMP, soluble in NMP and cresol only
[c] This work
[d] Ref. 14
[e] Ref. 15

Table 2 Structures of diamines used in polymer syntheses

Code	Structure	Code	Structure
MPD		BAP	
ODA		BAPB	
3,4-ODA		MBXD	

readily hydrolysed to the corresponding tetra-acid and then dehydrated to the corresponding CBA (**V**).

Despite the fact that there are very few reports of polymers having 1,2-linked residues in the main chain, and these are mainly polyesters of low molecular weight and/or poor thermal stability, we have demonstrated that the bis(ether anhydride) derived from catechol can be successfully incorporated into high-molecular-weight poly(ether imide)s by normal solution polymerization with aromatic diamines. When compared with other poly(ether imide)s of similar structure (derived from MPD), based on hydroquinone or resorcinol, the catechol-based polymers are seen to have comparable and good thermal stability.

Compared with the polymers prepared from hydroquinone and resorcinol-based bis(ether anhydride)s, polymers derived from the catechol-based bis(ether anhydride) and various diamines are very soluble. This fact makes the polymers readily processable from solution. In addition, the ability to pull fibres from the melt suggests that the polymers derived from catechol-based bis(ether anhydride) may also be melt processable, even at high molecular weight.

Thus, this study shows that nitrodisplacements can be extended to *o*-linked diols and can be used to provide high-molecular-weight, soluble, stable and processable poly(ether imide)s in solution from relatively inexpensive components. The polymers that become available provide an additional dimension to the development of structure–property relationships.

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