Polyimides with main-chain ethylene oxide units: synthesis and properties

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Abstract

This paper describes the synthesis of a new series of well-defined bis(ether anhydride)s based on ethylene oxide sequences of known length (up to six ethylene oxide units) with phthalic acid anhydride end-caps, and extends the synthesis of bisphenoxyamines based on ethylene oxide sequences to six ethylene oxide units. The dianhydrides and diamines were used in combination to synthesize a series of segmented polyimides of well-defined structures having defined sequences of from zero up to six ethylene oxide units separated by *N*-phenylphthalimide units. The polymers are characterized in terms of solubility, thermal stability, thermal transition behaviour, including crystal melting behaviour; glass-transition temperatures vary systematically with structure and composition. One polymer exhibits liquid crystallinity. The water absorption characteristics of the polymers, which vary from a hydrophobic aromatic polyimide to polymers containing up to 52.7 wt% ethylene oxide, were determined. The crystal melting behaviour is discussed in conjunction with data from other segmented polyimides containing similar structural units. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide; Poly(ethylene oxide); Segmented

We recently described the synthesis and selected properties of hydrophilic graft and segmented polyimides [1,2]. The polymers investigated had, in most cases, hydrophilic moieties of high-molecular-weight (>600 g mol^{-1}) based on poly(ethylene oxide) (PEO). These polyimide copolymers, which had high contents of hydrophilic units, exhibited a number of interesting properties. Several of them were highly flexible and elastomeric and some were water soluble [1]. When investigated for membrane applications, as additives in polyimide membranes, the polymers exhibited hydrophilic surfaces and reduced protein adsorption [2]. In many respects the segmented polyimides exhibited properties more familiar in segmented polyurethanes. However, the PEO components were based on commercial Jeffamine® mono-functional and di-functional aliphatic amines and problems were encountered in the synthesis and characterization of the copolymers. Graft copolymers were prepared by reacting preformed polyimides, functionalised with pendant carboxy groups, with Jeffamine mono-amines; it was not possible to characterize these polymers accurately with any certainty. There was also some uncertainty in the composition and molecular weights of the Jeffamine diamines used to form segmented polyimides by reaction

with dianhydrides and subsequent imidization. Both sets of Jeffamines had relatively broad molecular weight distributions which led to further uncertainty over the detailed structures and composition of the polyimides.

It was therefore decided to prepare a family of segmented polyimides with well-defined hydrophilic components. The new polyimides described here have PEO sequences in both the dianhydride and diamine moieties and have generic structure (**I**); the diamines used had terminal aromatic units to avoid problems previously identified with some
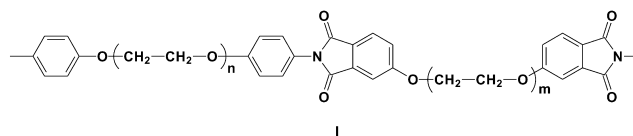
aliphatic amines [1]. Polyimides with PEO units in the diamine moieties have been prepared previously by De Visser et al. [3] by Feld et al. [4,5] and by Harris and coworkers [6–8] who all used short-chain PEO diamines. De Visser et al. linked the PEO units from poly(ethylene glycol)s to phenylamine groups through ester linkages [3]. Subsequently, Feld et al. used poly(ethylene glycols) with exact numbers (up to four) EO units and attached the phenylamine groups to them through ether linkages, using a nitro-activated fluorodisplacement reaction and subsequent reduction of the nitro groups to amines, Scheme 1. We

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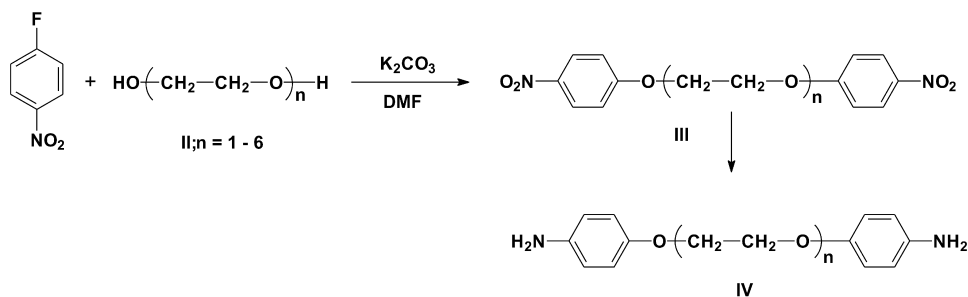
Scheme 1.

have now used these fluorodisplacement reactions to extend the synthesis to PEO sequences up to six (n) EO units. In addition, and to synthesize species **I**, we applied cyano-activated nitrodisplacement reaction to incorporate PEO sequences of up to six (m) EO units into dianhydrides, Scheme 2. Then, by using different combinations of PEO-containing dianhydrides and diamines, we prepared segmented polyimides **I** in which n and m were varied independently to give polyimides with from zero to exactly twelve ($n + m$) EO units per repeat unit of the polymer, Scheme 3. This approach provided a family of 49 possible polyimides with absolutely defined structures and with properties varying from those of a conventional and previously known aromatic polyimide ($n = m = 0$) [9,10] to those of PEO with regular distributions of main-chain *N*-phenylphthalimide units. It was possible to adopt this approach because dihydroxy-terminated poly(ethylene glycol)s with up to six EO units are available commercially as pure compounds. Longer hydroxy-terminated PEO species are only available as oligomeric PEOs with distributions of molecular weights. The decision to restrict this study to pure species was made on the basis of potential implications on the development of *meso*-phase structures in the final polymers.

In this paper, we record the synthesis and characterization of the additional diamines with longer PEO units, describe the synthesis and characterization of new dianhydrides with PEO sequences, and their bis(ether dinitrile) intermediates, and the synthesis of the segmented polyimides **I** derived from them. Also described here are the equilibrium water

contents (EWCs) of the polymers, their thermal transition behaviours, and preliminary observations on their crystallinity and liquid crystalline behaviour. More details of the solid-state and liquid crystalline structures developed in these and related materials will be reported separately in conjunction with data for polymers prepared from the PEO-based diamines and commercial or other aromatic dianhydrides.

1. Experimental

1.1. Materials

4-Nitrophthalodinitrile was obtained from TCI, 4-fluoronitrobenzene from Fluorochem and ethylene glycols and other reagents were obtained from Aldrich.

1.2. Synthesis of poly(ethylene oxide) dinitroderivatives (III)

Following a similar procedure to that of Feld et al. [4,5] we prepared diamines based on PEO with terminal aromatic amine functions according to Scheme 1; reaction conditions were identical to those used previously to prepare aromatic bis(ether amine)s from aromatic diols [11]. Mixtures of 1 mol equivalent of poly(ethylene glycol) (**II**) and 2.2 mol equivalents of 1-fluoro-4-nitrobenzene were refluxed in *N,N*-dimethyl formamide (DMF) solution in the presence of anhydrous potassium carbonate for 3–4 h; toluene or xylene were used to remove water azeotropically and to

Scheme 2.

