Synthesis of bis(ether nitrile)s and bis(ether acid)s from simple aromatic diols by *meta*-fluoro displacement from 3-fluorobenzonitrile†

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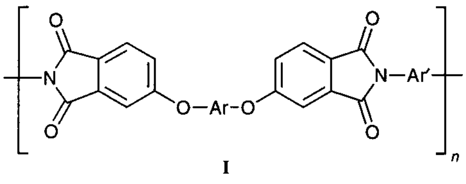
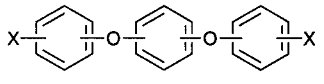
There is interest in synthesizing bis(ether acid)s and related compounds to use as monomers in order to prepare processable aromatic polymers, such as poly(ether amide)s and poly(ether ester)s. We have now found that it is possible to prepare efficiently bis(3-cyanophenoxy)phenylenes by fluoro displacement from 3-fluorobenzonitrile and phenylene diols or their derivatives, such as substituted catechols, and to convert those bis(ether nitrile)s to bis(3-carboxyphenoxy)phenylenes which can be used in the synthesis of poly(ether amide)s and poly(ether ester)s. The *meta*-fluoro displacement is performed at elevated temperatures in *N*-methylpyrrolidinone.

Following the development of processable poly(ether imide)s **I**,[1] we recently demonstrated that major enhancement in processability can be achieved by modifying the substitution pattern of the aromatic unit Ar between the ether linkages in **I**, especially by inclusion of 1,2-linked units derived from catechol or substituted catechols.[2] It is logical to extend these concepts to the synthesis of poly(ether amide)s and poly(ether ester)s to achieve similar improvements in processability over conventional aromatic polyamides.[3]



I



II

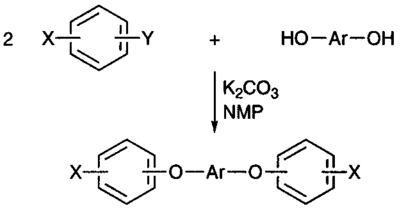
a $X = CO_2H$
b $X = CN$
c $X = COCl$
d $X = NO_2$
e $X = NH_2$

To achieve this end, poly(ether amide)s can be prepared from either/or both bis(ether acid)s or bis(ether amine)s of structure **II**, with different substitution patterns at each aromatic residue. Thus, the synthesis of substances with structure **II** is of interest. A number of bis(ether nitrile)s **IIa**, used in poly(benzoxazole) synthesis,[4] bis(ether acid)s **IIb**, a bis(ether acid chloride) **IIc**[5] and a bis(ether amine) **IIc**[6] have long been known. Evers *et al.*[5] used an aromatic nucleophilic displacement reaction between *p*-chlorobenzonitrile and various diols to prepare bis(ether nitrile)s directly, some of which were hydrolysed to the bis(ether acid)s. Thus, Evers *et al.* prepared bis(ether nitrile)s and bis(ether acid)s and devised a nomenclature based on the substitution patterns of the rings, *e.g.* *ppp*$(COOH)_2$, *pop*$(COOH)_2$.[5] We have adapted this system to allow for substituents on the rings, thus we have, for example, *p*(3Me)*op*$(COOH)_2$ for the diacid in which the terminal rings are *para*-linked and unsubstituted while the central ring is *ortho*-linked and carries a 3-methyl substituent. For unsubstituted species **II** which are symmetrical, *i.e.* the outer rings have the same substitution pattern, there are nine possible isomers: *ppp*$(X)_2$, *pmp*$(X)_2$, *pop*$(X)_2$, *mpm*$(X)_2$, *opo*$(X)_2$, *etc.*

Where substitution patterns of the terminal rings are *para* or *ortho*, formation of the ether linkages by aromatic nucleophilic displacement (S_NAr) reactions between a diol (to form the central ring) and a suitably activated nitro- or halo-benzene (Scheme 1) is easily achieved; Evers *et al.*[5] used chloro displacement reactions while we used fluoro displacement.[3] In these reactions an activating group X may be a precursor of a desired X in structures **II**. Thus, $-CN$ or $-NO_2$ groups are activating groups and are also precursors to $-COOH$ and $-NH_2$, respectively. The leaving group Y is preferably NO_2 or F and is strongly activated if it is *ortho*- or *para*- to X. In this way we have prepared a variety of *pop*X_2 and *ooo*X_2 bis(ether acid)s and bis(ether amine)s from catechol and substituted catechols and have used these in the synthesis of poly(ether amide)s and poly(ether ester)s.[3] These syntheses are relatively trivial. *pop*$(CN)_2$ and *pop*$(COOH)_2$ have also recently been prepared by others and used in the synthesis of poly(ether amide)s.[7,8]

