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A comparison of poly(ether imide)s from diamines with 2-aminophenoxy or 4-aminophenoxy units: Synthesis, characterization and properties

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Abstract

A series of new 3- and 4-ring bis(2-aminophenoxy) aromatic diamines were prepared. These, and corresponding, conventional bis(4-aminophenoxy) diamines were reacted with several aromatic bis(ether anhydride)s to form poly(ether imide)s. The diamines with 4-aminophenoxy groups gave high-molecular-weight polymers that were cast into films with good mechanical properties. In contrast, in almost all cases, diamines with 2-aminophenoxy groups only gave low-molecular-weight powdery products that could not be cast into coherent films. The low-molecular-weight products, prepared from stoichiometrically equal amounts of monomers, were examined by mass spectrometry and shown, in most cases, to consist primarily of cyclic oligomers; traces of linear oligomers were identified in some samples. Apart from a polyimide prepared from pyromellitic dianhydride and 4,4′-bis(2″-aminophenoxy)biphenyl, the only products found to contain significant proportions of linear oligomers were those prepared with a stoichiometric imbalance of monomers. End groups of the various linear oligomers were identified. The 2-aminophenoxy groups predispose the oligomers to cyclize as amic acids, and to remain as cyclics on imidization. In some cases [1+1] cyclic oligomers were observed although the most common species were the [2+2] cyclic dimers.

Keywords: Poly(ether imide)s; Macrocycles; Bis(2-aminophenoxy) diamines

1. Introduction

Polyimides have long been recognised as high-performance polymers that lack processability. Following the development of the commercial poly(ether imide) Ultem® [1], which combines good thermal stability, good mouldability and solubility in selected solvents, numerous papers reported poly(ether imide)s of different structures. These studies primarily involved poly(ether imide)s with ether linkages incorporated into the dianhydride moieties [2–7]. We contributed to these studies, synthesizing new bis(ether anhydride)s with aromatic [8–14], or aliphatic [15], units of different structure and substitution patterns.

Studies directed to understanding the influence of aromatic substitution patterns have primarily involved *para*- and *meta*-linked aromatic rings including rings in aromatic diamines [16], and rings adjacent to ether linkages in poly(ether imide)s [2,17]. There have been very few studies of the influences of *ortho*-linked units in such polymers. Comparisons have been made recently between polyimides with different substitution patterns in the phthalimide moiety [18–23].

We have focussed on synthesizing polymers containing *ortho*-linked aromatic units in dianhydride and diamine moieties and comparing them with more-conventional poly(ether imide)s. In bis(ether anhydride)s, ether linkages can be at either the 3- or the more-conventional 4-position of the phthalic anhydride unit and, hence, of the *N*-phenylphthalimide moiety of the poly(ether imide). A limited number of such polymers have been prepared previously [2,24–27]. In a companion study, we explored further the comparison of polymers with such structures [28]. We have demonstrated

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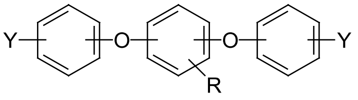
that *ortho*-linked phenylene units, derived from catechol or its derivatives [8–12], can be incorporated into bis(ether anhydride)s from which thermally-stable, high-molecular-weight polyimides can be obtained. Subsequently, we developed a route to bis(ether amine)s in which phenoxy amine units are attached to aromatic units, primarily phenylenes, with different substitution patterns [29]. In addition to incorporating catechol-related units into the bis(4-aminophenoxy)benzenes it is possible to have the ether linkages *ortho* to the amino group; this is the focus of the current paper.

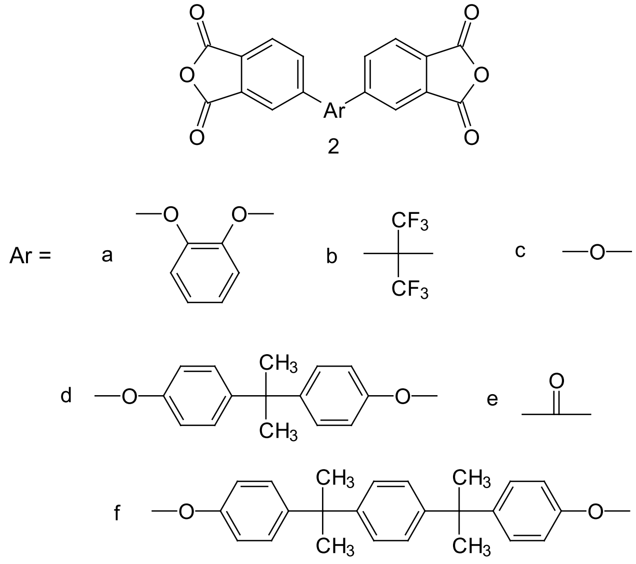
For bis(aminophenoxy)benzenes (**1a**) there are nine possible isomers with different substitution patterns, assuming the terminal units Y have the same substitution pattern and species are symmetrical. Evers introduced a nomenclature for such compounds based on the substitution pattern at each ring, e.g. *ppp*, *pmp*, etc. and the nature of the functional group [30]. Accordingly, dinitro compound **1b** in which Ys in the outer rings are *para* to the ether linkage and the central ring is derived from catechol is designated *pop*$(NO_2)_2$. We adopted this nomenclature and adapted it for the presence of substituents R. Thus the corresponding dinitro compound prepared from 3-methyl catechol (R = 3-methyl) is *p*3Me*op*$(NO_2)_2$ [29,31]; the identity and location of the substituent precedes the designation of the relevant ring.

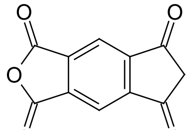


1 a Y = NH_2 , b Y = NO_2

We, and others, have now used several of these bis(ether amine)s in the synthesis of poly(ether imide)s and poly(ether amide)s [31–33]. To date most of that work involved bis(ether amine)s with terminal *para*-aminophenoxy residues. The work included the synthesis of bis(ether amine)s with a central catechol-derived unit which incorporated an *ortho*-linked unit into the diamine moiety of the polymer (i.e. *pop*$(NH_2)_2$) and led to thermally-stable, high-molecular-weight poly(ether imide)s and poly(ether amide)s.

More recently, we reported the synthesis of bis(ether amine)s with *ortho*-aminophenoxy units and, specifically, the diamine 1,2-bis(2′-aminophenoxy)benzene (i.e. *ooo*$(NH_2)_2$) which incorporates three *ortho*-phenylene units into the diamine moiety [34]. When this diamine was polymerized with the bis(ether anhydride), **2a**, derived from catechol, to form a poly(ether imide) with four *ortho*-phenylene units per repeat unit of the polymer, it was established that only low-molecular-weight poly(ether imide)s, with a high content of macrocyclic oligomers, could be obtained [34]. This observation contrasted with to the high-molecular-weight poly(ether imide)s formed from other bis(ether anhydride)s and diamines that incorporated a smaller number of *ortho*-phenylenes per repeat unit.





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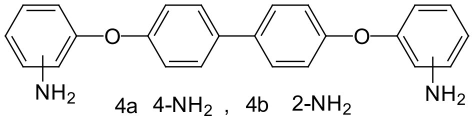
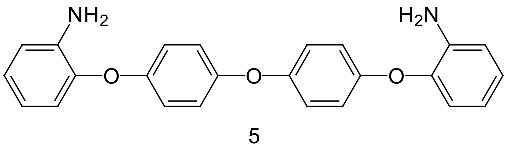
In this paper, we focus on the influence of substitution patterns in bis(aminophenoxy)benzenes on the polyimides formed with bis(ether anhydride)s **2b**–**2f** or dianhydride **3**. In the course of this work we establish that while bis(*para*-aminophenoxy)benzenes yield high-molecular-weight poly(ether imide)s with good mechanical properties, bis(*ortho*-aminophenoxy)benzenes yield, almost exclusively, low-molecular-weight polymers. We therefore, investigated the nature of several of the low-molecular-weight products to obtain information on the structures of the macromolecules present. We also examined polyimides from other bis(*ortho*-aminophenoxy) aromatic compounds (**4b** and **5**) to elucidate the factors which are important in controlling propensities for macrocycle formation; the corresponding *para*-aminophenoxy diamine **4a** is well known and yields high-molecular-weight polymers [11,35]. We are unaware of any report of the *para*-amino equivalent of **5** being prepared or used in polyimide synthesis, but it is likely to yield insoluble polymers. To identify **4** and **5** we adapt Evers' nomenclature further and designate **4b** as *o*4,4′biph*o*$(NH_2)_2$ and **5** as *oppo*$(NH_2)_2$.



4a 4-NH_2 , 4b 2-NH_2



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This paper describes an exercise undertaken to illustrate the possibilities and limitations of techniques, as well as deriving information on the role of substitution patterns on the natures of the products formed.

2. Experimental

2.1. Reagents

Fluoronitrobenzenes were obtained from Fluorochem. Dianhydride **1e** was obtained from TCI, Tokyo, Japan. Dianhydride **1d** was synthesized previously using a standard nitrodisplacement reaction between 4-nitrophthalodinitrile and bisphenol A with subsequent hydrolysis of the tetranitrile and dehydration of the resulting tetracarboxylic acid [9]; dianhydride **1f** was prepared similarly. Other dianhydrides, reagents and solvents were obtained from Aldrich or were general laboratory reagents.

2.2. Synthesis of bis(ortho-aminophenoxy)benzenes

Diamine *ppp*(NH_2)$_2$ (commonly known as TPE-Q) is well-known [36]. We recently reported the synthesis of related bis(*para*-aminophenoxy)benzenes and *ooo*(NH_2)$_2$ using aromatic nucleophilic displacement reactions (S_NAr) to prepare the dinitro compounds and reducing them to diamines [29,31,34]. Here we report the synthesis of new bis(*ortho*-nitrophenoxy)benzenes **8** and their conversions to bis(*ortho*-aminophenoxy)benzenes **9**, according to Scheme 1. Additionally, we used diamines **4b** and **5** which were prepared similarly by Paprotny; bis(4-hydroxyphenyl) ether was obtained from Kennedy and Klim. Intermediate dinitro compounds were not fully characterized but were converted directly to diamines. The synthesis of one dinitro compound and one diamine only are described in detail below. Characterization data for all the new compounds, prepared similarly, are presented in Tables 1 and 2.

2.2.1. Synthesis of opo(NO_2)$_2$

Under dry conditions, and in a flask equipped with Dean-Stark condensers, nitrogen gas inlets and stirrers, hydroquinone **6**(R = H, OH groups para) (0.2 mol) was reacted with, 2-fluoronitrobenzene **7**(X = F) (0.4 mol + 0.05 mol excess) in the presence of anhydrous potassium carbonate (80 g) in *N*,*N*-dimethyl formamide (DMF) solution (250 cm^3) with added xylene (50 cm^3); the latter was used to remove water azeotropically and control the reflux temperature (130–135 °C). The mixture was refluxed under nitrogen for 5 h. After 2.5 h xylene and DMF (100 cm^3) were distilled off. The hot reaction mixture was poured into ice/water mixture and stirred vigorously. The resulting precipitate was filtered off and washed with distilled water until neutral. Absolute ethanol (1200 cm^3) was added to the wet precipitate which was heated to boiling point and the solution was left to crystallize overnight, yielding yellow crystals of *opo*(NO_2)$_2$.

