Poly(ether imide)s with hindering substituents in the anhydride moiety: synthesis, properties and gas permeabilities

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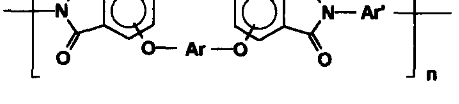
The synthesis of a series of bis(ether anhydride)s with hindering substituents, especially t-butyl and methyl, has been developed using nucleophilic displacement reactions between nitrophthalodinitriles and substituted hydroquinones, bisphenols and a naphthalene diol. The bis(ether anhydride)s have been successfully incorporated into poly(ether imide)s with hindering residues by polymerization with diamines, with and without alkyl substituents. The thermal and mechanical properties of a number of the polymers and their permeabilities to several gases have been determined. The properties of the polymers are discussed, along with those of related polymers. It is shown that the properties are strongly controlled by their structural features. In particular, the flexibilities of polymer backbones and substituents are found to influence glass transition temperatures and, in conjunction with the influence of chain rigidity on packing, to influence gas permeabilities and permselectivities.

(Keywords: poly(ether imide); nitrodisplacement; gas permeability)

INTRODUCTION

During a programme designed to develop improved materials for gas-separation membranes we synthesized several new polyimides and poly(ether imide)s (I). The combination of solvent solubility and robust mechanical properties makes poly(ether imide)s especially interesting for membrane applications and ultimately allows easy fabrication of the required asymmetric membranes.



(I)

Our aim was to investigate structural features which influence combinations of permeabilities and selectivities for various gas separations for materials of high permeability, and to examine the well-known trade-off between gas permeability and selectivity, i.e. increased permeability is normally associated with reduced selectivity[1,2]. Poly(ether imide)s are a particularly attractive class of polymers for structure–property investigations as the synthetic chemistry is flexible and there is the potential for introducing numerous different structural moieties. Prediction of membrane properties in terms of polymer structure from first principles is not yet reliable. Consequently, poly(ether imide)s with different structures were prepared to vary their molecular packing and segmental mobility and, hence, their gas separation behaviour.

Our previously published results demonstrate that bulky substituents in poly(ether imide)s, especially groups in Ar and Ar′ residues *ortho* to the linkages to the phthalimide residues, greatly enhance gas permeabilities without loss of selectivity[3,4]. These substituents hinder rotation about the linkages to the phthalimide residue and raise glass transition temperatures. We concluded that such bulky substituents hinder chain packing, increasing the amount and modifying the distribution of free volume in the glassy polymer matrix. This conclusion agrees with the views of Koros *et al.*[1] who, in a review of gas permeability through polymer membranes, stated that in glassy polymers 'Suppression of interchain packing by addition of bulky groups—which also cause simultaneous inhibition of interchain motion around flexible hinge points—tends to increase permeability without unacceptable loss in selectivity'. Very bulky substituents, e.g. trimethyl silyl, also enhance permeabilities in rubbery polymers[5,6].

This study focuses on the synthesis of a series of poly(ether imide)s with bulky residues, especially with t-butyl groups in the bis(ether anhydride) moiety, and studies their permeabilities and thermal and mechanical properties.

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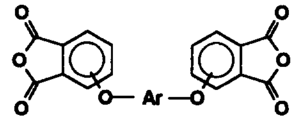
Although there are previous claims in the patent literature for poly(ether imide)s with hindered bisphenols or substituted hydroquinone units in the bis(ether anhydride) moiety, substituents are mainly small alkyl (e.g. methyl, including methyl on hydroquinone[7–9] or tetramethyl[7–11], or isopropyl[11,12] substituents on bisphenols) or small aromatic substituents (e.g. phenyl and benzyloxy[12]), and are mainly cited in patent claims without supporting examples. There appears to be one such claim for poly(ether imide)s with bulky t-butyl groups on hydroquinone residues in the dianhydride moiety[13] (without example) and one case of multiply substituted hydroquinone within the diamine moiety[14]. There is also a report of an aromatic polyester with pendent t-butyl groups[15]. However, there are few reports of aromatic polymers, especially poly(ether imide)s, with t-butyl substituents, particularly in the anhydride moiety. There is also little information on poly(ether imide)s with multiply substituted hydroquinone residues.



(II)

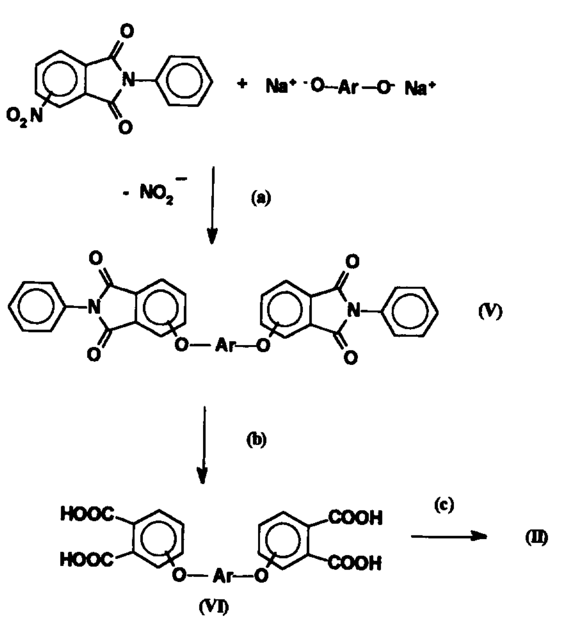
The synthesis of new poly(ether imide)s from bis(ether anhydride)s with bulky substituents and commercially available aromatic diamines (H_2N-Ar′-NH_2) required the development of new bis(ether anhydride)s, of general structure II, in which Ar is one of several aromatic units with bulky substituents. This work led us to investigate the limitations of nitrodisplacement procedures for diols (III) of different structures (*Table 1*).

This paper therefore describes the synthesis of a selected series of new bis(ether anhydride)s with bulky substituents on bisphenol and hydroquinone residues and some limitations to bis(ether anhydride) synthesis; a more general analysis of nitrodisplacement reactions will be presented subsequently. The synthesis of poly(ether imide)s from these hindered bis(ether anhydride)s with several diamines (IV), including hindered diamines, is also described (*Table 2*). Gas permeabilities and mechanical properties of the polymers were determined; data presented were measured on solvent-cast, dense polymer films.

NITRODISPLACEMENT REACTIONS

Bis(ether anhydride)s are conveniently prepared using a nucleophilic displacement of a nitro or halide group from a phthalic acid derivative, e.g. 3- or 4-nitrophthalic acid derivative, by reaction with an aromatic diol or its alkali metal salt. The literature describes two major procedures suitable for the synthesis of bis(ether anhydride)s based on phthalic acid derivatives and different diols; these procedures have been reviewed by Takekoshi[16]. We found that several diols with bulky substituents which are not amenable to nitrodisplacement by one process, but are susceptible to oxidative side reactions, may be converted to bis(ether anhydride)s by the other.

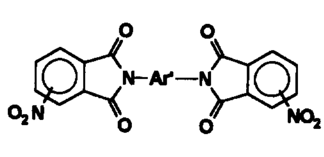
Ether linkages in bis(ether phthalic acid anhydride)s are usually formed by reaction of a nitrophthalic acid derivative in dimethylsulfoxide (DMSO); reaction conditions preclude direct use of nitrophthalic anhydrides. There is a recent report that 4-fluorophthalic anhydride can be used directly in displacement reactions with aromatic diols in diphenylsulfone in the presence of high concentrations of potassium fluoride[17,18]; reported yields are low and we are not concerned with this alternative here.



Scheme 1

The most commonly used displacement reactions are those between nitrophthalimides, commonly *N*-phenyl nitrophthalimides, and bisphenolates, derived from diols (III) (*Scheme 1*)[19–23]. The bis(ether phthalimide)s (V) so formed are hydrolysed to the tetraacids (VI) and then cyclized to the bis(ether anhydride)s (II).