A problem has been to prepare such materials in which the substitution pattern in the outer rings is *meta*, *e.g.* as *mpm*X_2, *mmm*X_2 or *mom*X_2, efficiently because, according to the rules of S_NAr reactions, if Y is *meta* to X it is not sufficiently activated to leave. Evers *et al.* recognised this problem and synthesized *mpm*$(COOH)_2$ by a two-stage process, reacting the sodium salt of *meta*-cresol with dibromobenzenes in pyridine in the presence of copper(I) chloride and oxidizing the resulting dialkyl species with potassium permanganate in pyridine to obtain the diacid in 38% overall yield.[5] Synthesis of the *mpm*$(CN)_2$ was a five-stage synthesis with a yield of 8.5%.

We have now demonstrated that, when X is $-CN$, *meta*-fluoro displacement is easily achieved in high yield according to Scheme 2 at elevated temperatures when fluorobenzonitrile **III** is reacted, under suitable conditions, with a diol **IV** (Table 1). Thus, *mom*$(CN)_2$-type bis(ether nitrile)s become immediately available and, after hydrolysis, bis(ether acid)s of



Scheme 1

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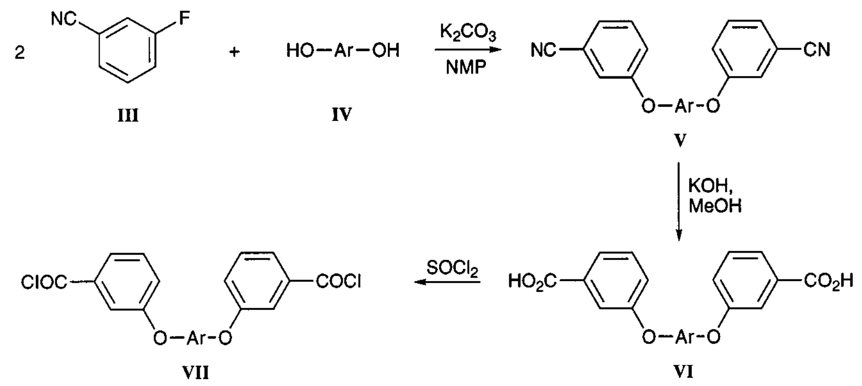
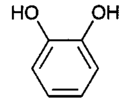
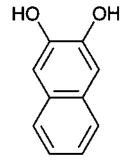
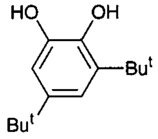
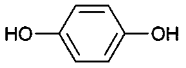
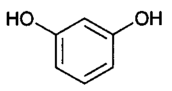
† Presented in part at 'Polycondensation '96', International Symposium on Polycondensation, Paris, 1996.



Scheme 2

Table 1 Diols used in fluoro displacement reactions with mnemonics used in bis(ether nitrile) and bis(ether acid) nomenclature

diol	code	mnemonic
	**IVa**	*o*
	**IVb**	(2,3N)*o*
	**IVc**	(3,5dtB)*o*
	**IVd**	*p*
	**IVe**	*m*

the type *mom*(COOH)$_2$ *etc.* and, subsequently, bis(ether acid chloride)s, including their derivatives from substituted catechols, are also available (Scheme 2). Bis(ether nitrile)s can be used directly in the synthesis of poly(benzobisoxazole)s;[4] bis(ether acid)s can be used in the synthesis of poly(ether amide)s and poly(ether ester)s. We report here the synthesis of the bis(ether nitrile)s and bis(ether acid)s from catechol, and 2,3-dihydroxynaphthalene, the bis(ether nitrile) from 3,5-di-*tert*-butylcatechol and other related materials. Diols **VIa–f** used are identified in Table 1 where their mnemonics used in the above nomenclature are defined. Polymers were prepared from some of the monomers to demonstrate their use in polymer synthesis.

Experimental

Materials

3-Fluorobenzonitrile was obtained from Fluorochem. Other reagents were obtained from Aldrich Chemical Company and were used without further purification (catechol was recrystallized from toluene) or were general laboratory reagents.