IV; n = 0 - 6   +   VII; m = 0 - 6
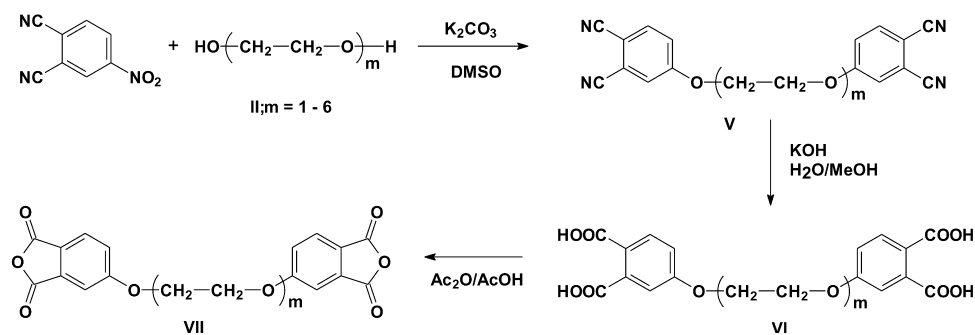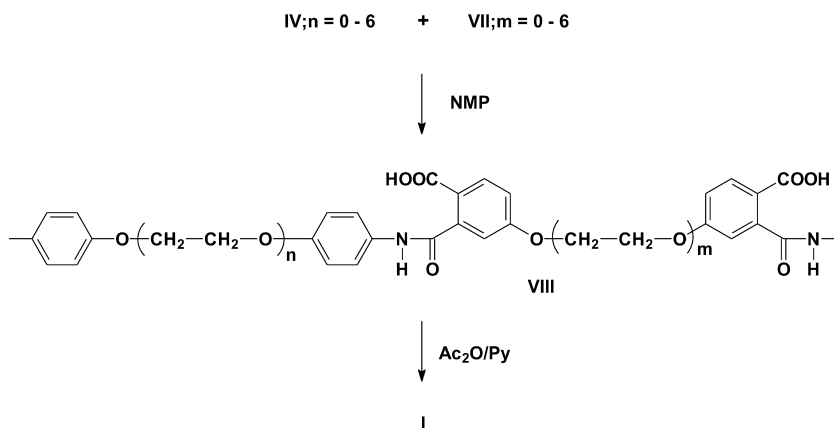
Scheme 3.

adjust the boiling point to 130–135 °C. Reaction mixtures were subsequently poured into cold water and the solid products were recrystallized. The fluorodisplacement reactions proceeded with yields in excess of 90%. Characterization data for previously described species **III**; $n = 1$–4 were almost identical with those reported previously. Designation of atoms as used in NMR analysis are identified in structures **IIIa** (X = NO$_2$) and **IVa** (X = NH$_2$).

1.2.1. 1,2-Bis(4-nitrophenoxy)ethane III; n = 1.

Yield 86%, recrystallized from toluene; mp 148.8–149.3 °C (lit.: 148–149 [4,5], 147 °C [12]).

1.2.2. Bis[2-(4-nitrophenoxy)ethyl]ether III; n = 2.

Yield 90%, recrystallized from ethanol/toluene; mp 156–157 °C (lit.: 155–156 [4,5], 154–157 °C [13]).

1.2.3. 1,2-Bis[2-(4-nitrophenoxy)ethoxy]ethane III; n = 3.

Yield 89%, recrystallized from ethanol; mp 96.5–97.5 °C (lit.: 96–97 °C [4,5]). ^{1}H NMR (CDCl$_3$), δ: 8.19 (m, 2H H(2), H(6), $J_{2,3} = 9.25$ Hz), 6.97 (m, 2H H(3), H(5)), 4.23, 3.91 (mm, 4H H(7),H(8), AA$'$BB$'$), 3.77 (s, 2H H(9)); ^{13}C NMR (CDCl$_3$), δ: Calc: C(1) 140.8, C(2), C(6) 124.7, C(3), C(5) 115.0, C(4) 165.7; Found: C(1) 141.98, C(2), C(6) 126.26, C(3), C(5) 114.95, 115.22, C(4) 164.2, C(7) 68.55, C(8) 69.84, C(9) 71.31.

1.2.4. Bis{2-[2-(4-nitrophenoxy)ethoxy]ethyl}ether III; n = 4.

Yield 83%, recrystallized from ethanol/water; mp 76–77 °C (lit.: 62–64 °C [4,5]).

1.2.5. 1,2-Bis{2-[2-(4-nitrophenoxy)ethoxy]ethoxy}ethane III; n = 5.

Yield 80.3%, recrystallized from ethanol; mp 91–92 °C. Elemental analysis: calcd for C$_{22}$H$_{28}$N$_2$O$_{10}$: C 55.00%, H 5.87%, N 5.83%; found: C 54.96%, H 5.87%, N 5.81%. ^{1}H NMR (CDCl$_3$), δ: 8.19 (m, 2H H(2), H(6), $J_{2,3} = 9.27$ Hz), 6.98 (m, 2H H(3), H(5)), 4.22, 3.89 (mm,

4H H(7), H(8), AA$'$BB$'$), 3.72, 3.67 (mm, 4H H(9), H(10), AA$'$BB$'$), 3.66 (s, 2H H(11)); ^{13}C NMR (CDCl$_3$), δ: Calc: C(1) 140.8, C(2), C(6) 124.7, C(3), C(5) 114.5, C(4) 163.7; Found C(1) 141.6, C(2), C(6) 125.8, C(3), C(5) 114.5, C(4) 163.8, C(7) 68.2, C(8) 69.3, C(9) 70.5, C(10) 70.58, C(11) 70.9. Accurate mass calcd for C$_{22}$H$_{29}$N$_2$O$_{10}$ [M + H$^+$]: 481.18222 Da; found (FAB): 481.18317 Da.

1.2.6. Bis(2-{2-[2-(4-nitrophenoxy)ethoxy]ethoxy}ethyl)-ether III; n = 6.

Yield 80% recrystallized from ethanol; mp 63–64 °C. Elemental analysis: calcd for C$_{24}$H$_{32}$N$_2$O$_{11}$: C 54.95%, H 6.14%, N 5.34%; found: C 54.86%, H 6.16%, N 5.34%. Accurate mass, calcd for C$_{24}$H$_{33}$N$_2$O$_{11}$ [M + H]$^+$: 525.20844 Da; found (FAB): 525.20965 Da.
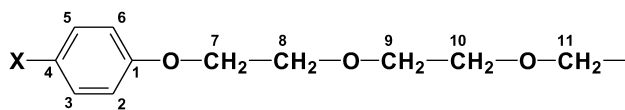
IIIa (X =NO$_2$) ,   IVa (X = NH$_2$)

1.3. Synthesis of poly(ethylene oxide) diamines (IV)

Dinitro compounds (**III**) were reduced to the corresponding diamines (**IV**) by a procedure described in detail previously [11]. Compounds **III** were dissolved/suspended in ethanol and 10%Pd/C was added to the boiling solution followed by dropwise adition of hydrazine monohydrate. After refluxing for 3 h the products were isolated by pouring into water. The products were subsequently recrystallized from small volumes of ethanol. Characterization data for previously known diamines were identical with literature data.

