Synthesis of Bis(ether anhydride)s for Poly(ether imide)s Having 1,2-Linked Units by Nitrodisplacement with Catechol Derivatives

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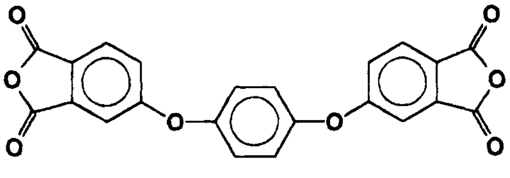
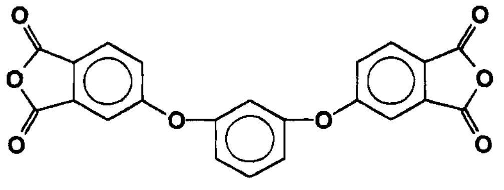
ABSTRACT: This paper extends a recent announcement that catechol will undergo nitrodisplacement with 4-nitrophthalonitrile to form a bis(ether dinitrile) to a series of substituted catechols and to reaction with 3-nitrophthalonitrile. For all catechols studied the bis(ether dinitrile)s were readily hydrolyzed to bis(ether diacid)s and converted to bis(ether anhydride)s. The bis(ether anhydride)s were converted to high-molecular-weight polymers with bis(4-aminophenyl) ether in solution polymerization with chemical imidization. The polymers formed have lower glass transition temperatures than polymers based on the hydroquinone-based bis(ether anhydride) and have far greater solubilities and processability than corresponding polymers based on hydroquinone and resorcinol-based bis(ether anhydride)s.

The synthesis of thermally-stable, high-molecular-weight polymers containing 1,2-linked, main-chain aromatic units is relatively unusual. Polyesters derived from 2-hydroxybenzoic acid are unstable to thermal elimination of main-chain units[1,2] and are often of low molecular weight.[3] There are also reports of copolyesters incorporating catechol units which are more thermally stable but are often of relatively low molecular weight.[4]

There are now many reports in the literature of bis(ether anhydride)s, as precursors to high-molecular-weight poly(ether imide)s, synthesized by nitrodisplacement reactions between aromatic diols, or their sodium salts, and 3- or 4-nitrophthalic acid derivatives.[5–9] In addition to bisphenols, several papers and patents (with many unsubstantiated claims) disclose nitrodisplacement reactions with hydroquinone and resorcinol and their derivatives[10,11] and subsequent conversion of the intermediates to bis(ether anhydride)s, i.e., the incorporation of 1,4- and 1,3-linked aromatic units to bis(ether anhydride)s through ether linkages to form, for example, hydroquinone bis(ether anhydride) (HBA, **I**) from hydroquinone and resorcinol bis(ether anhydride (RBA, **II**) from resorcinol.[7] Bis(ether anhydride)s **I** and **II** are readily converted to poly(ether imide)s having the cited main-chain units.



(I)



(II)

While there are few confirmed reports of successful nitrodisplacement reactions with substituted hydroquinone and resorcinol derivatives, we recently reported facile nitrodisplacement reactions between several substituted hydroquinones (with single or multiple methyl, *tert*-butyl, or other substituents) and 3- or 4-nitrophthalodinitriles.[12,13] The resulting bis(ether dinitrile)s were hydrolyzed to the corresponding bis(ether diacid)s and dehydrated to the bis(ether anhydride)s. The synthesis and properties of a selection of possible poly(ether imide)s derived from these bis(ether anhydride)s was also reported. While there are, therefore, several examples of poly(ether imide)s with 1,4- and 1,3-linked main-chain units, there are no previous reports of bis(ether anhydride)s and, hence, poly(ether imide)s with 1,2-linked, main-chain, phenylene–ether units derived from 1,2-dihydroxybenzene (catechol) or its derivatives in anhydride units.

The number and variety of processable poly(ether imide)s which can be synthesized is limited, in part, by the bis(ether anhydride)s which can be synthesized. The number of bis(ether anhydride)s is, in turn, limited by the diols which will undergo nucleophilic displacement reactions with phthalic acid derivatives, preferably with nitrophthalodinitriles. Given the excellent thermal and oxidative stability of poly(phenyl ether)s in general,[14] the synthesis of polymers with *o*-diphenoxy residues as well as thermally stable imide units, in addition to the isomeric poly(ether imide)s based on **I** and **II** with para- and meta-linked units, appeared a desirable goal.