Synthesis of 1,2-bis(3-cyanophenoxy)benzene [*mom*(COOH)$_2$]

Procedure A. Catechol (>99%) (44 g, 0.4 mol) and 500 ml *N*-methylpyrrolidone (NMP) were placed in a flask equipped with magnetic stirrer bar, thermometer, nitrogen inlet, Dean Stark trap and reflux condenser. The mixture was thoroughly deoxygenated with a stream of nitrogen. Anhydrous potassium carbonate (100 g) and xylene (100 ml) were added. Under a stream of nitrogen, the mixture was brought to the boil and dried azeotropically. 3-Fluorobenzonitrile (100 g) was added and reflux continued for 6 h with a flask temperature of 178–184 °C. Then, over a period of 2 h, most of the xylene was distilled off while the temperature rose to 204 °C. The dark brown mixture was precipitated into 4 l of ice–water mixture, the solid was filtered off and washed with deionized water until neutral. The brown crystalline mass was recrystallized from 1.5 l of methanol and 200 ml of water to yield 109 g (crude yield 87.3%) of brown crystals. The crude dinitrile was treated with Norit decolourizing agent and recrystallized from 1 l of methanol and 80–100 ml of water three times. The final yield of white crystals was 83 g (66.5% theoretical), mp 99–100 °C, with a further 6.4 g of slightly coloured crystals; details are recorded in Table 2.

Procedure B. This procedure was similar to Procedure A except that toluene was used to remove water azeotropically; flask temperature was 140 °C. The product was isolated as in Procedure A and purified by two recrystallizations with decolourizing charcoal from methanol–water (5 : 1); results are presented in Table 2.

Procedure C. This procedure was identical to Procedure B except that dimethylformamide (DMF) was used as solvent; the reaction temperature was 120 °C and results are presented in Table 2.

Preparation of 1,2-bis(3-carboxyphenoxy)benzene [*mom* (COOH)$_2$]. Bis(ether nitrile) *mom*(CN)$_2$ (80 g) was placed in a round-bottomed flask with a solution of 80 g of potassium hydroxide in 130 ml of water, followed by 100 ml of methanol. The mixture was refluxed for 10 h, after which evolution of ammonia could not be detected. The mixture was diluted to 2.5 l and acidified to pH 1.5. The product was filtered off and dispersed in 2.5 l of deionized water, warmed to 80–90 °C, filtered and washed three times with deionized water. The wet cake was dissolved in 2 l of acetic acid and tetrahydrofuran (THF) (4 : 1). Other diacids were prepared similarly from the corresponding bis(ether nitrile)s, and data are given in Table 3; the discrepancy between melting points of *mmm*(COOH)$_2$ found in this work and ref. 4 is unexplained but our analytical, NMR and melting point data were confirmed from independent syntheses by two workers.

Table 2 Synthesis of bis(ether nitrile)s

designation[a]	procedure		elemental analysis (%) C	H	N	melting point/°C	yield (%)
mom(CN)$_2$		calc.	76.91	3.87	8.97		
	A	found				99–100	87 (crude)
	B		77.1	3.81	8.93	99.2–99.7	70
	C						20
mpm(CN)$_2$		calc.	76.91	3.87	8.97	143.4–143.7	78
	A	found	76.91	3.87	8.90	139.5–141[b]	
mmm(CN)$_2$		calc.	76.91	3.87	8.97	90.2–90.6	49
	A	found	76.76	3.84	8.89	81–82[c]	
m(2,3N)*om*(CN)$_2$		calc.	79.54	3.89	7.73	157–158	51
	B	found	79.77	3.88	7.71		
m(3,5dtB)*om*(CN)$_2$		calc.	79.21	6.64	6.60	118–119	52
	B	found	79.38	6.67	6.58		
pop(CN)$_2$	C	calc.	76.91	3.87	8.97	116.8–117.3	96
		found	76.90	3.84	8.94	116.5–117.5[b]	
						117–118[d]	
						116.5–118[e]	
ooo(CN)$_2$	C	calc.	76.91	3.87	8.97	105.4–105.8	85
		found	77.07	3.85	9.02		

