# Synthesis of bulky bis(ether anhydride)s and poly(ether imide)s with bulky main-chain units[†]

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A series of bis(ether anhydride)s has been synthesized from very bulky bisphenols. Poly(ether imide)s have been synthesized from these bis(ether anhydride)s and two diamines in order to provide a series of poly(ether imide)s with bulky main-chain units. The polymers have been characterized in terms of molecular weight, solubility, glass-transition temperature and thermal stability in order to identify a series of high-performance polymers which are processable and potentially useful for applications which require soluble poly(ether imide)s for fabrication into, for example, gas separation membranes.

Polyimides are now well established as high-performance polymers with a number of applications including microchip encapsulation, films and membranes.[1] Their lack of solubility requires that they are normally applied as poly(amic acid) intermediates which are subsequently imidized. There have been many attempts to produce more soluble and processable alternatives. A successful development was the commercial poly(ether imide) Ultem;[2] the incorporation of main-chain ether linkages imparts solubility and melt processability. Subsequently, several groups have atttempted to produce other members of this family (1) in order to further enhance processability and tailor properties for specific applications; in 1, Ar is an aromatic unit derived from an aromatic diol and species 1 are usually derived from a bis(ether anhydride), formed by a reaction sequence involving nitro displacement between the diol and a suitable nitrophthalic acid derivative (often a nitrophthalodinitrile), and a diamine. Approaches which have been used to enhance solubility include incorporating substituent groups on Ar and/or Ar′ groups and changing the susbstitution patterns of aromatic residues.[3–6]

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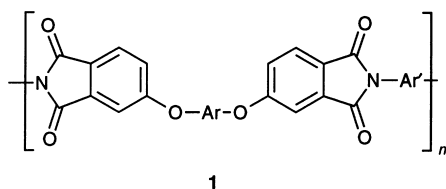
One of the main potential applications of poly(ether imide)s is as membranes for gas separation, which requires the polymers to be soluble for fabrication into hollow-fibre, asymmetric membranes. Two factors are important in producing optimum membrane properties. The polymers must show good permeability of gases and good selectivity in gas separation. It has long been recognised that bulky groups enhance gas permeability.[7] Amongst other studies by various groups, we have demonstrated a pattern of substituent type on selectivity.[5,8] We found that groups which were bulky enhanced gas permeability while substituents which reduced main-chain rotation enhanced selectivity. These factors together probably decrease the efficiency of chain packing and bulky, stiff units, which are probably difficult to pack in an efficient manner, appear to impart favourable properties.

Because a combination of bulky units and chain rigidity might enhance both permeability and selectivity in gas separation, we have investigated the possibilities of introducing

inherently rigid, bulky main-chain units into poly(ether imide)s. To this end we have identified a number of available bulky diols **2a–e** and have investigated their abilities to undergo nitro displacement reactions with 4-nitrophthalodinitrile and thus be converted into bis(ether anhydride)s **5a–e** (Scheme 1). We have also undertaken a preliminary assessment of the abilities of the anhydrides to undergo polymerization with diamines (Scheme 2) to produce processable poly(ether imide)s which might have useful properties for specific applications. Here we describe the results of these studies and report on the glass-transition temperatures, molecular weights, solubilities, thermal stabilities and colour of these polymers.

There has, over many years, been considerable interest in polymers containing moieties derived from adamantane and the literature has been reviewed.[9] Recent papers have reported polyimides,[10] poly(ether ketone)s,[11] polyphenylenes[12] and polybenzoxazoles.[13] One reason for interest in such polymers is the inherent thermal and chemical stability of the adamantane unit. This report includes the synthesis of poly(ether imide)s with main-chain adamantane-1,3-diyl units and their preliminary characterization. More recently we prepared a series of poly(ether imide)s with pendant adamantyl units, and the properties of these polymers and a comparison with polymers with main-chain units will be reported separately.[14]

Experimental

Diols (and their sources) used to prepare bis(ether anhydride)s were: 4,4′-(adamantane-1,3-diyl)diphenol **2a** (Aldrich), 6,6′-dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichromane **2b** (TCI), 1,1′-bi-2-naphthol **2c** (Aldrich), 4,4′-bicyclo[2.2.1]heptane-2,2-diyldiphenol **2d** and 4,4′-tricyclo[5.2.1.0^{2,6}]decane-8,8-diyldiphenol **2e**; the latter two diols were gifts from Kodak Ltd. 4-Nitrophthalodinitrile was obtained from TCI, 4,4′-oxydianiline was an ultrapure sample from BP. *m*-Phenylenediamine (Fluka) was sublimed prior to use. Other solvents and reagents used were obtained from sources specified previously and were used as supplied.