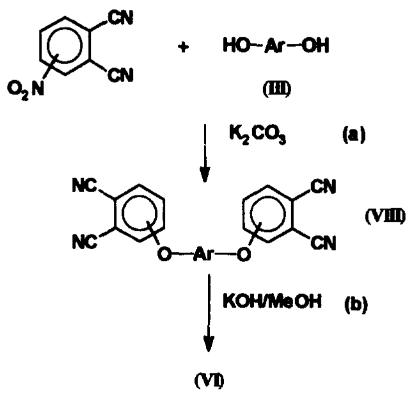
In principle, displacement reaction (a) in *Scheme 1* can be used to form a poly(ether imide) directly by using a bis(nitrophthalimide) of type VII. While this reaction has been reported to yield high-molecular-weight polymers by performing the reaction in non-polar[24] or phenolic solvents[25] (or in the melt[26]), we found these polymerizations to be less than satisfactory generally because of the limited solubility of the poly(ether imide)s formed in the solvent used[27]. We also found that reactions in cresol, a recommended solvent, can be subject to complications[27,28]. In addition, this latter route to poly(ether imide)s is only a possibility for those diols which undergo nitrodisplacement with nitrophthalimide in virtually 100% yield.



(VII)

The alternative nitrodisplacement reaction is that between nitrophthalodinitrile and diol (III) in DMSO in the presence of an alkali metal carbonate[29,30], e.g. K_2CO_3 [*Scheme 2*, reaction (a)]. This reaction produces the tetranitrile (VIII) which is then hydrolysed to tetraacid (VI) [*Scheme 2*, reaction (b)] and hence to the bis(ether anhydride) (II) [*Scheme 1*, reaction (c)].

In synthesizing bis(ether anhydride)s, as precursors to poly(ether imide)s, we found that many diols, e.g. substituted hydroquinones and hindered bisphenols, which will not react satisfactorily by *Scheme 1* will react satisfactorily by *Scheme 2*. We also identified structural



Scheme 2

limitations to diols (III) which can be used satisfactorily in *Scheme 2*.

EXPERIMENTAL

Materials

4-Nitrophthalic acid anhydride, 4-nitrophthalimide and 3-nitrophthalimide (Lancaster Synthesis) were used as supplied. 4-Nitrophthalodinitrile and 3-nitrophthalodinitrile were synthesized as described or were obtained from TCI, Tokyo, Japan and used as supplied. 2,5-Di-t-butyl hydroquinone and trimethylhydroquinone were supplied by Aldrich Chemical Co., and 2,5-di-t-amyl hydroquinone and 4,4′-butylidene-bis-(6-t-butyl-*m*-cresol)

Table 1 Identification of aromatic residues (Ar) used in the syntheses

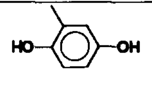
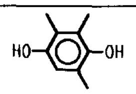
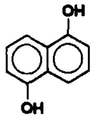
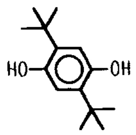
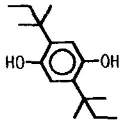
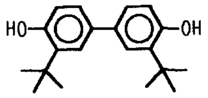
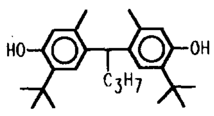
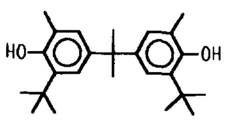
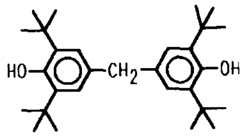
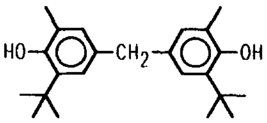
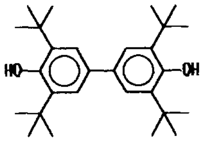
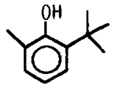
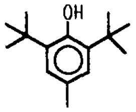
Code	Structure	Code	Structure
a		b	
c		d	
e		f	
g		h	
i		j	
k			
l		m	

Table 2 Diamines H_2N-Ar′-NH_2 (IV) used in the polymer syntheses

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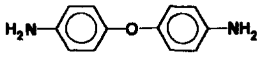
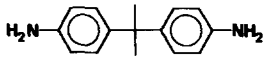
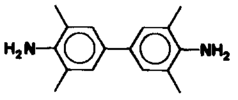
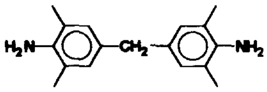
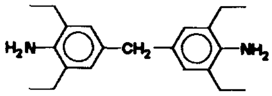
A		B	
C		D	
E			

Table 3 Synthesis of bis(ether phthalimide)s (V) by *Scheme 1*

Ar residue		Elemental analysis C	H	N	Yield (%)	Product colour
a	Calc	74.2	3.88	4.94		
(4-isomer)	Found	73.50	3.92	4.90	9.1	Brown-grey
(3-isomer)	Found	73.58	3.91	4.83	53	Light brown
b						Sienna-earth
c						Black tar-like

were supplied by TCI, Tokyo, Japan. 4,4′-Dihydroxy-3,3′-di-t-butylbiphenol was obtained from du Pont. 2,2-Bis-(4-hydroxy-3-methyl-5-t-butylphenyl)propane and 2,2-bis-(4-hydroxy-3-methyl-5-t-butylphenyl) methane were synthesized. Ultrapure 4,4′-diamino-diphenylether was provided by British Petroleum, 3,3′,5,5′-tetramethylbenzidene was obtained from Aldrich Chemical Co., 3,3′,5,5′-tetramethyl-4,4′-diaminophenylmethane was a development product from Seika and Co. and 3,3′,5,5′-tetraethyl-4,4′-diaminophenylmethane was supplied by Lonza. 2,2-Bis-(4-aminophenyl)propane was synthesized as described previously[4]. All anhydrous solvents were obtained from Aldrich Chemical Co.

Synthesis of intermediates

2,2-Bis-(4-aminophenyl)propane was prepared by reacting aniline hydrochloride with acetone in appropriate stoichiometric amounts in a sealed glass vessel at 145°C for 7 days (yield 55%; m.p. 132–133°C). *N*-phenyl nitrophthalimide was synthesized from 4-nitrophthalic acid anhydride as described previously[4].

Synthesis of bis(ether phthalimide)s and bis(ether anhydride)s. Bis(ether phthalimide)s were synthesized (*Table 3*) and bis(ether anhydride)s derived from them according to the procedures described previously by Takekoshi *et al.*[23] and as reported in a previous publication[4].

Synthesis of diols. (1) Preparation of bis-(4-hydroxy-3-methyl-5-t-butylphenyl)methane. To 82 g (0.5 mmol) of 2-methyl-6-t-butylphenol was added 82 ml of glacial acetic acid followed by 21 ml of formaldehyde solution (37% w/v) and, while stirring, 15 ml of concentrated hydrochloric acid was added. The solution was left at room temperature for 96 h. Then, 300 ml of hexane was added and the solid filtered off and washed with 300 ml of hexane. The off-white crystals were recrystallized from hexane (500 ml) to yield 55 g (65% theoretical yield based on formaldehyde) of white crystals (m.p. 101–102°C). Elemental analysis: calculated for $C_{23}H_{32}O_2$: C 81.17%, H 9.41%; found: C 81.57%, H 9.71%.

(2) Preparation of 2,2-bis-(4-hydroxy-3-methyl-5-t-butylphenyl)propane. Twenty-two grams of 2-t-butyl-6-methylphenol were diluted with 25 ml of glacial acetic acid and 3.8 g of acetone was added followed by 4 ml of concentrated hydrochloric acid. The solution was kept at room temperature for 2 months. Then, 100 ml of hexane was added and the mixture was washed with water, saturated sodium bicarbonate and water again and was then dried over calcium chloride. After partial evaporation of solvent a crystalline product was recovered which was recrystallized from hexane to yield 5 g (20% theoretical yield) of white crystals (m.p. 131–132°C). Elemental analysis: calculated for $C_{25}H_{36}O_2$: C 81.52%, H 9.78%; found: C 81.32%, H 9.85%.

Synthesis of nitrophthalodinitriles. The procedure of McClelland *et al.*[31] was used to prepare samples of 4- and 3-nitrophthalamides from 4- or 3-nitrophthalimide in concentrated ammonia solution; yields were in excess of 92%. Nitrophthalimides were converted to nitrophthalodinitriles according to the procedure of Hall *et al.*[32] by reaction with trifluoroacetic anhydride in dry dioxane and pyridine at 0°C. After dilution with water, extraction with ethyl acetate and washing with water, dilute hydrochloric acid, water and brine (5% sodium chloride), the solvent was removed *in vacuo* and the product was recrystallized from acetone/hexane (50:70); yield 80%. Elemental analysis: calculated for $C_8H_3N_3O_2$: C, 55.49%; H, 1.73%; N, 24.27%; found for 4-phthalodinitrile: C, 55.32%; H, 1.63%; N, 24.18%. Similar results were obtained for the 3-isomer.

