ELSEVIER

Polymer 40 (1999) 469–486

polymer

1,2-Bis(carboxyphenoxy)arylenes and aramids and polyarylates therefrom: synthesis and properties

G.C. Eastmond[a,*], J. Paprotny[a], R.S. Irwin[1b]

[a]*Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK*
[b]*E.I. du Pont de Nemours and Co. Inc., Experimental Station, Wilmington, DE 19880, USA*

Received 2 February 1998; revised 11 March 1998

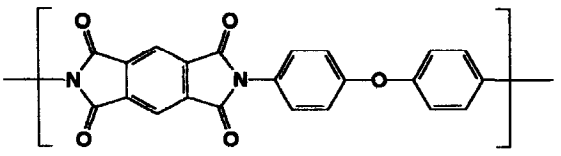
Abstract

The synthesis of a new series of aromatic bis(ether acid)s and bis(ether acid chloride)s by fluorodisplacement with catechol or its derivatives has been developed and exemplified. These monomers allow the synthesis of new aramids (poly(ether amide)s), polyarylates (poly(ether ester)s) and copolyarylates in which *ortho*-phenylene units are enchained through ether linkages. These polymers are significantly more flexible and, therefore, more soluble than conventional aromatic polyamides and polyesters. They have useful levels of thermal stability, associated with relatively high glass-transition temperatures (> 200°C), are processable from solution or the melt, and are potentially crystallizable. Liquid crystalline poly(ether ester)s were prepared. Polyamides prepared from bis(ether acid)s in which all three aromatic rings, separated by ether linkages, are all *ortho*-substituted gave low-molecular weight polymers.

Keywords: Catechol; 1,2-Bis(cyanophenoxy)arylenes; 1,2-Bis(carboxyphenoxy)arylenes

1. Introduction

Several high-performance polymers, including aromatic polyimides, polyamides, poly(ether sulphone)s and poly (ether ketone)s, have achieved commercial importance as moulding resins, coatings, films or fibres. Their relatively high stiffness favours high melting points and limited solubility and necessitates less-conventional processing conditions. Consequent manufacturing costs present a barrier to more widespread civilian use. The polypyromellitimide of 4,4′-oxydianiline (I) (Kapton®) must be processed from its soluble precursor poly(amide acid). The very stiff poly(1,4-phenyleneterephthalamide) (Kevlar® aramid fibre) has very limited solubility in its organic polymerization medium, and is spun from strong acid solution. The less stiff *meta*-isomer (Nomex® aramid fibre) can be spun from the polymerization solvent, but only in the presence of dissolved inorganic chlorides. For both aramids, solvent recovery, corrosion and waste disposal are significant costs. There is a need for new polymers with enhanced (low cost) processability but without undue loss of properties.



(I)

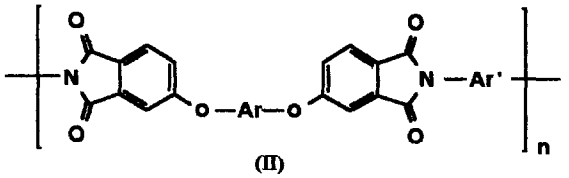
It is, therefore, relevant to review factors which are important in reducing processing costs and which contribute to high-temperature performance. Developing a practicable polymer involves optimising these factors; such considerations influenced our studies. Features required to maintain ultimate properties at elevated temperatures are chemical and dimensional stability under stress. Potential alternatives to Nomex® must not melt or embrittle on exposure to flame and must otherwise retain dimensional stability, wear resistance and tactile aesthetics during long-term use. The polymer must also be processable from non-corrosive solvents or from the melt. Parameters which control these properties include molecular flexibility, crystallizability and molecular weight, which also bear on flex life and abrasion resistance.

Aromatic polyimides offer the best potential for ultimate properties. Kapton® (I), however, is stiff, unprocessable and expensive. Attempts to enhance molecular flexibility and processability of polyimides have resulted in loss of properties. A major advance in this direction was the

* Corresponding author.
[1] Present address: 714 Ambleside Dr., Wilmington, DE 19808, USA.

0032-3861/98/$ - see front matter
PII: S0032-3861(98)00228-6

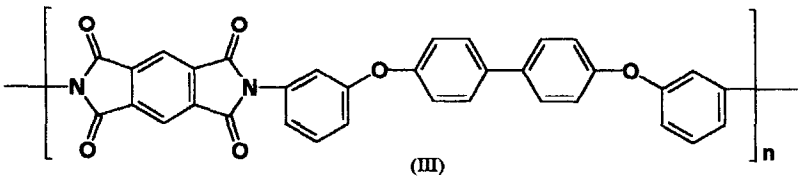
formation of thermally stable ether linkages by aromatic nucleophilic displacement, usually nitrodisplacement, reactions [1,2]. This step led to poly(ether imide)s (II) and the commercial polymer Ultem® (General Electric), wherein Ar is the 2,2-bis(4-phenylene)propane moiety and Ar(is *meta*-phenylene [3].



(II)

Ultem® is melt-processable, soluble in a limited number of solvents and has a relatively high glass-transition temperature (T_g) of 217°C. In fibre form (oriented) it is amorphous, has reduced resistance to solvents and chemical attack [4], and its dimensional stability is inadequate for use as a fibre at high temperatures (Irwin RS, unpublished results); undrawn, it creeps under load above 150°C [3]. Mechanical properties deteriorate above 70°C; its β-relaxation is below 100°C [4]. Stiffer poly(ether imide)s may be melt spun at very high temperatures, but only at low molecular weights where flex resistance is very low (Memeger W, Irwin RSI, unpublished results).

Introducing crystallinity gave a thermoplastic polyimide (III) (Mitsui-Toatsu N-TPI, Aurum® in fibre form, T_g 250°C, $M_n \sim 5000$ g mol^{-1}) with improved dimensional stability. This polymer has rigid and flexible moieties. Crystallization is relatively slow and the stiff units, which induce crystallinity, produce a high melt-processing temperature (> 388°C) [5]. However, fibres, deficient in abrasion and flex resistance, lack dimensional stability under load above T_g (Irwin RS, unpublished results).

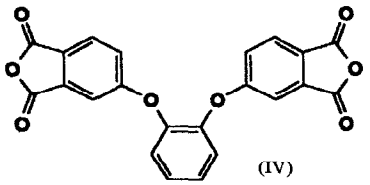


(III)

Alternatives to polyimides are aromatic polyamides (aramids) and polyesters (polyarylates). Most commercial aramids and polyarylates have flex lives (> 100 000 cycles) about two orders of magnitude higher than melt-extruded polyimides (Irwin RS, unpublished results). However, a solution-spun, crystalline, high-molecular weight polyimide of structure (I) had a comparable flex performance, indicating that there is no intrinsic barrier to producing polyimides with good flex resistance[2].

The superiority of aromatic polyamides (aramids), in terms of flex and abrasion resistances and dimensional stability, is because their relatively flexible chain structures and inter-chain hydrogen bonding enhance crystallizability. However, their long-term, upper-working temperatures, about 220°C, are low; an amidine rearrangement slowly causes chain scission and embrittlement at high temperatures [6]. Polyarylates, with greater intrinsic thermal stability, lack the high-temperature dimensional stability aided by hydrogen bonding.

Many different poly(ether imide)s have now been synthesized [7,8]. We recently discovered that poly(ether imide)s in which Ar is *ortho*-phenylene, prepared from (IV), are far more processable than their *meta*- or *para*-phenylene analogues. Properties are slightly inferior to but comparable with their *para*-, or *meta*-linked analogues [9–12]. Thus the combination of *ortho*-phenylene units and ether linkages imparts processability in poly(ether imide)s.



(IV)

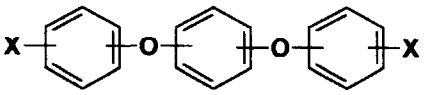
We have now investigated the possibility of transferring the improved processability achieved in polyimides to aramids and polyarylates. There are few polyamides with main-chain ether linkages, and especially with *ortho*-linked main-chain units; a polyamide derived from 2,3-bis(4-aminophenoxy)naphthalene has been reported [13]. There are also few satisfactory syntheses of polyarylates with *ortho*-linked main-chain units. Polyarylates from *ortho*-hydroxybenzoic acid are thermally unstable [14]. Copolyarylates with *ortho*-linked units (incorporated through ester linkages) are more stable and exhibit liquid crystallinity, but such studies are few [15]. We therefore used bis(ether acid)s in the synthesis of new poly(ether amide)s and poly(ether ester)s [16] and now report a preliminary analysis of their properties.

2. Bis(carboxyphenoxy and aminophenoxy)phenylenes

Considerable effort has recently been directed towards extending the concept of using ether linkages and modified aromatic substitution patterns, especially the introduction of *ortho*-linked units, to enhance processability in aromatic polymers [8]. Here, we investigate poly(ether amide)s and poly(ether ester)s which contain units (V) where the central phenylene unit is *ortho*-substituted. These are part of a

[2] Flex life is determined for 12 replicate specimens of single filaments, as the number of cycles of alternately bending the filament through an acute angle about a narrow gauge wire, then straightening, until 50% of the specimens have failed. The number of cycles to 50% failure is recorded.

larger family of aromatic polymers with different substitution patterns at the various phenylene units. In monomers (V), X is one of the functional group specified. In polymers, X is an amide or ester linkage to another main chain unit. These investigations necessitated the synthesis of new monomers and their use in polymers; both aspects are reported.



(V)

(a) X = COOH (b) X = CN (c) X = COCl (d) X = NO_2 (e) X = NH_2

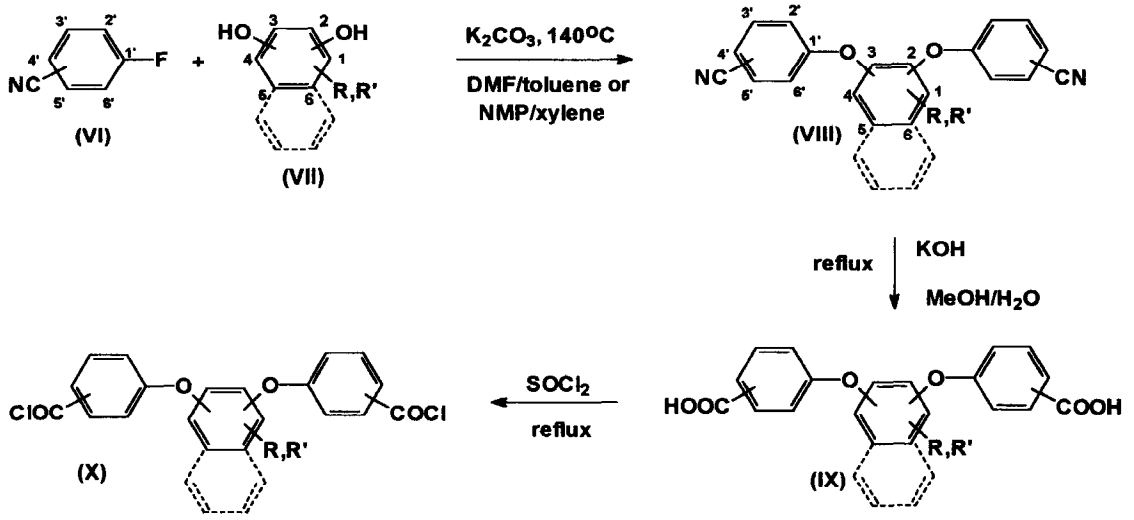
For species (V), in which the terminal units have the same substitution pattern, there are nine possible variants. Evers et al. introduced a nomenclature based on their substitution patterns, *ppp*, *pmp*, *opo* etc.; thus diacid (Va), where the outer rings are *para*-substituted and the central ring is *ortho*-substituted, is *pop*$(COOH)_2$ [17]. For substituted catechols we extend this nomenclature. Thus, *p*(3F)*op*$(COOH)_2$ is *pop*$(COOH)_2$ diacid in which the central ring carries a 3-fluoro substituent. In discussing polymer properties we favour this nomenclature, in which the substitution pattern is immediately identified. However, for monomer syntheses we adopt a conventional, self-consistent code identified in Scheme 1 and Scheme 2; in some places compounds are identified by both nomenclatures to avoid uncertainty.