[a] Systematic names: *mom*(CN)$_2$ = 1,2-bis(3-cyanophenoxy)benzene; *mpm*(CN)$_2$ = 1,4-bis(3-cyanophenoxy)benzene; *mmm*(CN)$_2$ = 1,3-bis(3-cyanophenoxy)benzene; *m*(2,3N)*om*(CN)$_2$ = 2,3-bis(3-cyanophenoxy)naphthalene; *m*(3,5dtB)*om*(CN)$_2$ = 1,2-bis(3-cyanophenoxy)-3,5-di-*tert*-butylbenzene; *pop*(CN)$_2$ = 1,2-bis(4-cyanophenoxy)benzene; *ooo*(CN)$_2$ = 1,2-bis(2-cyanophenoxy)benzene. [b] Ref. 5. [c] Ref. 9. [d] Ref. 7. [e] Ref. 8.

Table 3 Synthesis of bis(ether acid)s and a bis(ether acid chloride)

designation		elemental analysis (%) C	H	Cl	melting point/°C	yield (%)
mom(COOH)$_2$[a]	calc.	68.57	4.03		265–267	99
	found	68.49	3.99			
mpm(COOH)$_2$	calc.	68.57	4.03		318.9–319.2	
	found	68.57	4.03		305–313[b]	70
mmm(COOH)$_2$	calc.	68.57	4.03		205.5–206.1	
	found	68.40	4.04		269–274[b]	80
m(2,3N)*om*(COOH)$_2$	calc.	72.00	4.03		260–262	89
	found	72.14	3.98			
pop(COOH)$_2$	calc.	68.57	4.03		257–258	84
	found	68.57	4.02		257–258[c]	
					255–256[d]	
ooo(COOH)$_2$	calc.	68.57	4.03		184–185	90
	found	68.60	3.97			
mom(COCl)$_2$	calc.	62.03	3.12	18.31	74–76	63
	found	61.89	3.12	17.47		

[a] Systematic names: *mom*(COOH)$_2$ = 1,2-bis(3-carboxyphenoxy)benzene; *mpm*(COOH)$_2$ = 1,4-bis(3-carboxyphenoxy)benzene; *mmm*(COOH)$_2$ = 1,3-bis(3-carboxyphenoxy)benzene; *m*(2,3N)*om*(COOH)$_2$ = 2,3-bis(3-carboxyphenoxy)naphthalene; *pop*(COOH)$_2$ = 1,2-bis(4-carboxyphenoxy)benzene; *ooo*(COOH)$_2$ = 1,2-bis(2-carboxyphenoxy)benzene; *mom*(COCl)$_2$ = 1,2-bis[3-(chlorocarbonyl)phenoxy]benzene. [b] Ref. 5. [c] Ref. 7. [d] Ref. 8.

Syntheses of 1,2-bis(4-cyanophenoxy)benzene [*pop*(CN)$_2$], 1,2-bis(2-cyanophenoxy)benzene [*ooo*(CN)$_2$] and their corresponding diacids *pop*(COOH)$_2$ and *ooo*(COOH)$_2$. Fluoro displacements from *p*-fluorobenzonitrile and *o*-fluorobenzonitrile were performed with catechol according to procedure *C* to yield *pop*(CN)$_2$ and *ooo*(CN)$_2$, respectively. The bis(ether nitrile)s were hydrolysed to *pop*(COOH)$_2$ and *ooo*(COOH)$_2$ as described above for *mom*(COOH)$_2$. Details are given in ref. 3 and results in Tables 2 and 3.

Preparation of 1,2-bis(3-chlorocarbonylphenoxy)benzene [*mom*(COCl)$_2$]. 1,2-Bis(3-carboxyphenoxy)benzene (10 mmol) was boiled under reflux, protected with a calcium chloride guard tube, in a nitrogen atmosphere with *ca.* 20 mmol of thionyl chloride for 2 h. Excess thionyl chloride was distilled off under vacuum which was finally reduced to 0.2–0.5 Torr. The crude acid chloride was dissolved in 50 ml of cyclohexane, about one third of which was then distilled off, and the residual solution left to crystallize. The crude acid chloride was sublimed from a thoroughly degassed melt at *ca.* 200 °C at 0.5 Torr pressure (Table 3).