1.3.1. 1,2-Bis(4-aminophenoxy)ethane IV; n = 1.

Yield 88.5%, mp 178.4–179 °C (lit. 179–180 °C [4,5], 176 °C [14]).

1.3.2. Bis[2-(4-aminophenoxy)ethyl] ether **IV**; *n* = 2.
Yield 85%, mp 59.3–60.3 °C (lit. 59–60 °C [4,5]).

1.3.3. 1,2-Bis[2-(4-aminophenoxy)ethoxy]ethane **IV**; *n* = 3.
Yield 87.6%, mp 92.2–92.6 °C (lit. 93–95 °C [4,5]). ^{1}H NMR (CDCl$_3$), δ: 6.75 (m, 2H H(3), H(5), $J_{2,3}$ = 8.8 Hz), 6.61 (m, 2H H(2), H(6)), 4.04, 3.81 (mm, 4H H(7), H(8), AA$'$BB$'$), 3.73 (s, 2H H(9)), 3.42 (s, 2H, NH$_2$); ^{13}C NMR (CDCl$_3$), δ: Calc: C(1) 139.6, C(2), C(6) 116.2, C(3), C(5) 115.0, C(4) 150.1; Found C(1) 140.1, C(2), C(6) 116.2, 116.5, C(3), C(5) 115.8, 115.9, C(4) 151.8, C(7) 68.1, C(8) 69.9, C(9) 70.7.

1.3.4. Bis{2-[2-(4-aminophenoxy)ethoxy]ethyl}ether **IV**; *n* = 4.
Yield 92%, this product was obtained as a viscous oil as reported in the literature [4,5]. Elemental analysis: calcd for C$_{20}$H$_{28}$N$_2$O$_5$: C 63.81%, H 7.49%, N 7.44%; found: C 63.51%, H 7.78%, N 7.48%.

*1.3.5. 1,2-Bis{2-[2-(4-aminophenoxy)ethoxy]ethoxy}ethane* **IV**; *n* = 5.
Yield 94.4%, mp 54–55 °C. Elemental analysis: calcd for C$_{22}$H$_{32}$N$_2$O$_6$: C 62.83%, H 7.67%, N 6.66%; found: C 62.33%, H 7.78%, N 6.55%. Accurate mass calcd for C$_{22}$H$_{32}$N$_2$O$_6$ 420.22604 Da; found for M$^+$ (FAB) 420.22699 Da.

1.3.6. Bis(2-{2-[2-(4-aminophenoxy)ethoxy]ethoxy}ethyl)-ether **IV**; *n* = 6.
Yield 98.6%, mp 56–57 °C. Elemental analysis: calcd for C$_{24}$H$_{36}$N$_2$O$_7$: C 62.05%, H 7.81%, N 6.03%; found: C 62.12%, H 7.88%, N 6.05%. Accurate mass calcd for C$_{24}$H$_{36}$N$_2$O$_7$ 464.25226 Da; found from EI$^+$ mass spectrum (solid probe): 464.25156 Da.

1.3. Synthesis of poly(ethylene oxide) bisphthalodinitrile derivatives (V).

The bisphthalodinitrile derivatives (**V**) of the PEO oligomers, used in synthesis of the corresponding bisphthalic anhydrides (**VII**) and hence in syntheses of polyimides, were prepared by a cyano-activated nitrodisplacement reaction (Scheme 2), as described previously for the synthesis of aromatic bis(ether dinitrile)s [15]. Thus, 2 mol equivalents of 4-nitrophthalodinitrile were dissolved in DMSO to which 1 mol equivalent of poly(ethylene glycol) and anhydrous potassium carbonate were added. Mixtures were allowed to react overnight at room temperature under a nitrogen atmosphere after which an additional 10% 4-nitrophthalodinitrile and potassium carbonate were added and reaction was continued for another 6 h. Products were isolated by pouring reaction mixtures into large volumes of iced water. After washing, the products were recrystallized. Where necessary, products were decolourised prior to recrystallization. The results of the syntheses and some characterization data are presented in Table 1. Samples **V**; *n* = 3, **V**; *n* = 4 were further characterized by NMR. Designations of atoms used in NMR analysis are identified in structure **Va**.
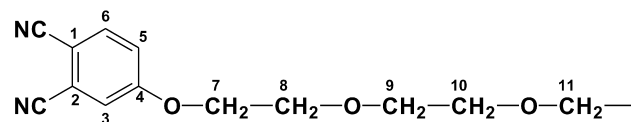
Va

Data for **V**; *n* = 3 are ^{1}H NMR (CDCl$_3$), δ: 7.71 (d 1H H(6), $J_{5,6}$ = 8.8 Hz), 7.32 (d, 1H H(3), $J_{3,5}$ = 2.6 Hz), 7.22 (dd, 1H H(5)), 4.24, 3.89 (mm, 4H H(7), H(8), AA$'$BB$'$), 3.72 (s, 2H H(9)); ^{13}C NMR (CDCl$_3$), δ: Calc: C(1) 99.0, C(2) 117.7, C(3) 118.3, C(4) 164.4, C(5) 118.6, C(6) 134.1;

Table 1
Synthesis and characterization of bisphthalodinitriles **V** derived from poly(ethylene glycol)s **II**

Diol	Elemental analysis (%)				Accurate mass (Da)	Yield (%)	M.Pt (°C)
II*n*		C	H	N			
1	Calcd	68.78	3.20	17.82		40	230–231
	Found	68.38	3.12	18.19			
2	Calcd	67.03	3.93	15.63		61^a	147–148
	Found	66.88	3.88	15.86			
3	Calcd	65.66	4.5.0	13.92	402.13281	13	167–169
	Found	65.54	4.50	13.98	402.13276		
4	Calcd	64.56	4.96	12.54	464.19339^b	–^{c}	110–115
	Found	645.34	4.94	12.77	464.19461^b		
5	Calcd	63.66	5.34	11.42		56^a	105–109^d
	Found	63.47	5.32	11.38			
6	Calcd	62.91	5.65	10.48		42	Oil
	Found	62.98	5.63	10.55			

^{a} Caesium carbonate used as base.
^{b} Quasi-molecular ion [M + NH$_4$]$^+$ confirmed; chemical ionisation using NH$_3$ reagent gas.
^{c} Not recorded.
^{d} Possible clearing temperature for liquid crystalline phase 116 °C.