Species (V) can now be synthesized by aromatic nucleophilic displacement reactions from suitably activated species, 4-fluorobenzonitrile (VI) (Scheme 1) or 4-nitrofluorobenzene (XI) (Scheme 2), by an aromatic diol (VII). Terminal units in the products, (VIII) or (XII), may be modified to produce monomers (IX), (X) and (XIII).

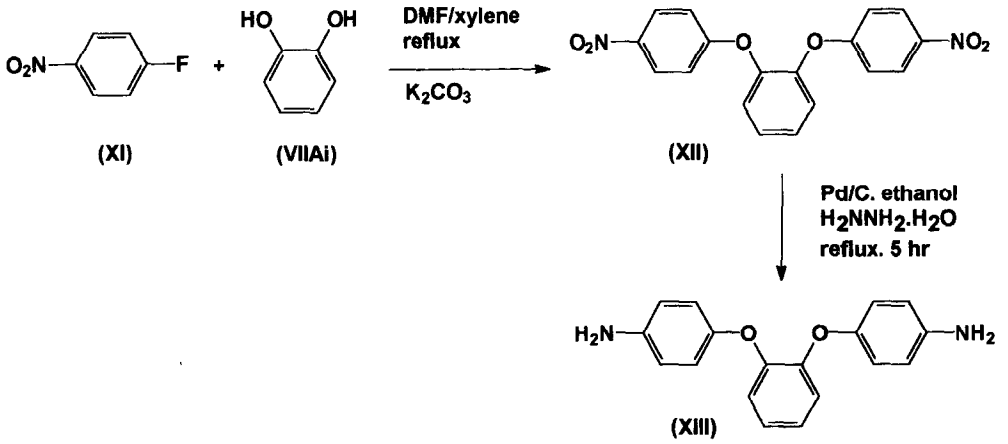
In this paper we are primarily concerned with substances in which the terminal units are *para*- and the central unit is *ortho*-substituted, i.e. with *pop*$(COOH)_2$ (IXaAi) and its derivatives, with the corresponding bis(ether amine) (XIII) and with poly(ether amide)s and poly(ether ester)s derived therefrom. This paper also describes the synthesis of the corresponding bis(ether acid)s in which substitution on the terminal aromatic rings is *ortho*, i.e. (IXbAi,ii,iv) or *ooo*X_2 species, and polymerization of them; we believe no such monomers have been reported previously [18].

With the development of aromatic nucleophilic displacement reactions, the synthesis of substances such as (VIII) and (XII), where nitrile and nitro groups activate halo- or nitrodisplacement, in which substitution at the outer rings is *ortho* or *para*, is relatively straightforward, although such compounds are almost unknown. More problematic is the synthesis of similar species in which the outer rings are *meta*-substituted, *mom*$(CN)_2$, *mmm*$(CN)_2$ and *mpm*$(CN)_2$, and their corresponding diacids, but we recently reported their syntheses [19].

Diacid *ppp*$(COOH)_2$ (IXaBi, Scheme 1) and acid chloride (XaBi) were first synthesized by Malichenko et al. [20]. Dinitrile *pmp*$(CN)_2$ (VIIIaCi) was synthesized by Bartlett



Scheme 1.



Scheme 2.

et al. using a solvent-assisted Ullmann condensation with 4-bromo-benzonitrile [21]. Subsequently, Evers et al. [17] prepared *ppp*(COOH)$_2$ (IXaBi), *pmp*(COOH)$_2$ (IXaCi) and *pop*(COOH)$_2$ (IXaAi) using nitrodisplacement reactions, developed by Takekoshi et al. [22], to synthesize the bis(ether nitrile)s VIIIaBi, VIIIaCi and VIIIaAi which were hydrolysed to diacids. These workers did not report the synthesis of poly(ether amide)s or poly(ether ester)s. Bis(ether amine) (XIII), *pop*(NH$_2$)$_2$, was described by Kurita and Williams who used it in the synthesis of polyimides [23]. These workers used a chlorodisplacement reaction from *para*-nitrochlorobenzene to form the ether linkages as did Yang and co-workers [13,24]. Gannett and Gibbs refer to diamines such as (Vd) but do not describe their syntheses [25].

We have now explored the use of fluorodisplacement reactions (Scheme 1) to prepare (VIIIaAi), (VIIIaBi) and (VIIIaCi), and analogues of (VIIIaAi) from catechol derivatives, as precursors to bis(ether acid)s. Thus we determined the effectiveness of fluorodisplacement in ether formation, developed new monomers and were enabled to explore the role of substitution patterns on polymer properties. Very recently the use of fluorodisplacement reactions has been reported in the syntheses of bis(ether acid) (*pop*(COOH)$_2$) (VIIIaAi) by Tan and Venkatasubraian [26] and of *pop*-(COOH)$_2$, *pmp*(COOH)$_2$ and *ppp*(COOH)$_2$ by Hsiao and Chang [27]. We also used fluorodisplacement to prepare *pop*(NO$_2$)$_2$ (XII) and, hence, *pop*(NH$_2$)$_2$ (XIII), and related substituted diamines, which we used in the synthesis of poly(ether amide)s [28].

Until recently, there has been little use of bisphenoxyphenylene-type monomers in the synthesis of polyamides. Ueda et al. used *ppp*(COOH)$_2$ with *meta*-phenylene diamine in the synthesis of polyamides; no properties were reported [29]. Tan and Venkatasubraian disclosed the synthesis of crosslinkable poly(ether amide)s from *pop*(COOH)$_2$ and a diamine with a pendant cyclobutane ring [26]. Hsiao and Chang reported poly(ether amide)s from *pop*(COOH)$_2$, *ppp*(COOH)$_2$ and *pmp*(COOH)$_2$ with a series of diamines and described some properties of these materials [27].

3. Experimental

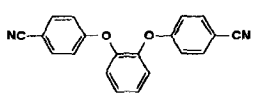
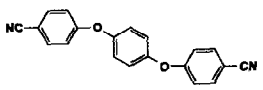
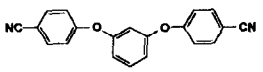
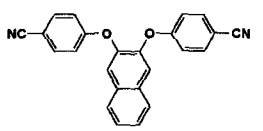
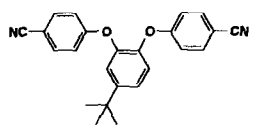
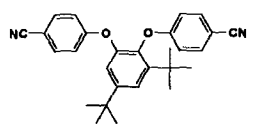
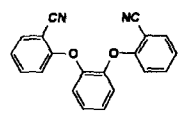
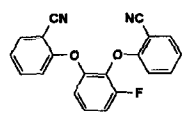
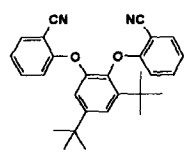
3.1. Materials

4-Fluorobenzonitrile, 2-fluorobenzonitrile and 4-nitrofluorobenzene were obtained from Fluorochem. Catechol, obtained from Aldrich Chem. Co., was recrystallized from toluene prior to use. *meta*-Phenylene diamine was purchased from Fluka and was purified by sublimation. *para*-Phenylene diamine, hydroquinone, resorcinol hydroquinone diacetate, resorcinol diacetate, 4-hydroxybenzoic acid (used in the synthesis of 4-acetoxybenzoic acid), triphenyl phosphite, dibutyl tin oxide and *meta*-terphenyl were all purchased from Aldrich. Hydrazine hydrate was from Fluka. All other materials were general laboratory reagents.

3.2. Synthesis of monomers and precursors

The syntheses of *pop*(CN)$_2$, *pmp*(CN)$_2$ and *ppp*(CN)$_2$ have been described a number of times; in the initial syntheses, using nitrodisplacement, Evers obtained yields of 45–80%. Here we describe a synthesis, using fluorodisplacement in *N*-methylpyrollidinone (NMP) as solvent, which we used to synthesize the bis(ether nitrile)s from catechol derivatives used in this work; 2,3-dihydroxynaphthalene is used in this example (Scheme 1 and Table 1). The details are very similar for all catechol derivatives and only significant differences are pointed out; results of the syntheses are presented in Table 1. Our preferred and optimised procedure, which gives higher yields of pure materials uses *N,N*-dimethyl formamide (DMF) as solvent and xylene to remove water as its azeotrope is virtually identical to that described elsewhere [27].

Table 1
Characteristics and analytical data for bis(ether nitrile)s

Bis(ether nitrile)		Elemental analysis				Recrystallization solvent	Melting point / °C	Yield %
Structure	Designation		C	H	N			
	*pop*(CN)$_2$ (VIIIaAi)	Calcd	76.91	3.87	8.97	methanol/ water (5:1)	116.7-117.3	96[a]
		Found	76.90	3.84	8.94		116.5-117.5[c]	79[b]
							116.5-118[d]	82[d]
	*ppp*(CN)$_2$ (VIIIaBi)	Calcd	76.91	3.87	8.97	*n*-propanol	213.8-214.7	79[a]
		Found	76.81	3.78	8.92		212-213[d]	
							213[e]	
	*pmp*(CN)$_2$ (VIIIaCi)	Calcd	76.91	3.87	8.97	ethanol	125.8-126.5	68[a]
		Found	76.67	3.76	8.88		123.5-125[c]	
							122-123[d]	
	*p*(2,3N)*op*(CN)$_2$ (VIIIaDi)	Calcd	79.54	3.89	7.73	ethanol/ water (15:1)	137.5-138.2	89[b]
		Found	79.59	3.88	7.70			
	*p*(4-*t*-B)*op*(CN)$_2$ (VIIIaAiii)	Calcd	78.24	5.47	7.60	methanol/ water (3:1)	119-120	96[b]
		Found	78.44	5.46	7.58			
	*p*(3,5d-*t*-B)*op*(CN)$_2$ (VIIIaAiv)	Calcd	79.21	6.64	6.60	ethanol	187-188	90[b]
		Found	79.20	6.62	6.58			
	*ooo*(CN)$_2$ (VIIIbAi)	Calcd	76.91	3.87	8.97	methanol/ water (8:1)	105.4-105.8	85[a]
		Found	77.07	3.85	9.02			
	*o*(3F)*oo*(CN)$_2$ (VIIIbAii)	Calcd	72.72	3.35	8.48	ethanol/ water (4:1)	98-99	89[a]
		Found	72.39	3.28	8.38			
	*o*(3,5d-*t*-B)*oo*(CN)$_2$ (VIIIbAiv)	Calcd	79.21	6.64	6.60	ethanol	172-173	90[a]
		Found	79.20	6.66	6.57			

[a]Synthesis in DMF[b]Synthesis in NMP[c]Lit. value [17][d]Lit. value [27][e]Lit. value [30]

3.2.1. Synthesis of 2,3-bis-(4′-cyanophenoxy)naphthalene *p(2,3N)op(CN)$_2$ (VIIIaDi)*

2,3-Dihydroxynaphthalene (VIIDi) (0.1 mol), NMP (150 ml), 4′-fluorobenzonitrile (VIa) (0.2 mol), anhydrous potassium carbonate (26 g) and toluene (30 ml) were placed in a three-necked flask equipped with a magnetic stirring bar, thermometer and a Dean-Stark trap connected to a reflux condenser. The contents of the flask, while stirred,

were brought to the boil (140°C), water was collected in the Dean-Stark trap. Boiling was continued for 6 h after the evolution of water ceased. Toluene was then distilled off until the temperature in the flask rose to 200°C. The contents were poured into cold, stirred water (1.5 l). The precipitate (a brown mud) was filtered off and washed several times with deionized water. While wet, the product was recrystallized from ethanol/water (15:1) to give *p*(2,3N)*op*$(CN)_2$ (VIIIaDi) in 89.2% yield.