Preparation of polymers by the phosphorylation technique. Anhydrous calcium chloride (0.6 g) and lithium chloride (0.2 g) were dissolved in anhydrous NMP (13 ml), under a nitrogen atmosphere. Anhydrous pyridine (4 ml) was added, followed by 1,2-bis(3-carboxyphenoxy)benzene (0.70 g, 2 mmol) and *para*-phenylenediamine (PPD; 2 mmol). The mixture was stirred under nitrogen and triphenyl phosphite (2 ml) was added. The temperature was raised to 105 °C for 5 h when additional triphenyl phosphite (1 ml) and pyridine (1 ml) were added and the mixture was stirred at 110 °C. The resulting viscous liquid was poured into 300 ml of methanol–water (80:20). The polymer was filtered off and extracted with boiling methanol for 1 h. The yield of polymer was 0.78 g. Other poly(ether amide)s were prepared similarly from *pop*(COOH)$_2$ and *m*-phenylenediamine (MPD) and from *m*(2,3N)*om*(COOH)$_2$ with MPD.

Polymers from 1,2-bis(3-chlorocarbonylphenoxy)benzene [*mom*(COCl)$_2$] and MPD. MPD (1 mmol) was dissolved in 7 ml of *N*,*N*-dimethylacetamide (DMAC) containing 8.7% CaCl$_2$ and 0.7 ml of pyridine. The mixture was cooled to

$-14\,^{\circ}C$, *mom*$(COCl)_2$ (1 mmol) was added and the mixture was stirred vigorously for 2.5 h during which period it became very viscous. The mixture was kept overnight at *ca.* 0 °C in a refrigerator, followed by 24 h at room temperature. The polymer was precipitated into MeOH–H_2O, twice extracted with boiling MeOH and dried.

Syntheses of poly(ether ester) by transesterification. *mom*$(COOH)_2$ (3.0 mmol), hydroquinone diacetate (3.0 mmol), dibutylin oxide (0.002 g) and *m*-terphenyl (3–4 g) were melted and stirred under nitrogen. Within 1–1.5 h the temperature was raised to 340 °C. The reaction was run for 5–8 h, gradually raising the temperature to 370–380 °C. After cooling to 110 °C the viscous melt was poured into acetone or into toluene–methanol (40:60). The polymer was filtered off and extracted with boiling acetone or methanol and dried. Yields of polymer were *ca.* 80%. Polymers were subjected to preliminary testing for solubility and for ability to pull fibres from the melt.

Instruments

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX400 spectrometer. Accurate molar masses were determined on a VG Analytical 7070E mass spectrometer.

Results and Discussion

Synthesis of monomers and precursors

Experiments demonstrated that the efficient synthesis of bis(ether nitrile)s, precursors to bis(ether acid)s, where CN is *meta* to the ether linkage is very sensitive to reaction conditions. Conditions for fluoro displacement from *meta*-fluorobenzonitrile were optimised for the parent *mom*$(CN)_2$ as Procedure A. These reaction conditions were also applied to the syntheses of *mpm*$(CN)_2$ and *mmm*$(CN)_2$ with the results presented in Table 2.

Bis(ether nitrile)s were also prepared from 2,3-dihydroxynaphthalene and 3,5-di-*tert*-butylcatechol to give *m*(2,3N)*om*$(CN)_2$ and *m*(3,5dtB)*om*$(CN)_2$, respectively; the syntheses of these materials were not optimised, and conditions used were Procedure B. Results are presented in Table 2. Data for *mom*$(CN)_2$ show that success in these reactions, in terms of yield and cleanliness of product, is very dependent on the reaction temperature. We previously found, when synthesizing *pop*$(CN)_2$ and *ooo*$(CN)_2$, that cleaner products were obtained by performing the nitrodisplacement reaction in DMF, Procedure C (Table 2); purity of the bis(ether nitrile) intermediates assists in producing pure bis(ether acid)s necessary for synthesis of high molecular mass polymers. However, in the synthesis of *mom*$(CN)_2$-type species Procedure C was unsatisfactory; reaction yields were low (*ca.* 20%) and products black. It was only with difficulty that a satisfactory sample of *mom*$(CN)_2$ was obtained by Procedure C, despite giving a 96% yield of pure *pop*$(CN)_2$. Optimum conditions for the synthesis of *mom*$(CN)_2$ are NMP as solvent with a reflux temperature of *ca.* 180 °C. Thus, conditions required to produce good yields of pure products from *meta*-activated species differ significantly from those where *ortho*- or *para*-activation is used. It is also necessary to perform the reactions under an atmosphere of nitrogen to minimise side reactions which lead to dark products. Nevertheless, it is now clear that pure materials of type *mom*$(CN)_2$ can readily be achieved (Table 2).