As a result of our previous study, in which we attempted to synthesize poly(ether imide)s with bulky side groups, we undertook an investigation to identify which diols will undergo nitrodisplacement with 3- or 4-nitrophthalodinitrile.[15] As a result of our investigations we identified a pattern of behavior which has some predictive capability; the results of that investigation will be reported subsequently. These investigations indicated that there is no good reason why 1,2-dihydroxybenzene and its derivatives should not undergo nitrodisplacement with nitrophthalodinitriles; failure in nitrodisplacement reactions is usually associated with the occurrence of competing oxidative processes, and the standard redox potential of catechol (795 mV[16]) is high. Indeed, there is one report of nitrodisplacement reactions in *N,N*-dimethylformamide with catechol and 4-*tert*-butylcatechol to form bis(ether dinitrile)s **III** and **Vd** which were used in the synthesis of phthalocya-

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Table 1. Identification of Catechol Derivatives (IXa–g) Used

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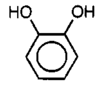
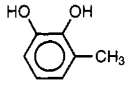
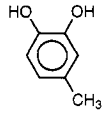
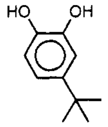
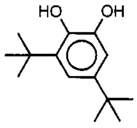
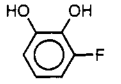
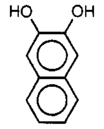
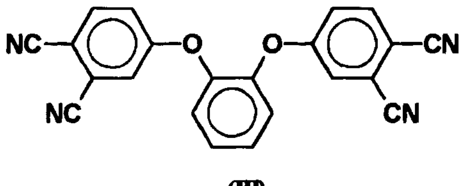
a		b	
c		d	
e		f	
g			

nines.[17] Such processes could allow the synthesis of bis(ether anhydride)s and poly(ether imide)s with 1,2-units linked through thermally-stable ether linkages. There are also recent reports of a chlorodisplacement reaction between 2,3-dihydroxynaphthalene and *p*-nitrochlorobenzene to form an ortho-linked dinitro compound which was reduced to the equivalent diamine and used in polyimide synthesis.[18,19]

Very recently we reported, in a preliminary publication, the first synthesis of bis(ether anhydride)s for poly(ether imide) synthesis based on catechol.[20,21] We demonstrated that catechol will readily undergo nitrodisplacement with 4-nitrophthalodinitrile in dimethyl sulfoxide to yield the bis(ether dinitrile) **III**, which is then readily hydrolyzed and dehydrated to the bis(ether anhydride) **IV**. The bis(ether anhydride) was reacted with a limited series of diamines to demonstrate the synthesis of high-molecular-weight poly(ether imide)s with 1,2-linked, main-chain, aromatic residues. The polymers were shown by thermogravimetric analysis (TGA) to have good thermal stability.



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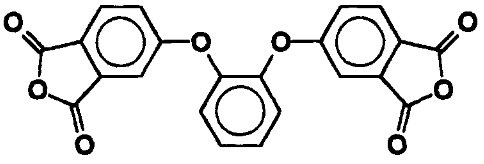
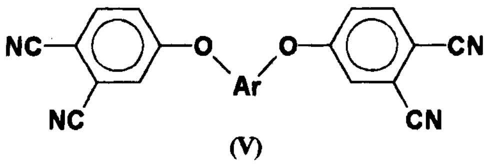


(IV)

In this paper we now show that nitrodisplacement between nitrophthalodinitriles and aromatic dihydroxy compounds in which the hydroxyl groups are ortho (i.e., substituted catechols and 2,3-dihydroxynaphthalene) is generally facile. Thus, we extend our previous report to nitrodisplacements between substituted catechols (**IXb–g**; Table 1) and 4-nitrophthalodinitrile (to form a series of bis(ether dinitrile)s **Vb–g**) and between **IXa** and the more reactive 3-nitrophthalodinitrile (to form bis(ether dinitrile) **VI**). The bis(ether dinitrile)s **V** are readily converted to bis(ether anhydride)s **VIIb–g**, and we report the synthesis of a selection of high-molecular-weight poly(ether imide)s **VIII** from them. The synthesis, characterization, and properties of a number of other polymers will be reported subsequently.



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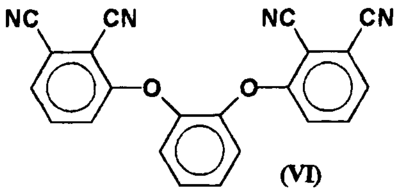

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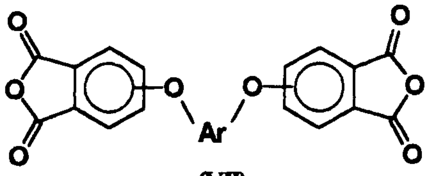

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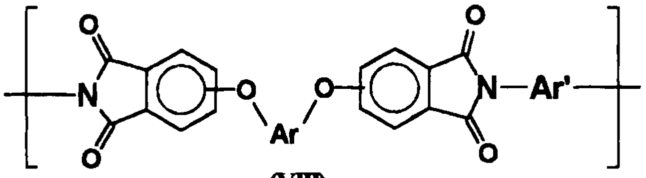


(VIII)

This paper, therefore, demonstrates the synthesis of a new group of bis(ether anhydride)s which leads to a whole new class of high-molecular-weight, thermally-stable poly(ether imide)s which are far more soluble than their analogues with 1,3- and 1,4-phenylene units and have higher molecular weights than are generally available in other polymers (copolyarylates) with 1,2-linked main-chain units. The polymers are, thus, more processable, in solution or from the melt, than their counterparts derived from hydroquinone or resorcinol-based bis(ether anhydride)s.