Synthesis of tetranitriles. All tetranitriles (VIIIb,d–h) were synthesized according to the same procedure, only the scale and details of isolation and purification of the products varied. The full details of the procedure are given for the synthesis of 1,4-bis-(3,4-dicyanophenoxy)-2,5-di-t-butyl benzene (IIId). In other cases only the scale and variations are detailed. Individual diols (III) are identified in *Table 1*, and the elemental analysis data for all products are given in *Table 4*. The identities of the products were further confirmed by i.r. and n.m.r. spectroscopy.

(1) Preparation of 1,4-bis-(3,4-dicyanophenoxy)-2,5-di-t-butyl benzene (VIIId, 4-isomer). 4-Nitrophthalodinitrile (17.38 g, 0.1 mol) was dissolved in 150 ml of anhydrous DMSO in a 250 ml three-necked flask fitted with a stirrer, nitrogen-gas inlet and thermometer. Then, 11.1 g (0.05 mol) of 2,5-di-t-butyl hydroquinone (IIId) was added to the mixture followed by 20 g of anhydrous potassium carbonate. The mixture was stirred at room temperature with a stream of dry, oxygen-free (white spot) nitrogen passing through the flask for 24 h. The reaction mixture was then poured into 1200 ml of water to produce a solid

Table 4 Synthesis of tetranitriles and dinitriles by *Scheme 2*

Ar residue		Elemental analysis C	H	N	Yield (%)	Melting point (°C)
b	Calc.	74.25	3.96	13.86	70	287.5–288.3
	Found	74.19	3.95	13.95		
c	Calc.	75.72	2.91	13.59	91	264–265
	Found	74.44	2.89	13.17		
d	Calc.	75.94	5.48	11.81		
(4-isomer)	Found	75.81	5.50	11.47	91.3	299[a]
(3-isomer)	Found	75.61	5.48	11.98	90.2	332[a]
e	Calc.	76.49	5.98	11.16	75	297.8–298.7
	Found	75.82	5.84	11.34		
f	Calc.	78.55	5.45	10.18	89	206.6–209
	Found	78.31	5.63	11.50		
g	Calc.	79.50	6.62	8.83	82.27	184.8–187
	Found	79.27	6.76	8.89		
h	Calc.	79.35	6.45	9.03	59.3	104.8–107.6
	Found	79.25	6.78	8.85		
l	Calc.	78.62	6.20	9.66	9.65	111–116
	Found	78.61	6.25	9.78		
m	Calc.	79.77	7.51	8.09	<10[b]	175.6–176.5
	Found	79.80	7.48	8.16		

[a] Determined by d.s.c.
[b] After four recrystallizations

product which was washed five times with water and three times with methanol. The product (20 g, 85% yield) in the form of a white powder was recrystallized from acetonitrile to yield white crystals of VIIId (4-isomer).

(2) Preparation of 1,4-bis-(2,3-dicyanophenoxy)-2,5-di-t-butyl benzene (VIIId, 3-isomer). The procedure adopted was identical with that for 1,4-bis-(3,4-dicyanophenoxy)-2,5-di-t-butyl benzene except that 3-nitrophthalodinitrile was used and the reaction was performed on half scale. The solid precipitate produced on pouring the reaction mixture into water was filtered and washed until the effluent was neutral. The product was further washed with boiling methanol until it became a greyish-white powder (10.6 g, 90.2% yield). After recrystallization from boiling acetonitrile white crystals of VIId (3-isomer) were obtained.

(3) Preparation of 1,4-bis-(3,4-dicyanophenoxy)-2,5-di-t-amyl benzene (VIIIe) (scale: 50 mmol of 4-nitrophthalodinitrile). The mixture was reacted at 60–70°C for 2 h and then at room temperature for 20 h. After the reaction mixture was poured into water and the precipitate washed with water, the precipitate was washed with methanol and then treated with boiling methanol, filtered while hot and dried.

(4) Preparation of 4,4′-bis-(3,4-dicyanophenoxy)-3,3′-di-t-butyl-1,1′-biphenyl (VIIIf) [scale: 0.1 mol (plus 10% excess) of 4-nitrophthalonitrile]. The isolated product was heated to boiling in methanol (200 ml) and filtered off; this procedure was repeated twice. The precipitate was then dried to yield 28.46 g of off-white powder. The crude material was recrystallized from 600 ml of acetonitrile to yield pure VIIIf.

(5) Preparation of 1,1′-bis-[4-(3,4-dicyanophenoxy)-2-methyl-5-t-butyl-phenyl]butane (VIIIg) (scale: 50 mmol of 4-nitrophthalonitrile). The reaction was carried out for 10 h at 60°C and 14 h at room temperature. The reaction flask was fitted with a calcium chloride guard tube. The precipitated product was washed with methanol to remove coloured impurities, and dried.

(6) Preparation of 1,4-bis-(3,4-dicyanophenoxy)-2,3,5-trimethyl benzene (VIIIb) (scale: 0.0809 mol of 4-nitrophthalodinitrile). The isolated product, washed with boiling methanol until it became white, was recrystallized from boiling acetonitrile to give slightly yellow crystals of VIIIb.

(7) Preparation of 2,2-bis-[4-(3,4-dicyanophenoxy)-3-methyl-5-t-butyl-phenyl]propane (VIIIh) (scale: 6.3 mmol of 4-nitrophthalodinitrile). After precipitating the mixture into water, 2.0 g of crude VIIIh was recovered and recrystallized from hexane.

Unsuccessful syntheses of tetranitriles. The same procedure as that adopted for the syntheses of tetranitriles above was used unsuccessfully in attempting the following syntheses. No attempts were made to identify the major products.

(1) Attempted preparation of bis-[4-(3,4-dicyanophenoxy)-3,5-di-t-butyl-phenyl]methane (VIIIi). 4-Nitrophthalodinitrile (1.73 g, 10 mmol) was dissolved in 15 ml of anhydrous DMSO followed by 2.123 g (0.5 mmol) of IIIi. After the material had dissolved, 2.6 g of potassium carbonate was added. The reaction mixture became deep violet in colour and was left, with stirring, for 24 h. The mixture was precipitated into 300 ml of water and filtered to yield 3.2 g of a yellow powder readily soluble in methanol which changed colour to deep purple when treated with sodium hydroxide. A similar experiment carried out with caesium carbonate yielded, after recrystallization, long gold-coloured needles soluble in methanol; the colour again changed when treated with sodium hydroxide. Elemental analysis showed that the product contained 82.17% C, 10.1% H and no nitrogen.

(2) Attempted preparation of bis-[4-(3,4-dicyanophenoxy)-3-methyl-5-t-butyl-phenyl]methane (VIIIj). 4-Nitrophthalodinitrile (6.92 g, 40 mmol) was dissolved in 40 ml of anhydrous DMSO followed by 6.8 g (20 mmol) of IIIj. The attempt to achieve a nitrodisplacement reaction and synthesize a tetranitrile failed. The unidentified, recovered product (20.3 g) was readily soluble in methanol and changed colour when treated with sodium hydroxide.

(3) Attempted preparation of bis-[4-(3,4-dicyanophenoxy)-3,5-di-t-butyl-phenyl]biphenyl (VIIIk). 4-Nitrophthalodinitrile (3.6 g, 0.021 mmol) was dissolved in 50 ml of anhydrous DMSO followed by 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl (IIIk) (4.1 g, 0.01 mmol). The solution became deep orange. After the bisphenol had dissolved, potassium carbonate (5 g) was added and the resulting suspension was stirred for 24 h. When the mixture was poured into water a brick-coloured precipitate formed which was filtered off and washed with water and then with methanol. The solid was recrystallized from acetonitrile to yield 3.32 g of brown crystalline needles with a blue metallic iridescence. Elemental analysis showed that the solid contained 82.06% C and 9.80% H and no nitrogen. Accurate mass spectrometry showed the product had a mass of 408.303 and mass spectrum identical with those for 3,3′,5,5′-tetra-t-butyldiphenoquinone which had been formed pure and in 81.4% yield.

Synthesis of model dinitriles. Model dinitriles were synthesized from nitrophthalodinitrile and monophenols using exactly the same procedure as adopted for the synthesis of teranitriles. Elemental analysis data are given in *Table 4*. The identities of the products were further confirmed by n.m.r. spectroscopy.