Diols were reacted with 4-nitrophthalodinitrile in dimethyl sulfoxide (DMSO) solution in the presence of anhydrous potassium carbonate at room temperature to produce bis(ether dinitrile)s **3a–e**,[15] exactly as described in previous publications.[5,6] Reactions were typically performed using 10 mmol of diol and 20 mmol of 4-nitrophthalodinitrile and were continued for 24 h. Products were isolated by pouring reaction mixtures into water and washing the products with methanol. Similarly, the bis(ether dinitrile)s were hydrolysed to bis(ether diacid)s **4a–e** with potassium hydroxide, isolated and then dehydrated to bis(ether anhydride)s **5a–e** with glacial acetic
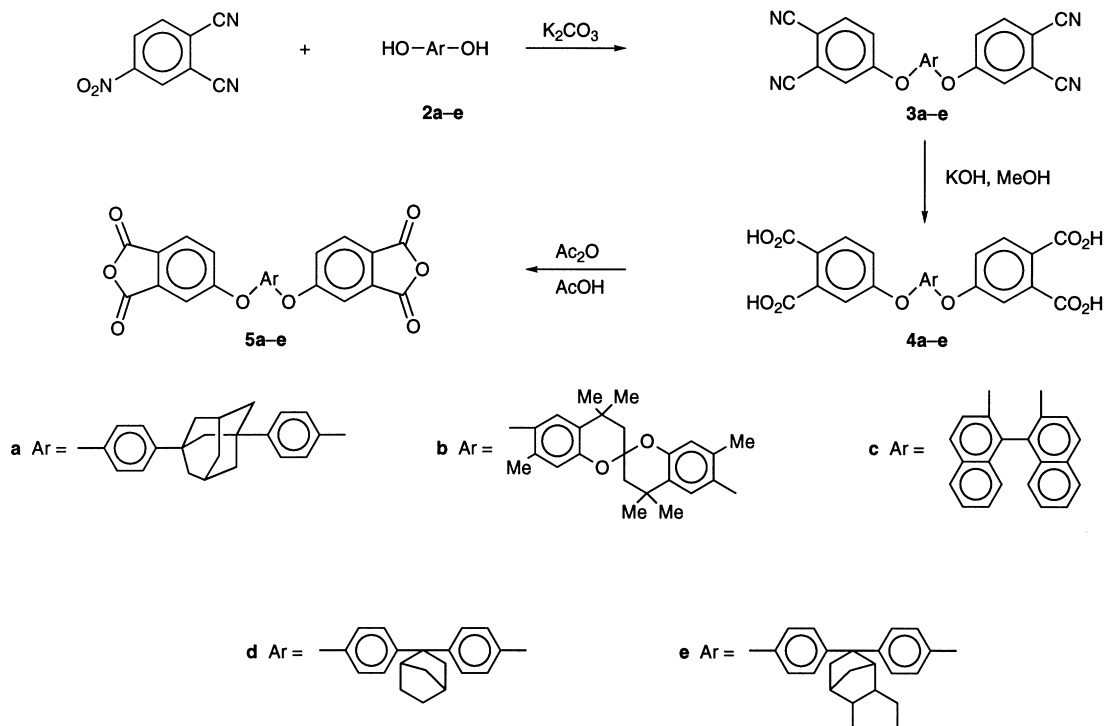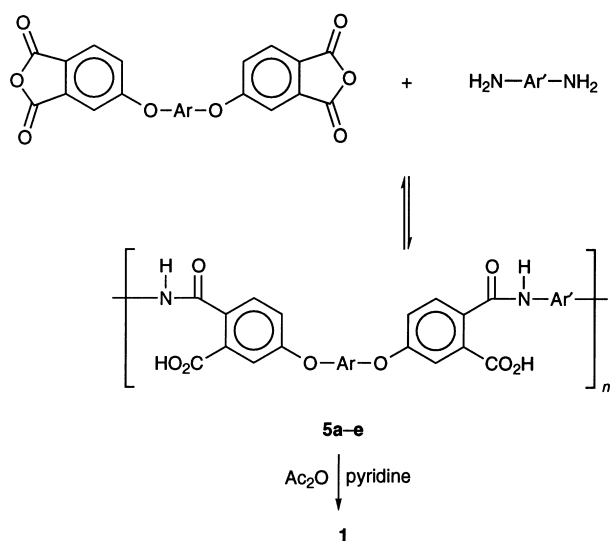
Scheme 1