Table 2
Variation in reaction conditions for synthesis of poly(ethylene glycol) bisphthalodinitriles **V**

Diol **II**n	Temp. (°C)	Solvent	Base added	Time (h)	Yield (%)	Green dye	Comments[a]
1	20	DMSO	K_2CO_3	24	40	N	Decol., 2
1	20	HMPA	Na salt of diol	2.5	76	Y	Decol., 2
1	4	HMPA	Na salt of diol	5	96	N	1
2	20	DMSO	Cs_2CO_3	24	61	Y[b]	Decol., 1
3	20	DMSO	K_2CO_3	24	13	Y	Decol., 2
3	20	DMSO	K_2CO_3	48[c]	47	Y	Decol., 2
4	20	DMSO	K_2CO_3	24	–	Y	3
4	105	DMSO	K_2CO_3	12	42	Y	Decol., 3
4	20	DMSO	Cs_2CO_3	20	53	Y	Decol., 2
5	20	DMSO	Cs_2CO_3	48	56	Y	Decol., 2
6	20	DMSO	K_2CO_3	52	42	Y	Decol., 0
6	8	DMSO	K_2CO_3	4	68	Y	Decol., 0
6	20	DMSO	Cs_2CO_3	48	47	Y	Decol., 2

[a] Indicates whether decolourization was necessary and number of subsequent recrystallizations needed to obtain a pure product.

[b] Green dye isolated as crystalline product.

[c] Half of 4-nitrophthalodinitrile added initially and half after 24 h.

Found: C(1) 107.6, C(2) 117.4, C(3), C(5) 119.6, 119.8, C(4) 161.9, C(6) 135.2, C(7) 68.6, C(8) 69.4, C(9) 70.9, CN 115.2, 115.6. Data for **V**; $n = 4$: ^{1}H NMR (CDCl$_3$), δ: 7.71 (d 1H H(6), $J_{5,6} = 8.7$ Hz), 7.32 (d, 1H H(3) $J_{3,5} = 2.6$ Hz), 7.22 (dd, 1H H(5)), 4.24, 3.88 (mm, 4H H(7), H(8), AA′BB′), 3.70, 3.66 (mm, 4H H H(9), (10), AA′BB′); ^{13}C NMR (CDCl$_3$), δ: Calc: C(1) 99.0, C(2) 117.7, C(3) 118.3, C(4) 164.4, C(5) 118.6, C(6) 134.1; Found: C(1) 107.5, C(2) 117.4, C(3), C(5) 119.6, 119.8, C(4) 162.0, C(6) 135.2, C(7) 68.6, C(8) 69.3, C(9) 70.6, C(10) 71.0, CN 115.3, 115.6.

Subsequent to converting species **V** into anhydrides **VII** and using these in polymer syntheses, a few experiments were conducted in an attempt to improve the yields of **V**. In different experiments the reaction temperature or the added base were changed. The results of these experiments are recorded in Table 2.

1.3.1. Nitrodisplacement reactions in hexamethyl-phosphoramide (HMPA)

In addition to using **II** as reactant (Scheme 2), a small number of experiments were performed in which **II** was first converted to its disodium salt in hexamethylphosphoramide and then reacted with 4-nitrophthalodinitrile. Thus, 60% sodium hydride (0.84 g, 20 mmol plus an small excess) was washed with hexane under a nitrogen atmosphere. HMPA (20 ml) was added followed by ethylene glycol (0.62 g, 10 mmol). The mixture was stirred for 40 min at 40 °C and then cooled to about 4 °C; the mixture solidified at lower temperatures. 4-Nitrophthalodinitrile (3.6 g, 20 mmol plus excess) was added to the disodium salt and the mixture was stirred for 5 h at 4 °C, after which it was poured into ~150 ml water, filtered, washed twice and dried to yield 3.0 g of **III**; $n = 1$, yield 95.5%; reaction at 20 °C gave a less pure product Table 2. A sample for elemental analysis was recystallized from acetonitrile to give a product melting point 230–231 °C; elemental analysis: calcd

for C$_{18}$H$_{10}$N$_4$O$_2$: C 68.78%, H 3.20% N 17.82%; found: C 68.86%, H 3.18%, N 18.04%.

1.4. Synthesis of bisphthalic anhydride derivatives (VII) of poly(ethylene glycol)s

Bisphthalodinitriles **V** were converted into dianhydrides (**VII**) by hydrolyzing the nitrile functions to carboxylic acids (**VI**) and dehydrating to form **VII**, Scheme 2. The procedures adopted were exactly the same as those used to hydrolyse aromatic bis(ether dinitrile)s and to dehydrate the tetraacids [15]. Thus, species **V** were suspended in equivolume mixtures of a 50 wt% aqueous solution of potassium hydroxide and methanol. After refluxing, until evolution of ammonia had ceased, solutions were diluted with deionised water and acidified to pH 1.5–2 with concentrated hydrochloric acid. The solids **VI** were washed until neutral and dried. Intermediates **VI** were not characterized in detail but were immediately dehydrated to **VII** by refluxing in equivolume mixtures of acetic anhydride and glacial acetic acid for 30 min and left to cool when the dianhydrides **VII** crystallized from solution. The products were isolated and characterized. The results are given in Table 3.

1.5. Synthesis of segmented polyimides

Segmented polyimides were prepared by a standard two-stage procedure in which **IV** and **VII** were reacted together in exactly equimolar proportions in an aprotic solvent, normally *N*-methylpyrrolidinone (NMP), to give poly(amic acid)s (**VIII**) which were then dehydrated with equivolume mixtures of acetic anhydride and pyridine, Scheme 3. The polymer-forming reaction was allowed to proceed overnight to give viscous solutions of **VIII**. Imidization reactions were normally allowed to proceed for several hours after which polymers **I** were isolated by precipitation into methanol.

Table 3
Synthesis and characterization of bisphthalic anhydrides **VII** derived from poly(ethylene glycol)s **II**

Diol **II**n	Elemental analysis			Accurate mass (Da)	Yield (%)	M.Pt (°C)
		C%	H%			
1	Calcd	61.02	2.84		86	215–216
	Found	60.63	2.71			
2	Calcd	60.30	3.54		97	156–157
	Found	60.18	3.52			
3	Calcd	59.73	4.10	442.09000	86	126–127
	Found	59.40	4.07	442.08935		
4	Calcd	59.26	4.55		70	97–99
	Found	59.23	4.56			
5	Calcd	58.86	4.94		100	84–85
	Found	57.71	5.03			
6	Calcd	58.53	5.26		100	Oily resin
	Found	56.29	5.03			

1.6. Polymer and monomer characterization

Molecular weights of polymers **I** were determined by gel permeation chromatography using an instrument based on polystyrene PL-gel columns calibrated with polystyrene standards (Polymer Laboratories), Knauer pump (flow rate 1 ml min^{-1}) and refractive index detector. The mobile phase was NMP/LiCl (0.1 M). Thermal transition temperatures were determined with the aid of a Perkin Elmer DSC2 using a heating rate of 20 °C min^{-1} to determine glass-transition temperatures and lower rates of heating and cooling, typically 2.5 or 10 °C min^{-1}, to determine crystal melting and crystallization temperatures, respectively; maximum temperatures employed were 420 °C. Thermal transition behaviour in an optical polarizing microscope was investigated with the aid of a Mettler heating stage. Thermogravimetric analysis was performed using a Perkin Elmer 7 Series thermal analysis system with a heating rate of 20 °C min^{-1} in air. NMR spectra were recorded on a Bruker AMX-400 spectrometer. X-ray diffractograms were obtained with the aid of a Hiltonbrooks DG2 powder diffractometer. Accurate masses were confirmed using a VG7070E magnetic sector mass spectrometer.