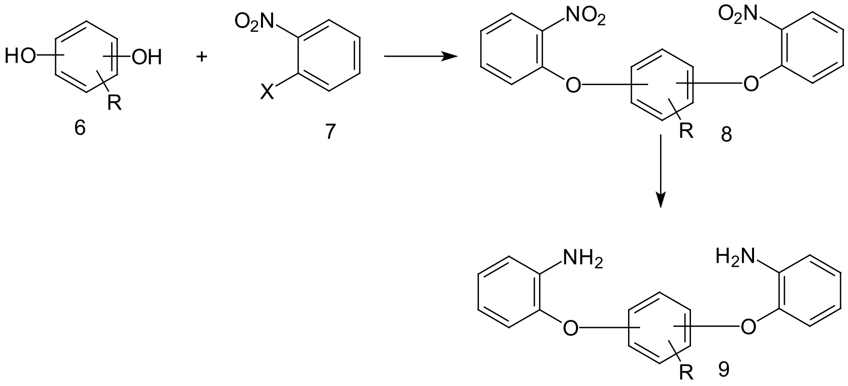
2.2.2. Synthesis of opo(NH_2)$_2$

1,4-Bis(2-nitrophenoxy)benzene *opo*(NO_2)$_2$ (35 g) was mixed with ethanol (385 cm^3) and heated to boiling, when 10% Pd/C (1 g) was added. While under reflux, hydrazine monohydrate (109 cm^3) was added; refluxing was continued for about 4 h. The catalyst was filtered from the solution of diamine. After reducing the volume to about 10% by evaporating solvent, crude diamine *opo*(NH_2)$_2$ was precipitated by addition of water, filtered off and washed with water. Wet diamine was recrystallized from a small quantity of ethanol and recrystallized from dichloromethane.

2.2.3. Characterization data

We previously reported some characterization data for *pop*(NO_2)$_2$, *pop*(NH_2)$_2$ [31] and *ooo*(NH_2)$_2$ [34]. NMR data for *pop*(NO_2)$_2$ and *pop*(NH_2)$_2$ were reported previously and here we record data for *ooo*(NH_2)$_2$ and a limited selection of related products used to substantiate the expected substitution patterns of the reaction products. Data were recorded using a spectrometer operating at 400 MHz with samples in $CDCl_3$ solution. Assignments were made, according to the numbering scheme defined in Fig. 1, with the aid of 2D C–H correlations; estimated chemical shifts are in parentheses.

ooo(NH_2)$_2$: ^{1}H NMR; δ (ppm) 3.66 (2H, amine), 7.04 (m, 4H, H(3,4,5,6), (6.69, 6.73)), 6.64 (m, 1H, H(3′), (6.42)), 6.90 (m, 1H, H(4′), (6.57)), 6.74, 6.77 (m, 2H, H5′, 6′), (6.52, 6.53)). ^{13}C NMR; 147.2 (C(1, 2) (148.3)), 118.9, 119.9, 124.1, 124.2



Scheme 1.

Table 1
Synthesis of bis(*ortho*-nitrophenoxy) compounds **8**

Compound		Elemental analysis			Mp (°C)	Yield (%)
		C	H	N		
*o*3Me*oo*(NO$_2$)$_2$[a]	Calc.	62.3	3.9	7.6	146–147	88
	Found	62.3	3.9	7.6		
*o*4Me*oo*(NO$_2$)$_2$[a]	Calc.	62.3	3.9	7.6	102–104	63
	Found	62.1	3.9	7.6		
opo(NO$_2$)$_2$	Calc.	61.4	3.4	7.9	157–158	84
	Found	61.5	3.5	8.0		
*o*Me*po*(NO$_2$)$_2$[a]	Calc.	62.3	3.9	7.6	124–125	75
	Found	62.3	3.9	7.7		
*o*tBu*po*(NO$_2$)$_2$[a]	Calc.	64.7	4.9	6.9	141–142	95
	Found	64.7	5.0	6.9		
*o*4,4’biph*o*(NO$_2$)$_2$	Calc.	67.28	3.76	6.53		
	Found	67.39	3.74	6.52		
oppo(NO$_2$)$_2$	Calc.	64.84	3.62	6.30		
	Found	64.88	3.64	6.31		

[a] Me and *t*Bu denote a methyl or *t*-butyl substituent, respectively, in the position indicated.

(C(3, 6; 3′, 4′) (120.7; 116.8, 124.3)), 144.13 (C(1′) (144.4)), 138.0 (C(2′) (137.1)), 116.4, 118.4 (C(5′, 6′) (120.3, 120.0)).

opo(NH$_2$)$_2$: ^{1}H NMR; δ (ppm) 3.80 (2H, amine),6.93 (s, 4H, H(2, 3, 5, 6) (6.69)), 6.95 (m, 1H, H(4′), (6.57)), 6.69 (m, 1H, H(5′) (6.52)), 6.81, 6.83 (m, 2H H(3′, 6′)). ^{13}C NMR 152.7 C(1, 4) (152.6), 119.35C(2, 3, 5, 6) (120.7), 144.4 C(1′) (144.4, 138.4 C(2′) (137.1), 116.4 C(3′) (116.8), 124.5 C(4′) (124.3), 118.7, 119.4 C(5′, 6′) (120.3, 120.0)).

o3Meoo(NO$_2$)$_2$: ^{1}H NMR; δ (ppm) 7.1 (m, 2H H(5, 6) (6.61, 6.47)), 7.2 (m, 1H H(4) (6.53)), 7.9 (m, 2H H(3′, 3″) (8.12)), 6.57, 6.9 (m, 2H H(4′, 4″) (7.08), 7.4–7.5 (m, 2H H(5′, 5″) (6.57)), 7.0–7.2 (m, 2H H(6′, 6″) (7.04)). ^{13}C NMR 142.8 C(1) (148.2), 147 C(2) (149), 128 C(3) (129.6), 126.7 C(4) (125.7), 123.1, 122.1 C(5, 6) (124.9, 118.2), 150.2, 150.6 C(1′, 1″) (152.9), 138.9, 140.1 C(2′, 2″) (139), 125.6, 125.8 C(3′, 3″) (114.3), 116.0, 118.9 C(4′, 4″) (124.3), 119.5 C(6′, 6″) (120).

The above NMR data, coupled with those published previously [31], substantiate the substitution patterns of the novel *ortho*-aminophenoxy diamines. In addition, data for *o*3Me*oo*(NO$_2$)$_2$ demonstrate that the 3-methyl residue on the central phenylene unit renders the two *ortho*-nitrophenoxy units non-equivalent, presumably by restricting rotation about the ether linkage ortho to the methyl group.

2.3. Synthesis of polyimides

All polyimides investigated were synthesized by the same conventional two-stage solution polymerisation (Scheme 2), except that high-molecular-weight products, as evidenced by highly viscous solutions, were isolated by precipitation into methanol to give fibrous or bead-like precipitates, while low-molecular-weight polymers, indicated by non-viscous solutions, were isolated by precipitation into methanol/water (3:1 v/v) or water (where specified in the text) to give fine powders. Two example syntheses, one of a high-molecular-weight polymer and one of a low-molecular-weight product are given below; characterization data for all the polymers prepared are given in Table 3.

Table 2
Synthesis of bis(*ortho*-aminophenoxy) compounds **9**

Compound		Elemental analysis			Mp (°C)	Yield (%)
		C	H	N		
*o*3Me*oo*(NH$_2$)$_2$	Calc.	74.5	5.9	9.1	97–98	69
	Found	74.2	6.0	9.1		
*o*4Me*oo*(NH$_2$)$_2$	Calc.	74.5	5.9	9.1	84–85	70
	Found	74.4	6.0	9.1		
opo(NH$_2$)$_2$	Calc.	74.0	5.5	9.6	105–106	78
	Found	74.1	5.6	9.6		
*o*Me*po*(NH$_2$)$_2$	Calc.	74.5	5.9	9.1	117–118	86
	Found	74.3	6.0	9.1		
*o*tBupo(NH$_2$)$_2$	Calc.	75.8	7.0	8.0	106–107	94
	Found	75.8	7.0	8.1		
*o*4,4’Biph*o*(NH$_2$)$_2$[a]	Calc.	78.24	5.47	7.61	174–175	92
	Found	78.18	5.48	7.61		
oppo(NH$_2$)$_2$[b]	Calc.	74.98	5.24	7.26	79–81	96
	Found	74.95	5.28	7.35		

[a] Accurate mass calculated: 368.15247; found: 368.15282.

[b] Accurate mass calculated: 384.14737; found: 384.14766.

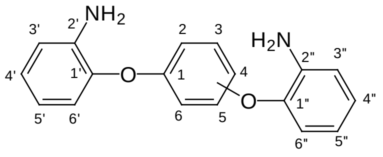


Fig. 1. Structure designation as used in NMR analysis.

2.3.1. Synthesis of polyimide from pop($(NH_2)_2$) and 6FDA

1,2-Bis(4-aminophenoxy)benzene (1 mmol) was dissolved in 5 cm^3 *N*-methylpyrrolidinone (NMP) at room temperature and an exactly stoichiometric equivalence of 6FDA was added with stirring. The reaction mixture was left overnight to form a viscous solution of the intermediate poly(amic acid) (Scheme 2, step **a**) which was then chemically imidized, by adding 2 cm^3 of an equiv-volume mixture of acetic anhydride and pyridine at room temperature (Scheme 2, step **b**), to form the corresponding poly(ether imide) **11**. After leaving the reaction mixture for 6 h the high-molecular-weight polymer was precipitated into methanol. The coarse precipitate was washed with boiling methanol to remove residual solvent.

2.3.2. Synthesis of polyimide from opo($(NH_2)_2$) and 6FDA

1,4-Bis(2-aminophenoxy)benzene (1 mmol) was dissolved in 5 cm^3 *N*-methylpyrrolidinone (NMP) at room temperature and an exactly stoichiometric equivalence of 6FDA was added with stirring. The reaction mixture was left overnight to form a non-viscous solution of the intermediate poly(amic acid) (Scheme 2, step **a**) which was then chemically imidized, by adding 2 cm^3 of an equiv-volume mixture of acetic anhydride and pyridine at room temperature (Scheme 2, step **b**), to form the corresponding poly(ether imide) **11**. After leaving the reaction mixture for 6 h the high-molecular-weight polymer was precipitated into methanol–water (3:1 v/v) mixture. The powdery precipitate was washed with boiling methanol–water to remove residual solvent.