(1) Preparation of 4-(2′-t-butyl-5′-methylphenoxy)phthalodinitrile. From 5 mmol of 2-t-butyl-5-methyl phenol (aromatic residue l) and 10 mmol of 4-nitrophthalodinitrile in 10 ml of DMSO, 1.10 g of a crude dinitrile was obtained. After multiple recrystallizations from cyclohexane, an analytically pure sample was obtained in 10% yield. The final product (m.p. 111–116°C) had a strong absorption in the i.r. region (KBr disc) at 2230 cm^{-1}, characteristic of $C \equiv N$ stretching.

(2) Preparation of 4-(2′,6′-di-t-butyl-4′-methylphenoxy)-phthalodinitrile. From 10 mmol of 4-nitrophthalodinitrile and 10 mmol of 2′,6′-di-t-butyl-*p*-cresol (aromatic residue m) in 10 ml of DMSO, 2 g of brown powder was obtained. After four recrystallizations from cyclohexane 0.15 g (4.3% theoretical yield) of off-white needles (m.p. 175.6–176.5°C) were obtained. I.r. analysis showed a $C \equiv N$ stretching vibration at 2234 cm^{-1}.

Synthesis of bis(ether anhydride)s from tetranitriles. All bis(ether anhydride)s (IIb, d–h) were synthesized according to the same procedure, only the scale and details of isolation and purification of the product varied. The full details of the procedure are given for the synthesis of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene (IId). In other cases only the variations are detailed; elemental analysis data are given in *Table 5*. The identities of the products were further confirmed by i.r. and n.m.r. spectroscopy.

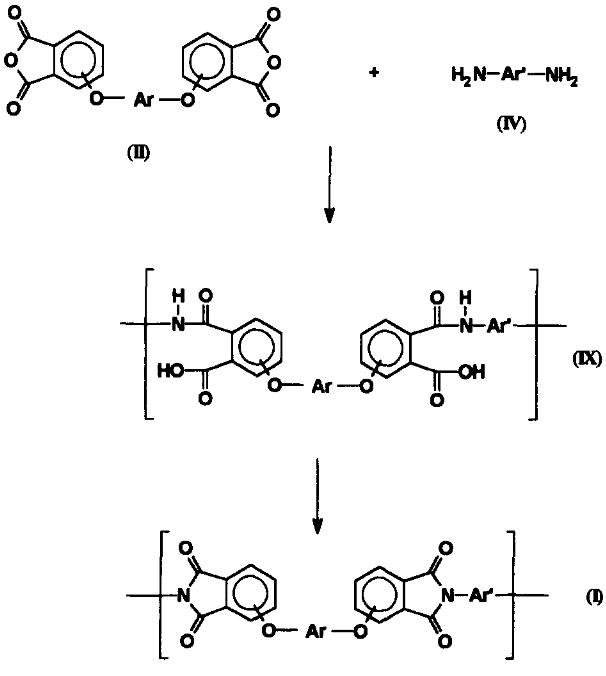
(1) Preparation of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer). Potassium hydroxide (25 g) was dissolved in 40 g of water in a 250 ml round-bottomed flask fitted with a reflux condenser, then 19 g of 1,4-bis-(3,4-dicyanophenoxy)-2,5-di-t-butyl benzene (VIIId, 4-isomer) were added to the heated solution, followed by 100 ml of methanol. The mixture was refluxed for 40 h by which time evolution of ammonia had ceased. The mixture was then diluted with water to 300 ml. The acidity was adjusted, by addition of concentrated hydrochloric acid solution, to pH 1.5–2. The resulting precipitate was filtered, washed three times with water and dried to yield 21.6 g (98% yield) of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene.

Then, 20 g of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene were dissolved in 200 ml of glacial acetic acid and 150 ml of acetic anhydride. The mixture was refluxed for 2 h. The resulting solid product, which crystallized on cooling, was filtered and recrystallized from 200 ml of acetic anhydride to give a 90% yield of the 4-isomer of IId.

Table 5 Synthesis of bis(ether anhydride)s

Ar residue	Elemental analysis			Yield (%)	Melting point (°C)
		C	H		
c	Calc.	69.02	2.65	91.8	255–256
	Found	68.30	2.60		
d	Calc.	70.04	5.06	90	250
(4-isomer)	Found	69.85	5.08		
(3-isomer)	Found	69.85	5.08	50	322[a]
e	Calc.	70.85	5.53	83	199–202
	Found	70.41	5.53		
f	Calc.	73.22	5.08	78.92	197.6–199.5
	Found	73.60	5.17		
g	Calc.	74.78	6.23	72.34	180.5–183.2
	Found	74.15	6.23		

[a] Determined by d.s.c.



Scheme 3

(2) Preparation of 1,4-bis-(2,3-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 3-isomer). The tetranitrile (VIIId, 3-isomer) was converted to the corresponding tetraacid and thence to the corresponding bis(ether anhydride) using an equivalent preparation to that used for 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene.

(3) Preparation of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-amyl benzene dianhydride (IIe). After hydrolysis of tetranitrile (VIIIe) the reaction mixture was acidified to pH 1 when an oily solid precipitated. The precipitate was digested using ether (3 × 100 ml) and the combined organic solutions were dried over magnesium sulfate and evaporated to give VIe. The tetraacid was dehydrated by refluxing, as for VId, for 3 h.

(4) Preparation of 4,4'-bis-(3,4-dicarboxyphenoxy)-3,3'-di-t-butyl-1,1'-biphenyl dianhydride (IIf). Hydrolysis of tetranitrile (VIIIf) was continued for 75 h and the mixture was subsequently acidified to pH 0.5. The tetraacid (VIf) was also dehydrated by boiling for 3 h. The product, which crystallized out on cooling, was filtered off and dried to yield crude bisanhydride (IIf) which was recrystallized from 60 ml of boiling acetic anhydride to yield 12.86 g of pure IIf and an additional 5.3 g as a second crop.

Although the general procedure normally gave bis(ether anhydride)s of sufficient purity to provide high-molecular-weight polymers, in the case of anhydride (IIf), even after a further three recrystallizations, the polymers subsequently prepared had peak molecular weights of only 18–22 $\mathrm{kg\,mol^{-1}}$. To obtain polymers with very high molecular weight additional recrystallization from acetonitrile (80 ml) and acetic anhydride (10 ml) was necessary.

(5) Preparation of 1,1-bis-[4-(3,4-dicarboxyphenoxy)-2-methyl-5-t-butyl-phenyl]butane dianhydride (IIh). Hydrolysis of VIIIh was continued for 56 h after which the reaction mixture was acidified to pH 1. To dehydrate the resulting tetraacid the reaction mixture was boiled for 1 h between the addition of acetic anhydride and acetic acid, boiling was continued for a further 1.5 h. Because no product crystallized out on cooling, half the volume of solvent was distilled off after which a crystalline product formed. The crude product (IIh) was recrystallized from 20 ml of acetic anhydride.

(6) Preparation of 1,4-bis-(3,4-dicarboxyphenoxy)-2,3,5-trimethyl benzene dianhydride (IIb). Tetranitrile VIIIb was converted to the corresponding VIb and then to the corresponding bis(ether anhydride) (IIb) by the standard procedure.

Synthesis of poly(ether imide)s

All poly(ether imide)s were made according to the same two-step synthesis (*Scheme 3*) involving formation of poly(amic acid) (IX) by adding a bis(ether anhydride) (II) to a diamine (IV) in dimethylacetamide (DMAC) solution (diamines are identified in *Table 2*). Poly(amic acid)s were subsequently imidized chemically with an equivolume mixture of pyridine and acetic anhydride. Anhydrides and diamines were weighed on an analytical balance to ensure exact stoichiometry of reagents. Details of the synthesis are given for one polymer. Scales of reactions and variations for others are presented. In all cases polymer yields were essentially quantitative.

(1) Preparation of poly(ether imide) from 4,4'-diaminodiphenylether (IVA) and 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer). IVA

(0.01 mol) was dissolved in 50 ml of anhydrous DMAC in a flask fitted with a magnetic stirrer, and 0.01 mol of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer) was added in one portion at room temperature. Within 4 h the mixture became very viscous and impossible to stir with the laboratory magnetic stirrer used. To this mixture was added 5 g of anhydrous pyridine and 5 g of acetic anhydride. The mixture became opaque after 2 h; after standing for 12 h it had formed a gel which was washed three times with methanol, dried and dissolved in dichloromethane. After precipitating into methanol and drying, the yield of polymer was 6.7 g.