In order to determine equilibrium water contents (EWCs) of the polymers, films of polymers were cast from chloroform solutions by slow evaporation and were subsequently dried in a vacuum oven. Equilibrium water contents were determined by soaking weighed samples in water for 24 h, or to constant weight, drying them by contacting with absorbent paper and weighing again. EWC was calculated as:

$$EWC = \frac{\text{Wt. wet film} - \text{Wt. dry film}}{\text{Wt. dry film}} 100.$$

2. Results and discussion

The synthesis of established ($n = 1 - 4$) and new ($n = 5, 6$) dinitro compounds **III** and corresponding diamines **IV** proceeded with high yields. Where previously known dinitro compounds and diamines were prepared the characterization data were essentially identical with previously reported data; NMR data are consistent with the less-detailed data reported previously [4,5], see Section 1. The new dinitro compounds **III**; $n = 5, 6$ and diamines **IV**; $n = 5, 6$ were prepared in high yields exactly as the previous compounds; their characterization data are recorded in Section 1.

In order to prepare **VII** with ethylene oxide sequences, cyano-activated nitrodisplacement reactions between the appropriate **II** and 4-nitrophthalodinitrile were undertaken. The same reaction conditions (with potassium carbonate as base) when used with aromatic dihydroxy compounds gave virtually quantitative yields of bis(ether dinitrile)s in most cases. In contrast, yields of **V** from **II** were poor, normally less than 60%; caesium carbonate was used with **II**; $n = 2$. In addition, the quality of the crude products **V** was inferior and it was normally necessary to decolourise and recrystallize them several times to obtain pure products; purification at this stage helps in the synthesis of pure **VII** necessary to achieve high-molecular-weight polyimides. A feature of these reactions was the formation of a green impurity, assumed to be a green dye. The formation of such impurities occurs infrequently in the synthesis of bis(ether dinitrile)s from aromatic diols under the same reaction conditions and there is no obvious set of circumstances which determines their formation. However, with aliphatic diols the green compound(s) was formed in almost all cases, apart from reaction with diol **II**; $n = 1$; the impurities were readily removed with decolourising charcoal.

Compounds **V** were hydrolysed to **VI** and dehydrated to **VII** according to Scheme 2. These reactions proceeded in high yield to give pure **VII** suitable for the synthesis of polyimides.

Although the dianhydrides **VII** prepared as described above were used successfully in the synthesis of polyimides

I, some additional experiments were performed in attempts to improve the yields of **V**, Table 2. An elevated reaction temperature (105 °C) did not improve the situation. Reduction of the reaction temperature from 20 to 8 °C with **II**; $n = 6$ gave a higher yield of purer product in a shorter time; presumably the occurrence of side reactions was reduced.

Replacing potassium carbonate by caesium carbonate had little influence on the results obtained with **II**; $n = 4, 6$. In the case of **II**; $n = 3$ it was possible to isolate the green impurity as a crystalline solid but no attempt was made to characterize it; it was possibly a phthalocyanine compound.

As an alternative to using the hydroxy compounds themselves in displacement reactions, it is common practice to use the alkali metal salts. The disodium salt of **II**; $n = 1$ was prepared in HMPA and was reacted with nitrophthalodinitrile. Data in Table 2 show that these reaction conditions gave higher yields of products, especially at temperatures below ambient; reaction at 4 °C gave a 96% yield of a product with no green impurity and which only required recrystallizing once. These reaction conditions offer potentially higher yields of purer products but at the risk of using a more hazardous solvent.

Lower members of the series of tetranitriles show some tendency for odd–even effects in their melting points; odd members have relatively high melting points superimposed on a general decline as molecular weight and EO content increase. **V**; $n = 5$ exhibited some unusual melting and crystallization behaviour. The sample appeared to melt at ~105 °C but optical microscopy showed the sample to remain birefringent. Optical microscopy and DSC showed a further transition at 116 °C with a further loss of order and blackout under crossed polars. The behaviour was similar to that expected from a liquid crystalline substance with a clearing temperature of 116 °C; without further investigation true liquid crystallinity is not claimed. **V**($n = 6$) could not be crystallized and was only obtained as an oil.

The yields of **VII** quoted in Table 3 are those of pure crystalline products, except for **VII**; $n = 6$ which was obtained as an oily resin which could not be crystallized. The melting points of **VII** did not show any odd–even effects.

Combining the different diamines and dianhydrides prepared with different values of n and m, leads to a potential family of 49 different polyimides. Most, but not all, of the possible combinations of **IV** and **VII** available were used in the syntheses of polymers **I**. The different combinations of **IV** and **VII** lead to a series of polymers which are essentially PEOs with different contents of polyimide moieties distributed through the polymers in a regular manner. Thus, **I**; $n = m = 0$ is a conventional aromatic polyimide. As EO units are introduced into **IV** and **VII** then the polymers steadily take on more PEO character. As n and m increase a series of isomeric polymer structures (identical values of $n + m$) are developed. Thus, **I**; $n = 1, m = 0$ is isomeric with **I**; $n = 0, m = 1$. With larger

numbers of EO units in the different moieties a larger number of isomers are possible. Thus, **I**; $n = 6, m = 0$, **I**; $n = 5, m = 1$, **I**; $n = 4, m = 2$, **I**; $n = 3, m = 3$, **I**; $n = 2, m = 4$, **I**; $n = 1, m = 5$, and **I**; $n = 0, m = 6$, are all isomers ($n + m = 6$) and are essentially PEO within which *N*-phenylphthalimide units are distributed differently; they all have an average of one *N*-phenylphthalimide unit per three EO units. It is therefore of interest to examine how the polymer properties vary with both overall composition and with detailed structure.

Polymer syntheses from various combinations of **IV** and **VII** usually led to very viscous solutions of **VIII**, indicating formation of high-molecular-weight polymer. Where polymers had suitable solubility in DMF/LiCl (0.1 M), the eluant of choice, molecular weights were determined by GPC. Several polymers had high molecular weights confirming that their monomers were synthesized to high purity. A polymer from dianhydride **VII**; $m = 6$ had low molecular weight, possibly reflecting lack of purity of the monomer which could not be crystallized. It was generally more difficult to prepare pure **VII** than **IV** from the same **II**.