Experimental Section

Materials. The structures and identification letters of the several catechol derivatives (**IXa–g**) used in this study are shown in Table 1; catechol and all its derivatives were obtained from Aldrich Chemical Co., except for 2,3-dihydroxynaphthalene which was obtained from Fluka. Catechol was recrystallized from toluene. 4-Nitrophthalodinitrile (TCI, Tokyo, Japan), anhydrous dimethylacetamide (DMAC; Aldrich Chemical Co.), and dimethyl sulfoxide (DMSO; Aldrich Chemical Co.) were used as supplied. Bis(4-aminophenyl) ether (ODA) was an ultrapure sample obtained from BP. Acetic anhydride, glacial acetic acid, pyridine, acetonitrile, methanol, chloroform, pyridine, *N*-methylpyrollidinone (NMP), potassium hydroxide, and anhydrous potassium carbonate were all general laboratory reagents.

3-Nitrophthalodinitrile was synthesized by the method of Hall et al.[22] in which 3-nitrophthalimide (Lancaster Synthesis) is reacted heterogeneously with a concentrated ammonia solution at room temperature. 3-Nitrophthalamide was filtered off after it precipitated from the reaction mixture on cooling overnight. After washing the nitrophthalamide with diethyl ether, it was dissolved in dry dioxane/pyridine at 0 °C and reacted with trifluoroacetic anhydride. After warming, the solution was diluted with water and extracted with ethyl

Scheme 1

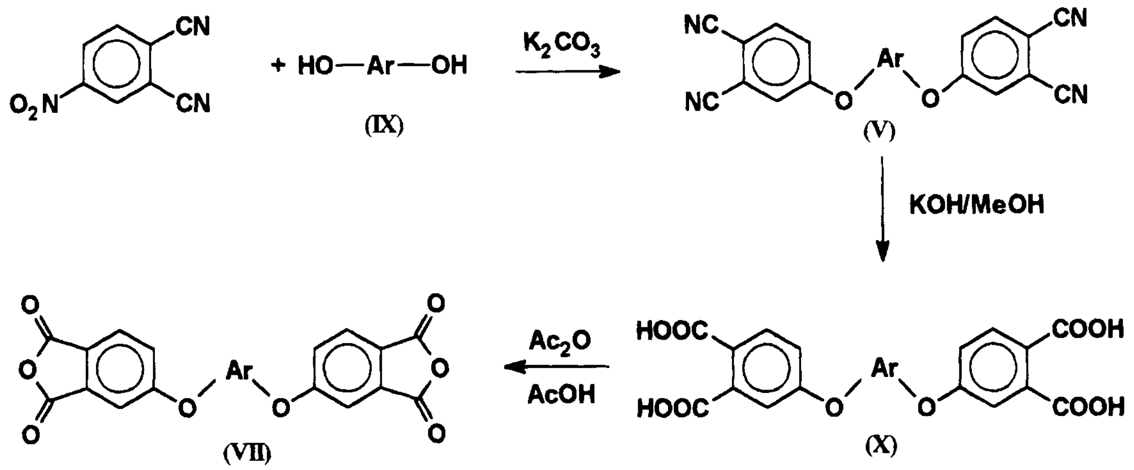


Table 2. Tetranitriles Vb–g and VI Synthesized from Diols IX

catechol HO–Ar–OH		elem anal.		crystallzn solvent	yield/%	mp/°C
		calcd	found			
IX[a]	C	72.92	72.83	MeOH/MeCN (5:1)	92.11	190.1–190.6
	H	2.76	2.76			
	N	15.67	15.57			
IXb	C	73.40	73.38	MeOH/MeCN (4:1)	83.8	194.3–195.3
	H	3.19	3.16			
	N	14.89	14.95			
IXc	C	73.40	73.31	MeOH/MeCN (4:1)	81.2	194–195
	H	3.19	3.15			
	N	14.89	14.99			
IXd	C	74.64	74.55	MeOH	76.6	161–162
	H	4.30	4.25			
	N	13.39	13.39			
IXe	C	75.94	76.07	MeCN	99.1	247–248
	H	5.48	5.51			
	N	11.81	11.86			
IXf	C	69.47	69.47	MeOH/MeCN (4:1)	80	198.5–199.5
	H	2.36	2.34			
	N	14.73	14.80			
IXg	C	75.72	75.50	MeCN	99.2	265–266
	H	2.91	2.89			
	N	13.59	13.51			

[a] Data from ref 20.

acetate. The product was washed with water, dilute hydrochloric acid, water, and brine. The nitrophthalodinitrile was finally recrystallized from acetone/hexane (50:70) to give colorless crystals.[13]

Polymer Characterization. Molecular weights of poly(ether imide)s were determined by gel permeation chromotography, using Polymer Laboratories PL-gel 5-μm columns, DMF with 1 M LiCl as eluant, a pumping rate of 1 mL min^{-1}, and a refractive index detector (Knauer). The system was calibrated with polystyrene standards (Polymer Laboratories).