(2) Preparation of polymer from 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t butyl benzene dianhydride (IId, 4-isomer) and tetramethylbenzidene (IVC) (scale 1 mmol). Poly(amic acid) formation was continued with stirring at 50°C for 1 h and the mixture was then kept at room temperature for 60 h. Imidization was allowed to proceed for 3 h at room temperature. After 15 min the mixture had become a solid gel. The mixture was added to methanol, washed with methanol and dried. Precipitation from chloroform gave a lemon-coloured polymer.

In a repeated synthesis, IVC (10 mmol) was dissolved in anhydrous DMAC and (IId, 4-isomer) was added with stirring. After 1 h at room temperature the mixture was heated to 70°C for 15 min, then stirred at room temperature for 72 h. The mixture was imidized at room temperature for 12 h. The polymer was isolated from the resulting yellow gel.

(3) Preparation of polymer from 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t butyl benzene dianhydride (IId, 4-isomer) and bis-(3,5-dimethyl-4-aminophenyl)methane (IVD) (scale 1 mmol). Poly(amic acid) formation was continued at 70°C for 75 min with stirring. The mixture became clear after 1 h and was then kept at room temperature for a further 48 h. Imidization was carried out for 3 h at room temperature. The lemon-coloured solution was precipitated into methanol. The crude product was reprecipitated from chloroform.

(4) Preparation of polymer from (IId, 4-isomer) and bis-(3,5-diethyl-4-aminophenyl)methane (IVE) (scale 8 mmol). Poly(amic acid) formation was continued at 60°C for 10 h. Imidization was carried out for 2 h at 60°C. The crude product was reprecipitated from chloroform to give a pale yellow polymer.

(5) Preparation of polymer from 1,4-bis-(3,4-dicarboxyphenoxy)-2-di-t-amyl benzene dianhydride (IIe) and (IVD) (scale 0.01 mmol). Poly(amic acid) formation was carried out at room temperature for 48 h. The extremely viscous mixture was diluted with DMAC. Imidization was continued for 24 h. The product was reprecipitated from chloroform.

(6) Preparation of a polymer from IVD and 4,4′-bis-(3,4-dicarboxyphenoxy)-3,3′-di-t-butyl-1,1′-biphenyl dianhydride (IIf) (scale 1 mmol). 4,4′-Bis-(3,3-dicarboxyphenoxy)-3,3′-di-t-butyl-1,1′-biphenyl dianhydride (IIf), recrystallized from a mixture of acetonitrile (80 ml) and acetic anhydride (10 ml), was used. Poly(amic acid) formation was allowed to proceed overnight, during which time the mixture became very viscous. Imidization was continued for 4 h after which the polymer was precipitated into methanol, washed and dried to yield a yellow polymer.

(7) Preparation of a polymer from IVD and 1,1-bis-[4-(3,4-dicarboxyphenoxy)-2-methyl-5-t-butyl-phenyl]-butane dianhydride (IIg) (scale 8 mmol). During polymerization for 48 h at room temperature the viscosity increased considerably, after which the mixture was stored at 30°C for 6 h. The mixture was imidized for 5 h and then precipitated into methanol.

(8) Preparation of polymer from IVA and 1,4-bis-(3,4 dicarboxyphenoxy)-2,3,5-trimethyl benzene dianhydride (IIb) (scale 0.002 mol). The polymerization mixture became very viscous within 30 min at room temperature and was left to react overnight. On imidization the viscosity increased and the mixture remained clear, but very viscous. After 6 h the solution was precipitated into methanol. The fibrous precipitate was filtered off and dried, and reprecipitated from chloroform.

(9) Preparation of polymer from IVB and 1,4-bis-(3,4-dicarboxyphenoxy)-2,3,5-trimethyl benzene dianhydride (IIb) (scale 0.01 mol). The polymerization mixture became very viscous after 30 min. This mixture was imidized for 6 h. The very viscous solution was diluted with DMAC. The polymer was precipitated and dried.

Synthesis of copoly(ether imide)s. Copoly(ether imide)s were prepared in exactly the same manner as poly(ether imide)s except that mixtures of anhydrides or diamines were used. The following descriptions only give, therefore, the scale of reaction (based on total anhydride or diamine) and individual details of syntheses.

(1) Preparation of polymer from 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer) and a mixture of IVA and IVB. IVA and IVB (0.005 mol of each) were dissolved in DMAC. 1,4-Bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer) was added. The solution became extremely viscous within 2 h. Imidization was continued overnight to form an opaque solid gel which was washed with methanol and the product dried. The polymer was reprecipitated from dichloromethane.

(2) Preparation of a polymer from IVD and a mixture of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer) and 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA). To 0.01 mol of IVD in DMAC, 0.008 mol of 1,4-bis-(3,4-dicarboxyphenoxy)-2,5-di-t-butyl benzene dianhydride (IId, 4-isomer) was added and the mixture heated to 50–60°C for 10 min to dissolve the anhydride. Then, 0.002 mol of BTDA was added. The mixture was allowed to react for 24 h and the poly(amic acid) was imidized for 6 h. The product was reprecipitated from chloroform. The whole of the synthesis and work-up was carried out in a laboratory illuminated with inactive sodium light.

(3) Preparation of polymer from 1,4-bis-(3,4-dicarboxyphenoxy)-2,3,5-trimethylbenzene dianhydride (IIb) and a mixture of IVA and IVB (0.005 mol of each). Dianhydride (0.01 mol, IIb) was added to a solution of IVA and IVB in DMAC. After 18 h the polymer was imidized and the mixture allowed to stand for 6 h, during which time a gel formed. The gel was washed with methanol, dried, and dissolved in 100 ml of chloroform from which solution the polymer was precipitated.

Polymer characterization

Molecular weights were determined by g.p.c. using tetrahydrofuran or chloroform as eluant and an u.v. detector (flow rate 1 ml min^{-1}). The system was calibrated with polystyrene standards. The molecular weights reported correspond to the peaks of the chromatograms

Table 6 Polymers and copolymers prepared

Polymer code	Anhydride	Amine	M_p (kg mol^{-1})	Comments	T_g (°C)
1	d (4-isomer)	A	205	Insol. in NMP, sol. in $CHCl_3$ sol. in CH_2Cl_2	263
2	d (3-isomer)	A		Gel in cold NMP	265
3	d (4-isomer)	A+B	190 121		277 271
4a 4b	d (4-isomer)	C	29, 85a		267 320
5	d (4-isomer)	D	66.7, 43.5		270 272
6	d (4-isomer)	E	43.5		234
7	e	D	106		240.7
8	d+BTDA	D	50		285.3
9	f	D	42.6		272.8
10	g	D	34		240
11	b	A		Sol. in cresol, hot NMP and DMAC	245–251
12	b	B	141		272
13	b	A+B	121		277

Table 7 Mechanical properties

Polymer code	Annealing conditions[a]	Modulus (GPA)		Strength (MPa)		Comments
		Mean	Max.	Mean	Max.	
1	a	2.75	3.09	60.86	65.42	Yields
	b	3.19	3.39	101.86	104.63	Yields
3	a	2.78	3.26	68.08	71.21	Yields
	b	3.65	4.09	114.4	129.6	Yields
4/85K[b]	a	2.88	3.28	68.95	74.41	Yields
	b	3.59	3.86	94.87	102.36	Yields
5/43K[b]	a	2.19		33.91		Yields
	b					Brittle
6						Brittle
12	a	3.40	3.72	65.00	66.24	Yields
	b	2.88	3.00	116.10	123.10	Yields
13	a	3.19	3.3	70.72	72.74	Yields
	b	2.96		116.46		Yields

[a] Annealing conditions: (a) dried under vacuum; (b) annealed under vacuum at 200°C for 1 week

[b] *n*K indicates molecular weight of sample used (in g mol^{-1})

and approximately to the weight-average molecular weights. Glass transition temperatures (T_gs) were determined using a Perkin–Elmer DSC II. All characterization data are given in *Table 6*.