3.2.2. Synthesis of 1,4-bis-(4′-cyanophenoxy)benzene (ppp$(CN)_2$) (VIIIaBi)

The procedure used was the same as that for the synthesis of 1,2-bis(4′-cyanophenoxy)benzene except the reaction was carried out on hydroquinone (5.54 g; 0.05 mol) with 4′-fluorobenzonitrile (12.18 g) and in DMF (200 ml); xylene was used to remove the water azeotrope and, as xylene was distilled off after reaction, DMF was added to retain the original volume. The crude product, obtained in 88% yield, was recrystallized twice from *n*-propanol (1 l), the second time after decolourizing with charcoal. The final yield of pure product was 79% (Table 1).

3.2.3. Synthesis of 1,3-bis-(4′-cyanophenoxy)benzene (pmp$(CN)_2$) (VIIIaCi)

The same procedure was used for the synthesis of 1,3-bis-(4′-cyanophenoxy) benzene except the reaction was carried out on resorcinol (11 g; 0.1 mol) and 4′-fluorobenzonitrile (24.63 g) in 200 ml DMF. The crude product was recrystallized from ethanol (600 ml) to give a 68% yield of pure product (Table 1).

3.2.4. Syntheses of 1,2-bis(2′-cyanophenoxy)benzene (ooo$(CN)_2$) (VIIIbAi) and 1,2-bis(2′-cyanophenoxy)-3,5-di-tert-butylbenzene (o(3,5d-t-Bu)oo$(CN)_2$) (VIIIbAiv)

In a similar manner to that described above, catechol (0.1 mol) was reacted with 2′-fluorobenzonitrile (0.2 mol) in DMF at 125°C over a period of 10 h. The precipitate formed after pouring the reaction mixture into iced water was filtered off and washed several times with deionized water. The white product (*ooo*$(CN)_2$) was recrystallized from methanol/water (8:1). Similarly, 1,2-bis(2′-cyanophenoxy)-3,5-di-*tert*-butylbenzene was prepared by reacting 1,2-dihydroxy-3,5-di-*tert*-butylbenzene with 2-fluorobenzonitrile. The product (*o*(3,5d-*t*-Bu)*oo*$(CN)_2$) was recrystallized from ethanol and a 90.1% yield of pure product was obtained (Table 1).

3.2.5. Synthesis of 1,2-bis(4′-carboxyphenoxy)benzene (pop$(COOH)_2$) (IXaAi)

1,2-Bis(4′-cyanophenoxy)benzene (VIIIaAi) (113 g, 0.368 mol) was placed in a round-bottomed flask with methanol (150 ml) and the mixture was brought to the boil, cooled slightly and, while stirring, a solution of potassium hydroxide (120 g) in water (120 ml) was added. After refluxing for 1 h the potassium salt started to precipitate and, to prevent further precipitation, additional water was added as necessary; refluxing was continued for 10 h, after which no evolution of ammonia could be detected. The mixture was diluted to 2 l, boiled with decolourizing agent (Norit A, Aldrich; 2 tablespoons) for 3 h (this step may not be necessary in all syntheses), filtered through a filtering medium (Celite, Aldrich) and further diluted to 4 l. The mixture was then acidified with concentrated HCl to pH 1.5–2, stirred and warmed to 60–70°C for 1 h after which it was cooled to room temperature, filtered and washed thoroughly. The water-wet cake was dissolved in boiling acetic acid (1.8 l). Water (150 ml) was added and the mixture was left to crystallize overnight. After filtering, the solid product was dried to yield 110 g of white crystals of (IXaAi) and a further crop was recovered after partial evaporation. The product had a melting point of 255–259°C; melting was peculiar, some liquid formed at 255–257°C and coexisted with birefringent crystals which melted sharply at 258–259°C. Analytical data are presented in Table 2.

3.2.6. Synthesis of 1,4-bis-(4′-carboxyphenoxy)benzene (ppp$(COOH)_2$) (IXaBi)

The synthetic procedure was the same as that used for *pop*$(COOH)_2$ except that heating to complete the elimination of ammonia took 60 h; additional water (50 ml), KOH and propanol were added during this period. The yield was 88% (Table 2).

3.2.7. Synthesis of 1,3-bis-(4′-carboxyphenoxy)benzene (pmp$(COOH)_2$) (IXaCi)

The same procedure as used for *pop*$(COOH)_2$ synthesis was used. The solution became clear after heating for 16 h; additional KOH (5 g) was added to ensure complete hydrolysis. The diacid was isolated as for *pop*$(COOH)_2$ and the yield was 92% (Table 2).

3.2.8. Synthesis of 1,2-bis-(4′-carboxyphenoxy)benzene dichloride (pop$(COCl)_2$) (XaAi)

1,2-Bis-(4′-carboxyphenoxy)benzene (IXaAi) (10 mmol) was boiled under reflux (with a calcium chloride guard tube) in a nitrogen atmosphere with thionyl chloride (about 20 mmol) for 2 h. Excess thionyl chloride was distilled off, while heating with a water bath, under vacuum which was ultimately reduced to 0.20–0.5 Torr. The resulting, crude acid chloride was dissolved in cyclohexane (50 ml) of which about one-third was then distilled off. The residual solution was left to crystallize. The crude acid chloride was sublimed from a thoroughly degassed melt at about 200°C at 0.5 Torr pressure. The yield was 81% of *pop*$(COCl)_2$; analytical data and melting point are presented in Table 2.

3.2.9. Synthesis of other acid chlorides

Acid chlorides were prepared from other acids by the same procedure except for final recrystallization. 2,3-Bis-(4′-carboxyphenoxy)naphthalene dichloride (XaDi) was recrystallized from cyclohexane/toluene (1:1), 1,2-bis-(4′-carboxyphenoxy)-3,5-di-*tert*-butylbenzene dichloride was

Table 2
Characteristics and analytical data for bis(ether acid)s, and bis(ether acid chloride)s

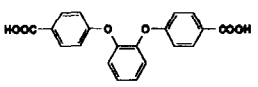
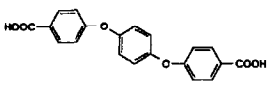
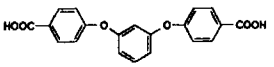
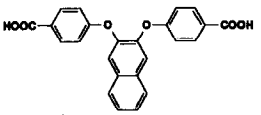
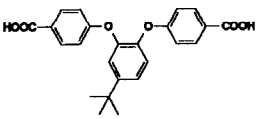
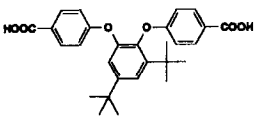
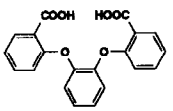
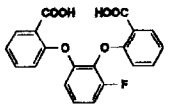
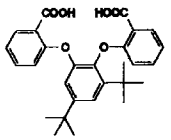
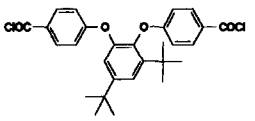
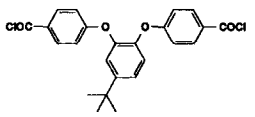
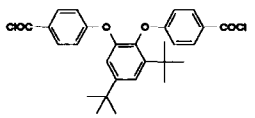
Diacid		Elemental analysis				Melting point	Yield
Structure	Designation		C	H	Cl	(°C)	%
	*pop*(COOH)$_2$ (IXaAi)	Calcd Found	68.57 68.57	4.03 4.02		255-258[a] 255-256[d]	84
	*ppp*(COOH)$_2$ (IXaBi)	Found	68.33	4.04		332-333 331-333[b] 313-315[c] 322-324[a]	88
	*pmp*(COOH)$_2$ (IXaCi)	Found	68.35	4.07		305-306 300-302[b] 299-301[d]	
	*p*(2,3N)*op*-(COOH)$_2$ (IXaDi)	Calcd Found	72.00 71.53	4.03 3.93		282-285	87
	*p*(4-*t*-B)-*op*(COOH)$_2$ (IXaAiii)	Calc. Found	70.92 70.99	5.54 5.47		231-232	90
	*p*(3,5-d-*t*-B)*op*(COOH)$_2$ (IXaAiv)	Calcd Found	72.70 72.83	6.53 6.53		251-253	87
	*ooo*(COOH)$_2$ (IXbAi)	Calcd Found	68.57 68.60	4.03 3.97		184-185	90
	*o*(3F)*oo*(COOH)$_2$ (IXbAii)	Calcd Found	65.22 65.15	3.55 3.58		207-210	92
	*o*(3,5d-*t*-B)-*oo*(COOH)$_2$ (IXbAiv)	Calcd Found	72.70 72.81	6.53 6.53		265-267	

Table 2 *continued*

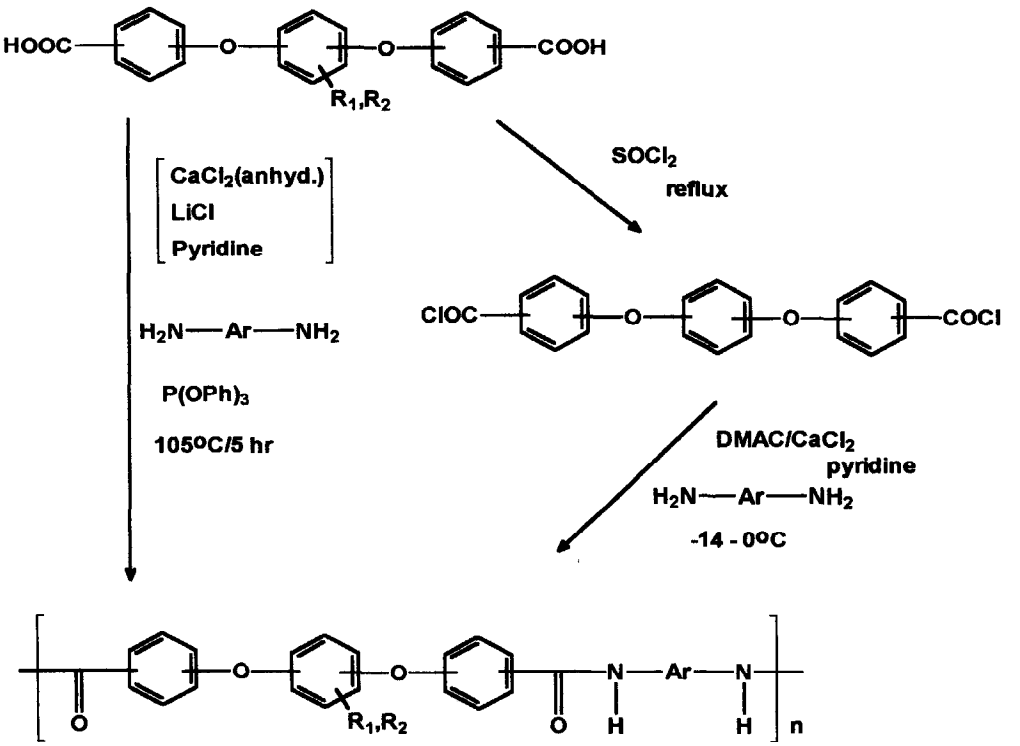
	*p*(3,5d-*t*-B)-*op*(COCl)$_2$ (XaAiv)	Calcd	67.33	5.65	14.19	157-160	82
		Found	67.63	5.82	13.62		
	*p*(4-*t*-B)*op*(COCl)$_2$ (XaAiii)	Calcd	65.02	4,54	15.99	107-110	66
		Found	65.54	4.80	17.27		
	*p*(3,5d-*t*-B)-*op*(COCl)$_2$ (XaAiv)	Calcd	67.33	5.65	14.19	157-160	82
		Found	67.63	5.82	13.62		

[a]Double melting, as described in text[b]Ref. [17][c]Ref. [20][d]Ref. [27]

recrystallized from a minimum of cyclohexane and 1,2-bis-(4′-carbophenoxy)-4-*tert*-butylbenzene dichloride was recrystallized from cyclohexane.