Hydrolyses of all *mxm*$(CN)_2$ species (*x* represents any substitution pattern of the central aromatic ring or other aromatic species) are readily achieved and a typical set of reaction conditions is described above. Hydrolysis produces pure bis(ether acid) in high yield (Table 3). Further, to prepare high molecular mass polyamides it is most convenient to react acid chlorides with diamines and, to this end, *mom*$(COOH)_2$ was converted to *mom*$(COCl)_2$ by reaction with thionyl chloride (Table 3).

Thus, it is now possible to prepare readily a series of monomers, bis(ether nitrile)s, bis(ether acid)s and bis(ether acid chloride)s of type **II** in which the terminal aromatic rings are *meta*-substituted. These monomers can be, and have been, used in the synthesis of poly(ether amide)s or poly(ether ester)s. The synthesis of representative poly(ether amide)s is described in the preceding section.

In contrast, synthesis of equivalent dinitro species **IId**, precursors to diamines **IIe**, by fluoro displacement from *meta*-fluoronitrobenzene is not effective under comparable conditions. When the corresponding fluoro displacement reaction was performed with catechol under reaction conditions equivalent to Procedures A or B only black tars were recovered and we failed to extract pure dinitro compound.

It is of interest to consider the effectiveness of the displacement reaction with *meta*-activated species. Electron-withdrawing groups *meta* to a leaving group are less activating than the same group in an *ortho*- or *para*-position. Even so, *meta*-nitro and nitrile groups do have some activating propensity. Terrier has commented that, 'while two nitro groups may provide sufficient activation to allow clean S_NAr processes to occur, single *meta*-nitro groups are too weakly activated for S_NAr processes and there is a high tendency to react by alternative pathways'.[10] In addition, it is usual to consider that the nitrile group is less activating than the nitro group.[10] However, in this work, we find that, at elevated temperatures, a single nitrile group in a *meta*-position is sufficient to activate fluoro displacement and there is no reason to believe that reaction proceeds by other than a normal S_NAr process.

meta-Nitro displacement reactions are uncommon but are known in, for example, nitro displacement from *meta*-dinitrobenzene by methoxide or thiophenoxide anion in hexamethylphosphoramide (HMPA) at room temperature,[11] between the same reagents in chlorobenzene (80 °C) under phase transfer conditions[12] and by potassium fluoride in HMPA at 180 °C.[13] Idoux *et al.* have shown that *m*-NO_2 and *m*-CN will activate nitro displacement and *m*-NO_2 fluoro displacement by 2,2,2-trifluoroethoxide anion at 25 °C.[14] Yoshikawa *et al.* have now demonstrated that it is possible, by reacting *m*-dinitrobenzene in aprotic solvents with various bisphenols, to achieve *m*-nitro displacement in the presence of a base such as potassium carbonate at elevated temperatures. They achieved good yields ($>90\%$) with many bisphenols but $<60\%$ with hydroquinone and did not report results with other phenylene diols.[15] The use of diols without prior formation of the phenoxide anion is important with catechol and its derivatives because of oxidative side reactions and there is no prior report of catechols being used in *m*-nitro displacement or *m*-fluoro displacement reactions.

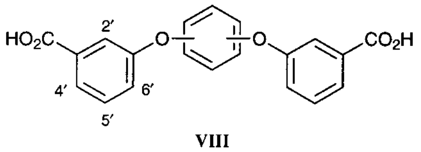
Kirst and Una showed that fluoro displacement between nitrofluorobenzenes and methoxide with a *para*-nitro group is faster than with a *meta*-nitro group by a factor of *ca.* 10^3 at 100 °C; this factor decreases at higher temperatures.[16] Taking values of σ^- for *para*-CN and *meta*-CN as 0.88 and 0.56, respectively, it is estimated that, at 100 °C, *para*-CN is less reactive than *para*-NO_2 by a factor of *ca.* 100 and that *meta*-CN is less reactive than *para*-CN by a factor of *ca.* 80.[17] These data still predict that *meta*-NO_2 would be more reactive than *meta*-CN. Despite our observation that *meta*-CN-activated fluoro displacement is more effective than the *meta*-NO_2-activated reaction, there is no obvious reason to invoke a pathway other than normal fluoro displacement.