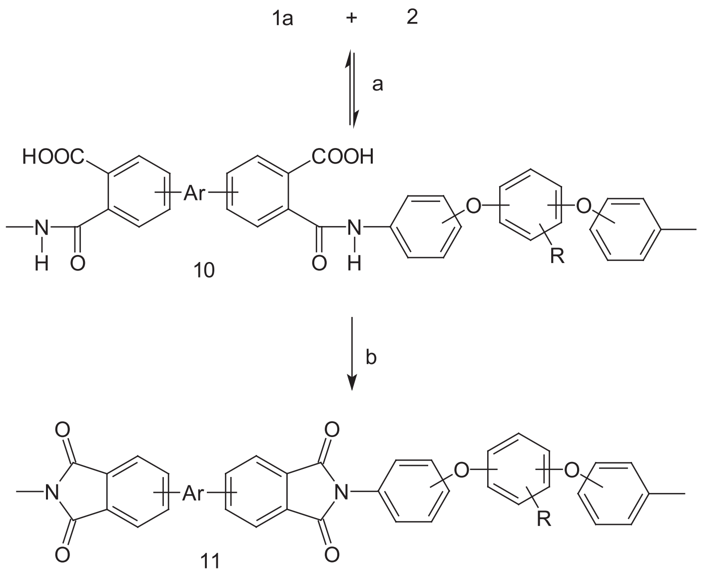
2.4. Techniques

Polymer molecular weights were determined by gel permeation chromatography (GPC) using DMF/LiCl(0.1 M) (for polymers prepared from 4-ring diamines) or tetrahydrofuran (for polymers from 3-ring diamines) as the mobile phase with a flow rate of 1 $cm^3\ min^{-1}$, columns packed with 5 μm-PL gel polystyrene (Polymer Laboratories), a refractive index detector and the instrument was calibrated with polystyrene standards (Polymer Laboratories). Glass-transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) with the aid of a DuPont 912 differential scanning calorimeter, or a Perkin–Elmer DSC2, using a heating rate of 10 °C min^{-1}; T_gs were determined on the second or subsequent heating cycle. Tensile properties were determined with the aid of an Instron Tensile Tester using dumb-bell-shaped samples with a gauge length of 46 mm and a cross-head speed of 5 mm min^{-1}; samples were cut from films ∼0.5 mm thick cast from dichloromethane or chloroform, dried and room temperature and subsequently under vacuum at 100–150 °C.

Samples were analysed by electrospray ionization mass spectrometry (ESI-MS) or MALDI-TOF mass spectrometry (MT-MS) without added cationization agents, as described in the Supporting Information.

3. Results and discussion

A variety of polyimides were prepared from various combinations of dianhydride **2** or **3** with a diamine **1a**, **4** or **5**. The polymers were initially characterized in terms of solubility, molecular weight (where soluble in an appropriate solvent) and T_g. Further characterization in terms of mechanical properties was performed according to the suitability of polymers for film formation, or by mass spectrometry for low-molecular-weight polymers and other selected polymers.



Scheme 2.

Table 3
Characteristics of polymers prepared

Diamine	Dianhydride	Solubility	M_p (kg mol^{-1})	$\bar{M}_n$ (kg mol^{-1})	T_g (°C)
pop(NH$_2$)$_2$	BTDA	Insol.	–	–	191
*p*3Me*op*(NH$_2$)$_2$	BTDA	Insol.	–	–	253
*p*4Me*op*(NH$_2$)$_2$	BTDA	Insol.	–	–	225
ooo(NH$_2$)$_2$	BTDA	Insol.	–	–	–
*o*4Me*oo*(NH$_2$)$_2$	BTDA	Insol.	–	–	–
pop(NH$_2$)$_2$	ODPA	Insol.	–	–	232
*p*3Me*op*(NH$_2$)$_2$	ODPA	Insol. THF, sol. DCM	–	–	228
*p*4Me*op*(NH$_2$)$_2$	ODPA	Insol	–	–	–
ooo(NH$_2$)$_2$	ODPA	Insol. THF, sol DCM	–	–	171
*o*3Me*oo*(NH$_2$)$_2$	ODPA	Sol.	14	4.6	160
*o*4Me*oo*(NH$_2$)$_2$	ODPA	THF, insol. DCM	0.98	0.73	–
opo(NH$_2$)$_2$	ODPA	Sol.	15	4.4	169
ppp(NH$_2$)$_2$	6FDA	Sol.	113	27	238
*p*Me*pp*(NH$_2$)$_2$	6FDA	Sol.	69		248
pop(NH$_2$)$_2$	6FDA	Sol.	(i) 118, (ii) 30	(i) 18, (ii) 10	233
*p*3Me*op*(NH$_2$)$_2$	6FDA	Sol.	77	22	210
*p*4Me*op*(NH$_2$)$_2$	6FDA	Sol.	(i) 111, (ii) 132	(i) 29, (ii) 17	239
ooo(NH$_2$)$_2$	6FDA	Sol.	(i) 41, (ii) 36	(i) 5.8, (ii) 9.4	220
*o*3Me*oo*(NH$_2$)$_2$	6FDA	Sol.	41	6.3	230
*o*4Me*oo*(NH$_2$)$_2$	6FDA	Sol.	50	5.3	167
opo(NH$_2$)$_2$	6FDA	Sol.	25	3.3	232
*o*tBu*po*(NH$_2$)$_2$	6FDA	Sol.	15		235
ppp(NH$_2$)$_2$	BPADA	Sol.	44	14	200
*p*Me*pp*(NH$_2$)$_2$	BPADA	Sol.	75		202
pop(NH$_2$)$_2$	BPADA	Sol.	(i) 128, (ii) 67	(i) 25, (ii) 10	191
*p*3Me*op*(NH$_2$)$_2$	BPADA	Sol.	139	25	196
*p*4Me*op*(NH$_2$)$_2$	BPADA	Sol.	125	25	194
ooo(NH$_2$)$_2$	BPADA	Sol.	35	9.5	134
*o*3Me*oo*(NH$_2$)$_2$	BPADA	Sol.	29	8.8	197
*o*4Me*oo*(NH$_2$)$_2$	BPADA	Sol.	34	9.9	185
opo(NH$_2$)$_2$	BPADA	Sol.	31	9.3	198
*o*tBu*po*(NH$_2$)$_2$	BPADA	Sol.	18		197
BAPB	6FDA		355	37	
BAPB	BPADA		196	95	
*o*4,4′biph*o*(NH$_2$)$_2$	6FDA		22	4	250
*o*4,4′biph*o*(NH$_2$)$_2$	BPADA		10	1	201
*o*4,4′biph*o*(NH$_2$)$_2$	BPPDA		68		225
*o*4,4′biph*o*(NH$_2$)$_2$	PMDA	Insol.	–	–	266
oppo(NH$_2$)$_2$	6FDA		45	7	225
oppo(NH$_2$)$_2$	BPADA		39	9	201
oppo(NH$_2$)$_2$	PMDA		20	2	262

(i) and (ii) indicate samples in repeat syntheses.

Polymers are designated by the code adopted for diamines and the conventional abbreviation for the specific dianhydride (Table 3); the conventional abbreviations used are: for **1a** CBA, for **1b** 6FDA, for **1c** ODPA, for the dianhydride **1d** (formed from bisphenol-A) BPADA, for **1e** BTDA, for **1f** (formed from bisphenol-P) BPPDA and for **3** PMDA.

3.1. Solubility and molecular weight

Data for the several polyimides are listed in Table 3. Solubilities were tested in tetrahydrofuran (THF), dichloromethane (DCM) and chloroform; sol. and insol. indicate soluble and insoluble in all three solvents, respectively.

All polymers prepared from BTDA (**1e**, benzophenone tetracarboxylic acid dianhydride) were insoluble in all solvents used which precluded molecular weight determination and these polymers were not characterized except for determining their T_gs. Several of them formed physically crosslinked gels on imidization, in common with many other typical polyimides prepared in solution. Similarly, polymers prepared from ODPA (**1c**, oxydiphthalic anhydride) had limited solubility, which restricted their characterization; as seen in other work, the presence of *ortho*-catenated units and methyl substituents aided solubility.

In contrast, because of the enhanced solubility imparted by ether linkages, especially with *ortho*-catenation, and the presence of the hexafluoroisopropylidine unit, most polymers prepared from dianhydrides 6FDA (**1b**) or BPADA (**1d**) had sufficient solubility in GPC eluants to enable molecular weight determination. Data obtained from these several polymers show a major distinction between two groups of polymers. Those prepared from *para*-aminophenoxy diamines, whether the catenation of the central phenylene was para or ortho, produced highly viscous solutions of poly(amic acid) and high-molecular-weight polyimides with peak molecular weights (M_p) in excess of 70 kg mol^{-1}, and up to 140 kg mol^{-1}, as measured by GPC against polystyrene standards, with low contents of oligomers. We are aware that values of molecular weights of poly(ether imide)s, as measured by GPC, are usually exaggerated. We previously compared absolute number-average molecular weights obtained by membrane osmometry with values obtained by GPC and results showed that the latter were too high by a factor of 2–3 [13] (the large differences between apparent and true molecular weights cannot apply at the lower limit of the calibration where molecular weights smaller than molar masses of unpolymerized monomers would be implied). Molecular weights quoted are therefore approximate but useful for comparative purposes. Poly(ether imide)s with M_p in excess of 70 kg mol^{-1} have, in our experience, been found suitable for preparing strong, tough films with good mechanical properties. In contrast, except for the poly(ether imide) prepared from *o*4,4′bipho$(NH_2)_2$ and **2f**, all polymers prepared from *ortho*-aminophenoxy diamines gave low-molecular-weight products from non-viscous solutions of poly(amic acid)s. The polyimides all had M_p less than 50 kg mol^{-1}, with high contents of low-molecular-weight oligomers; number-average molecular weights were less than 10 kg mol^{-1}. In the case of the oligomeric products it was possible to observe peaks for individual oligomers. These data reinforce the previous observation that the polyimide from dianhydride **2a** (CBA), and *ooo*$(NH_2)_2$ gave a low-molecular-weight polymer [34], in contrast to corresponding polyimides prepared from *ppp*$(NH_2)_2$, *pmp*$(NH_2)_2$ and *pop*$(NH_2)_2$ or **4a** which gave high-molecular-weight polymers ($M_p >$ 160 kg mol^{-1}). We conclude that it is the *ortho*-aminophenoxy unit that predisposes polymerizations to yield low-molecular-weight polymers; the exception noted above will be discussed later.

The distinction between the two groups of polymers is clearly seen from a comparison of typical chromatograms. Fig. 2 presents gel permeation chromatograms of three typical polyimides prepared in this study. That in Fig. 2(a) is from the polymer prepared from *ppp*$(NH_2)_2$ and 6FDA and shows that most of the product elutes within the envelope for the high-molecular-weight polymer, with little content of oligomeric material. In contrast, the chromatogram for the polymer prepared from *opo*$(NH_2)_2$ and ODPA, in Fig. 2(b), shows a major peak at rather lower molecular weight (greater elution time) and a larger mass fraction of oligomeric material, partially resolved into separate oligomers. Similar data were obtained for the polymer from *o*3Me*oo*$(NH_2)_2$ and ODPA (Fig. 2(c)). This distinction is typical between polymers prepared from bis(*para*-aminophenoxy)benzenes and from bis(*ortho*-aminophenoxy)benzenes; the former show little content of oligomers and the latter a high content of oligomers.