3.2.10. Synthesis of 1,2-bis(4′-nitrophenoxy)benzene (pop(NO$_2$)$_2$) (XII)

Catechol (22 g, 0.2 mol) was placed in a three-necked round-bottomed flask equipped with nitrogen inlet, thermometer and Dean-Stark trap with reflux condenser, together with DMF (250 ml), *para*-nitrofluorobenzene (64 g; 0.4 mol + 7.6 g excess), anhydrous potassium carbonate (80 g) and xylene (50 ml). The mixture was refluxed under nitrogen for 5 h, then, within 2.5 h, liquid (xylene plus DMF; 100 ml) was distilled off and the hot liquid was poured into ice/water mixture (2 l) with vigorous stirring. The resulting brown solid was filtered off and thoroughly washed with deionized water until neutral. The wet cake was boiled in ethanol (1200 ml) and left to crystallize overnight to yield (including a second crop) 65 g (92% theoretical) of yellow crystals of (XII), melting point 134–135°C (lit. 136–138 [23]). Elemental analysis: Calcd for $C_{18}H_{12}N_2O_6$: C, 61.36%; H, 3.43%; N, 7.95%; found: C, 61.34%; H, 3.43%; N, 7.92%.



Scheme 3.

3.2.11. Synthesis of 1,2-bis(4′-aminophenoxy)benzene (pop(NH_2)$_2$) (XIII)

1,2-Bis(4′-nitrophenoxy)benzene (XII) (64.20 g; 0.182 mol), prepared as described above, was charged into a 3 l round-bottomed flask equipped with a magnetic stirrer bar, reflux condenser and dropping funnel together with ethanol (700 ml) and 5% palladium on charcoal (2 g). The mixture was brought to the boil when hydrazine hydrate (200 ml) was added dropwise during a period of 1.5 h. The mixture was refluxed for a further 3 h. The hot mixture was then filtered over a filter agent and left overnight to crystallize when the crystals were separated; the liquid volume was reduced to 400 ml, and an additional crop of crystals was filtered off. The combined crystalline product was recrystallized twice from methanol/water (3:1) to yield off-white crystals (41.2 g) of (XIII). By reducing the liquid volume further an additional crop of 5.7 g of crystals was obtained (overall yield 88% theoretical). Melting point 135–136°C (lit. 137–138 [23]). Elemental analysis: Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95%; H, 5.51%; N, 9.59%; found: C, 74.10%; H, 5.62%; N, 9.77%.

3.2.11.1. Polymer syntheses. Polymers were prepared from the diacids, diacid chlorides and diamines described above by a variety of procedures (Scheme 3).

3.2.12. Preparations of poly(ether amide)s by the phosphorylation technique

A series of poly(ether amide)s were prepared initially by the so-called phosphorylation technique [31], which usually produces products of limited molecular weight, in order to establish the solubilities of the poly(ether amide)s under consideration.

3.2.12.1. Preparation of poly(ether amide)s from 1,2-bis-(4′-carboxyphenoxy) benzene (pop(COOH)$_2$) and para-phenylene diamine (PPD). In a typical synthesis, a solution of anhydrous calcium chloride (0.6 g) and lithium chloride (0.2 g) was prepared in anhydrous NMP (13 ml) under a nitrogen atmosphere. Anhydrous pyridine (4 ml) was added, followed by *pop*-(COOH)$_2$ (IXaAi) (0.70 g; 2 mmol) and PPD (2 mmol). The mixture was stirred under nitrogen and triphenyl phosphite was added (2 ml).

Table 3
Synthesis and properties of poly(ether amide)s

Diacid or diacid chloride	Diamine	Procedure	i.v. (dl g^{-1})	Molecular weight (kg mol^{-1})	Comments
ppp(COOH)$_2$	PPD	Phosphorylation			Soluble in conc. H_2SO_4, insol. in NMP, DMF.
ppp(COOH)$_2$	MPD	Phosphorylation			Soluble in conc. H_2SO_4, insol. in NMP, DMF.
pmp(COOH)$_2$	PPD	Phosphorylation			Soluble in conc. H_2SO_4, insol. in NMP, DMF.
pmp(COOH)$_2$	MPD	Phosphorylation			Soluble in conc. H_2SO_4, insol. in NMP, DMF.
pop(COOH)$_2$	PPD	Phosphorylation		39	Fusible to form fibres, sol. in DMF, DMAC, NMP and cresol
mpm(COOH)$_2$	PPD	Phosphorylation			Soluble in conc. H_2SO_4
mpm(COOH)$_2$	MPD	Phosphorylation			Soluble in conc. H_2SO_4
mmm(COOH)$_2$	PPD	Phosphorylation			Soluble in conc. H_2SO_4, methanesulphonic acid
mmm(COOH)$_2$	MPD	Phosphorylation			Soluble in conc. H_2SO_4, methanesulphonic acid
mom(COOH)$_2$	PPD	Phosphorylation			Fusible, forms fibres, soluble in NMP
mom(COOH)$_2$	MPD	Phosphorylation			Fusible, forms fibres, soluble in NMP
ooo(COOH)$_2$	PPD	Phosphorylation			Fusible, forms fibres, soluble in NMP
ooo(COOH)$_2$	MPD	Phosphorylation			Fusible, forms fibres, soluble in NMP
pop(COOH)$_2$	PPD	Acid chloride	1.16	75	Soluble in NMP
pop(COOH)$_2$	MPD	Acid chloride	1.18	104	Fusible, short fibres, soluble in NMP
pop(COOH)$_2$	*pop*(NH_2)$_2$	Acid chloride	1.11	111	Infusible, soluble in NMP
mom(COOH)$_2$	MPD	Acid chloride			Long fibres, sol. in NMP
p(4-*t*-B)-*op*(COOH)$_2$	PPD	Acid chloride	0.70		
p(4-*t*-B)-*op*(COOH)$_2$	MPD	Acid chloride	0.54	34	
p(4-*t*-B)-*op*(COOH)$_2$	*pop*(NH_2)$_2$	Acid chloride	0.32		
p(2,3N)*op*-(COOH)$_2$	PPD	Acid chloride	0.32		
p(2,3N)*op*-(COOH)$_2$	MPD	Acid chloride	insol.		
p(2,3N)*op*-(COOH)$_2$	*pop*(NH_2)$_2$	Acid chloride	0.63		
p(3,5d-*t*-B)-*op*(COOH)$_2$	PPD	Acid chloride	0.60		
p(3,5d-*t*-B)-*op*(COOH)$_2$	MPD	Acid chloride	0.07		
p(3,5d-*t*-B)-op(COOH)$_2$	*pop*(NH_2)$_2$	Acid chloride	0.65		
IPA	PPD	Acid chloride			Soluble in conc. H_2SO_4
IPA	*pop*(NH_2)$_2$	Acid chloride			Fusible, long fibres, soluble in NMP
TPA	MPD	Acid chloride			Soluble in conc. H_2SO_4, NMP/$CaCl_2$
TPA	*pop*(NH_2)$_2$	Acid chloride			Plastic melt, no fibres, sol. in NMP

The temperature was raised to 105°C for 5 h when an additional triphenyl phosphite (1 ml) and pyridine (1 ml) were added and the mixture was stirred at 110°C. The viscous liquid was then poured into methanol/water (80/20) (300 ml). The polymer was filtered off and extracted with boiling methanol for 1 h. The yield of polymer was 0.78 g.

The same procedure was used for other polymers identified in Table 3 as having been made by the phosphorylation technique.

3.2.13. Preparations of poly(ether amide)s using preformed acid chloride

In order to prepare poly(ether amide)s of higher molecular weight, which would allow a more realistic assessment of properties, a series of poly(ether amide)s were prepared from bis(ether acid chloride)s to produce samples of the soluble polymers.

3.2.13.1. Preparation of polymers from 1,2-bis-(4'-carboxyphenoxy) benzene dichloride (XaAi) and PPD. PPD (1 mmol) was dissolved in DMAC (7 ml) containing $CaCl_2$ (8.7 wt%) and pyridine (0.7 ml). The mixture was cooled to −14°C and *pop*$(COCl)_2$ (1 mmol) was added and the mixture stirred vigorously for 2.5 h, during which period it became very viscous. The mixture was then kept at about 0°C overnight, then at room temperature for 24 h. The polymer was precipitated into MeOH/H_2O, extracted twice with boiling MeOH and dried.

Other poly(ether amide)s identified in Table 3 were prepared by identical procedures.

3.2.14. Syntheses of aromatic poly(ether ester)s and copoly(ether ester)s

Polyarylates, derived from the catechol diacid (IXaAi), were synthesized by different procedures as described below.

3.2.14.1. Preparation of polyarylates by transesterification (Scheme 4). The diacid (3.0 mmol) and diol diacetate (3.0 mmol) were, together with dibutyltin oxide (0.002 g), melted and stirred under nitrogen with *meta*-terphenyl (3–4 g) as solvent. Within 1–1.5 h the temperature was raised to 340°C. The reaction was run for 5–8 h while gradually raising the temperature to 370–380°C. After cooling to about 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 about 80%. The polymers and copolymers were subjected to preliminary testing for solubility and for ability to pull fibres from the melt, Table 4.