Scheme 2

acid and acetic anhydride as described previously; these procedures are summarized in Scheme 1. Elemental analysis data for the bis(ether dinitrile)s and bis(ether anhydride)s, together with their melting points and yields, are given in Tables 1 and 2, respectively.

Poly(ether imide)s were prepared from the bis(ether anhydride)s in a two-stage process involving initial formation of poly(amic acid) by reaction with diamine in N-methylpyrrolidone (NMP) or N,N-dimethylacetamide (DMAC) and subsequent chemical imidization with an acetic anhydride–pyridine mixture (1:1, v/v) as described in previous publications and summarized in Scheme 2.[5,6]

Molecular weights were determined by gel-permeation chromatography using DMF–1 M LiCl as eluent, PL-gel polystyrene columns and polystyrene standards (both from Polymer Laboratories) with refractive index detection (Knauer detector). Glass-transition temperatures were determined using a Perkin-Elmer DSC2 differential scanning calorimeter. Thermogravimetric analysis (TGA) was undertaken on Perkin-

Elmer Series 7 instruments. Measurements were made under nitrogen at The Leverhulme Centre for Innovative Catalysis, University of Liverpool, with a heating rate of $40\,^\circ$C min^{-1}, samples were annealed for 6 h at $170\,^\circ$C *in vacuo*, and in air at The University of Sussex with a heating rate of $10\,^\circ$C min^{-1}.

Results and Discussion

All diols **2a–e** satisfactorily underwent nitro displacement reaction with 4-nitrophthalodinitrile according to Scheme 1 to give pure bis(ether dinitrile)s **3a–e** in good yield. The elemental analysis data for the bis(ether dinitrile)s are given in Table 1. Each bis(ether dinitrile) was readily hydrolysed by potassium hydroxide to its corresponding bis(ether acid) **4** which was isolated. The bis(ether acid)s were not characterized but were directly dehydrated to the bis(ether anhydride). The bis(ether anhydride)s **5a–e** were characterized by elemental analyses and melting points, supported by spectrocopy; details of elemental analyses, yields and melting points, together with the solvents used for recrystallization, are reported in Table 2.

In order to test the feasibility of preparing poly(ether imide)s from the several bis(ether anhydride)s, each bis(ether anhydride) was reacted with one or two aromatic diamines [usually *m*-phenylenediamine (MPD) and 4,4′-oxydianiline (ODA)] in NMP or DMAC, to prepare poly(amic acid)s which were then chemically imidized with an acetic anhydride–pyridine mixture. After precipitation into methanol, the poly(ether imide)s were boiled with methanol in order to remove residual NMP. Where soluble in NMP–1 M LiCl, the molecular weights of the poly(ether imide)s were determined and in all cases the glass-transition temperatures of the polymers were measured by differential scanning calorimetry. The results are reported in Table 3.