Glass transition temperatures (T_gs) were determined by differential scanning calorimetry with the aid of a Perkin-Elmer DSC2. Accurate masses of precursors were determined by mass spectrometry on a Fisons TRIO-100 quadrapole mass spectrometer (70 eV) in electron ionization mode.

Nitrodisplacement Reactions

The general reaction scheme employed for nitrodisplacement reactions is shown in Scheme 1. In this scheme 4-nitrophthalodinitrile is reacted with diol **IX** in anhydrous DMSO in the presence of potassium carbonate as an acid acceptor to generate bis(ether dinitrile) **V** which is then hydrolyzed to bis(ether diacid) and dehydrated to bis(ether anhydride) **VII**. The detailed procedures were almost identical for all catechols used. For **IXa** itself the detailed procedure has been presented previously.[20,21] In this paper we give the detailed procedures for each step in the reaction in Scheme 1 for the synthesis of anhydride **VIIc** from 3-methylcatechol (**IXb**) and list the minor differences for other diols. We also give in detail the procedure for nitrodisplacement between 3-nitrophthalodinitrile and **IXa**. The reaction products **Vb–g** and **IV** from nitrodisplacement and the anhydrides **VII** were characterized, and details of elemental analysis data and melting points for the several reaction products are given in Tables 2 and 3; the intermediate acids **X** were not characterized in detail. The elemental analysis data were supported by spectroscopic data (infrared and NMR) and by mass spectrometry; for example, all bis(ether dinitrile)s **V** exhibited strong, sharp, characteristic infrared absorptions (C≡N stretch) at ν = 2231–2235 cm^{-1} which were totally absent in the bis(ether anhydride)s **VII**.

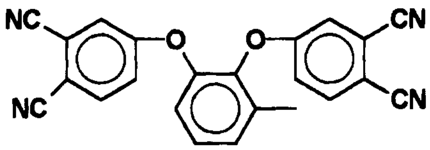
Preparation of 1,2-Bis(3,4-dicyanophenoxy)-3-methylbenzene (Vb). A total of 3.60 g (0.02 mol plus 0.14 g of excess) of 4-nitrophthalodinitrile was dissolved in 50 mL of anhydrous DMSO in a 100-mL three-necked flask fitted with a magnetic stirbar and under a nitrogen atmosphere. A total of 1.24 g (0.01 mol) of **IXb** was added to the mixture followed by 5 g of anhydrous potassium carbonate. The reaction mixture was stirred at room temperature for 24 h and then precipitated into 400 mL of water. The yellow solid was washed with water until the washings were neutral. The wet product

Table 3. Dianhydrides VIIb–h: Identification Codes, Analytical Data and Melting Points

catechol HO–Ar–OH	code		elem anal.		crystallzn solvent[b]	yield/%	mp/°C
			calcd	found			
IXa[a]	CBA	C	65.67	65.69	Ac_2O	80.8	187.1–187.6
		H	2.48	2.45			
IXb	3-MCBA	C	66.3	66.28	MeCN/Ac_2O (1:1)	95.7	208–209
		H	2.8	2.84			
IXc	4-MCBA	C	66.3	66.44	MeCN/Ac_2O (3:1)	87.7	179–180
		H	2.8	2.81			
IXd	4-tBCBA	C	68.12	68.10	MeCN/Ac_2O (9:1)	86.1	158–159
		H	3.93	3.90			
IXe	3,5-tBCBA	C	70.03	69.93	MeCN/Ac_2O (6:1)	89.6	147–148
		H	5.05	5.25			
IXf	3-FCBA	C	62.86	62.48	MeCN/Ac_2O (10:1)	85.43	177–178
		H	2.15	2.57			
IXg	2,3-NCBA	C	69.02	68.95	AcOH/Ac_2O (1:1)	95.0	264.6–265.4
		H	2.65	2.57			

[a] Data from ref 20. [b] MeCN = acetonitrile; Ac_2O = acetic anhydride; AcOH = acetic acid.