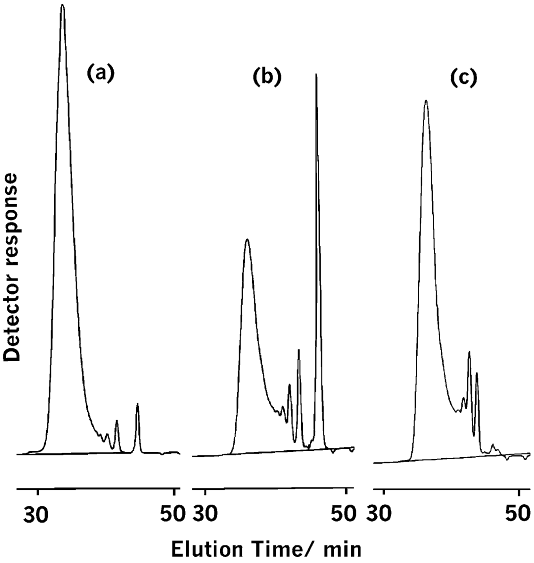


Fig. 2. Comparison of gel permeation chromatograms for poly(ether imide)s prepared from: (a) 6FDA and *ppp*$(NH_2)_2$; (b) ODPA and *opo*$(NH_2)_2$; (c) ODPA and *o3Meoo*$(NH_2)_2$.

3.2. Thermal properties

Glass-transition temperature data might have been expected to provide an extensive structure–property relationship for such a large series of closely-related polymers. Thus, *para*-catenated units, which tend to stiffen polymer chains, and alkyl substituents, which increase the bulkiness of the polymer, are normally considered to raise T_gs. The identification of structure–property relationships in this work, however, was compromised by the major differences in molecular weight. Molecular weights of many products fell in the range where T_gs are molecular-weight dependent, and the potential influence of a high content of cyclic oligomers (see later) further confuses the issue. Nevertheless, where sensible comparisons can be made, either for high-molecular-weight polymers or polymers of comparable molecular weight, the usual trends are apparent, with some modification.

For example, series of polymers based on *ppp*$(NH_2)_2$, *pop*$(NH_2)_2$, *opo*$(NH_2)_2$ and *ooo*$(NH_2)_2$ diamines, provide systematic increases in numbers of *ortho*-catenated units per repeat structure of the polymer chain, but this does not lead to systematic changes in T_g. For such polymers prepared from 6FDA T_gs do decrease in the above sequence from 238 to 220 °C. Within that sequence the fall of 1 °C in T_g from *pop*$(NH_2)_2$ to *opo*$(NH_2)_2$ is associated with a major decrease in molecular weight. It is probable that, for comparable molecular weights, the *opo*$(NH_2)_2$ unit might result in a higher T_g than the *pop*$(NH_2)_2$ unit. Indeed, for the equivalent series of polymers prepared from BPADA T_g falls from 200 to 134 °C, but T_g for the polymer prepared from *opo*$(NH_2)_2$ is greater than that prepared from *pop*$(NH_2)_2$. Thus, the *ortho*-phenylene in an *ortho*-aminophenoxy unit is not as effective in reducing T_g as a central catechol-derived unit; we have previously demonstrated that polymers prepared from dianhydride **1a** have T_gs lower than those from the equivalent dianhydride prepared from hydroquinone [8]. Examination of space-filling models shows that bis(*para*-aminophenoxy)benzene residues force adjacent phthalimide units away from each other, enhancing overall chain flexibility. In contrast, bis(*ortho*-aminophenoxy) benzene residues force neighbouring phthalimide units together, restricting chain flexibility which raises T_g, and reverses the trend that *ortho*-catenated units reduce T_g compared with *para*-catenated units.

For polyimides based on alkyl-substituted bis(aminophenoxy)benzenes trends are more systematic; the trends are not totally consistent and are complicated by certain subtleties and differences in or absences of molecular weight data. For insoluble polymers based on BTDA, the polymer from *p*3Me*op*$(NH_2)_2$ has a higher T_g than that from *pop*$(NH_2)_2$ as would be anticipated.

For polymers prepared from 6FDA and BPADA, T_gs for the polyimides from *p*Me*pp*$(NH_2)_2$ are higher than for those from *ppp*$(NH_2)_2$, despite the lower molecular weight of the polymer from the former diamine in the case of 6FDA. For polyimides prepared from BPADA, for the series of polymers from *pop*$(NH_2)_2$ and *ooo*$(NH_2)_2$ diamines, methyl substituents on the central *ortho*-catenated phenylene raise T_g above those from the unsubstituted diamines. Furthermore, the 3-methyl substituents raise T_g more than the isomeric 4-methyl substituent. The latter trend is entirely consistent with expectation since space-filling models clearly indicate that, while the 4-methyl substituent does not restrict rotation around the ether linkage to the adjacent *N*-phenylphthalimide unit, the 3-methyl substituent severely restricts such rotation, and hence enhances the bulk of the smallest structural sequence involved in producing changes in chain conformation associated with T_g; NMR data described above are also consistent with restricted rotation around the ether linkage ortho to the ether linkage in *o*3Me*oo*$(NH_2)_2$. The same trend is apparent in polymers from BTDA and *pop*$(NH_2)_2$-type diamines. These trends are not upheld consistently elsewhere, in some cases by virtue of differences or uncertainties in molecular weights of the polymers involved. For example, for polymers prepared from 6FDA, that from *p*4Me*op*$(NH_2)_2$ has a higher T_g than that from the unsubstituted *pop*$(NH_2)_2$ but the polymer from *p*3Me*op*$(NH_2)_2$ has a lower T_g; the low T_g for the *p*3Me*op*$(NH_2)_2$ polymer is almost certainly attributable to its relatively lower molecular weight. Also for polyimides from 6FDA, that formed from *o*3Me*oo*$(NH_2)_2$ has a higher T_g than that from *ooo*$(NH_2)_2$, but the polymer from *o*4Me*oo*$(NH_2)_2$ has an apparently lower T_g, despite the similarity in molecular weight; this is unexplained at present.

3.3. Mechanical properties

Only polymers with peak molecular weights in excess of about 70 kg mol^{-1} could be solvent cast into films tough enough to allow mechanical properties to be determined; polymers of lower molecular weight produced brittle films too friable to be tested. Thus, only those polymers prepared from bis(*para*-aminophenoxy) diamines gave polymers suitable for testing. The several mechanical property data obtained are given in Table 4.

Data in Table 4 are very similar to those reported for innumerable other poly(ether imide)s and polyimides, other than those with particularly advantageous properties, in that tensile moduli are of the order of 3 GPa. Extensions to break are variable but ultimate tensile strengths are lower than those we have reported previously for poly(ether imide)s. We have also noted previously that extensions to break are somewhat variable, with no apparent explanation for the different values observed [11]. Here, we note that extensions to break for polyimides based on *ppp*$(NH_2)_2$ and *p*Me*pp*$(NH_2)_2$ are significantly higher than those based on diamines with *ortho*-catenated phenylenes.

Table 4
Tensile property data for polymers prepared from bis(*para*-aminophenoxy) diamines

Diamine	Dianhydride	Tensile properties		
		Young's modulus (GPa)	Extension at break (%)	Ultimate tensile strength (MPa)
*p*3Me*op*$(NH_2)_2$	ODPA	3.26	3.38	82.67
ppp$(NH_2)_2$	6FDA	3.14	29.91	74.18
*p*Me*pp*$(NH_2)_2$	6FDA	3.04	31.64	70.05
pop$(NH_2)_2$	6FDA	3.44	3.16	87.2
*p*3Me*op*$(NH_2)_2$	6FDA	2.88	2.93	84.27
*p*4Me*op*$(NH_2)_2$	6FDA	3.34	2.73	77.71
ppp$(NH_2)_2$	BPADA	2.57	24.23	14.56
*p*Me*pp*$(NH_2)_2$	BPADA	2.73	35.39	52.35
pop$(NH_2)_2$	BPADA	3.12	16.26	56.38
*p*3Me*op*$(NH_2)_2$	BPADA	2.39	8.39	45.15
*p*4Me*op*$(NH_2)_2$	BPADA	3.89	9.77	42.76

Given the inability to prepare high-molecular-weight polymers from bis(*ortho*-aminophenoxy) diamines we determined to investigate the nature of the products from those diamines with various dianhydrides.

3.4. The nature of oligomeric poly(ether imide)s

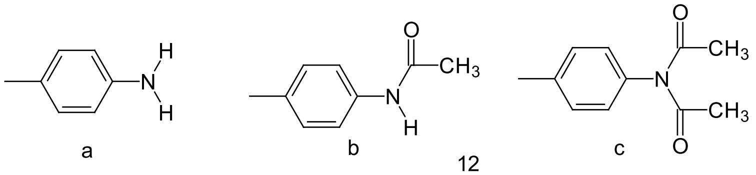
To elucidate the nature of the low-molecular-weight products from *ortho*-aminophenoxy diamines, which are so different from the high-molecular-weight poly(ether imide)s produced from *para*-aminophenoxy diamines, we analysed the products by mass spectrometry. This analysis investigates factors responsible for the formation of high or low-molecular weight products and describes information available from related materials, e.g. different numbers of *ortho*-phenylene groups per repeat unit and different rigidities, using data obtained under different conditions. Thus, we analysed products by either MT-MS or ESI-MS. We used the total reaction product from the polymerization reaction as sample (MT-MS) or, in some cases, extracts produced by various solvents (MT-MS or ESI-MS).

These studies follow on from our initial observation that a polymer formed from CBA (**2a**) and *ooo*$(NH_2)_2$, with four *ortho*-phenylenes per repeat unit, was of low average molecular weight [34]. GPC showed that sample to contain a high-molecular-weight component; peak molecular weight 30 kg mol^{-1} measured against polystyrene standards. GPC and MT-MS demonstrated that a large proportion of that product was low-molecular-weight oligomers and that a large proportion of these, at least, were macrocylic oligomers.

Macrocyclic oligomers (M_n) identified were [$n+n$] species, where $n=2$–10 [34]; no signal from the [1+1] cyclic oligomer was visible; M_n represents a macrocycle with n repeat units M. It was possible that a [1+1] species formed might have been lost when the product was isolated by precipitation into methanol, as there is no intrinsic reason why a cyclic [1+1] species could not have been formed; see Supporting Information.

Here, we consider products prepared from BPADA, 6FDA or PMDA with various 1,2- and 1,4-bis(*ortho*-aminophenoxy) benzenes and other diamines with *ortho*-aminophenoxy groups, and selected bis(*para*-aminophenoxy)benzenes. The products, after imidization, were isolated by precipitation into different precipitants and, in some cases, oligomers were extracted by different solvents.