The exact compositions of species with *meta*-outer rings were confirmed by accurate mass determinations by mass spectrometry. The calculated molar mass for *mxm*$(COOH)_2$ species is 350.07904 and observed masses were 350.07889, 350.07855 and 350.07889 for *mpm*$(COOH)_2$, *mmm*$(COOH)_2$ and *mom*$(COOH)_2$ respectively; the calculated value for

Table 4 ^1H NMR parameters for bis(ether acid)s in [$^2H_7$]DMF; chemical shifts and coupling constants for designated protons and proton pairs

diacid		chemical shifts and coupling constants
mpm	δ	H(2,3,5,6)7.24;H(2′,5′)7.60;H(4′)7.80;H(6′)7.35
	J/Hz	(2′,4′)1.50;(2′,6′)2.54;(4′,5′)7.69;(4′,6′)1.07(5′,6′)8.24
mmm	δ	H(2)6.86;H(4,6)6.93;H(5)7.50;H(2′)7.63;H(4′)7.82;H(5′)7.60;H(6′)7.39
	J/Hz	(2,4)2.35;(4,5)8.21;(2′,4′)1.54;(2′,6′)2.58;(4′,5′)7.70;(4′,6′)0.98;(5′,6′)8.18
mom	δ	H(3,4,5,6)7.36;H(2′)7.45;H(4′)7.73;H(5′)7.50;H(6′)7.18
	J/Hz	(2′,4′)1.49;(2′,6′)2.67;(4′,5′)7.64;(4′,6′)1.03;(5′,6′)8.22
pop	δ	H(3,4,5,6)7.34;H(2′)7.01;H(3′)8.0
	J/Hz	(2′,3′)8.98
ooo	δ	H(3)7.01;H(4,5)7.19;H(6)7.01;H(3′)7.90;H(4′)7.25;H(5′)7.56;H(6′)7.10
	J/Hz	(3′,4′)7.78;(3′,5′)1.48;(4′,5′)7.33;(4′,6′)0.95;(5′,6′)8.22

m(2,3N)*om*$(COOH)_2$ was 400.09518 compared with an experimental value of 400.09518; errors were all less than 0.0005. Any alternative pathway might be expected involve isomerization and formation of isomers during reaction but no such change of substitution pattern occurs. NMR evidence is quite clear that *meta*-fluoro displacement with diols gives rise to *meta*-nitrile ethers. Splitting patterns for *mom*, *mpm*, *mmm*, *ppp*, *pmp*, *pop* and *ooo* bis(ether nitrile)s and bis(ether acid)s are all different and entirely consistent with the products of the various species being obtained by normal aromatic nucleophilic displacement reactions with retention of substitution patterns. Thus, for all species **VIII** with *meta*-substitution in the outer rings, ^1H NMR spectra show distinctive spectra with very similar chemical shifts and coupling constants for those protons (Table 4); in Table 4 primes are used to denote protons in the outer aromatic rings, absence of primes refers to protons on the central ring. This pattern is quite different from those for *para*- and *ortho*-substitution in the outer rings. In addition, the splitting pattern for protons on the central rings for *mom*$(COOH)_2$ and *pop*$(COOH)_2$ are identical complex multiplets characteristic of an AA′BB′ system with a small coupling constant; the pattern for *ooo*$(COOH)_2$ is somewhat different and is resolved into two multiplets but still characteristic of an AA′BB′ system with a slightly increased coupling constant. Further, the calculated chemical shifts for all protons in the outer rings and for all carbons in all rings are almost identical with those observed from ^1H and ^{13}C NMR.[18] Thus, there is no doubt that initial substitution patterns of the rings are maintained during the S_NAr process.