It is noticeable that the glass-transition temperatures (T_g) of the polymers are almost independent of the diamine used and are dominated by the bis(ether anhydride) structure; in several series of poly(ether imide)s, derived from various diphenols or dihydroxyphenylenes, those based on ODA have glass-transition temperatures about $10\,^\circ$C lower than those based on MPD. We previously noted a reduced dependance of T_g on diamine structure in poly(ether imide)s based on

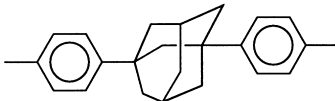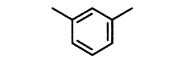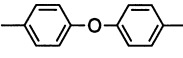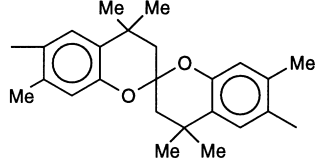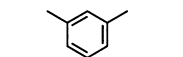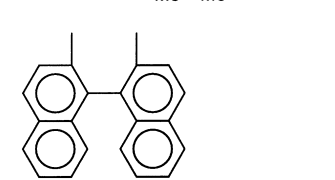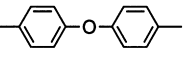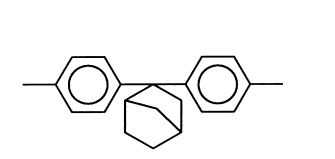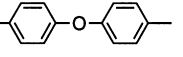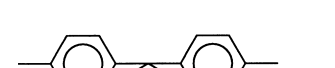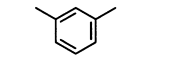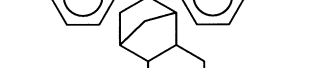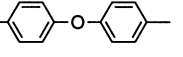**Table 1** Synthesis of bis(ether dinitrile)s

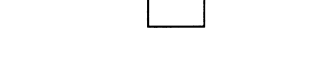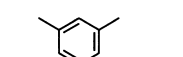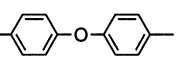| bis(ether dinitrile)		elemental analysis			recrystallization solvent	yield (%)		mp/°C
		C	H	N		pure	crude	
3a	Calc.	79.72	4.89	9.79	MeCN	87	96	188–189
	Found	79.68	4.86	9.84				
3b	Calc.	75.46	5.19	9.02	MeCN	87	98	276–277
	Found	74.60	5.30	9.02				
3c	Calc.	80.28	3.36	10.03	MeCN–MeOH	79	99	253–254
	Found	80.18	3.36	10.08				
3d	Calc.	78.93	4.54	10.51	MeCN–MeOH(1:2)	78	91	197–198
	Found	79.00	4.51	10.56				
3e	Calc.	79.60	4.92	9.78	MeCN	95	—	143–145
	Found	79.66	4.92	9.75				

Table 2 Synthesis of bis(ether anhydride)s

bis(ether anhydride)		elemental analysis		recrystallization solvent	yield (%)	mp/°C
		C	H			
5a	Calc.	74.50	4.60	Ac$_2$O	73	184–186
	Found	74.53	4.59			
5b	Calc.	70.90	4.88	Ac$_2$O–MeCN	87	290–291
	Found	70.27	4.80			
5c	Calc.	74.73	3.13	Ac$_2$O	88	221–222
	Found	73.64	3.05			
5d	Calc.	73.42	4.54	Ac$_2$O	95	111–112
	Found	73.33	4.22			
5e	Calc.	74.50	4.60	Ac$_2$O–MeCN	85	168–169
	Found	74.60	4.59			

Table 3 Properties of polymers

Ar	Ar′	M^w/kg mol^{-1}	T_g/°C
		119	255
		106	253
		83	271
		122	268
		—	254
		—	250
		98	248
		52	255
		70	253

naphthalene-derived bis(ether anhydride)s.[16] When used for practical gas separation membranes it is necessary for polymers to operate at high temperatures and the glass-transition temperatures of the polymers based on bulky anhydrides are consistent with use for this purpose. It is anticipated that polymers with significantly higher glass-transition temperatures could be prepared by polymerization of the bis(ether anhydride)s with rigid diamines, especially those with hindering substituents *ortho* to the phthalimide unit; we anticipate that glass-transition temperatures in excess of 300 °C can readily be achieved.

In general the polymers had little colour. Those based on MPD were essentially colourless and did not discolour when heated in air to temperatures up to 250 °C. In addition, all polymers were soluble in chloroform and, when prepared from such solutions, solvent-cast films were creasable and did not fracture and hence had useful mechanical properties; mechanical properties have not yet been determined. The low colour is consistent with reduced interchain interactions between *N*-phenylphthalimide units which, in turn, is indicative of less efficient chain packing, due to the bulky nature of the units close to the phthalimide residues. The units could prevent close approach of phthalimide units and could give rise to high permeability for gas separation membranes.