The polymers prepared demonstrated a variety of properties according to their differing molecular structures. Thus **I**; $n = m = 0$ was a conventional insoluble aromatic polyimide while **I**; $n = m = 6$ was a very soft hydrophilic material. The range of solubilities is illustrated in Table 4 which shows a grid defining the polymer structures in terms of values of n and m; Table 4 also defines the polymers synthesized. Isomeric polymers having identical values of $(n + m)$ and, hence, the same EO content lie on lines of unit slope through the grid. As might be anticipated, the more highly aromatic polymers are largely insoluble. As the EO content increases, the solubility tends to increase, and polymers become soluble in less powerful solvents. Thus, species **I** with small numbers of EO units per repeat are soluble in the aprotic solvent NMP while those with large numbers of EO units are also soluble in chlorform. Table 4 shows that polymers **I** with EO units only in the dianhydride moiety are more soluble than their isomers with EO units in the diamine moiety only; such polymers are also more hydrophilic, see later. **I**; $n = 1, m = 2$ formed thermally reversible gels in NMP.

Lack of solubility of some polymers restricted their characterization, in terms of molecular weight, and their film-forming capabilities. The viscosities of solutions of their intermediates **VIII** indicated the formation of high-molecular-weight polymers in general and this was borne out in highly viscous solutions of the soluble polymers. The film-forming characteristics of the polymers are given in Table 4 in parentheses. Lack of solubility in a readily removable solvent such as chloroform restricted film formation from polymers with high aromatic contents, while low T_gs resulted in soft polymers at high EO contents. In some cases rather poor quality films were formed which might have been a result of limited solubility and crystallization (described later). Poor film formation was not a

Table 4
Solubilities, properties of cast films and molecular weights (in parentheses, kg mol^{-1}) of segmented polyimides **I** according to the numbers of ethylene oxide units in diamine (n) and dianhydride (m) moieties

m	n						
	0	1	2	3	4	5	6
0	i	i	i	i	NMPh	NMPh	NMPw
	aa	–	–	–	–	–	Opaque(93)
1	NMP	i	NMP	s(128)	s(44)	s(112)	s(87,104)
	−99	–	−62	–	Poor	Good	Good
2	s(79)	NMP,trg	NMP	s(113)	s(37)	s(105)	s(95)
	Poor	–	−51	Good	Good	–	Good
3	NMP	NMPw	s	s	s	s	s
	−(24)	–	Good	Good	Good	Good	Good
4	s	NMP	s(66)	s(87)	s	s(67)	s(95)
	–	−95	Good	Good	Good	Good	Good
5		s		s	s	s	s
		–		Good	Good	Poor	Poor
6	s	s(18)		s			s
	Uncastable	Poor, trg		Too soft			V. poor, soft, tacky

i: indicates insoluble in NMP and other solvents; NMP: indicates solubility in cold NMP; NMPh: indicates solubility in hot NMP; NMPw: indicates solubility in warm NMP; s: indicates solubility in NMP and chloroform; trg: indicates a thermally reversible gel; aa: castable only from poly(amic acid) solution.

consequence of low molecular weight (except possibly polymers from **VII**; $m = 6$) as all components were sufficiently pure that they gave high-molecular-weight polymers in least some combinations.

Thermal transition behaviours of polymers **I** vary markedly with detailed structure. Thus, polymer **I**; $n = m = 0$, reported previously [9,10], is an amorphous polyimide with a typically high glass-transition temperature while **I**; $n = m = 6$ is an amorphous, very flexible material at room temperature. Values of the glass-transition temperatures (T_gs) of most polymers prepared were determined by differential scanning calorimetry (DSC) with the results

shown in Table 5. For some of the highly aromatic polyimides no T_g was observed, probably because the thermal transition was weak. For the remainder of the polymers **I** there was a general overall trend of T_g with polymer composition; values of T_g decreased as the EO content increased. While the individual values of T_g observed are recorded in Table 5, the smooth trend with structure is shown graphically in Fig. 1.

As the overall T_g data show a systematic trend with composition, it is of interest to examine if there is any quantitative relationship between the values. The various
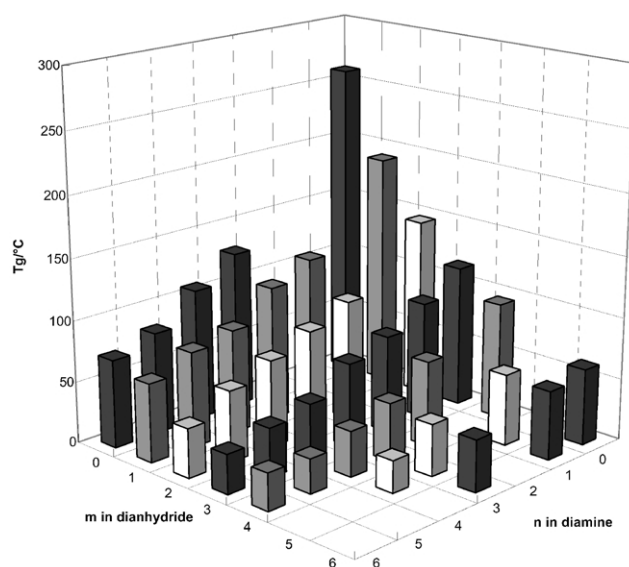
Table 5
Glass-transition temperatures (°C) of segmented polyimides **I** according to the numbers of ethylene oxide units in diamine (n) and dianhydride (m) moieties; calculated values are in parentheses

m	n						
	0	1	2	3	4	5	6
0	–	Nf	Nf	129	108	83	72
	(270[a])	(201)	(155)	(122)	(98)	(79)	(64)
1	191	Nf	124	110	85	78	64
	(201)	(155)	(122)	(98)	(79)	(64)	(51)
2	146		98	84	71	58	40
	(155)	(122)	(98)	(79)	(64)	(51)	(41)
3	116	96	79	68	47	40	32
	(122)	(98)	(79)	(64)	(51)	(41)	(32)
4	95		69	47	37	28	30
	(98)	(79)	(64)	(51)	(41)	(32)	(24)
5		58		42	26		
	(79)	(64)	(51)	(41)	(32)	(24)	(18)
6	62	56		42			
	(64)	(51)	(41)	(32)	(24)	(18)	(12)

[a] Literature, Ref. [8].