The main feature in all mass spectra was the appearance of signals from macrocyclic oligomers. In addition to major obvious signals, spectra were examined for sets of minor peaks separated by the repeat unit mass, which might have arisen from series of related oligomers. Structures **12** and **13**, possibly formed on imidization of **10** or on isolation by precipitation into water or methanol, were considered as potential endgroups for linear oligomers.



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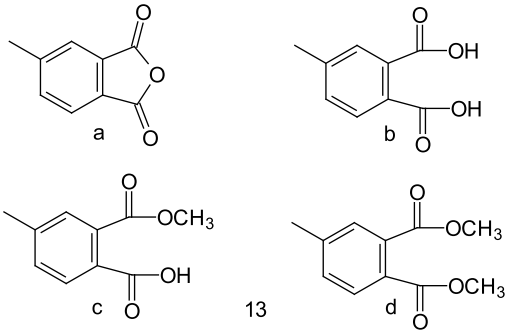

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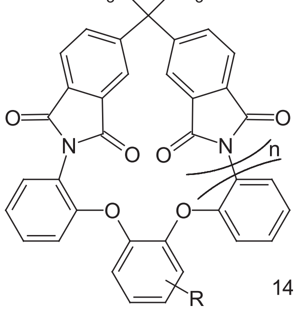
All combinations of these endgroups were considered as possibly present in linear oligomers, either [$n+n$] oligomers with one amine-derived and one anhydride-derived terminal units, or oligomers with two amine-derived units or two terminal anhydride units. The possible presence of unimidized amic acid units in cyclic or linear oligomers was also considered.

In the following sections, we outline the main conclusions derived by mass spectrometric analysis of various reaction products, describe the variety of species observed and show a few representative spectra to illustrate major features. The bulk of the spectra, their analyses and detailed descriptions of species observed are presented in the Supporting Information, which can be consulted for further details.

3.4.1. Products from 6FDA (2b) and 3-ring diamines

3.4.1.1. Products from ooo(NH_2)$_2$. Products from 6FDA and *ooo*(NH_2)$_2$ were examined by ESI-MS. Using methanol, a precipitant for high-molecular-weight polymer, to extract species for analysis, only signals attributable to macrocycles **14**, R=H, $n=2$–4 were observed, Fig. 3, with signals for $[M_n+Na]^+$ dominant. Clearly, the spectrum was dominated by cyclics with $n=2$, and low contents of species with $n=3, 4$. Additional signals were observed from these species with methanol adducts. Details varied between samples with $[M_n+Na+CH_3OH]^+$ ($n=2$, 3 and 4) and $[M_n+Na+2CH_3OH]^+$ ($n=2$) from one sample and up to four molecules of methanol as adducts for $n=2$ cyclics in another; see inset to Fig. 3. No signals could be attributed to other cyclic or linear species. One sample gave no peak from any [1+1] cyclic species, but a second gave small signals for adducts $[M_1+Na+CH_3OH]^+$ and $[M_1+Na+2CH_3OH]^+$; space-filling models indicate that the [1+1] cyclic oligomer has almost no conformational flexibility but has a pocket which could possibly accommodate methanol molecules; see Supporting Information. No peaks could be attributed to any linear oligomer.



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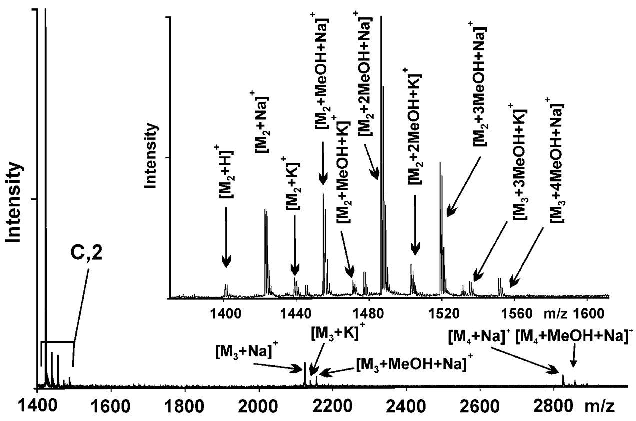


Fig. 3. ESI-MS spectrum (solvent methanol) of products formed from 6FDA and *ooo*(NH_2)$_2$. Main diagram: peaks from cyclic oligomers **14**, R = H with *n* = 2, 3 and 4, group of signals from the cyclic dimer marked **C,2**; Inset: detailed signals from cyclic dimer.

Adding DMF, a good solvent, to the methanol used for extraction, enhanced dissolution of higher oligomers. Signals attributed to cyclics up to *n* = 7 were observed (*n* = 2 species dominated), with signals from methanol adducts and a small signal from $[M_2+Na+DMF]^+$. Relative intensities of identical species were independent of solvent used. Thus, detailed ESI-MS results depend on the medium used for sample preparation and possibly on the conditions for dissolution. ESI-MS might not be so generally useful as MT-MS for high-performance polymeric materials.

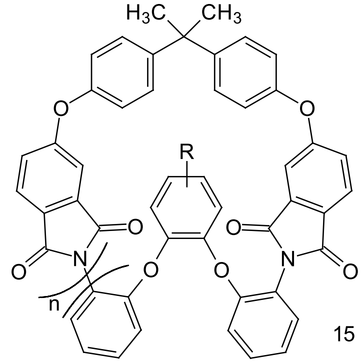
3.4.1.2. The influence of methyl substituents. The influence of alkyl substituents, which might restrict bond rotation and affect propensities for cyclization, in polymers prepared from **2b** with *o*3Me*oo*(NH_2)$_2$ or *o*4Me*oo*(NH_2)$_2$ was investigated; it was anticipated that the 3-methyl substituent might reduce macrocyle formation most, by restricting bond rotation (as indicated by space-filling models) and ring closure.

Methanol extracts of samples prepared from **2b** and *o*4Me*oo*(NH_2)$_2$ or *o*3Me*oo*(NH_2)$_2$, **14**, R = 4Me and **14**, R = 3Me, respectively, were examined by ESI-MS. Both samples exhibited peaks for cyclics only, *n* = 1–5 for **14**, R = 4Me and 1–4 for **14**, R = 3Me; in both cases peaks for *n* = 2 were dominant. For **14**, R = 4Me the peak for $[M_1+Na]^+$ was strong, 35% of the intensity of $[M_2+Na]^+$. Both samples had peaks for species with one molecule of methanol as adduct; this was the strongest peak for the [1 + 1] cyclics for **14**, R = 3Me. Using methanol/DMF mixtures to extract samples, similar results were observed. In this case a DMF adduct gave the strongest signal for [1 + 1] cyclics for **14**, R = 4Me, while peaks for solvent adducts for the [1 + 1] cyclic **14**, R = 3Me were small; for **14**, R = 3Me cyclics species up to *n* = 6 were observed.

Thus, there was little difference in results obtained using diamines with methyl substituents in the 3- or 4-position. No signals attributable to any linear oligomers were observed in products prepared from 6FDA and either of the methyl-substituted diamines.

3.4.2. Products from BPADA and methyl-substituted diamines

ESI-MS spectra from a polymer prepared from BPADA (**2d**) and *o*3Me*oo*(NH_2)$_2$, using methanol as solvent, had peaks for cyclics **15**, R = 3Me, *n* = 1, 2 and 3 only. With CH_3OH/DMF(2:1) as solvent, peaks for cyclics up to *n* = 4 were observed. In both solvents signals from solvent adducts were relatively weaker than for polymers based on 6FDA.



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A sample prepared from **2d** and *o*4Me*oo*(NH_2)$_2$ was fractionated from dichloromethane solution into methanol. The first fraction exhibited only high-molecular-weight polymer by GPC. Subsequent fractions contained oligomers, the distribution of which moved to lower molecular weights in successive fractions. The MT-MS spectrum from a later fraction showed only cyclic oligomers **15**, R = 4Me, *n* = 2–8, with no signal from [1 + 1] cyclics.

3.4.3. Minor peaks in spectra of products from 6FDA (2b) or BPADA (2d)

The predominant signals from the polymers prepared from **2b** or **2d** with *o*3Me*oo*(NH_2)$_2$ or *o*4Me*oo*(NH_2)$_2$ were for cyclic oligomeric polyimides only. Tiny peaks (together representing less than 5% of the total peak intensity) were visible in some spectra. In an attempt to attribute the minor peaks, all combinations of the end groups listed above (structures **12** and **13**) were considered as candidates for linear oligomers but no correspondence of masses was identified. Nor could the peaks be attributed to multiply-charged species or to species with amic acid residues. There was no evidence linking them to unrecognised side reactions during synthesis or impurities in one or other diamine. We concluded that the minor peaks had no significance.

In summary, for polymers prepared from *ooo*(NH_2)$_2$, *o*3Me*oo*(NH_2)$_2$, or *o*4Me*oo*(NH_2)$_2$ with either **2b** or **2d** only evidence for cyclic oligomers was obtained by ESI-MS or MT-MS. However, it cannot be concluded at this stage that only cyclic oligomers, and no linear oligomers, are present in the polymers as it is possible that, for some reason of solubility or otherwise, linear oligomers were not observed.

3.4.4. Effects of stoichiometric imbalances

To enforce the formation of linear oligomers, polymers were prepared from **2b** and *o*4Me*oo*(NH_2)$_2$ with stoichiometric imbalances to ensure the presence of excess endgroups that could not be eliminated by macrocyle formation. Indeed, macrocycle formation, removing equal quantities of the two monomers, would exacerbate any initial stoichiometric imbalance in residual monomers. Polymers were prepared with an excess of diamine or an excess of dianhydride, 10 mol% in each case.

Because of the low solubility of most dianhydrides, it is common practice, in the solution synthesis of polyimides, to add solid dianhydride to a solution of diamine. However, using excess dianhydride in this way, slow dissolution could result in a stiochiometric equivalence of reagents being achieved and reacting in solution before all dianhydride had dissolved. Thus, a high-molecular-weight product or a high concentration of cyclics could be achieved even if the final reaction mixture contained excess dianhydride. Therefore, solutions of individual reagents were prepared and mixed to ensure a stoichiometric imbalance of reactants in solution at all stages. The resulting poly(amic acid)s were imidized as usual. Part of each sample was isolated by precipitation into water and part into methanol. All samples were examined by MT-MS by dissolving them in THF or chloroform.

3.4.4.1. Effect of excess dianhydride. The product prepared with excess dianhydride, precipitated into water, and dissolved in either solvent gave almost identical results. The major peaks formed two distinct series with separations of 714 Da in each case, Fig. 4. One set (designated C,*n*) corresponded to cyclic oligomers **14**, R = 4Me, *n* = 1–4. The other set (designated A,*n*) corresponded to linear oligomers **16**, *n* = 1–10, with two anhydride-derived ends that had been hydrolysed to diacid on precipitation into water.