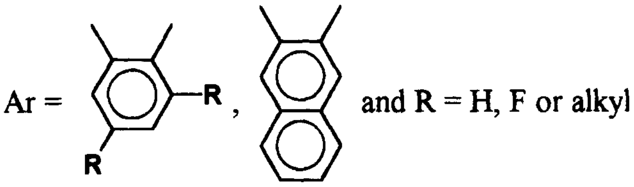
was recrystallized twice from methanol/acetonitrile (4:1) to yield 2.80 g of pure white bis(ether dinitrile) **Vb** and 0.35 g of a less pure product (83.8% theoretical yield). The product had the formula:



Synthesis of Other Bis(ether dinitrile)s with 4-Nitrophthalodinitrile. Nitrodisplacement with **IXc** was performed identically to yield 3.08 g of off-white crystals of **Vc**. Similarly, with **IXd** the yield was 3.2 g of off-white crystals of **Vd**; the relatively low yield was due to loss of product because of its high solubility in methanol. With **IXe** the initial product was white, and after washing three times with water and three times with methanol, the product was 4.70 g (99.1% theoretical) of snow-white crystals which were recrystallized from acetonitrile to yield 4.1 g of final product. Nitrodisplacement with **IXf** similarly yielded 3.04 g of off-white crystals of **Vf**. With **IXg** the initial product was off-white and was washed with water until the washings were neutral and then with methanol to give 4.12 g of crude bis(ether dinitrile) **Vg** which was recrystallized from 240 cm^3 of acetonitrile.

Preparation of 1,2-Bis(2,3-dicyanophenoxy)benzene (VI). A total of 3 g (0.0173 mol) of 3-nitrophthalodinitrile was dissolved in 15 mL of anhydrous DMSO in a 50-mL three-necked flask fitted with a stirrer, nitrogen-gas inlet, and thermometer. A total of 0.95 g (0.00863 mol) of **IXa** followed by 2 g of potassium carbonate was added to the reaction mixture. The mixture was stirred at room temperature with a stream of dry, oxygen-free nitrogen passing through the flask for 26 h. The product was isolated by pouring the reaction mixture into 300 mL of water. The resultant solid precipitate was filtered off and washed until the effluent was neutral. The product (an off-white powder) was recrystallized from methanol/acetonitrile (20/80) to yield off-white crystals of **VI**. The melting point was 158–159 °C. Elem anal. Calcd for $C_{22}H_{10}N_4O_2$: C, 72.92; H, 2.76; N, 15.67. Found: C, 72.57; H, 2.72; N, 15.43.

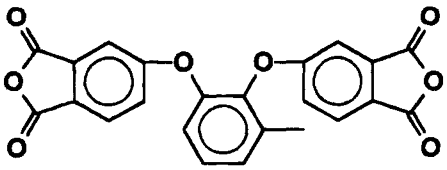
General Procedure for the Hydrolysis of 1,2-Bis(3,4-cyanophenoxy)benzenes. A total of 0.1 mol of a 1,2-bis(3,4-cyanophenoxy)benzene derivative (bis(ether dinitrile)) (**Vb–g**) was suspended in 100 g of a 50 wt % aqueous solution of potassium hydroxide. Then 100 mL (or more if needed to wet the solid) of methanol was added. The mixture was boiled under reflux. Within the first 2–4 h the solid bis(ether dinitrile) dissolved. Reflux was continued until the evolution of ammonia ceased. The solution was then diluted with deionized water to 1.5–2 L and acidified with concentrated hydrochloric acid to pH 1.5–2. The solid bis(ether diacid) **Xb–g** was filtered off and washed with deionized water until neutral, and no chloride ions could be detected. The the bis(ether diacid) product with formula **X**, especially where



was dried. Yields were generally in the range 92–98% of theoretical; products were not characterized in detail.

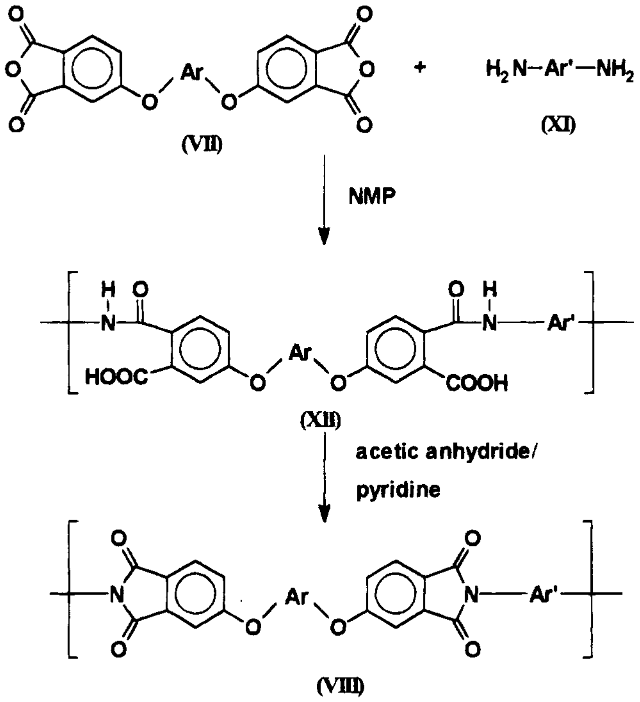
Preparation of Dianhydrides VII–g from Bis(ether diacid)s Xb–g. The same general procedure was used to dehydrate bis(ether diacid)s **Xb–g** to form the dianhydrides **VIIb–g**. The detailed procedure is described for the synthesis of **VIIb** and **VIIg**. For all other acids the procedure was identical with that for **Xb** except for the solvents used for recrystallization which are specified in Table 3, along with analytical data and melting points for all dianhydrides.