Fig. 1. Variation in glass-transition temperatures of segmented polyimides **I** with the numbers of ethylene oxide units in diamine (**n**) and dianhydride (**m**) moieties.

polymers can be considered as copolymers of aromatic and aliphatic units. As the diamines have phenoxy end-groups the polymers can be considered as copolymers of the aromatic polyimide from oxydiphthalic anhydride (ODPA) **VII**; $m = 0$ and bis(4-aminophenoxy)ether (ODA) **IV**; $n = 0$ and PEO. The aromatic polyimide from ODPA and ODA has previously been reported to have a T_g of 270 °C (543 K) [9,10]. Several values have been quoted for the T_g of PEO and most workers agree with a value of about 200 K (−70 °C, approximately). Various procedures have been proposed to combine T_gs of components to estimate values of T_gs of copolymers. One of the most popular is the Fox equation [16]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

where T_g is T_g of the copolymer and w_1 of T_g for the several polymers were calculated and these are shown in Table 5 (in parentheses) for comparison with experimental values; calculated values for isomeric polymers are, of course, identical. In general, it can be seen that the Fox equation provides a good estimate of the observed values. The Gordon–Taylor equation [17]

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

gives poor agreement between observed and calculated values. In many cases, the observed values and those derived from the Fox equation agree to within five degrees. In some cases larger discrepancies are observed, especially at the top right-hand part of Table 5 where there are a few differences of up to about ten degrees. However, given the simplicity of the calculation and uncertainty in the absolute values of the T_gs of the components the general agreement is very good. It can be seen that, in large measure, the inevitable identity of T_gs calculated for isomeric species is largely maintained in the observed values except for some drift to higher experimental values for polymers rich in EO units in the diamine moiety and dilute in EO in the dianhydride moiety. The origin of this drift is not obvious but might be related to relative rigidity in the polymers where the rigid phthalimide parts of the *N*-phenylphthalimde units are in close proximity, allowing intermolecular interactions to develop between aromatic units; aromatic polyimides develop intermolecular charge transfer interactions. Alternatively the effect might be a consequence of crystallinity and a raising of T_g of the residual amorphous polymer; see later.

In addition to T_gs, several polymers exhibited sharp endotherms on heating, consistent with crystal melting and, in one case, with liquid crystallinity. Table 6 presents the temperatures of the endotherms observed by DSC on heating and exotherms on cooling. Optical microscopy and wide-angle X-ray diffraction also provided information consistent with crystallinity in some polymers; see later. Most polymers studied were found to be amorphous; these

Table 6
Temperatures (°C) of crystal melting endotherms and crystallization exotherms (in parentheses) in segmented polyimides **I** with the numbers of ethylene oxide units in diamine (n) and dianhydride (m) moieties. Ratios of glass-transition temperatures to crystal-melting temperatures are shown in square brackets

m	n						
	0	1	2	3	4	5	6
0			373 (330)	311, 330 (297) [0.67]	285 (268) [0.68]	259 (238) [0.67]	232, 246 (210) [0.66]
1			276, 289 (247) [0.70]	235 (193) [0.75]	180 (152) [0.79]	173 (140) [0.79]	140, 166 (122) [0.82, 0.77]
2		290 (238) [0.71]			143[a] – [0.83]		114,131[a] – [0.77]
3		240, 252 (220) [0.70]					
4		225 (172)					
5		174, 195 (160[b], 144[c]) [0.71]					
6		171, 182 (159) [0.72]					

[a] After annealing overnight at 80 °C.
[b] First cooling.
[c] Second cooling.

correspond to blank cells in Table 6. However, it should not be assumed that all these polymers are totally uncrystallizable as it was observed that in several polymers the exotherms and endotherms, indicative of crystallinity, only developed after repeated heating and cooling between 180 and about 300 °C or on annealing above T_g.

Repeated scanning to about 300 °C or above brings into question the thermal stability of the polymers containing EO units as PEO degrades at 280 °C [18]. Thermal stabilities of representative polymers were determined by thermogravimetric analysis with results detailed in Table 7. Thermal degradation occurred in two distinct steps. Table 7 records the temperatures for 5% weight loss, the temperatures for maximum rate of weight loss in the first stage of decomposition, the percentage weight losses in the first step and the ethylene oxide contents of the polymers. The data clearly demonstrate that EO sequences with *N*-phenylphthalimide termini are resistant to thermal degradation to about 400 °C, at least, and that degradation would not have occurred during the thermal treatments in the DSC or optical microscope used to induce or determine crystallinity. It is also clear that weight losses in the first stage of decomposition do not correspond to the EO contents of the polymers. The degradation characteristics, including decomposition onset temperatures, are akin to those of wholly aromatic polyimides and the EO sequences do not constitute

Table 7
Thermogravimetric analysis of polymers **I** with various values of n and m

| n	m	Temp. for 5% wt loss (°C)	Temp. for max. rate of wt. loss (°C) (first step)	Weight loss in first stage (at 550 °C)	EO content (wt%)
2	0	475	500	38	15.7
6	0	421	480	50	35.8
6	2	410	470	72	42.6
4	1	451	490	69	31.7

thermally weak links in the polymers. This observation is in accord with previous data on similar polymers reported by Cheng et al. [7]

Several crystallizable polymers identified in Table 6 exhibited one clear melting endotherm, consistent with simple crystal melting. Peak temperatures of crystallization exotherms observed are recorded in parentheses in Table 6. It is difficult to be definitive over equilibrium transition temperatures as the melting and crystallization peaks frequently only appeared after several cycles of heating and cooling and, in some cases, the transition temperatures gradually moved to reproducible values, see, for example, **I**; $n = 1, m = 5$. Additional polymers might be crystallizable under certain annealing conditions. Multiple melting endotherms for a few of the polymers were separated by not more than about 10 °C and probably represent pre-melting of poor-quality crystalline units, while others were separated by more than 20 °C. It was therefore appropriate to obtain additional evidence to establish crystallinity and to determine between multiple melting transitions, associated with melting and recrystallization, and/or liquid crystallinity.

Although crystal melting and the glass-transition are of different origin there is a well-established empirical relation between T_g and T_m for most crystallizable polymers [19–24]. The ratio T_g/T_m in most cases is about 0.67; lower values (0.5 or less) are observed for some symmetrical polymers and higher values (0.75 or greater) for unsymmetrical polymers. It is of interest to note values of this ratio for the crystallizable polymers identified so far in this investigation. Values of T_g/T_m are given in Table 6 in square brackets and are calculated from the higher of the two endotherms (where two are observed) except for **I**; $n = 6, m = 1$ where values are reported for both endotherms; for **I**; $n = 6, m = 1$ the lower endotherm is probably the melting point and the higher a clearing temperature on loss of liquid crystallinity, while in other polymers the higher is probably the true melting point. It is seen from Table 6 that most values of T_g/T_m observed are about 0.67 for polymers with EO units in the diamine only. Higher values, 0.7 or greater, up to about 0.8 for **I**; $n = 4, 5, 6, m = 1$, were observed for polymers with EO units in both moieties. Most of the polymers studied are highly symmetrical along the backbone except for the slight asymmetry associated with the position of the ether linkage in the phthalimide units. Thus, these polymers

conform well with observations reported for other crystallizable polymers.