Physical properties

Sample preparation. Dense polymer films were prepared by solvent casting from 2 wt% solutions in chloroform. Solutions were filtered through Millipore prefilters (type AP15) into flat-bottomed Petri dishes (Anumbra). Polymer films were pretreated at 200°C under vacuum to remove residual solvent.

Tensile properties. Dumb-bells were cut from films (~0.05 mm thick) and properties were determined using a crosshead speed of 5 mm min^{-1} and a gauge length of 46 mm. Data are given in *Table 7*.

Gas permeability measurements. Gas permeabilities were measured in a gas diffusion rig, as described previously[4], by allowing gas (purity >99%) to diffuse through the membrane from known pressure to vacuum. Permeability measurements were made under steady-state conditions. Permeabilities were determined individually for hydrogen, carbon dioxide, oxygen, nitrogen and methane at applied pressures of 100 to 700 kPa. The permeability data shown in *Table 8* were determined at ~650 kPa. Details of the permeation cell are reported elsewhere[33].

RESULTS

In the early stages we found that, in accordance with literature reports, we could prepare pure bis(ether anhydride)s in very high yields from a number of simple

Table 8 Gas permeabilities

Polymer code	Membrane thickness (μm)	Permeabilities (Barrer)					Permselectivities		
		P_{CO_2}	P_{CH_4}	P_{O_2}	P_{N_2}	P_{H_2}	O_2/N_2	CO_2/CH_4	H_2/CH_4
1	40	19.0	0.874	4.51	0.914	43.3	4.9	22	50
3	57	20.9	0.918	5.33	0.964	52.1	5.5	23	57
4a	67	94.7	5.55	21.7	4.89	146.1	4.4	17	26
4b	41		6.73			175			26
5	36	48.9	2.58	12.0	2.46	100.2	4.9	19	39
6	58		3.79			69.9			18
7	67	29.3	2.04	7.03	1.78	56.3	3.9	14	28
8	78		1.81	9.28	1.89	81.8	4.9		45
9	69	29.5	1.51	8.06	1.47	68.9	5.5	20	46
12	41	7.80	0.256	2.02	0.343	24.9	5.9	30	97
13	66	5.72	0.177	1.46	0.259	20.8	5.6	32	118

bisphenols and from hydroquinone (IIIc) by *Scheme 1*. We have previously detailed the syntheses of bis(*N*-phenylphthalimide ether)s in good yield from bisphenol-A (85%), bis(4-hydroxyphenyl) ether (82%), bisphenol-P (86%) and bis(4-hydroxy-3,4-dimethylphenyl) methane (78%). However, when we attempted to apply the same procedure to a number of other hindered bisphenols, especially those with substituents *ortho* to the hydroxyl groups, and to substituted hydroquinones the yields from the nitrodisplacement reactions were often very low and the products were very impure (*Table 3*). Although, in some cases, elemental analyses were in reasonable accord with the desired compounds the products were insufficiently pure to produce bis(ether anhydride)s of the purity required to produce high-molecular-weight polymers. In many cases the diols, when reacted to form their disodium salts, gave highly coloured solutions and black products when reacted with *N*-phenylnitrophthalimide. In these cases the major products were unidentified.

However, where *Scheme 1* failed to produce pure bis(ether anhydride)s, nitrodisplacement reactions were, in many cases, satisfactorily accomplished by *Scheme 2* (*Table 4*). The tetranitriles so formed were readily hydrolysed to tetraacids and subsequently dehydrated to bis(ether anhydride)s (*Table 5*).

In all cases, the bis(ether anhydride)s described were readily converted into high-molecular-weight polyimides (see later). The satisfactory synthesis of high-molecular-weight polymers is the best proof that pure bis(ether anhydride)s, free of monoanhydride which would act as an endcap, had been prepared. The synthesis of pure bis(ether anhydride) is facilitated by the synthesis of pure tetranitriles, free from any dinitrile produced by nitrodisplacement at one -OH group of the diol. It is much easier to purify the tetranitrile than the tetraacids or bis(ether anhydride)s produced subsequently. Purification of the tetranitrile is the most important step in synthesizing monomers and producing high-molecular-weight polymers.

We note, however, that not all diols undergo nitrodisplacement satisfactorily according to *Scheme 2*. In particular, some bisphenols with bulky substituents *ortho* to the hydroxyl group, especially with methylene bridging groups, i.e. IIi and IIj, failed to undergo nitrodisplacement satisfactorily. While IIIj fails to undergo nitrodisplacement, 4,4′-dihydroxydiphenyl-(3-methyl-5-t-butyl) propane (IIIh) satisfactorily undergoes nitrodisplacement to form a tetranitrile, implicating the role of the bridging moiety. In addition, IIIi, which also has a methylene bridge, does not undergo displacement and neither does IIIk. It is easy to attribute failure to undergo nitrodisplacement to steric restrictions generated by the bulky *ortho* substituents. However, steric restrictions are not the sole origin of these difficulties with nitrodisplacement, as evidenced by a comparison of IIIj and IIIh.

We have demonstrated that both IIIl and IIIm (*Table 4*) undergo nitrodisplacement according to *Scheme 2*, albeit with low yield. Steric restrictions are identical with those involved in the above failures. Also, it has recently been reported that 2,2-bis-(3,5-di-t-butyl-4-hydroxyphenyl) propane and IIIk will undergo fluorodisplacement with bis-(4-fluorophthalimide) derivatives, to form the equivalent ether linkage to phthalic acid residues[18]. Although relatively poor yields in the nitrodisplacement reactions and the formation of low-molecular-weight polymer in the fluorodisplacement polymerizations suggest that the displacement reactions are not efficient, at least they are not totally impossible on steric grounds. We will discuss the reasons for some bisphenols failing to undergo nitrodisplacement more fully in a subsequent paper which will deal with a broader study of nitrodisplacement reactions.

Synthesis of tetraacids and bis(ether anhydride)s

In all cases where tetranitriles (VIIId–h) were successfully prepared, the tetraacids and bis(ether anhydride)s were also readily obtained in good yield (*Table 5*). The standard procedures described above generally gave bis(ether anhydride)s of sufficient purity to produce high-molecular-weight polymers. However, in the case of VIf further recrystallization of the bis(ether anhydride) from acetonitrile was required prior to polymer synthesis.

Synthesis of poly(ether imide)s and copoly(ether imide)s

A selection of the possible poly(ether imide)s derived from the new bis(ether anhydride)s with hindering substituents were prepared without any attempt being made to produce materials with optimum permeability or mechanical properties. Polymers were prepared by the two-stage process outlined in *Scheme 3*, described above in detail for the polymer derived from bis(ether anhydride) (IId) and diamine (IVA) . The diamines used are listed in *Table 2*. Polymer preparation involved reacting a bis(ether anhydride) (II) with a diamine (IV) in solution in *N*-methylpyrrolidinone (NMP) or DMAC, to form the poly(amic acid) (IX), and then dehydrating with an acetic anhydride/pyridine mixture to form the poly(ether imide) (I). In the synthesis of copolymers either a bis(ether anhydride) was added to a solution of a mixture of diamines or a mixture of bis(ether anhydride)s was added to a solution of the diamine.

The molecular weights of the polymers and copolymers prepared are given in *Table 6*.

Physical and mechanical properties

The T_gs of the several polymers prepared are given in *Table 6* and their mechanical properties are summarized in *Table 7*. In considering the properties of the polymers prepared in this work it is instructive to compare the data with those we reported previously for a series of isomeric poly(ether imide)s, several of which also carried bulky (methyl) groups to hinder rotation about the linkages between the several aromatic residues. In making the comparisons it should be noted that some of the polymers prepared in this study have relatively low molecular weights (<80 kg mol^{-1}) and for such polymers it is possible that properties are slightly molecular-weight dependent.

In our previous study we found that poly(ether imide)s, based on similar structural units and with no hindering groups on aromatic residues in positions *ortho* to the bonds linking those residues to the phthalimide unit, had T_gs below 250°C. Incorporation of hindering methyl groups (two at each link to the phthalimide residue), in either the diol or diamine residues, increased T_g to 260–300°C. (It has been reported by others that incorporation of two methyl groups *ortho* to the link to the carbonate residue in bisphenol-A polycarbonate increases T_g by 40°C[34]). We also observed that if both residues had two hindering groups *ortho* to the links to the phthalimide residues T_gs were not less than 420°C. In this study, we note that most of the polymers studied have T_gs between 230°C and 285°C, although even bulkier hindering groups are present. Langsam and Burgoyne also found that one t-butyl group linked *ortho* to phthalimide residues raised the T_gs less than did two *ortho* methyl groups, even though the t-butyl group has a greater volume than two methyls[35]. Thus, the work of Langsam and Burgoyne[35], our previous results and the results of this study show a common pattern in that bulky substituents *ortho* to links to phthalimide residues, in either anhydride or amine moieties, increase T_gs and that two methyl groups have more effect than one t-butyl group. Bulky groups in anhydride residues have more effect than in amine residues as restrictions on rotation in amine residues has less influence on conformational changes[4].