Preparation of 1,2-Bis(3,4-dicarboxyphenoxy)-3-methylbenzene Dianhydride (VIIb). A total of 0.01 mol of 1,2-bis(3,4-dicarboxyphenoxy)-3-methylbenzene (**Xb**), prepared from **Vb** as described above, was suspended in 30 mL of warm glacial acetic acid, and 30 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 bis(ether anhydride) were recrystallized from acetonitrile/acetic anhydride (1:1, v/v) to yield off-white long needles of **VIIb** of structure



Preparation of Dianhydride VIIg from Bis(ether diacid) Xg. A total of 3.47 g (0.007 mol) of 2,3-bis(3,4-dicarboxyphenoxy)naphthalene (**Xg**), synthesized according to the procedure described above from the

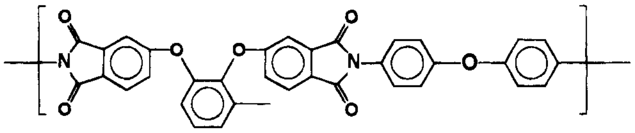
Scheme 2



bis(ether dinitrile) **Vg**, was suspended in 15 mL of acetic acid and brought to a boil; 100 mL of acetic anhydride was added in aliquots, and the mixture was boiled gently for 40 min. After leaving overnight to cool, the white crystals which precipitated were filtered off and dried under vacuum at 140 °C to yield 3.05 g (95% of theoretical yield) of the bis(ether anhydride) **VIIg**.

Polymerization Reactions. Poly(ether imide)s **VIII** were synthesized in solution in a conventional two-stage process involving intermediate formation of poly(amic acid) **XII** (Scheme 2). According to this procedure, exactly equimolar quantities of dianhydride **VII** and diamine **XI** were reacted together in a suitable aprotic solvent to form **XII** which was then dehydrated and cyclized to **VIII**. Details are given for the synthesis of one poly(ether imide). All other synthesis were performed in an identical manner, and all polymers (poly(amic acid)s and poly(ether imide)s) remained in solution during synthesis. Only the syntheses of poly(ether imide)s prepared with ODA as diamine are presented here, to illustrate the use of each anhydride. The synthesis and characterization of other polymers, with different diamines, will be presented in a subsequent publication along with a description of some properties. The formation of polymers from catechol bis(ether anhydride) CBA and various diamines, including ODA, and of polymers from HBA and RBA with several diamines has been reported previously.[20]

Preparation of Polymer from 1,2-Bis(3,4-carboxyphenoxy)-3-methylbenzene Dianhydride (3-MCBA, VIIb) and ODA. A total of 0.001 mol of ODA was dissolved in 5 mL of anhydrous dimethylacetamide (DMAC) in a flask fitted with a magnetic stirbar. A total of 0.001 mol of 3-MCBA was added, in one portion, with stirring at room temperature. After 20 h the highly viscous solution was imidized with 2 mL of a 50:50 mixture of acetic anhydride and pyridine. The mixture was allowed to stand, with stirring, for 6 h. The mixture was then precipitated dropwise into 100 mL of methanol and was boiled in methanol to remove residual solvent. The polymer was filtered off and dried, redissolved in 5 mL of chloroform, and reprecipitated. The structure of the polymer was



Results and Discussion

There are now many reports of the synthesis of bis(ether anhydride)s and poly(ether imide)s derived from various diols. The diols are usually incorporated into the bis(ether anhydride) monomers by a nitrodisplacement reaction with a phthalic acid derivative. While there are several reports on the successful use of bisphenols in this context, there are few reports of the use of dihydroxybenzenes and their derivatives in nitrodisplacement reactions. Nitrodisplacement reactions with hydroquinone and resorcinol themselves have been described previously,[7-11] but there is little information on displacements with their derivatives.

During our previous studies of nitrodisplacement reactions, aimed at the synthesis of poly(ether imide)s for gas separation membranes, we demonstrated that nitrodisplacement between diol and 3- or 4-nitrophthalonitrile is the preferred route for diols which are susceptible to oxidation processes.[13] Thus we were able to demonstrate that Scheme 1 works satisfactorily for several substituted hydroquinones and resorcinols.