Of relevance to potential applications is the thermal stabilities of the polymers. Thermal stabilities of the polymers prepared from the bis(ether anhydride)s **5a**, **b**, **d** and **e** with MPD by DTA have been examined under a nitrogen atmosphere by TGA. The results are presented in Fig. 1 which shows that all the polymers have good thermal stability. The data in Fig. 1 exaggerate the true stabilities of the polymers beause the heating rate used was 40 °C min^{-1}. In comparison, data obtained with the same polymer based on **2a** (in air) at a heating rate of 10 °C min^{-1} showed the same shape of thermogram but initial decomposition started at 405 °C. Nevertheless, the data in Fig. 1 provide comparative data for the samples investigated and show the patterns of behaviour on thermal decomposition. Initial decomposition of all samples occurs at a similar temperature with decomposition of the polymer based on adamantane starting to decompose at a slightly lower temperature; similar initial decomposition temperatures probably indicate a common mode of chain scission, *e.g.* at the ether linkage to the phthalimide; polyimides which do not have such ether linkages, *e.g.* Kapton, are more stable. All samples show decomposition in two stages, in common with many other data on related polymers. Decomposition of the polymer based on spirobichromane is somewhat distinctive in showing a rapid loss of 30 wt% over a relatively small temperature rise; this step is probably indicative of a mode of decomposition associated with the spirobichromane moiety rather than the aromatic structures common to all the polymers and other

poly(ether imide)s. Loss of 30% does not correspond to loss of the total diol unit or to its central aliphatic structure. Rather, the weight loss corresponds approximately to loss of one substituted chromane unit per repeat, which might be eliminated following scission of an aryl ether linkage adjacent to the phthalimide unit.

Conclusions

It has been demonstrated that 4,4′-(adamantane-1,3-diyl)diphenol **2a**, 6,6′-dihydroxy-4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichromane **2b**, 1,1′-bi-2-naphthol **2c**, 4,4′-bicyclo-[2.2.1]-heptane-2,2-diyldiphenol **2d** and 4,4′-tricyclo- [5.2.1.0^{2,6}]-decane-8,8-diyldiphenol **2e** all undergo nitro displacement with 4-nitrophthalodinitrile to give bis(ether dinitrile)s which can be converted to bis(ether anhydride)s. The bis(ether anhydride)s react with aromatic diamines to give poly(ether imide)s with bulky main-chain units which are soluble in chloroform and are processable from solution in chloroform or aprotic solvents. Where soluble in DMF–1 M LiCl, the molecular weights of the polymers were determined and the polymers were shown to have high molecular weight; molecular weights of polymers based on **5c** and ODA and **5d** and MPD were not determined because of their insolubility in the medium used. The polymers have little colour and those based on MPD are virtually colourless. Glass-transition temperatures are in the range 240–270 °C and the polymers based on MPD show good thermal stability.

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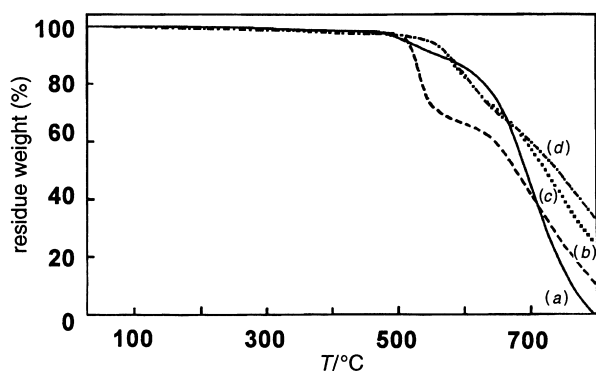16 G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, 1996 **6**, 1459.

Fig. 1 Thermogravimetric analysis data for poly(ether imide)s based on bis(ether anhydride)s (*a*) **5a**, (*b*) **5b**, (*c*) **5d** and (*d*) **5e** with MPD, heating rate 40 °C min^{-1}, nitrogen atmosphere