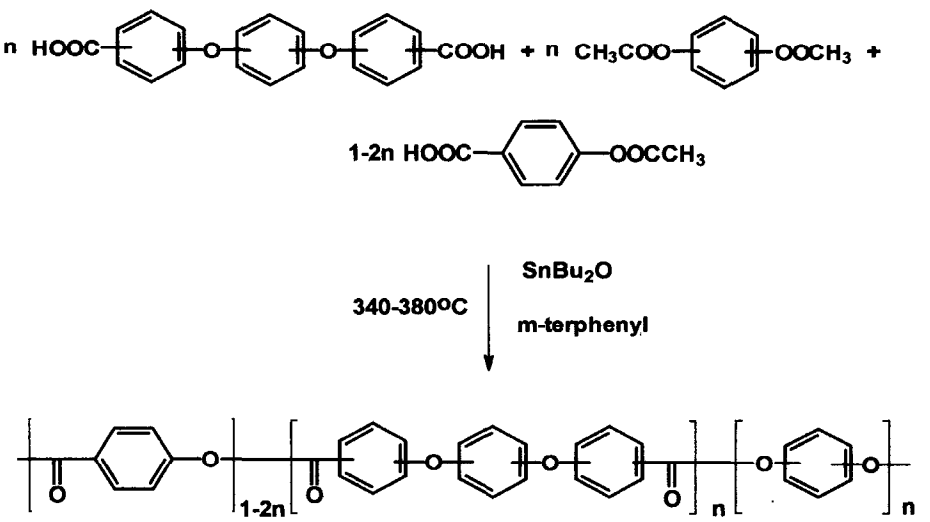
3.2.14.2. Preparation of polyarylates by reaction of acid chloride. In order to form polyesters using acid chlorides, acid chloride (XaAi) (1 mmol) and diol (1 mmol) were refluxed together in dichlorobenzene for 3 h. The polymer was isolated by precipitation into methanol, was extracted with methanol and dried. An example is given in Table 4.

3.2.15. Preparation of copolyarylates by transesterification

Exactly the same reaction conditions were applied as for the preparation of poly(ether ester)s by transesterification, except that *para*-acetoxybenzoic acid was added in different proportions such that there was an overall stoichiometric balance of acid and protected hydroxyl functionalities (Scheme 4). Examples are given in Table 4 in which *pop*-$(COOH)_2$ or *p*(3,5d-*t*-B)*op*$(COOH)_2$ was reacted with hydroquinone diacetate and *para*-acetoxybenzoic acid.

3.3. Techniques

Polymer molecular weights were determined by gel permeation chromatography (gpc) using DMF/LiCl(0.1 M)



Scheme 4.

Table 4
Synthesis and properties of polyarylates and copolyarylates

Diacid	Other reagent	Method	T_g (°C)	Comments
pop(COOH)$_2$	Hydroquinone diacetate	Transesterification	112	Soluble in boiling dichlorobenzene: long fibres from melt
pop(COOH)$_2$	Hydroquinone	Acid chloride	120	Fusible, short fibres pulled just below decomp. temp. Soluble in NMP
pop(COOH)$_2$	Resorcinol diacetate	Transesterification		Very soluble in THF, fibres pulled from melt
p(2,3N)*op*(COOH)$_2$	Hydroquinone diacetate	Transesterification	133	Soluble in chloroform, THF, long fibres from melt
p(4-*t*-B)*op*(COOH)$_2$	Hydroquinone diacetate	Transesterification	138	Soluble in chloroform, very long (50 cm) fibres from melt
p(3,5d-*t*-B)*op*(COOH)$_2$	Hydroquinone diacetate	Transesterification	186	Soluble in chloroform, long fibres from melt
mom(COOH)$_2$	Hydroquinone diacetate	Transesterification	nf	Short brittle fibres from melt
pop(COOH)$_2$ (0.1)	Hydroquinone diacetate(0.1), *p*-ABA (0.8)	Transesterification	no T_g T_m 270, T_c 244	Infusible
pop(COOH)$_2$ (0.25)	Hydroquinone diacetate(0.25), *p*-ABA (0.5)	Transesterification	126	Fusible, long fibres pulled from melt, opaque solution in NMP, liquid crystalline
p(4-*t*-B)-*op*(COOH)$_2$ (0.15)	Hydroquinone diacetate(0.15), *p*-ABA (0.7)	Transesterification	nf	Soluble in hot cresol, dichloroacetic acid or NMP, opaque solutions, very short fibres from melt

p-ABA, *para*-acetoxybenzoic acid; nf, not found

as the mobile phase with a flow rate of 1 cm^3 min^{-1}, columns packed with 5μ-PL gel polystyrene (Polymer Laboratories), a refractive index detector and the instrument was calibrated with polystyrene standards (Polymer Laboratories). Inherent viscosities were measured in 4% LiCl in DMAC.

Glass-transition temperatures (T_g) were determined by differential scanning calorimetry (d.s.c.) with the aid of a Perkin-Elmer DSC2. Optical anisotropies were examined using a polarizing microscope fitted with a heating stage to heat samples up to 300°C. Thermogravimetric analysis (t.g.a.) was performed on a Perkin-Elmer Series 7 instrument.

Values of orientation angle and apparent crystallite size in drawn fibres were determined by X-ray diffraction measurements on bundles of filaments (about 5 mm diameter). The orientation angle was determined from the arc length at half maximum optical density on film and the apparent crystallite size was determined from peak widths at half height; details of the procedures are presented elsewhere [32].

For the determination of mechanical properties, cast films were cut into 0.25″ wide strips with a sharp blade. Some strips were stretched maximally, short of breaking, by hand while in brief contact with a heated pin (1.0″ diam.) at various selected temperatures. Linear densities of fibre strips, drawn and undrawn, were determined using a vibrascope according to ASTM Method D1577 and applied to the determination of a longitudinal stress–strain curve with the aid of an Instron Tensile Tester Type 1122 according to ASTM Method 2101. Specimens of 1.0 gauge length were clamped between the jaws of the instrument and elongated at a constant rate of 0.6″ min^{-1}, i.e. 60% min^{-1} at room temperature. Force–elongation data were used to determine tenacity (force just prior to break), percentage elongation at break, initial modulus and work to break (proportional to the area under the stress–strain curve). Reported data (Table 6) are averages of at least two replica tests.

4. Results and discussion

4.1. Monomer synthesis

The relatively new nucleophilic displacement reactions, discussed here, provide better routes to the ether linkages in precursors to the required bis(ether acid) (and bis(ether amine)) monomers, in terms of yields and purity, than do the more traditional routes. Solvent-assisted Ullmann condensation, used by Bartlett et al. [21] gave a yield of *pmp*(CN)$_2$, i.e. 1,3-bis(4′-cyanophenoxy)benzene, from 4-bromobenzonitrile of only 21%. Aromatic nucleophilic displacement reactions require an electron-withdrawing (activating) group and a leaving group on one component which reacts with either an alkali metal salt of a dihydroxy compound or with a dihydroxy compound directly in the presence of a base, such as potassium carbonate, in an aprotic solvent. The activating group needs to be a suitable precursor for conversion to acid; nitrile is suitable and was used here. Nitro groups are activating and can be reduced to amine in the synthesis of bis(ether amine)s. The major leaving groups are halogen or nitro. It is generally considered that reactivities are in the order F, $NO_2 \gg Cl > Br$; relative propensities of F and NO_2 as leaving groups appear to depend on context.

Kurita and Williams employed chlorodisplacement from *para*-chloronitrobenzene to prepare *pop*(NO$_2$)$_2$ in 60% yield from catechol in DMSO solution in the presence of

potassium *tert*-butoxide [23]. Evers et al. used nitrodisplacement to prepare *ppp*$(CN)_2$ and other dinitriles [17], following the procedure of Takekoshi et al. [22], with yields of 45–85%. In our hands, nitrodisplacement reaction with 4-nitrobenzonitrile in DMF with potassium carbonate at 130–140°C gave yields of 70–80%.

For comparison with the above procedures, we have now examined fluorodisplacement reactions in NMP or DMF for the synthesis of bis(ether nitrile)s (Section 3 and Scheme 1). Higher yields and purer products were obtained in DMF, compared with NMP used earlier. For optimal yields the use of high temperatures was a key factor; thus, in DMF, xylene was used to remove the eliminated water as its azeotrope; toluene had been used in NMP. These facile reactions gave higher yields than chloro- or nitrodisplacement reactions; yields are quoted in Table 1 along with analytical data and melting points for the products. Similar results were obtained by Hsiao and Chang for the syntheses of *pop*$(CN)_2$, *ppp*$(CN)_2$ and *pmp*$(CN)_2$ [27]. Analytical data were supported by nmr spectroscopy (^1H and ^{13}C). Crude products were generally purer than those obtained from nitrodisplacement processes and recrystallization was not always necessary. We therefore prefer the fluorodisplacement route to the precursors for the desired bis(ether acid) monomers.

Bis(ether nitrile)s were readily hydrolysed to the corresponding bis(ether acid)s by boiling with potassium hydroxide in aqueous methanol (Scheme 1). Yields of snow-white crystals, after recrystallization from acetic acid, exceeded 84%. Similar results were obtained for a series of substituted bis(ether acid)s, including *ooo*-$(COOH)_2$ and its derivatives (Table 2). Hsiao and Chang used similar procedures and obtained similar results in the syntheses of *pop*$(COOH)_2$, *ppp*$(COOH)_2$ and *pmp*$(COOH)_2$ [27], although our yields were rather higher. The bis(ether acid) *pop*$(COOH)_2$ was further converted to crystalline bis(ether acid chloride) *pop*$(COCl)_2$ by direct reaction with excess thionyl chloride. The crude product was recrystallized from cyclohexane as described in Section 3, to give a good yield of pure product; *pop*$(COCl)_2$ was additionally sublimed from the melt. Similar procedures were used in the synthesis of additional bis(ether acid chloride)s. Analytical data and melting points are given in Table 2.

The syntheses outlined above provide a series of bis(ether acid) monomers which can be used, possibly in conjunction with related bis(ether amine)s prepared as in Scheme 2 (Table 2)[28], to prepare polymers with flexible main-chain ether linkages, especially *ortho*-linked phenylene units. Thus, polyamides with *ortho*-linked phenylene units can be prepared from *pop*$(COOH)_2$ or *pop*$(COCl)_2$ and a variety of diamines including the diamine *pop*$(NH_2)_2$. For comparison, polyamides were also prepared from *ppp*$(COOH)_2$ and *pmp*$(COOH)_2$. Poly(ether ester)s and copoly(ether ester)s were prepared from *pop*$(COOH)_2$, *pop*$(COCl)_2$ and related monomers (Table 4) with a variety of diols.

4.2. Polymer syntheses

4.2.1. Poly(ether amide)s

Different procedures were used to synthesize poly(ether amide)s containing various combinations of *para*-, *meta*- and *ortho*-moieties. The phosphorylation route, described by Higashi and co-workers [31], was used initially to prepare poly(ether amide)s from *ppp*$(COOH)_2$, *pmp*$(COOH)_2$, *mom*(COOH)2, *pop*$(COOH)_2$ and *ooo*$(COOH)_2$. No special precautions were taken in order to maximise molecular weights [33] and, under the usual conditions employed here, only low-molecular weight polymers were obtained. However, this procedure is simple and satisfactory for the preparation of polymers in order to assess their solubilities. Details of the phosphorylation procedure used are given in Section 3, and data on the polymers prepared are given in Table 3.

High-molecular-weight polyamides are better synthesized using a reaction between preformed acid chloride and diamine. Polymers judged likely to be soluble in non-aggressive solvents were made to high molecular weight in this way. Thus, polymers were prepared from *pop*$(COCl)_2$ and other bis(ether acid)s containing *ortho*-units with the three diamines PPD, MPD and *pop*$(NH_2)_2$ (Table 3). Viscosities of these polymerization mixtures were normally high and the nature of the precipitated polymer indicated high-molecular-weight products. Polymers prepared by the acid chloride route could be solvent-cast into tough, coherent films; polymers made by the phosphorylation route gave friable films.