In a preliminary paper, we recently reported the successful nitrodisplacement reactions between 4-nitrophthalodinitrile and catechol; we also demonstrated that, as in Scheme 1, the resulting bis(ether dinitrile) **V** can be hydrolyzed and converted to the corresponding bis(ether anhydride) **VII**. The results now presented in Table 2 demonstrate that this finding can also be applied to substituted catechols, and to nitrodisplacement with 3-nitrophthalodinitrile, to produce a variety of bis(ether dinitrile)s with ortho-linked aromatic residues. Nitrodisplacement with catechol derivatives is facile, irrespective of whether the substituents are electron-donating or electron-withdrawing and even if very bulky substituents are attached to the catechol residue. As in our previous study, we found that purity of the bis(ether dinitrile) ultimately controls success in producing high-molecular-weight poly(ether imide)s after subsequent conversion of the bis(ether dinitrile) to bis(ether anhydride) and, hence, to poly(ether imide).

In nitrodisplacement reactions, 3-nitrophthalodinitrile is generally more reactive than 4-nitrophthalonitrile, in that the nitrodisplacement reactions proceed more rapidly. However, while nitrodisplacement between 4-nitrophthalic esters and sodium 4-methylphenoxide proceeds satisfactorily with a major yield of phenolic ether, reaction between 3-nitrophthalic esters and sodium 4-methylphenoxide yields a variety of reaction products with no major component, indicating a series of side reactions.[23] Also, for displacements between 4-nitrophthalic esters and 4-methylphenol with potassium carbonate as catalyst the yield of phenol ether is low.[23] For nitrodisplacement with nitrophthalodinitriles, using potassium carbonate as catalyst, the high yields of bis(ether dinitrile) obtained in this work (Table 2) indicate no serious intervention of side reactions between 4-nitrophthalodinitrile and any catechol derivative or between catechol and 3-nitrophthalodinitrile; the relatively low yield for **Vd** was of pure material and largely reflects losses on recrystallization of a very soluble product. Thus, nitrodisplacements with catechols are as well-behaved as those with hydroquinone or resorcinol and their derivatives.

Table 4. Characteristics of Polymers

anhydride	mol wt/$\times 10^3$	T_g/°C	solubility
CBA	287	209	s
3-MCBA	42.4	216, 218	s
4-MCBA	79.2	213	s
4-tBCBA	58	219	s
3,5-tBCBA	16.8	228	s
3-FCBA	235	216	s
2,3-NBA	85	235	s
HBA	78 (0.96 dL/g[b])	239[a] 237[b]	NMP
RBA	(0.70 dL/g[b])	209[b]	NMP (swells)

[a] Data determined in this work. [b] Data taken from the paper by Takekoshi.[24]

In almost all cases the bis(ether dinitrile)s **V** were readily hydrolyzed to bis(ether diacid)s **XI** by methanolic potassium hydroxide. Although the bis(ether diacid)s were not isolated as pure compounds for characterization, it is clear that intermediate yields were high as the yields of anhydride prepared from them, and based on bis(ether dinitrile), were high.

For all the substituted catechols reported, cyclodehydration of the bis(ether diacid) to bis(ether anhydride) **VII** was clean and was achieved with good yield; analytical data for the bis(ether anhydride)s are presented in Table 3.

The bis(ether anhydride)s were converted to poly(ether imide)s by reaction with diamines in a conventional two-stage solution process in aprotic solvent (Scheme 2). The viscosities of the reaction mixtures became high as poly(amic acid)s were formed, indicating the formation of high-molecular-weight polymer. When imidized all polymers remained in solution, unlike many other poly(ether imide)s based on ODA as diamine with 1,4- or 1,3-linked dihydroxybenzene residues, i.e., poly(ether imide)s based on HBA or RBA residues. That is, the polymers based on catechol derivatives are more soluble than the corresponding polymers based on hydroquinone or resorcinol.

Solubilities of the polymers were tested in a number of solvents. We found, in general, that the solvent power toward poly(ether imide)s for several solvents increases in the order CH_2Cl_2, $CHCl_3$ < DMF < DMAC < NMP < cresol. All polymers based on catechol and its derivatives were soluble in all the above-named solvents. In contrast, the polymers based on hydroquinone and resorcinol-based anhydrides, HBA and RBA, respectively, only dissolved or swelled in NMP and more aggressive solvents. Thus, all polymers derived from catechol derivatives and ODA can be readily processed from solution.

For several of the poly(ether imide)s based on catechol derivatives, fibers could be pulled from a molten pool of polymer, indicating that the polymers are amenable to melt processing.

The polymers prepared all had high molecular weights, as measured by gel permeation chromotography calibrated with polystyrene standards. The molecular weights quoted in Table 4 are peak molecular weights, i.e., those corresponding to the peaks of the chromatograms; these molecular weights correspond approximately to weight-average molecular weights in so far as polystyrene standards provide a measure of molecular weight. The chromatograms indicated normal unimodal molecular weight distributions with polydispersities of about 2 and only traces of oligomers. The high molecular weights of the polymers confirm that the monomer syntheses were successful in producing pure materials.