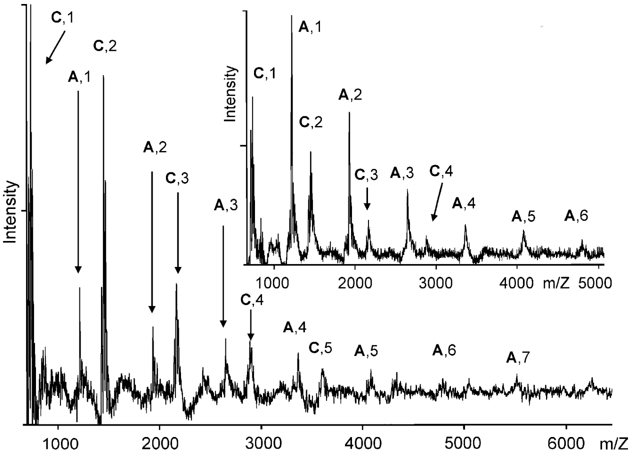
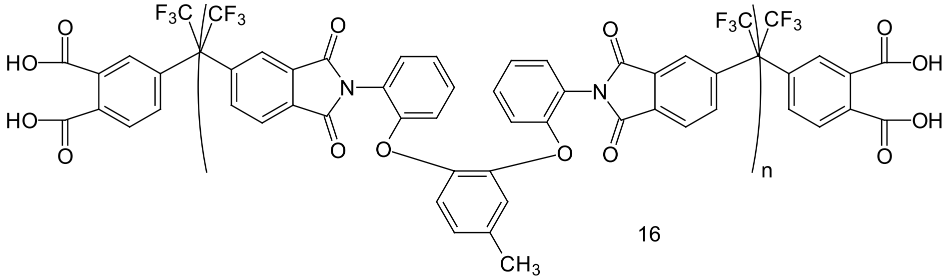


Fig. 4. MT-MS spectrum obtained from the product prepared from 6FDA and *o*4Me*oo*(NH_2)$_2$ with 10 mol% excess dianhydride. Main spectrum obtained using THF and inset obtained using chloroform as solvents. Cyclic species with n repeat units are designated C,*n* and linear species with n diamine and ($n+1$) dianhydride units designated A,*n*.



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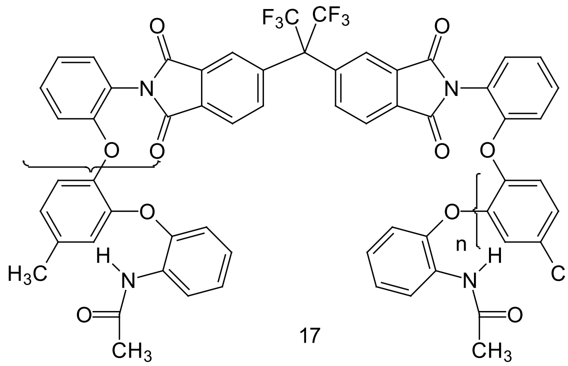
In spectra obtained using THF as solvent, peaks for cyclic oligomers dominated; Fig. 4, major spectrum. For samples prepared using chloroform as solvent, linear oligomers were dominant; Fig. 4 inset. Since, the same species must have been present in the isolated product, these differences reflect the sensitivity of the systems to the procedures and media used for product isolation and sample preparation.

3.4.4.2. Effects of excess diamine. For the polyimide prepared with excess diamine, isolated by precipitation into water, there were two main sets of peaks corresponding to (primarily) cyclic and linear oligomers; see Supporting Information.

Groups of peaks that included cyclic oligomers **14**, R = 4Me were complex. Within those sets of peaks, with *n* up to 9 and for which the [1 + 1] species were the most intense, were small peaks from linear [*n* + *n*] oligomers with one unreacted amine end (**12a**) and one anhydride end hydrolysed to diacid (**13b**).

The main sets of peaks for linear oligomers, *n* up to 11, corresponded to amine-ended species **17** with both ends monoacetylated, as **12b**, by acetic anhydride during imidization. Although the signals could have arisen from species with one end unacetylated (**12a**) and the other diacetylated (**12c**) this scenario seems unlikely. In addition, there were peaks attributable to amine-ended linear oligomers with other endgroups; viz. one unreacted amine (**12a**) and one monoacetylated amine (**12b**); one monoacetylated amine and one diacetylated amine (**12c**). Of these several peaks, one corresponded to an amine-ended oligomer with one end monoacetylated and one end diacetylated; the latter endgroup is an acyclic *N*-phenylimide or *N*-phenyl diacetamide. No signals were attributable to amine-ended oligomers with two unreacted or two diacetylated ends.



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Literature on diacetylation of phenylamines is limited, nevertheless, there are precedents for forming *N*-phenyl-diacetamides. Dehn reported formation of *N*-phenyl-diacetamide by acetylation of *N*-phenylacetamide with acetyl chloride in dilute solution in ether in sunlight at ambient temperatures [37]. Young reviewed early studies on the formation of diacetanilide by acetylation of acetanilide and concluded that the second acetylation of aniline proceeds more easily than anticipated [38]. Sudborough noted that the second acetylation is favoured by the presence of substituents *ortho* to the initial amine group [39]. This view is consistent with that of McCombie et al. who described the diacetylation of 2-(halophenoxy)anilines by refluxing with a mixture of acetic anhydride and acetic acid [40]. Al-Awadi and Al-Omran reported 72% yields of *N*-phenyl diacetamide on heating aniline with acetyl chloride for 2 h in the presence of pyridine [41]. Following these precedents, we suggest that under the conditions of the imidization reaction, i.e. in the presence of excess acetic anhydride with pyridine as scavenger, for prolonged periods, and with a phenoxy substituent *ortho* to the amine, it is probable that at least a proportion of the initial amine endgroups were converted to *N*-phenyl-diacetamide. With the agreement between calculated and observed masses of the oligomers and lack of correspondence with any other conceivable structure, we propose that the set of linear oligomers responsible for the designated peaks in each group have one diacetamide endgroup.

On the basis of the intensities of species observed, we further conclude that species with one unacetylated end and one diacetylated end made little or no contribution to the signals attributable to species with two monoacetylated ends, despite uncertainty due to identity of masses of the isomers, although their presence cannot be ruled out.

The sample prepared from **2b** with excess *o*4Me*oo*$(NH_2)_2$, isolated by precipitation into methanol and dissolved in THF for analysis, gave the same sets of peaks, but peaks for cyclics were relatively less intense than those for the linear, amine-ended oligomers with monoacetylated ends. Amongst signals for the other amine-ended oligomers there was a signal for the oligomer $n=1$ with Na^+ with one end unreacted and one monoacetylated. There was also an isolated peak at 857 Da attributable to a linear [1 + 1] oligomer with one diacetylated, amine-derived end, and one anhydride-derived end hydrolysed to diacid.

The observation of a variety of linear oligomers in samples prepared with a stoichiometric imbalances of monomers supports the concept that, in the samples prepared with a stoichiometric equivalence of monomers, only cyclic oligomers were present. The results discussed so far demonstrate that 1,2-bis(2-aminophenoxy)benzenes, i.e. with three *ortho*-phenylenes per repeat unit, predispose systems to formation of macrocyclic oligomer rather than chain growth.

3.4.5. Products prepared from *opo*$(NH_2)_2$

In case, it is the sequence of three adjacent *ortho*-linked phenylenes that predisposes growing polymers from diamines with *ortho*-phenylene groups to cyclize, we examined representative products prepared from *opo*$(NH_2)_2$, which also gave rise to low-molecular-weight products, but which have a more extended structure and only introduces two *ortho*-linked phenylenes into the repeat unit.

Products prepared from *opo*$(NH_2)_2$ with either BPADA (**2d**) or 6FDA (**2b**), examined by ESI-MS with methanol/DMF as solvent, gave distinct signals for $[n+n]$ cyclic oligomers with $n=1$, 2 and 3 (up to $n=4$ for **2b**) together with various solvent adducts. In each case, the only other signal attributable to any oligomer was of very low intensity and attributed to a linear species from one bis(ether anhydride) and two diamines with monoacetylated terminal groups.

These results indicate that it is not the presence of three *ortho*-linked groups in the diamine, which predisposes species to cyclize relative to chain growth, but the presence of *ortho*-amino units themselves. To test this concept and to extend the scope of this study, we investigated combinations of diamine and dianhydride with greater disparity between their relative lengths and of the units they incorporate into the polymer. Thus, we investigated the combination of a short rigid dianhydride **3**, as well as the dianhydrides used above, with a long, 4-ring diamine **4** or **5**.

3.4.6. Products prepared from 4-ring diamines

In the case of **3** with **5** or **4b** the polymers, examined by MT-MS, exhibited peaks for cyclics **18** or **19**, $n=2$–9 in both cases. Peaks for cyclics $[M_n+Na]^+$ for $n=2$–7 were the major peaks for **3** with **5**, as depicted in Fig. 5. There were no signals from [1 + 1] oligomers; space-filling models do not exclude formation of such species that might have been lost during

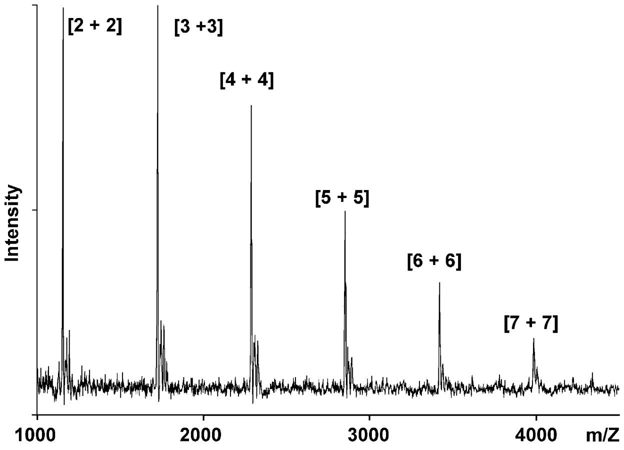
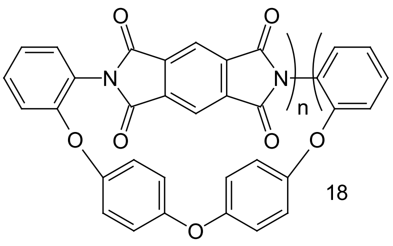
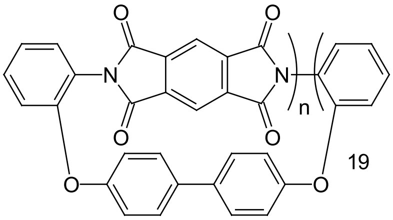


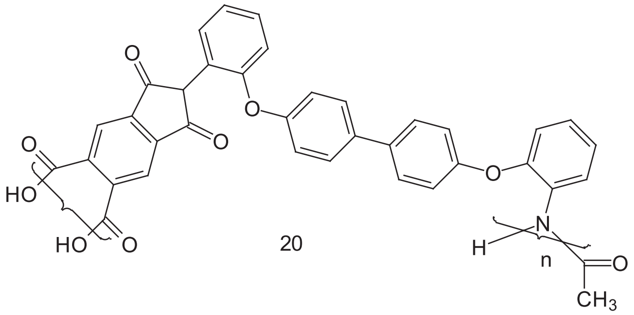
Fig. 5. MT-MS spectrum obtained from a fraction of the product prepared from PMDA and *oppo*$(NH_2)_2$; peaks arising from cyclic $[n+n]$ oligomers.