Polymers 12 and 13, based on diol (IIIb) with diamines (IVA) and (IVB), respectively, have T_gs of $\sim$270°C, which are in accord with those reported previously. In these polymers there are three hindering methyl residues per two ether linkages and no groups hindering rotation about the amine link to the imide ring.

Other polymers have much bulkier pendent groups, i.e. t-butyl. The major groups of these polymers have anhydride residues (IId), based on di-t-butyl hydroquinone, and IVA and/or IVB or IVD diamine units and these have T_gs of $\sim$270°C. For polymer 4, which has a rigid biphenyl unit in the diamine residue (associated also with pendent methyl groups), T_g is higher, while for polymer 6 the diamine unit (IVE) reduces T_g. The lower T_g for 6, compared with 5, results from the presence of pendent ethyl residues which, although bulky, are flexible; flexible side groups are well known to reduce T_gs in other systems. Polymer 7, which has IIIe and IVD residues, is isomeric with 6 (IIId and IVE) and has a slightly higher T_g, possibly because the added bulk of the t-amyl residues in the anhydride raises T_g more than the equivalent added bulk in amine residues; both t-amyl and ethyl will impart some side-chain flexibility as well as bulk. Polymer 10, which has a flexible pendent n-butyl group, has a relatively low T_g; its T_g may be in the molecular-weight-dependent region. In contrast, polymer 9, which has only two t-butyl groups but a rigid biphenyl residue, has a T_g in line with other polymers.

It is noticeable that polymers with diol residues IIIb and IIId have generally similar T_gs although the bulk of the latter is greater. Also, none of the polymers have T_gs as high as some of those observed previously for polymers with only pendent methyl residue. One difference between the polymers prepared in this study and the previous ones is that in the earlier polymers there were always two hindering residues per link to the phthalimide residues. In these polymers there is often only one, or at least one link with one bulky group adjacent to the ether linkages. These observations are consistent with space-filling molecular models which show that two methyl groups *ortho* to the ether link act like a claw and lock the adjacent phenyl rings orthogonal to each other, while one t-butyl residue permits the phenyl rings to change their relationship to each other and also allows further conformational changes through rotations about the ether linkage of $\sim$120°. Thus, polymers with one t-butyl group adjacent to ether linkages are much more flexible than those with two *o*-methyl groups.

In examining the mechanical properties of the polymers it was found that only those polymers with molecular weight (M_p) of >80 kg mol^{-1} yield under tension, especially after annealing at 200°C for some time. Only polymers 1 and 3 have mechanical properties comparable with those of the commercial poly(ether imide) Ultem 1000 but all polymers have respectable tensile properties.

Gas permeabilities

A major aim of the current study was to investigate the influence of bulky substituents, especially t-butyl groups *ortho* to the ether linkages to the phthalimide residues in poly(ether imide)s, on gas permeabilities. Permeabilities to methane, carbon dioxide, hydrogen, nitrogen and oxygen were determined for a number of the polymers prepared and the results are summarized in *Table 8* together with selectivities for several common gas separations.

It is relevant to compare the data presented here with data from other polymers with hindering residues, prepared and treated under comparable conditions, which we reported recently and which include polymers with some common groupings[4] and with the data on other polymers reviewed by Koros *et al.*[1] and by Robeson[2].

One feature of the data reported here is the high gas permeabilities achieved for glassy polymers; data for polymer 4, in particular, are at the higher end of the range for glassy polymers quoted in the review by Koros

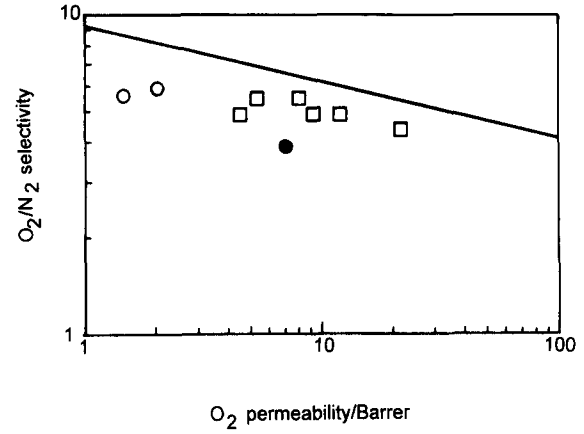


Figure 1 Comparison of permselectivities in oxygen/nitrogen separations with oxygen permeability for poly(ether imide)s prepared in this study and having methyl substituents (○), t-butyl substituents (□) or flexible (amyl) substituents(●) with the upper-bound relationship, defining best known performance, taken from Robeson[2]

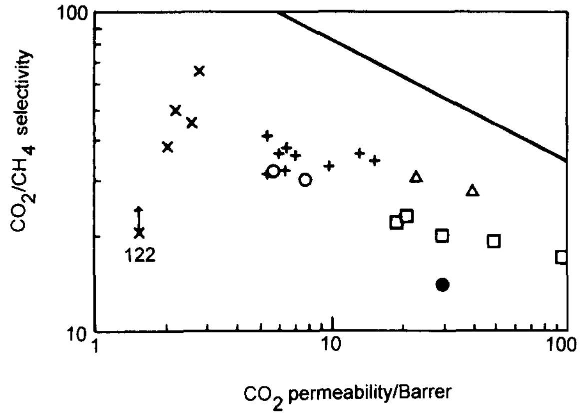


Figure 2 Comparison of permselectivities in carbon dioxide/methane separations with carbon dioxide permeability for poly(ether imide)s prepared in this study and having methyl substituents (○), t-butyl substituents (□) or flexible (amyl) substituents (●) with the upper-bound relationship, defining best known performance, taken from Robeson[2]. Data from a previous study[4] for poly(ether imide)s having no hindering substituents (×), methyl substituents in either anhydride or diamine moiety (+) and methyl substituents in both moieties (△) are included

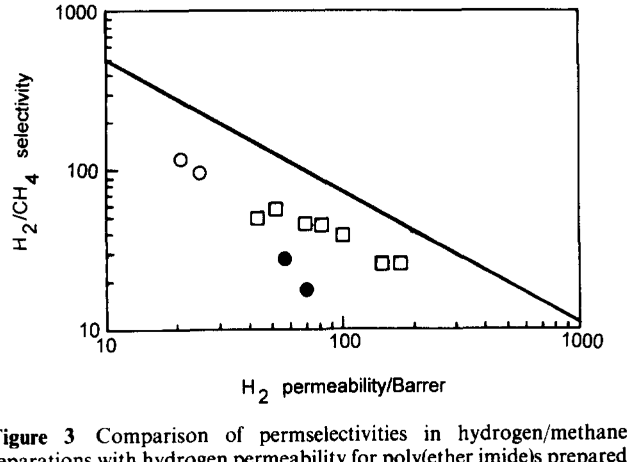


Figure 3 Comparison of permselectivities in hydrogen/methane separations with hydrogen permeability for poly(ether imide)s prepared in this study and having methyl substituents (○), t-butyl substituents (□) or flexible (amyl or ethyl) substituents (●) with the upper-bound relationship, defining best known performance, taken from Robeson[2]

et al.[1] and in the review by Robeson[2], for glassy polymers with selectivities for CO_2/CH_4 separations of $> \sim 10$.

Data presented in this paper are consistent with data for most other polymer groups in showing a general trade-off between high permeability and high selectivity. There are few data in the literature on permeabilities through glassy polymers with bulky substituents but, in our previous paper, we noted a strong tendency for polymers with multiple hindering (methyl) residues to have similar permselectivities (of ~ 30 or even higher and coupled with carbon dioxide permeabilities of >6 barrer) for carbon dioxide–methane separations. All polymers studied in this paper have hindering residues but the data do not consistently show such high selectivities.