Attempts were made to characterize some of the poly(ether amide)s in terms of molecular weight. Gel permeation chromatograms often showed the presence of a small low-molecular-weight peak, well-divorced from the main polymer peak. These peaks distort any attempt to obtain realistic values for the number-average molecular weight of the polymer and the molecular weights quoted in Table 3 correspond to the peaks of the chromatograms and approximate to weight-average molecular weights for the high-molecular weight component; molecular weights were calculated on the basis of a polystyrene calibration. Some of the molecular weights determined were higher than expected for aromatic polyamides. We therefore determined the molecular weight of a standard Nomex® (poly(1,3-phenyleneisophthalamide)) sample in the same way. The Nomex® had been characterized by S. Threefoot at Du Pont using g.p.c. in DMAc/4%LiCl; the number- and weight-average molecular weights determined were 17 and 93.6 kg mol^{-1}, respectively, and the polymer had an inherent viscosity of 1.5 dl g^{-1} in the same solvent. The corresponding molecular weights determined by gel permeation chromatography in DMF/LiCl (0.1 M) during this work were 46 and 330 kg mol^{-1}, respectively. The discrepancies between the values is approximately a factor of three to four and if such a factor is applied to the molecular weights determined for other poly(ether amide)s then the values calculated are more

reasonable. Similar, unrealistic high molecular weights, up to 400 kg mol^{-1}, were determined for another series of poly(ether amide)s based on new bis(ether amine)s [28]. We therefore determined inherent viscosities (i.v.) of several of the poly(ether amide)s (Table 3) as an additional guide to molecular weights.

Viscosity data show that polymers prepared from *pop*-$(COCl)_2$ were of high molecular weight; inherent viscosities were in excess of unity. Polymers prepared from the substituted derivatives of *pop*$(COCl)_2$ had lower inherent viscosities and molecular weights. In some cases only low-molecular-weight products, inherent viscosities below 0.5 dl g^{-1}, were obtained. The reasons for the lower molecular weights are not clear. It is uncertain at this stage as to whether or not the substituents on the catechol moiety restrict chain conformations in such a way as to favour the formation of cyclic polymers or if the reason is monomer purity.

In comparison with the major high-molecular-weight peak and small oligomer peak found in the gel permeation chromatograms of the polyamides formed from bis(ether acid)s with terminal *para*-carboxy groups, chromatograms for polyamides formed from bis(ether acid)s with the *ooo*-substitution pattern had major peaks at 'high' molecular weight (about 30 as opposed to 90 kg mol^{-1}) and distinct evidence for a high content of oligomeric material. The oligomers probably have a high cyclic content (Eastmond GC, Paprotny J, unpublished results).

4.2.2. Poly(ether ester)s

Previous attempts to prepare polyarylates and copolyarylates with *ortho*-substituted units are very limited. Polymers prepared from *ortho*-hydroxybenzoic acid were found to be thermally unstable [14]. Copolymers in which catechol, along with another diol, was reacted with terephthalic acid led to polymers which were more stable but which had low T_g [15]; the catechol unit was incorporated through ester linkages. In this work *ortho*-units are incorporated though ether linkages and provide a new group of poly(ether ester)s.

To illustrate the formation of poly(ether ester)s with *ortho*-substituted units, we synthesized a small selection of poly(ether ester)s and copoly(ether ester)s from *pop*-$(COOH)_2$, either by reacting the acid chloride *pop*$(COOCl)_2$ with an aromatic diol, or by transesterification of *pop*-$(COOH)_2$, or a related bis(ether acid), with a diol diacetate, as described in Section 3. Copolymers were prepared from bis(ether acid), diol diacetate and *para*-acetoxybenzoic acid. The syntheses are summarized in Scheme 4 and the results are presented in Table 4; when Scheme 4 was used to synthesize homopoly(ether ester)s no hydroxyester, only diester, was used. Synthesis by transesterification, using *meta*-terphenyl as solvent, was found to be the more useful method for producing polymers of high molecular weight.

4.3. Polymer properties

4.3.1. Poly(ether amide)s

4.3.1.1. Polymer solubilities. One of our interests in synthesizing poly(ether amide)s of different structure was to investigate the influence of aromatic substitution patterns on polymer properties as well as identifying the possibility of preparing processable polyamides. Thus we prepared a series of poly(ether amide)s with different aromatic substitution patterns in the diacid monomer and assessed their solubilities in various solvents (Table 5); several of these tests were made on polymers initially prepared by the phosphorylation route. Our results are consistent with other data recently published on related materials.

Kevlar® aramid, the commercial all *para*-polyamide fibre from terephthalic acid and PPD, and Nomex® aramid, the all *meta*-polyamide fibre from isophthalic acid and MPD, are only soluble in concentrated sulfuric acid and, in the latter case, NMP (or DMAc) with calcium chloride. Aramids with

Table 5
Thermal properties of poly(ether amide)s formed from bis(ether acid chloride)s and diamines

Acid	Amine	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C) in N_2 (air)	Residue (%) at 600°C [700°C] in N_2 (air)	Gradient–hot bar		
							Sticks (°C)	Melts (°C)	Fibres
pop$(COOH)_2$	PPD	223	267	441	415 (390)	40 (0)	> 400	> 400	None
	MPD	221			390 (380)	60 (18)	325	365	Short, brittle
	pop$(NH_2)_2$	192		286	390 (380)	44 (6)	280	354	Short, brittle
p(2,3N)*op*$(COOH)_2$	PPD	235	~320	391	410	54 [50]	250	285	Very weak
	MPD	246			410	67 [61]	239	288	Weak
	pop$(NH_2)_2$	201			410	91 [89]	213	249	Weak
p(4-*tert*-B)*op*$(COOH)_2$	PPD	225–250			410	57 [47]	248	294	Weak, brittle
	MPD	217			395	46 [42]	229	262	Short, brittle
	pop$(NH_2)_2$	194			415	48 [33]	213	255	Long, weak
p(3,5d-*t*-B)*op*$(COOH)_2$	PPD	269			410	43 [38]	288	327	Long, weak
	MPD	247			410	35 [31]	265	305	Brittle
	pop$(NH_2)_2$	218			420	38 [28]	225	275	Long, weak

mixtures of *meta*- and *para*-linkages were also insoluble in simple aprotic solvents. Thus, the polyamide from terephthalic acid and MPD would only dissolve in NMP with added $CaCl_2$ and that from isophthalic acid and PPD would only dissolve in concentrated sulfuric acid (Table 4). In contrast, Yang and Cherng reported that polymers prepared from terephthalic acid or isophthalic acid and *pop*$(NH_2)_2$ are soluble in DMAc and NMP without added salts, except that the polymer from TPA was insoluble in DMAc without LiCl [24]. We observed similar results (Table 4). Yang and Cherng reported that the corresponding polyamides from *ppp*$(NH_2)_2$ and *pmp*$(NH_2)_2$ are insoluble in DMAc without added LiCl [24].

More recently, Hsiao and Chang also prepared poly(ether amide)s from bis(ether acid)s (IXaAi), (IXaBi) and (IXaCi) and a variety of diamines, by the phosphorylation method. They tested polymer solubilities in organic aprotic solvents and *meta*-cresol. In agreement with our findings (Table 3), they reported that polymers prepared from *pop*$(COOH)_2$ and conventional diamines were generally more soluble than those from the isomeric diacids *ppp*$(COOH)_2$ and *pmp*$(COOH)_2$ [27]. Hsiao and Chang reported that the polymers from all three acids and PPD were insoluble in all solvents used, while polymers prepared with MPD were all soluble in virtually all aprotic solvents used [27]. In contrast, we found that polymers prepared from *ppp*$(COOH)_2$ with both PPD and MPD were soluble only in concentrated sulfuric acid. The different behaviours of the MPD polymers may be due to different molecular weights. As our polymer was insoluble we were unable to determine its molecular weight; Hsiao and Chang reported a number-average molecular weight of 66 000 by g.p.c. with DMF eluant which is probably a significant overestimate (see above). We also found that polymers formed using various combinations of *meta*- and *para*-substituted units, but no *ortho*-substituted units, in the diacid with PPD and MPD were soluble only in concentrated sulfuric acid; polymers from *mmm*$(COOH)_2$ and PPD or MPD were additionally soluble in methanesulfonic acid (Table 3). In marked contrast, polymers from *pop*$(COOH)_2$ with PPD, MPD and *pop*$(NH_2)_2$ were all soluble in NMP as was the polymer from *mom*$(COOH)_2$ and PPD.

The overall consensus of data from poly(ether amide)s containing various combinations of *ortho*-, *meta*- and *para*-substituted units is that the only aromatic polyamides which show significant solubility in aprotic solvents, without added salts (which provide non-corrosive solutions) are those containing one or more *ortho*-substituted units per repeat.

We also prepared poly(ether amide)s using the various bis(ether acid)s prepared in this work which carried pendant substituents, fluorine or *tert*-butyl or having the *ortho*-substituted naphthalene unit as in *p*(2,3N)*op*$(COOH)_2$. All the polymers prepared from these monomers with PPD, MPD or *pop*$(NH_2)_2$, identified in Table 3, were soluble in simple aprotic solvents. Thus, it is established that incorporation of *ortho*-substituted main chains units into poly(ether amide)s gives rise to solution-processable aramids.

4.3.1.2. Thermal properties. Melt processability implies that polymers have thermal-transition temperatures within a suitable working range and that they are thermally stable at temperatures where they are sufficiently fluid. We therefore determined T_g values (and melting behaviour, if any) of the poly(ether amide)s by d.s.c. and their thermal stabilities by t.g.a. In this study we report only on the thermal properties of poly(ether amide)s with *ortho*-substituted units, with or without substituents, in the acid moiety.

The glass transition (and crystallization and melting) temperatures of the several poly(ether amide)s in question are summarised in Table 5. Most of the polymers prepared, when cast as films, were amorphous, with certain exceptions. Hsiao and Chang reported that all poly(ether amide)s based on *pop*$(COOH)_2$, with the exception of that prepared with 4,4′-bis(4-aminophenoxy)biphenyl, were amorphous while polymers prepared from *ppp*$(COOH)_2$ and *pmp*$(COOH)_2$ were generally crystalline.

Data in Table 5 show that T_g values of polymers prepared with PPD or MPD are all significantly above 200°C. Polymers prepared from *pop*$(COOH)_2$, or its substituted analogues, and *pop*$(NH_2)_2$ have T_g values at or just below 200°C; the polymer prepared from *p*(3,5d-*t*-Bu)*op*$(COOH)_2$ and *pop*$(NH_2)_2$ has T_g at 218°C. D.s.c. traces showed evidence of crystallization and crystal melting in some samples; we attribute the somewhat irreproducible behaviour to sensitivity of crystallization to details of thermal history and, possibly, solvent. Thus, a sample of the polymer from *pop*$(COOH)_2$ and PPD, precipitated into methanol showed no evidence for crystallinity; Hsiao and Chang failed to observe a T_g and in their sample found no evidence for crystallinity [27]. However, a sample which precipitated as fibrils from NMP solution into water under high shear showed a very weak T_g at 223°C, followed by an exotherm (23 J g^{-1}, about 15°C wide at a heating rate of 20°C min^{-1}) with a peak at 267°C and a distinct sharp endotherm (59 J g^{-1}) peaking at 441°C; the latter feature is very close to, and possibly overlaps to some extent, a strong exotherm at about 450°C, common to all samples, which corresponds to decomposition. We attribute the exotherm at 267°C to crystallization and the endotherm (441°C) to crystal melting. Thus, the polymer precipitated into water is amorphous but is susceptible to crystallization on heating above T_g. The polymer from *pop*$(COOH)_2$ and MPD showed only a weak T_g and no evidence of crystallization or crystal melting; the exotherm attributed to thermal decomposition was seen at about 425°C; Hsiao and Chang reported a T_g of 219°C for this polymer [27]. The polymer from *pop*$(COOH)_2$ and *pop*$(NH_2)_2$ showed a T_g at 192°C and a weak, broad crystal-melting endotherm at 286°C with no evidence for an intermediate crystallization exotherm; an as-precipitated sample showed no evidence for crystallization above T_g.