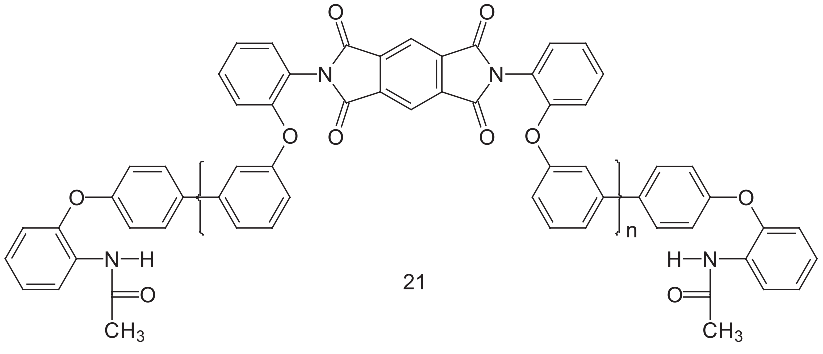
polymer isolation; see Supporting Information.


18


19

The product from **3** with **5** gave signals for the cyclic oligomers only. However, that from **3** with **4** did give signals attributable to two sets of linear oligomers, Fig. 6. One set, L,*n*, corresponded to [$n+n$] oligomers **20** that had failed to ring close; terminal amines were monoacetylated, **12b**, and the anhydride was hydrolysed to diacid, **13b**. The smallest such species observed was the [3+3] oligomer; intensity increased to $n=4$ and 5 and decreased at higher *n*. A second, more intense set, marked A,*n*, corresponded to species **21** ($n=2$–8) with two monoacetylated amine-derived ends.


20


21

Based on signals observed, species identified contained more diamine than dianhydride. There were no signals from species with two dianhydride ends but it is possible that such species, hydrolysed to acid (i.e. tetra acids), were lost on precipitation.

An acetone extract of the product from **3** and **4b** gave similar results with cyclics **19** and oligomers **21**, up to $n=7$; including a signal from **21**, $n=1$. The extract gave no peaks for oligomers **20** except for the species with $n=6$ and 7.

Comparing the results obtained from the two products prepared from **3**, it was found that, while *o*4,4′bipho(NH$_2$)$_2$ (**4b**) yielded a high proportion of linear oligomers, no linear oligomers were observed from the polymer prepared from *oppo*(NH$_2$)$_2$ (**5**). It seems unlikely that if the product from **3** with **5** contained linear oligomers they would not have been observed. Therefore, the observations indicate that the central rigid unit **4b** reduces the relative rate of ring closure in the poly(amic acid), especially at high n where linear oligomers predominate, compared with the more flexible **5**, which perhaps facilitates ring closure.

Diamines **4b** and **5** were also polymerized with longer dianhydrides **2b** and, the more flexible, **2d**. The polymer from **2b** and **4b**, examined by MT-MS, gave clear signals for cyclic oligomers, $n=2$–7 only, with no other peaks attributable to series of oligomers. A single, relatively-strong, peak was attributable to the linear [1+1] oligomer with a monoacetylated amine end and a diacid anhydride-derived end. A methanol extract exhibited signals from the cyclic oligomer $n=2$ only. These results differ from those observed for the product formed from **3**and **4b** described above.

Only signals for [$n+n$] cyclics, $n=2$–6 were apparent in the total product from **2b** and **5**. A methanol extract showed only peaks for cyclics $n=2$, 3 with different relative intensities, illustrating differences in solubility of the oligomers.

A methanol extract of the product from **2d** and **4b**, examined by MT-MS, gave clear peaks for the [1+1] cyclic and small peaks from a linear oligomer with one

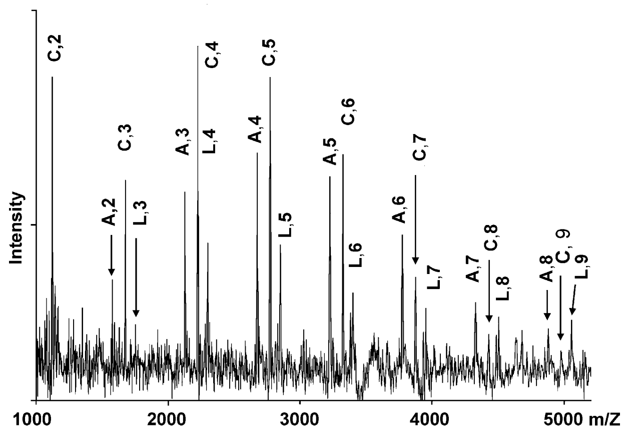


Fig. 6. MT-MS spectrum obtained from a fraction of the product prepared from PMDA and *o*4,4′bipho*o*$(NH_2)_2$. Peaks designated C,*n* arise from $[n+n]$ cyclic oligomers, those designated L,*n* arise from $[n+n]$ linear oligomers with n dianhydride and $(n+1)$ diamine units, as described in the text, those designated A,*n* arise from linear oligomers with *n* dianhydride and $(n+1)$ diamine units.

dianhydride and two diamines with monoacetylated terminal groups.

The product from **2d** and **5** gave signals for cyclic oligomers $n=2$–5. Several peaks were discernable in the mass region corresponding to $[1+1]$ cyclics. The major peak, at 877 Da, did not correspond to the $[1+1]$ cyclic imide with an associated cation, but did correspond to a $[1+1]$ cyclic in which only one amic acid residue had failed to cyclize. There were smaller peaks from the fully-imidized $[1+1]$ cyclic imide associated with H^+ and Na^+. A small isolated peak at 4836 Da was attributed to a linear amine-ended oligomer with both ends monoacetylated. A methanol extract of this polymer exhibited peaks for cyclic oligomers $[M_n+H]^+$, $n=1$ and 2 with that for $n=1$ by far the larger (intensity ratio 50:7). In the methanol extract no peak corresponded to the $[1+1]$ cyclic with an un-imidized amic acid residue.

Clearly, varying the relative lengths of diamine and dianhydride using the 4-ring *ortho*-aminophenoxy diamines of different rigidity does not greatly change the balance of products in favour of linear oligomers; cyclic oligomers were observed in all cases. Only in the combination of **3** with **4b**, with very disparate lengths of rigid units, was there a strong tendency to form linear oligomers. However, this combination showed that even the conformationally restricted $[1+1]$ cylic oligomer was formed. Although no $[1+1]$ cyclic species could be positively identified in the spectrum from the total product from **2d** and **4b**, such cyclic products were undoubtedly formed as seen in the methanol extract where the $[1+1]$ cylic oligomer was concentrated.

Thus, within the series of diamines used, there is no indication that longer diamines reduce the tendency to form low-molecular-weight polymers. This contrasts with the observation in a parallel study that compared polymers prepared from bis(ether anhydride)s with 3-phthalic anhydride or 4-phthalic anhydride units [28]. In that study it was observed that, while bis(ether anhydride)s with 4-phthalic anhydride units invariably produced high-molecular-weight poly(ether imide)s, bis(ether anhydride)s having 3-phthalic anhydride units produced low-molecular-weight polymers from a variety of 1- and 2-ring diamines and only with a longer diamine, 4,4′-bis(4″-aminophenoxy)biphenyl, were high-molecular-weight polymers formed. It is noticeable that in this study the longer bis(ether anhydride) **2f**, based on bis-phenol-*P*, in conjunction with **4b** was unique in producing high-molecular-weight polymer from a diamine with *ortho*-amino groups.

3.4.7. Products from bis-(4-aminophenoxy) benzenes

While the products from bis(2-aminophenoxy) diamines contain large proportions of oligomers, it is clear, from GPC data, that the products from *ppp*$(NH_2)_2$ with 6FDA (Fig. 2) and related products do contain very small amounts of oligomers, in addition to high-molecular-weight polymer. Using a mixture of methanol and DMF (1:1 v/v) we extracted sufficient oligomeric material from such products to examine by ESI-MS. Spectra from products from *ppp*$(NH_2)_2$, *pop*$(NH_2)_2$ or *p*4Me*op*$(NH_2)_2$ and 6FDA were almost identical (Supporting Information) in showing groups of peaks from $[2+2]$ and $[3+3]$ cyclics, with trace amounts of $[4+4]$ cyclics. In each case only signals from cyclics with methanol adduct molecules were observed. The dimers were primarily associated with 1–5 molecules of methanol, the trimers with 2–6 molecules of methanol and the cyclic tetramers with 3 or more molecules of methanol. In each case the largest signal from the dimers and trimers were for 3 and 4 adduct molecules, respectively.

These data demonstrate that polyimides from bis(4-aminophenoxy) diamines do form small cyclic species. These observations are consistent with the report by Kricheldorf et al. that polyimides based on 4,4′-diaminodiphenyl ether with non-aromatic dianhydrides contain primarily cyclic oligomers in their low-molecular-weight species [42]; these observations are discussed below. However, it is clear from GPC and mass spectrometric data presented here that the tendency to form oligomers is much smaller in reactions involving bis(4-aminophenoxy) diamines than for products from bis(2-aminophenoxy) diamines, which have large fractions of oligomers and lower-molecular-weight products overall. Thus, the tendency for chain growth, relative to cyclization is higher for reactions involving bis(4-aminophenoxy) diamines. This investigation makes no statement as to whether the higher-molecular-weight species from either class of diamines are linear or cyclic.

3.4.8. General considerations

The original theory of step polymerisations proposed by Carothers, and developed by Flory, considered only the formation of linear polymer chains, where the number-average degree of polymerisation $\overline{\mathrm{DP}}$ is given by

$$\overline{\mathrm{DP}} = \frac{1}{1-p} \tag{1}$$

(p is the extent of reaction), and the frequency distribution of chains by

$$n_x = p^{x-1}(1-p) \tag{2}$$

(n_x is the mole fraction of chains of degree of polymerisation x) [43]. It was soon recognised that polymerizations under thermodynamic or kinetic control can and do form macrocyclic products. Jacobson and Stockmayer first analysed this problem (JS theory) [44]. Assuming that all reactive chains are random-flight chains with free rotation and fixed bond angles and with a Gaussian distribution of end-to-end distances, they predicted that competition between cyclization and propagation in chains with mutually reactive ends and suitable end-to-end distances would lead to a population of cyclic oligomers, which decreases with increasing ring size as $n^{-1.5}$ [44].