A distinction between our previous results and the current data is that in the previous study all aromatic residues were bisphenols and all hindered units had two methyl groups *ortho* to each linkage to the phthalimide residues. In this study the emphasis is on the presence of t-butyl groups (on bisphenols or hydroquinone residues) or multiple methyl substituents on hydroquinone residues as hindering groups in the anhydride moiety; most polymers with t-butyl residues have only one hindering group per link to phthalimide residues. Thus, while some hindering residues are bulkier than used previously, in some measure rotation around links to the phthalimide residues is less hindered, as discussed above.

It is useful to compare the data presented here with the upper-bound relations for various gas pairs reported previously[2]. The upper-bound performances were determined from an analysis of the gas separation literature[2] and represent target 'benchmarks' for each gas pair where the trade-off between permeability and selectivity is pushed to the limits of known performance. *Figures 1, 2* and *3* compare data for O_2/N_2, CO_2/CH_4 and H_2/CH_4 separations, respectively, for the polymers synthesized here with the reported upper bounds.

Whilst the performances of these poly(ether imide)s are unimpressive for H_2/CH_4 and, especially, for CO_2/CH_4 separations, when compared with the upper bounds for O_2/N_2 separations the properties are more attractive. Polymer 9 is especially attractive, coming closest to the upper bound with an oxygen permeability of 8 Barrer and O_2/N_2 selectivity of 5.5.

Figures 1–3 show that for the set of poly(ether imide)s studied here the data are self-consistent, showing the usual trade-off between permeability and selectivity. All polymers show the same sequence of permeabilities for gases used as the abscissa in *Figures 1–3*. Relative selectivities vary a little for different separations. Poly(ether imide)s 6 and 7 show less favourable permselectivities, presumably because of the presence of more flexible pendent groups, namely ethyl in polymer 6 and t-amyl in polymer 7. The former shows the lowest selectivity for H_2/CH_4 separations.

Data from our previous study are incorporated into *Figure 2* and together with data from this study show distinct trends for related series of polymers for CO_2/CH_4 separations. The polymers with no hindering substituents have low CO_2 permeabilities, but one polymer has by far the highest selectivity and approaches the 'upper bound' most closely. Polymers with hindering substituents have higher permeabilities but, amonst these polymers, those with hindering methyl substituents, in either the anhydride or diamine residue, have higher selectivities than those with tertiary alkyl substituents such as t-butyl and especially t-amyl in the anhydride residue, whether or not there are methyl groups in the diamine residue. The best combination of permeabilities and selectivities are found for polymers prepared previously with pairs of *o*-methyls in both residues. It would now be interesting to determine if the enhanced selectivity of polymers with several methyl substituents is maintained in oxygen/nitrogen separations when excellent performances may become available.

Previously we found the linear relationship:

$$P_{CO_2} = (26.58 \pm 0.74) P_{CO_4} + (1.93 \pm 0.41)$$

between carbon dioxide and methane permeabilities for polymers with hindering residues[4], giving an approximate selectivity for CO_2/CH_4 separation of ~30. In this study permselectivities of this magnitude are obtained only for polymers 12 and 13 which have trimethylhydroquinone residues, i.e. hindering methyl groups, and for which the absolute permeabilities are comparable with those observed previously. (Polymers prepared previously which had higher permselectivities but lower absolute permeabilities had no hindering groups.) Polymers 12 and 13 have hindering groups only in the anhydride residues and in those units there are two hindering groups *ortho* to one of the links to the phthalimide residues.

Most polymers investigated in this study have one t-butyl (or t-amyl) group *ortho* to each link to the phthalimide residue, with or without hindering methyl groups in the diamine residue. As a group these polymers also exhibit similar selectivities, of ~20, for CO_2/CH_4 separations, in some cases this permselectivity is coupled with particularly high permeability.

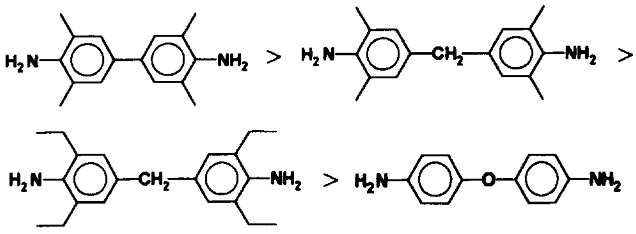
Thus, it is only those polymers with the lower permeabilities which have the high selectivities seen previously in other polymers with hindering residues. There appears to be a clear distinction between polymers with two *o*-methyl groups (high selectivity) and single *o*-t-butyl groups (high permeability) in the anhydride moiety (*Figure 2*). To obtain high permeabilities with a selectivity of 30 requires hindering groups in both residues; a polymer with the diol unit equivalent to IIC and diamine unit equivalent to IVD had a permeability to CO_2 of 40 Barrer with a selectivity of 27.3. Polymers with t-butyl residues, on the other hand are, as a group, associated with lower selectivities, although capable of having higher permeabilities. We conclude from these comparisons that the distribution of pore sizes in the two groups of polymers is different.

In our previous paper we identified a tendency for polymers with multiple methyl substituents to have both high T_g and high permeability, while maintaining good permselectivity in gas separation[4]. We attributed this combination of properties to inefficient packing of stiff, kinked polymers with limited conformations generating relatively large numbers of small pores; the large number of pores provides good permeability and the pore-size distribution gives good selectivity. The same trend is apparent in this study for polymers with multiple methyl substituents on hydroquinone residues in the anhydride moiety (polymers 12 and 13).

Other results from this study are consistent with single t-butyl groups preventing efficient packing of the polymer chains, so as to leave a sufficiently high concentration of pores to provide good permeability, but that the greater chain flexibility modifies chain packing in some way such that the distribution of pore sizes limits selectivity.

For the polymers with t-butyl substituents investigated in this study there is no obvious trend between high T_g and high permeability, although polymer 4 which, in addition to t-butyl groups, has hindering methyl groups on a rigid diamine moiety, has the highest permeability and the highest T_g observed for this group of polymers. Thus, preliminary indications are that polymers with one very bulky (and possibly flexible) substituent adjacent to phthalimide residues are more flexible and have lower T_gs but the substituents restrict packing to provide a structure with many pores, to impart high permeability, but with a size distribution which limits permselectivity. Ethyl and t-amyl groups give low T_gs and low selectivities (polymers 6 and 7).

Clearly, polymers with t-butyl groups in the bis(ether anhydride) residues and hindering methyls in the diamine residues have particularly high permeabilities. Comparing poly(ether imide)s based on bis(ether anhydride) (IId, 4-isomer), gas permeabilities vary with the diamine moiety (IV) according to the sequence:



where rigidity combined with *o*-methyl substituents is seen to produce the highest permeability.

CONCLUSIONS

It has been established that nitrodisplacement with nitrophthalodinitrile provides a more versatile route to new bis(ether anhydride)s than does nitrodisplacement with nitrophthalimide. Nitrodisplacement with nitrophthalodinitrile readily permits the incorporation of substituted hydroquinone, naphthalene and hindered bisphenol residues into bis(ether anhydride)s and poly(ether imide)s. Intervention of an alternative reaction to nitrodisplacement limits bis(ether anhydride) synthesis from diols with very severe steric constraints. Thus, poly(ether imide)s with bulky substituents and with good thermal and mechanical properties can be synthesized. Molecular weights in excess of $80\,kg\,mol^{-1}$ ensure that polymers are not brittle but yield under tension.

Polymers with very bulky substituents have high gas permeabilities. While very bulky (e.g. t-butyl) groups can give very high permeabilities, multiple methyl substituents, especially in anhydride residues, can provide higher permselectivities for gas separation. Selectivities in carbon dioxide/methane separations are ~20 for poly(ether imide)s with t-butyl substituents and ~30 for polymers with multiple methyl substituents; polymers without hindering substituents may have higher selectivities but have low permeabilities. t-Butyl groups give polymers with lower T_gs than do multiple methyl substituents, and flexible substituents give even lower T_gs and reduced selectivities in gas separations. Differences in thermal properties and permeabilities between polymers with t-butyl and multiple methyl substituents are understandable in terms of chain flexibility; methyl substituents enhance chain rigidity. Thermal property and gas permeability data from this and a previous study[4] indicate that specific structural features strongly influence structure–property relations in poly(ether imide)s; their influences cannot yet be quantified sufficiently to predict properties.

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