Similar studies were made on polymers prepared from bis(ether acid)s formed from catechol derivatives and the same diamines. For the bis(ether acid) prepared from 2,3-dihydroxynaphthalene, *p*(2,3N)*op*(COOH)$_2$, the polymer with PPD exhibited a well-defined T_g at 235°C, followed by a rather broad, ill-defined exotherm at about 320°C, and a well-defined, sharp melting endotherm (16 J g^{-1}) peaking at 391°C; as-precipitated samples showed no evidence for crystallization. The corresponding polymers prepared with MPD and *pop*(NH$_2$)$_2$ only exhibited T_g values with virtually no evidence for crystallization or crystal melting at the heating rates employed in these experiments.

Polymers with a *tert*-butyl-substituent in the acid moiety showed no clear evidence for crystallization or crystal melting at temperatures below that of thermal decomposition. The polymer with PPD had a weak, broad and ill-defined T_g at about 230°C, that with MPD had a stronger and more well-defined T_g at 217°C while that with *pop*(NH$_2$)$_2$ had a well-defined transition at 194°C. Introduction of two *tert*-butyl-substituents into the acid moiety also produced amorphous polymers with no evidence for crystallinity. Each polymer exhibited a distinct T_g at the temperatures quoted in Table 5;. the second *tert*-butyl group served to raise the T_g values of the several polymers.

Thus, the poly(ether amide)s are generally amorphous but some compositions show definite evidence for crystallizability in the melt. Under conditions so far used, the crystalline contents are low, as judged by transition enthalpies. Nevertheless, the data indicate that it may be possible, under suitable conditions of molecular weight and thermal treatment, to induce crystallinity and raise the effective upper-working temperatures.

T.g.a. data showed that all polymers prepared had thermal decomposition onset temperatures (T_d) in the range 390–420°C in nitrogen; onset temperatures in air, where measured, were only slightly lower. These onset temperatures are a little lower than the onset of decomposition (450°C) identified by d.s.c.; heating rates were different. There were some differences in residues at 600°C but these are not interpreted. There were also slight differences between the shapes of the thermograms for the individual samples. Almost all samples heated under nitrogen decomposed in a smooth single process, while samples heated in air tended to show two-stage decompositions; a small initial decomposition set in at the temperatures cited followed by a stronger decomposition about 50°C higher. Fig. 1 shows thermograms for three polymers prepared from *pop*-(COOH)$_2$ with *pop*(NH$_2$)$_2$, PPD and MPD, clearly the main features are largely uninfluenced by the structure of the diamine; the polymer formed from MPD decomposes a little more slowly as the temperature is raised. Detailed features have not been interpreted in terms of decomposition mechanisms.

The combination of results from d.s.c. observations and t.g.a. data indicate that possible melt-processing windows exist for all polymers studied. That is, there are large differences between T_g values, where polymers soften, and their T_d values. In the few cases where samples crystallized, crystal melting temperatures were probably too close to T_d values for the polymers to be melt processed between T_m and T_d. For these polymers it is probable that only solution processing is possible but, as the polymers in question are soluble in NMP, it is feasible that they could be processed (spun) from solution and crystallized in subsequent heating processes to give materials with good upper working temperatures.

4.3.1.3. Melt processability. In attempting to make a preliminary assessment of the melt-processing potentials, we attempted to pull fibres from melts using a gradient–hot-bar technique, as described previously [12]. Temperatures quoted in Table 5 for this technique are those at which the polymer sticks to the bar (usually slightly above T_g) and when the polymer forms a pool of molten polymer ('melts') from which we attempted to pull fibres.

Polymers prepared from *pop*(COOH)$_2$ with various diamines did not stick to the hot bar until temperatures well in excess of T_g were attained. These polymers, perhaps rather stiff, linear and potentially crystallizable, exhibited much reduced processing windows and either no fibres or only short brittle fibres could be pulled from melts.

Polymers prepared from the acids formed from catechol derivatives gave 'melts' at lower temperatures and, although fibres, in some cases long fibres, could be pulled from the melts, the fibres were rather weak or brittle. However, since it is established that at least some of the polymers investigated are crystallizable, at least under some conditions, it is possible that processing procedures could be developed to produce strong crystalline fibres. It is also probable that solution processing would be the most appropriate method for producing fibres from the new materials. For polymers which give strong amorphous films, when cast from solvents, hot pressing might produce samples with good properties. In making these observations, it should be remembered that many

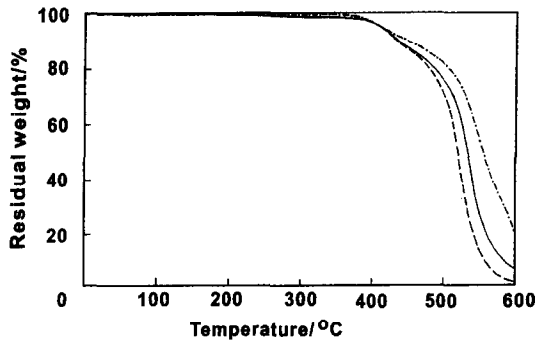


Fig. 1. Thermograms determined by thermo-gravimetric analysis on polyamides prepared from (——) *pop*(COOH)$_2$ and *pop*(NH$_2$)$_2$; (– – –) *pop*(COOH)$_2$ and PPD; (– • –) *pop*(COOH)$_2$ and MPD.

Table 6
Influence of isomerism on poly(ether amide) copolymers

Sample	Diacid(s)	Diamine(s)	Draw conditions		UTS (GPa)[a]	Elongation (%)[b]	Tensile modulus (GPa)[a]	Orientation angle (°)	Apparent crystallite size (Å)
			Ratio	Temp (°C)					
1	TPA	*ppp*$(NH_2)_2$	1.8	420	0.36	3.9	15.0		
2	TPA	*pop*$(NH_2)_2$	As cast		0.07	57	1.85	nil	15
			2.5	220	0.40(0.46)	9.0(9.7)	7.29(7.56)		
			2.9	237	0.46(0.53)	9.0(9.8)	7.53(8.52)		
			4.0	250	0.41(0.53)	9.6(16)	6.92(7.66)		
			5.1	260	0.46(0.57)	16(14)	6.05(6.42)	< 44	12
3	TPA	*ppp*$(NH_2)_2$/PPD (40:60)	8.5	400	1.91	4.2	30.9		
4	TPA	*pop*$(NH_2)_2$/PPD (50:50)	5	380	1.11	6.1	23.0	9	25
5	TPA	*pmp*$(NH_2)_2$/PPD (50:50)	5	390	1.19	5.2	23.5	15	29
6	*pop*$(COOH)_2$/TPA (50:50)	PPD	5	380	1.05	7.0	20.0	12	30
7	*pop*$(COOH)_2$/TPA (30:70)	PPD	2.3	395	0.64	3.5	24.2	16	43
8	TPA	3,4′-ODA/PPD(50:50)	10	495	3.37	5.0	76.6	12	10
9	TPA	4,4′-ODA/PPP(50:50)	5	400	1.96	5.4	37.1		

UTS (MPa) converted from tenacity (gpd) as 1 gpd = 123.5 Mpa, assuming a nominal density of 1.4 g cm^{-3}. 4,4′-ODA, bis(4-aminopheny)ether; 3,4′-ODA, 3,4′-diaminophenylether
[a]Average values; maximum values in parentheses

of the polymers examined in this preliminary study had low molecular weights and better mechanical properties will almost certainly be obtained when the molecular weights are optimised.

4.3.2. Copolyamides

In addition to producing homopoly(ether amide)s, it is possible to use the bis(ether acid)s, or corresponding bis(ether amine)s, as comonomers to reduce order in existing aramids and enhance processability. Here we report on experiments, performed on strips of polymer film, undertaken to assess drawability and properties of copolymers incorporating *ortho*-substituted units.

Table 6 presents data on a series of materials with different proportions of *para*- and other, especially *ortho*-, linkages. Data show that conversion of a proportion of units from *para* to *ortho*, samples 1 and 2, considerably reduces the draw temperature (from 420 to 260°C) and increases the draw ratio achievable. Simultaneously, tenacity (ultimate tensile strength, UTS) and elongation at break of the *ortho*-isomer increase with the draw ratio but the modulus, relative to the all *para* material, decreases. In copolymer 3, with all *para*-units, the proportion of ether linkages is reduced compared with sample 1 by introducing PPD as comonomer and the draw temperature is increased to 500°C. A similar effect was found in sample 4 compared with sample 2. Within the series of copolymers 3–5, in which PPD and a bis(ether amine) are used as comonomers and a proportion of the linkages are changed from *para* to *meta* to *ortho*, replacing the *para*-units in one diamine reduces the draw temperature (from 500 to 380°C), the draw ratio attainable, the tensile modulus and the tenacity; there is little difference in properties in using *pop*$(NH_2)_2$ or *pmp*$(NH_2)_2$. Similar results (modulus, tenacity and extension to break) were obtained for polymers based on the two diacids TPA and *pop*$(COOH)_2$, samples 6 and 7, where the draw temperature increased with increasing *para* (TPA) content, while the draw ratio was reduced. There was little major influence on other parameters by using two acids as comonomers as opposed to two diamines.

For sample 2 an increase in draw temperature increased the attainable draw ratio as a result of which the elongation at break increased, but other parameters changed little; the undrawn sample had a high elongation to break and low modulus and tenacity.

It is perhaps unexpected that the draw ratio achieved with sample 2 is greater than that with sample 1, as *para*-linkages are generally considered to impart less chain flexibility than other units. The lower moduli attained in all samples with less than 100% *para*-linkages suggests that in these materials there is a low level of chain alignment, consistent with reduced tenacity, despite reasonable orientation angles; values of orientation angle are influenced by relatively low contents of oriented crystalline material. The limited draw ratio achieved with the copolymers is consistent with crystallization during drawing. While a high content of ether and *ortho*-linkages can lead to a high draw ratio (cf. samples 1 and 2), the lower draw ratios in copolymers with *ortho*-units arise from entanglement of long rigid units, compared with a higher overall level of flexibility. X-ray diffraction data confirm that poly(ether amide)s are crystallizable, that crystallinity can be developed in samples with a high proportion of *ortho*-substituted units when drawn and that crystallinity can be retained in aramids with predomi-

nantly *para*-units when a large proportion of *ortho*-units are introduced (Table 6). Overall, the balance of properties with the relative contents of *ortho*- and *para*-linkages is subtle and warrants further study.

4.3.3. Poly(ether ester)s

Some properties, especially those relating to solubility and melt processability, of the poly(ether ester)s and copoly(ether ester)s prepared in this study are summarized in Table 4. From these data it is seen that, as with poly(ether amide)s and poly(ether imide)s, inclusion of *ortho*-substituted units into the acid moieties introduces solubility in relatively simple organic solvents, such as NMP and even chloroform or tetrahydrofuran. T_g values of several poly(ether ester)s are lower than those of the corresponding aramids, consistent with the absence of hydrogen bonding.

While most polyarylates examined were prepared by transesterification, comparison of the two polymers prepared from *pop*$(COOH)_2$ and hydroquinone shows that the acid chloride route gave a polymer with higher molecular weight, a higher T_g and reduced solubility. This same polymer was also more difficult to process from the melt.