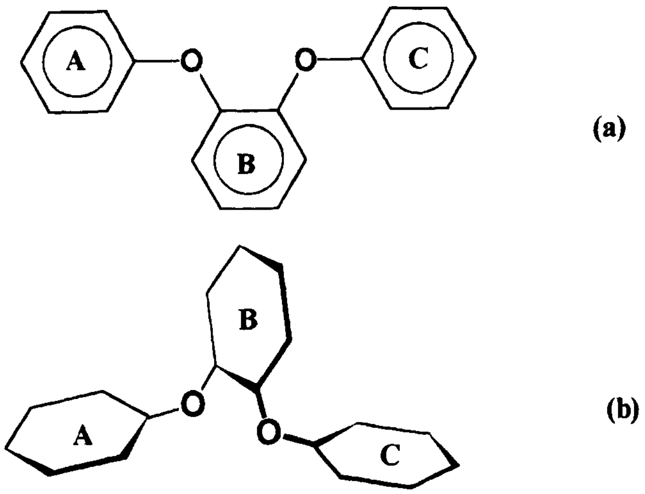
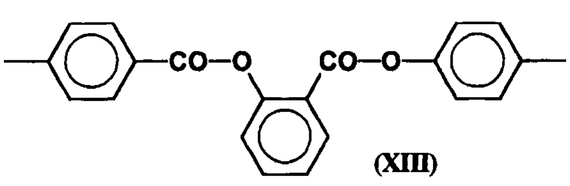


Figure 1. Representations of conformations of diphenoxyphenyl units present in catechol-based anhydrides and poly(ether imide)s.

Glass transition temperatures of the several poly(ether imide)s were measured by differential scanning calorimetry. For all the polymers based on catechol derivatives and ODA the T_gs were in excess of 200 °C and there was no evidence of thermal decomposition; thermogravimetric analysis of CBA polymers shows no decomposition below 480–520 °C in air.[20] T_gs are generally similar to those of the equivalent polymers based on RBA but rather lower than the polymers based on HBA. T_gs increased slightly with the bulkiness of the substituents, as is generally found in other polymer series.

The solubilities and T_gs of several polymers give some indication of the flexibility of the polymers as well as interactions between chains and with solvents. For the series of polymers investigated in this study the highest T_g is for the polymer based on HBA; this probably reflects the extended nature of the anhydride unit which can adopt a relatively planar configuration and probably allows relatively strong interchain interactions. T_g for the resorcinol-based polymer is significantly lower, probably reflecting the loss of the extended nature of the chain. For CBA-based polymer T_g is similar to that of the RBA polymer.

In a review of rigid polymers, Preston[25] comments that liquid crystallinity in polyesters with general structure **XIII**, based primarily on para-linked units, and



(XIII)

containing a relatively high proportion of hydroxybenzoic acid units[26] is possibly because the ortho-oriented rings are displaced laterally from the main chain and do not interfere with the interchain attractions of the para-orientated segments. Subsequently, Navarro[4] stated that "the formation of bent structures due to the presence of ortho links" will help prevent "the extended close packing of chains". In the case of the CBA units in the poly(ether imide)s described here, we are concerned with the conformations of the substituted bisether unit shown in Figure 1. Simple models show that it is impossible for rings A, B, and C to be coplanar with B lateral to the main-chain direction (Figure 1a). However, although we have not yet undertaken extensive studies, early indications from molecular modeling studies are that a low-energy conformation for the anhydride unit is one in which the aromatic rings A and C are almost coplanar and the plane of the central catechol ring B is perpendicular to that of A and C, shown schematically in Figure 1b, and the plane of ring B is almost perpendicular to the axis through rings A and C. This lateral arrangement of the catechol unit will hinder interchain packing and probably help to reduce T_g. However, rotations about the ether linkages do not appear to be very restricted, and it is uncertain if, in bulk polymer, space-filling requirements dominate to prevent adoption of this low-energy, free-chain conformation.

Conclusions

The results described in this paper demonstrate that our finding that catechol will undergo nitrodisplacement reaction with 4-nitrophthalonitrile can be extended to a series or related *o*-dihydroxybenzene derivatives with electron-donating or electron-withdrawing substituents and to 3-nitrophthalonitrile. The bis(ether dinitrile)s so formed are readily hydrolyzed to bis(ether diacid)s and cyclodehydrated to produce bis(ether anhydride)s.

Bis(ether anhydride)s derived from catechol derivatives are shown to react readily with diamines, ODA in this immediate study, to form high-molecular-weight poly(amic acid)s which can be dehydrated in solution to soluble high-molecular-weight poly(ether imide)s. The polymers so formed are more soluble in common solvents than the equivalent polymers derived from the bis(ether anhydride)s derived from hydroquinone or resorcinol.

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