VIII

Polymer syntheses

One of the most convincing proofs of producing bis(ether acid)s of high purity is the ability to produce high molecular mass polymers. In order to identify soluble poly(ether amide)s which might be made to high molecular mass in solution we undertook preliminary syntheses using the phosphorylation technique.[19] For those polymers found to be soluble in conventional solvents, example polymers were also synthesized using bis(ether acid chloride). In addition, an example poly(ether ester) was prepared by a transesterification procedure, as described above. Thus, polymers were prepared from *ppp*$(COOH)_2$, *pmp*$(COOH)_2$, *pop*$(COOH)_2$, *mpm*$(COOH)_2$, *mmm*$(COOH)_2$, *mom*$(COOH)_2$ and *ooo*$(COOH)_2$ with PPD and MPD by the phosphorylation procedure described above. Poly(ether amide)s prepared from *ppp*$(COOH)_2$, *pmp*$(COOH)_2$, *mpm*$(COOH)_2$ or *mmm*$(COOH)_2$ with PPD or MPD by the phosphorylation technique were only soluble in concentrated H_2SO_4 or methanesulfonic acid. Poly(ether amide)s similarly prepared from *pop*$(COOH)_2$, *mom*$(COOH)_2$ and *ooo*$(COOH)_2$ were soluble in NMP. An example high molecular mass poly(ether amide) was prepared from *mom*$(COCl)_2$ and MPD.

The low molecular mass poly(ether amide)s prepared from *mom*$(COOH)_2$ and PPD or MPD by the phosphorylation technique were fusible and short fibres could be pulled from the melts. The higher molecular mass poly(ether amide) prepared from *mom*$(COCl)_2$ and MPD was also fusible and long fibres could (>10 cm) be drawn from the melt. The poly(ether ester) prepared from *mom*$(COOH)_2$ and hydroquinone diacetate by the transesterification procedure described above was also fusible and short, brittle fibres could be drawn from the melt.

Conclusions

We have demonstrated the feasibility of performing efficient *meta*-displacement reactions between *m*-fluorobenzonitrile and phenylene diols, including catechol and its derivatives, to produce bis(ether nitrile)s in NMP at elevated temperatures and, from them, bis(ether acid)s which can be readily incorporated into poly(ether amide)s or poly(ether ester)s. This development completes the possibilities of making bis(ether acid)s and related compounds based on structure **II** with all possible substitution patterns at all aromatic rings.

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References

1 R. O. Johnson and H. S. Burhlis, *J. Polym. Sci., Polym. Symp.*, 1983, **70**, 129.
2 G. C. Eastmond and J. Paprotny, *Polymer*, 1994, **35**, 5148; G. C. Eastmond and J. Paprotny, *Macromolecules*, 1996, **29**, 1382.
3 G. C. Eastmond and J. Paprotny, *US Pat.*, filed 1995, WO 97/00903, 1997.
4 R. C. Evers, F. E. Arnold and T. E. Helminiak, *US Pat.* 4,229,566, 1980.
5 R. C. Evers, F. E. Arnold and T. E. Helminiak, *Polym. Prepr., Am. Chem. Soc., Polym. Div. Inc.*, 1990, **21**(1), 88; *Macromolecules*, 1981, **14**, 925.
6 T. P. Gannett and H. H. Gibbs, *US Pat.* 4,576,857, 1986.
7 L.-S. Tan and N. Venkatasubraian, *US Pat.* 5,514,769, 1996.
8 S.-H. Hsiao and C.-F. Chang, *Macromol. Chem. Phys.*, 1996, **197**, 1255.
9 R. K. Bartlett, G. O'Neill, N. G. Savill, S. L. S. Thomas and W. F. Wall, *Brit. Polym. J.*, 1970, **2**, 225.
10 F. Terrier, in *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group*, VCH, Weinheim, 1991, p. 10.
11 N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith and P. A. Wade, *J. Org. Chem.*, 1976, **41**, 1560.
12 F. Montanari, M. Pelosi and F. Rolla, *Chem. Ind.*, 1982, 412.

13 G. Bartoli, A. La Trofa, F. Naso and P. F. Todesco, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2671.

14 J. P. Idoux, M. L. Madenwald, B. S. Garcia and D-L. Chu, *J. Org. Chem.*, 1985, **50**, 1876.

15 Y. Yoshikawa, K. Yamaguchi, K. Sugimoto, Y. Tanabe and A. Yamaguchi, *Eur. Pat. Appl.*, A1 0192480, 1986; S. Tamai, A. Yamaguchi and M. Ohta, *Polymer*, 1996, **37**, 3683.

16 J. Hirst and S. J. Una, *J. Chem. Soc. B*, 1971, 2221.

17 D. Bethell, personal communication.

18 M. Gibas, personal communication.

19 N. Yamazaki, F. Higashi and J. Kawabata, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 2149; F. Higashi, S.-I. Ogata and Y. Aoki, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 2081.

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