Later, Stepto and Waywell synthesized polyurethanes from long, flexible monomers [45]. Product analysis showed the formation of significant proportions of cyclic oligomers and extrapolation of their data indicated that such products increased to 100% at complete conversion, in general agreement with the predictions of JS theory. Gordon and Temple analysed the system further in terms of reaction kinetics [46], and graph theory [47]. Subsequently, Stanford et al. adopted a statistical approach to rate theory [48]. All these approaches concluded that step polymerisations with perfect stoichiometry of reactants inevitably lead to 100% cyclics at complete conversion, with the formation of cyclics favoured at intermediate conversions in dilute reaction systems. Only for a stoichiometric imbalance of reactants did calculations predict a predominance of linear species at complete conversion. The underlying model was perhaps more applicable to flexible aliphatic reactants than stiff aromatic monomers. The theory has been modified to allow for stiff chains in ring-chain equilibria [49] and Kricheldorf et al. modified Eq. (1) to allow for different relative rates of propagation and cyclization in kinetically controlled polymerisations [50].

The polymer growth process relevant to this study, i.e. the formation of poly(amic acid), step a in Scheme 2, is an exothermic addition reaction. Equilibrium constants for step a in Scheme 2 are large and reactions (with subsequent chemical imidization of the products) normally lead to high-molecular-weight polymers; there is no reason to think that there is a major re-distribution of species on chemical imidization. These polymerisations are normally under kinetic control.

The data presented here, and previously [31,34], establish that diamines with *p*-aminophenoxy groups, on reaction with aromatic dianhydrides, lead to high-molecular-weight poly(amic acid)s and, after imidization, polyimides. Thus, the extents of reaction p are clearly high. At present it is not clear if those high-molecular-weight polymers are linear or cyclic. There is no reason to believe that the corresponding diamines with *ortho*-aminophenoxy groups are any less reactive and, indeed, they quickly react with isophthalic and terephthalic acids to yield high-molecular-weight polyamides. The high content of cyclic products observed in the present reaction products from various aromatic dianhydrides and diamines with *ortho*-aminophenoxy groups, reported here and in a previous note, is consistent with high extents of reaction and with JS theory and subsequent developments.

It is sometimes claimed that MT-MS and, by analogy, ESI-MS spectra do not truly represent the populations of species present in polymer samples. This is clearly so in the ESI-MS data reported here which show significant variations in populations of species with the solvent used. Thus, it might be claimed, the observation of cyclic species only in several samples does not preclude the presence of linear species. However, the clear observation of linear oligomers in samples prepared with stoichiometric imbalances of reagents establishes that there is no problem in identifying the presence of linear oligomers. Thus, the total absence of linear oligomers in samples prepared with a stoichiometric equivalence of monomers strongly supports the view that those samples do contain only cyclic species in the molecular weight range observed. These observations are clearly at odds with the original treatment of step polymerisations which predicts that in the frequency distribution low-molecular-weight linear species are the most populous, albeit at a low weight fraction.

Analysis of the observed populations of species presented in the Supporting Information is not consistent with either of the common theories; it should be noted, however, that the populations quoted are not definitive as they are for $[M_n+Na]^+$ species only and do not take account of related species associated with different adventitious ions or solvent adducts, which can give the strongest signals. However, using data sets uncomplicated in this way, plots of data to compare the exponent with the predicted value of -1.5 from JS theory show that several of the relevant plots are non-linear. Where a rough linear dependence between the logarithms of the populations of species and the degrees of polymerisation x can be identified, the exponents were between -2 and -5, with a value about -4 in most cases; these are clearly inconsistent with the value of -1.5 predicted for random-flight chains.

Linearization of Eq. (2), where reasonably linear plots were obtained, gave estimated values of the extent of reaction p between 0.16 and 0.6, which predicts number-average degrees of polymerisation between 1.2 and 2.6; such values are totally inconsistent with the high extents of reaction achieved and molecular weights observed. In all cases populations of species decreased more rapidly with increasing n than is consistent with a linear dependence between ln n and n.

Although diamines with *para*-aminophenoxy groups do give rise to some very-low-molecular-weight oligomers they exhibit a strong tendency for chain growth in preference to cyclization and only a very small weight fraction of oligomers is seen by GPC. In contrast, the results obtained here establish that diamines with *ortho*-aminophenoxy groups give rise to low-molecular-weight products overall and that these contain a high weight fraction of almost exclusively cyclic oligomers. All the available evidence is that these diamines introduce a strong tendency to cyclization of oligomeric species, as opposed to chain growth. Because the techniques used only provide information over a limited range of molecular weights, we are unable to comment on the nature of larger species. Therefore, we conclude that the *ortho*-aminophenoxy groups impart conformations on the active oligomeric chains of poly(amic acid) as to strongly enhance the probability of cyclization, even forming [1+1] cyclic species in some cases.

It appears, from an examination of space-filling models, that the sharp kink (60°), imposed by the *ortho*-amino group, imparts a recursive feature into the molecular conformation that enhances the proximity of reactive chain ends in oligomers and, hence, ring-closure. Almost the only exception to this generalization appears to be the reaction between **3** and **4b**, where the **3** unit is linear and the central rigid biphenyl unit of the diamine tends to force the endgroups apart and reduce the tendency for cyclization. It is also interesting to note that, although there is conformational flexibility at the amic acid residues in the poly(amic acid) intermediates, there is no problem in creating small cyclic oligomers of polyimides when the amic acid units are converted to rigid linear *N*,*N*′-diphenylpyromellitimde units; see Supporting Information. Kricheldorf et al. also reported an enhanced tendency to form macrocyles from terephthaloyl chloride and dihydroxybenzenes when *ortho*-dihydroxybenzene (catechol) was used as monomer [50].

It is notable that, for stoichiometric equivalences of monomers, apart from a very specific case involving **3**, almost all combinations of dianhydrides and diamines gave virtually exclusively cyclic oligomers. This generalization applies for a variety of different lengths of dianhydride and diamine. It is interesting to compare the results obtained here with those obtained in the parallel study involving bis(ether anhydride)s where the ether linkage is in the 3-position of the phthalic anhydride unit [28], as described in Section 3.4.6. In the single case of using the long, relatively-linear diamine **4b** with the long dianhydride **2f** from bisphenol-P were high-molecular-weight polymers prepared from a diamine with *ortho*-aminophenoxy units. Thus, it is conceivable that there is a subtle influence of the lengths of the monomers used and the tendency to form cyclic oligomers.

3.5. Correlation of mass spectrometry and gel permeation chromatography

Although, there are large discrepancies between molecular weights of polyimides determined by GPC and absolute values from membrane osmometry [13], it is tempting to explore the possibility that a correlation exists between GPC and mass spectrometric data for the lowest-molecular-weight species in several samples examined. To a first approximation, there is a rough correlation between the numbers of oligomeric peaks identifiable in the gel permeation chromatograms (Fig. 2(b) and (c)) and species identified in ESI-MS spectra. There is also a rough correlation between the masses of individual peaks where, for any individual sample, masses of individual peaks determined by GPC (polystyrene equivalent) are about 250–300 mass units lower than peaks in mass spetra. However, given the uncertainty as to what species might have been lost on sample isolation, and the validity of exact masses determined by GPC, it is not realistic to relate specific peaks and signals at this stage; better separation of individual species is required for that purpose.

4. Conclusions

Several conclusions can be drawn from the current studies relating to monomer and polymer syntheses and to the nature of the products of the polymerisation reactions. These are as follows:

(i) Fluorodisplacement reactions between *ortho*-fluoronitrobenzene and various dihydroxybenzenes, leading to bis(*ortho*-nitrophenoxy)benzenes is a generally facile process. The dinitro compounds are readily reduced to yield a new series of bis(*ortho*-aminophenoxy) diamines which can be used in polymer synthesis.

(ii) While *para*-aminophenoxy diamines lead to high-molecular-weight polyimides, *ortho*- aminophenoxy diamines lead to low-molecular-weight polyimides when prepared by a two-stage solution polymerisation with about 10% w/w solids. The high-molecular-weight polyimides prepared from *para*-aminophenoxy diamines with different dianhydrides yielded polymers which exhibited good mechanical properties, similar to those of countless other poly(ether imide)s. In contrast, the oligomeric products prepared from *ortho*-aminophenoxy diamines gave brittle polymers with inferior mechanical properties.

(iii) As a result of examining oligomeric polyimides prepared from bis(*ortho*-aminophenoxy) diamines by gel permeation chromatography and mass spectrometry, it is concluded that these species consist primarily, if not exclusively, of oligomeric, cyclic polyimides. There was no evidence for the presence of linear oligomeric species in most products prepared from a variety of diamines and dianhydrides with a stoichiometric equivalence of monomers. The lack of observation of linear species by mass spectrometry did not preclude the presence of linear species. However, the enforced presence of linear species, by preparing polymers with a stoichiometric imbalance of monomers and the subsequent observation of such species, reinforces the view that, when a stoichiometric balance of monomers involving *ortho*-aminophenoxy diamines was used, the products were probably exclusively cyclic, oligomeric polyimides. Only in specific cases, involving a disparity in lengths of the dianhydrides and diamines with rigid units, was evidence for the presence of especially low-molecular-weight linear oligomeric species observed.

(iv) Thus, it is concluded that bis(*ortho*-aminophenoxy) diamines exhibit a very strong disposition towards the synthesis of cyclic oligomeric polyimides. The *ortho*-aminophenoxy residues apparently exert a strong influence towards ring closure in the formation of poly(amic acid)s which is maintained on imidization to cyclic polyimides; irrespective of the dianhydride and of the number of aromatic rings (three or four) in the bis(*ortho*-aminophenoxy) diamines.

(v) Whereas *ortho*-linked main-chain phenylene units have been reported to lower T_gs of polymers, it is concluded that the *ortho*-phenylene unit from bis(*ortho*-aminophenoxy) diamines, situated between the *N* of the phthalimide moiety and the ether linkage in the diamine moiety, serves to raise the T_g of the products, for polymers of comparable molecular weight.

(vi) While methyl substituents in the diamine moieties raise T_g of polyimides generally, the 3-methyl group from *o*3Me*oo*$(NH_2)_2$ raises T_g more than the 4-methyl group in *o*4Me*oo*$(NH_2)_2$. This effect is a result of restricted rotation about the neighbouring ether linkage reducing the possibilities for conformational changes.

(vii) It is concluded from mass spectrometric studies that while ESI-MS, under the conditions used, only reveals lower oligomers than are observed with MT-MS. The range of molecular weights of oligomers can be enhanced by use of mixed solvents, which favour dissolution of higher-molecular-weight polymer. However, neither ESI-MS nor MT-MS gives definitive distributions of species present in the polymers examined. Use of solvent extracts can, for example, reveal the presence of different oligomers and, especially, [1+1] oligomers not always observed on analyzing the total products.

(viii) There is a marked tendency for macrocyclic polyimide oligomers to form adducts with solvents, especially methanol, which can interact with the imide ring. This tendency is probably enhanced by cavities in the small cyclic oligomers identified by examination of space-filling models; see Supporting Information.

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Supplementary data

Supplementary data associated with this article can be found at doi:10.1016/j.polymer.2006.01.036

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