Changing the substitution pattern in the diacid from *pop* to *mom* changed the thermal transition behaviour. No clear evidence of a T_g could be found in the polymer from *mom*$(COOH)_2$ and hydroquinone. Gel permeation chromatography showed this product to be oligomeric.

Introduction of bulky groups into *pop*$(COOH)_2$ increased the solubility of poly(ether ester)s formed with hydroquinone in solvents such as chloroform and THF and simultaneously increased T_g. Despite the higher T_g values, fibres could be very readily pulled from polymer melts without thermal decomposition.

The possibility of using *pop*-type diacids as comonomers in otherwise all-*para* polyarylates was examined. Thus, *pop*$(COOH)_2$ or *p*(4-*t*-Bu)*op*$(COOH)_2$ was introduced (along with a molar equivalent of hydroquinone to maintain stoichiometry) into poly(*para*-hydroxybenxoic acid). Reduction of the *para*-hydroxybenxoic acid content to 50 mol%, i.e. one of six phenylene rings in the polymer is *ortho*, led to a polymer which gave opaque solutions in NMP. The polymer had a T_g at 126°C and long fibres could be drawn from a liquid-crystalline melt. A smaller *pop*$(COOH)_2$ content (10 mol%) gave a polymer with a melting point at 270°C and, on cooling, a crystallization peak (T_c) at 244°C. The polymer was infusible and the powder in the d.s.c. pan did not sinter even up to 400°C. Similarly, a poly(ether ester) with 15 mol% *p*(4-*t*-Bu)*op*-$(COOH)_2$ gave a polymer soluble in strong solvents (Table 4) to give opaque solutions. No T_g was identified but the polymer sintered in the d.s.c. pan and it was possible to pull short fibres from a melt on a hot-plate. Weak T_g values are commensurate with liquid crystalline behaviour.

Thus incorporation of *ortho*-substituted units enhances solubility and processability but in these materials, where the *ortho*-phenylene units are enchained through ether linkages, the polymers may have higher T_g values than other copolymers where catechol is enchained through ester linkages [15].

A number of aromatic polyarylates exhibit liquid crystallinity and we examined the polymers prepared for optical anisotropy. Although d.s.c. failed to identify melting points in several poly(ether ester)s, evidence for melting behaviour was found by polarizing microscopy. Thus, no endothermic melting transitions were observed in poly(ether ester)s from *pop*$(COOH)_2$ and hydroquinone below 400°C, but samples formed anisotropic melts when heated to about 210°C and cooled to anisotropic solids. Similarly, the poly(ether ester) from *p*(2,3N)*op*$(COOH)_2$ formed an anisotropic melt at 170°C and became isotropic at 280°C; neither transition was observed by d.s.c. In contrast, neither poly(ether ester) with *tert*-butyl substituents formed anisotropic melts, but became isotropic fluids about 30°C above their respective T_g values.

The oligomeric poly(ether ester) from *mom*$(COOH)_2$ became an anisotropic melt at 220°C which persisted to 240°C when it gradually became isotropic; on cooling the solid was anisotropic.

The copoly(ether ester)s showed a variety of effects. The thermal transition behaviour of the sample from *pop*-$(COOH)_2$ with 80 mol% *para*-hydroxybenzoic acid is described above; this sample showed no optical anisotropy. Decreasing the *para*-hydroxybenzoic acid content to 50 mol% produced a material which formed an anisotropic liquid at 210°C, which persisted to at least 300°C, and formed an anisotropic solid on cooling. The copolymer with a *tert*-butyl substituent and intermediate (70 mol%) *para*-hydroxybenzoic acid was an anisotropic liquid from 260 to at least 300°C. Thus, direct evidence for liquid crystallinity was observed from 260 to at least 300°C in a number of the poly(ether ester)s formed.

5. Conclusions

In this paper we have demonstrated that a series of 1,2-bis(4′-carboxyphenoxy)arylenes and 1,2-bis(2′-carboxyphenoxy)arylenes can be readily prepared from catechol and its derivatives by reacting the relevant diol with 4-fluorobenzonitrile or 2-fluorobenzonitrile in NMP or DMF, in the presence of potassium carbonate; dinitriles so formed were hydrolysed to the corresponding diacids. Our preferred reaction conditions for optimum yields of dinitro compounds from 2- or 4-fluorobenzonitrile is reaction in DMF. However, as reported elsewhere, for fluorodisplacements from 3-fluorobenzonitrile reactions at higher temperature in NMP, in the presence of xylene to remove water as its azeotrope, gave higher yields of purer monomers [28]. It was demonstrated that these bis(ether acid)s, as their acid chlorides, can

be used successfully in the synthesis of new high-molecular-weight poly(ether amide)s and poly(ether ester)s. The general structure of the poly(ether amide)s is shown in Scheme 3, where Ar is *para*- or *meta*-phenylene or 1,2-bis(4′-phenoxy)benzene and R_1, R_2 are as used in Scheme 1. The structures of the poly(ether ester)s and copoly(ether ester)s are shown in Scheme 4, where for homopolymers $n = 1$.

1,2-Bis(2′-carboxyphenoxy)arylenes could also be prepared from catechol and its derivatives by an equivalent reaction with 2-fluorobenzonitrile. The bis(ether acid)s made in this way led to low-molecular-weight polymers.

The properties of poly(ether amide)s formed from 1,2-bis(4′-carboxyphenoxy)arylenes, i.e. bis(ether acid)s in which the terminal phenylene units are *para*-substituted and the central phenylene *ortho*-substituted, were determined. In comparison with poly(ether amide)s prepared from bis(ether acid)s with other substitution patterns, we established that those polymers with *ortho*-substituted units are far more soluble than their isomers. Thus, poly(ether amide)s with *ortho*-substituted units are processable from solution in aprotic solvents without added inorganic salts. The same polymers are also more readily processed from the melt. The poly(ether amide)s, as prepared, were mainly amorphous, but it was demonstrated that several of them are potentially crystallizable above their glass-transition temperatures. The poly(ether amide)s were all thermally stable to about 400°C. The processing windows available for melt processing poly(ether amide)s are small, but it was concluded that the polymers may be processed from solution and subsequently crystallized to produce high-tenacity polymers with high upper-working temperatures. The polymers, when crystalline, could be viable alternatives to existing poly(ether amide)s for some applications.

It was also demonstrated that the same bis(ether acid)s or bis(ether acid chloride)s can be used to synthesize new thermally stable poly(ether ester)s or copoly(ether ester)s, incorporating *ortho*-phenylene units into the polymer backbone. Several of the poly(ether ester)s and copoly(ether ester)s prepared were shown to exhibit liquid crystalline behaviour in the melt and form anisotropic solids on cooling. Glass-transition temperatures of some of the poly(ether ester)s were higher than for many polyarylates.

Acknowledgements

The authors wish to acknowledge the financial support of E.I. du Pont de Nemours & Co. Inc., Wilmington, DE, USA, which enabled this work to be undertaken.

References

[1] Wirth JG, Heath DR. US Pats 3787634, 3838097, 1974; Williams FJ, Donahue PE. J Org Chem 1977;(42):3414; Takekoshi T. In: Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. Glasgow: Blackie, 1990:38; Terrier F. Nucleophilic aromatic displacement: the influence of the nitro group. New York: VCH, 1991.
[2] Heath DR, Wirth JG. US Pats 3730946, 3763210, 3763211, 1973; 3787475, 1974; 3869499, 1975; Takekoshi T. Polymer J 1987;19:191.
[3] Johnson RO, Burlhis HS. Polym Sci J Polym Symp 1983;70:129.
[4] Böhringer B, Schilo D, Birkenfeld W, Odenthal W. Chemifaser/Textilindustrie, 1991;41/93:T12.
[5] New TPI, Mitsui-Toatsu Product Data Sheet.
[6] Irwin RS. In: Luise RR, editor. Applications of high temperature polymers. New York: CRC Press, 1997:150.
[7] Takekoshi T. J Polym Sci, Polym Symp 1986;74:93.
[8] Eastmond GC, Paprotny J. Reactive and Functional Polymers 1996;30:27.
[9] Eastmond GC, Paprotny J. US Pat 5434240, 1995.
[10] Eastmond GC, Paprotny J. Polymer 1994;35:5148.
[11] Eastmond GC, Paprotny J. Macromolecules 1995;28:2140.
[12] Eastmond GC, Paprotny J, Irwin RS. Macromolecules 1996;29:1382.
[13] Yang CP, Chen WT. Macromolecules 1993;26:4865.
[14] Feasey RG. Eur Pat Appl, 7732, 1979; Muramatsu H, Kodairu K, Matsuura K, Ito K. Kobunshi Ronbunshi 1982;39:651.
[15] Noël C, Friedrich C, Laupêtre F, Billard J, Bosio L, Strazielle C. Polymer 1984;25:263; Bilibin AYu, Tenkovtsev AV, Skorokhodov SS. Makromol. Chem. 1985;186:1575; Navarro F, Serrano JL. J Mater Chem 1991;1:895; Rankin P. PhD thesis, University of Leeds, 1993.
[16] Eastmond GC, Paprotny J. Inter Pat Applic, WO 97/00903, 1997; US Pat. Applic. filed 1995.
[17] Evers RC, Arnold FE, Helminiak TE. Macromolecules 1981;14:925.
[18] Beilstein CrossFire*plus*Reactions Database, from Beilstein Informationssyteme GmbH, Frankfurt, Germany.
[19] Eastmond GC, Paprotny J. J Mater Chem 1997;7:1321.
[20] Malichenko BF, Vilenskaya LN, Voronina OM. Zh Org Khim 1971;7:1924.
[21] Bartlett KK, O'Neill G, Savill NG, Thomas SLS, Wall WF. Br Polym J 1970;2:225.
[22] Takekoshi T, Wirth JG, Heath DR, Kochanowski JE, Manello JS, Webber MJ. Polym Prepr, Am Chem Soc, Polym Div Inc 1979;20(1):179.
[23] Kurita K, Williams RL. J Polym Sci, Polym Chem Ed 1974;12:1809.
[24] Yang C-P, Cherng J-J. J Polym Sci, Part A: Polym Chem 1995;33:2209.
[25] Gannett TP, Gibbs HH. US Pat 4576857, 1986.
[26] Tan L-S, Venkatasubraian N. US Pat 5514769, 1996.
[27] Hsiao S-H, Chang C-F. Macromol Chem Phys 1996;197:1255.
[28] Eastmond GC, Paprotny J. Synthesis, 1998:894.
[29] Ueda M, Kameyama A, Ikeda C. Polym J 1987;19:673.
[30] Takekoshi T, Wirth JG, Heath DR, Kochanowski JE, Manello JS, Weber MJ. Polym Prep, Am Chem Soc, Polym Div Inc 1979;20(1):179.
[31] Yamazaki N, Higashi F, Kawabata J. J Polym Sci, Polym Chem Ed 1974;12:2149; Higashi F, Ogata SI, Aoki Y. J Polym Sci, Polym Chem Ed 1982;20:2081.
[32] Irwin RS. US Pat 5310861 (to E.I. du Pont de Nemours and Co., Inc.), 1994.
[33] Ponomarev II, Mariani A, Russo S. Polymer 1992;33:4197; Russo S, Mariani A, Ignatov VN, Ponomarev II. Macromolecules 1993;26:4984; Mariani A, Mazzanti SLE, Russo S. Can J Chem—Rev Can Chemie 1995;73;1960.