Preliminary optical microscope observations indicated that **I**; $n = 1, m = 5$ does exhibit liquid crystallinity between the endotherms. Preliminary small-angle X-ray scattering (SAXS) data also indicated liquid crystallinity in this sample [25]. These preliminary findings contrast with data reported previously by Kricheldorf et al. [26] who found that polyimides **IXAb**(R = H), with the phenylenes in the diamine moiety *para*-substituted, i.e. similar to **IV** but with an alkane sequence in place of the EO sequence, exhibited liquid crystallinity. However, if a spacer was introduced into the dianhydride moiety (as in polyimides **IXB**, **IXC**) no liquid crystallinity was observed. In this study we find that an –O– spacer in **I**; $n = 1–6, m = 0$ does not impart liquid crystallinity but a slightly longer, flexible EO spacer in the specific case of **I**; $n = 6, m = 1$ does impart liquid crystalline behaviour, implying that rigidity in the dianhydride moiety is not a pre-requisite for liquid crystallinity. This result and adds to the structures known to give rise to liquid crystalline behaviour.
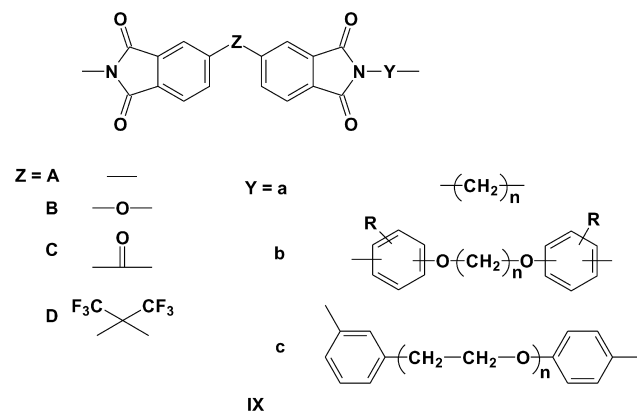
WAXS data, obtained for some samples which exhibited endotherms in DSC, confirmed their crystallinity. A series of powder diffractograms are shown in Fig. 2 and d-spacings derived from them are listed in Table 8. Polymer **I**; $n = 2, m = 0$ showed particularly strong, sharp diffraction peaks. Polymer **I**; $n = 4, m = 0$ showed virtually the same diffractogram, with very similar d-spacings, but with broader peaks. The smallest of the three major d-spacings for these two polymers was about 3.4 Å and is consistent
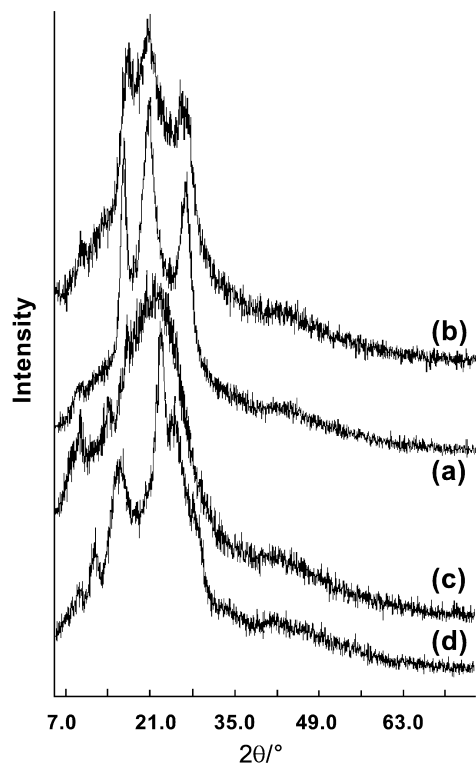
Fig. 2. Wide angle X-ray diffractograms for several crystalline polyimides I with different composition s: (a) **I**; **n = 2, m = 0**, (b) **I**; **n = 4, m = 0**, (c) **I**; **n = 3, m = 1**, (d) **I**; **n = 1, m = 4**.

with stacking of aromatic rings and, therefore, with association of aromatic units (hard segments) as occurs in segmented polyurethanes.

Polymer **I**; $n = 3, m = 1$, with EO units in both dianhydride and diamine moieties, showed a broad major diffraction peak (d ~4.1 Å). A comparable polymer **I**; $n = 1, m = 4$, but with the longer EO sequence in the dianhydride, showed sharper diffraction peaks. The broad peak for **I**; $n = 3, m = 1$ was probably a consequence of using precipitated polymer powders, and without any thermal treatment to induce crystallization, in order to prepare the diffractograms. Polymer **I**; $n = 1, m = 4$ showed the same prominent d-spacing of about 3.5 Å as did polymers with $m = 0$ described earlier. In polymers with $m = 0$ the

two N-phenylphthalimide units are linked by a single oxygen atom and probably act in concert to form associations of aromatic residues. In polymer **I**; $n = 1, m = 4$ all N-phenylphthalimide units are separated by EO spacers, so the d-spacing of 3.5 Å suggests that even single N-phenylphthalimide units have sufficiently strong intermolecular interactions to bring about association of the aromatic residues.

General lack of crystallinity in polymers **I** with two long EO spacers (n and $m > 2$) suggests that dilution of aromatic units and/or dominance of PEO sequences restricts the association of aromatic units into sufficient arrays to generate long-range order. It is still possible that some level of segregation of units and reinforcing by aromatic units exists in these polymers. Indeed, polymers **I**; $n = 4, m = 6$ and **I**; $n = 5, m = 6$ were elastomeric, consistent with association of the aromatic units to form physical crosslinks between the predominantly PEO chains; polymers **I**; $n = 3, m = 6$ and **I**; $n = 4, m = 5$ would stretch under tension but did not recover rapidly.

In addition to the dominant features, diffractograms in Fig. 2 show common small features. They all show a small feature at $2\theta \sim 9°$ corresponding to a d-spacing of 9.5–10 Å. Longer d-spacings, arising from repeat units along the chain, were not observable and are appropriate to observation by SAXS. Such studies are in progress and results will be reported in conjunction with data on liquid crystalline behaviour of these and related polymers in a subsequent publication.

The series of 49 possible polymers of this study, from $n = m = 0$ to $n = m = 6$, have a wide variety of EO contents. **I**; $n = m = 0$ is wholly aromatic and hydrophobic while **I**; $n = m = 6$ has chains whose lengths are dominated by EO sequences and is hydrophilic. Following our previous report [1], that grafted and segmented polyimides can be very hydrophilic, we determined the EWCs of films of these polymers; suitable films could not be formed from all polymers prepared. Values of EWC are recorded in Table 9 along with weight fractions of EO (in parentheses) in the polymers; despite the polymer **I**; $n = m = 6$ having six EO residues per N-phenylphthalimide unit it contains only 52.7 wt% EO. The data clearly demonstrate a lack of water uptake by polymers with little EO content and large water uptakes for polymers with high EO contents. The variations recorded in Table 9 are more-clearly apparent in Fig. 3 which presents the data graphically. Polymers with $m = 6$ were generally too friable when swollen to allow good values of EWC to be determined. Nevertheless, the fact that **I**; $n = m = 6$ formed a highly swollen hydrogel but did not dissolve is further evidence for the presence of physical crosslinks formed by association of N-phenylphthalimide units.

Data in Table 9 and Fig. 3 show that in general EWCs increase with increasing EO content and, although EWCs were determined using a simple procedure and small samples, reducing the potential accuracy of the results,

Table 8
X-ray powder diffraction data for representative polymers **I**

n	m						
2	0	2θ (°)	25.920	20.023	16.994		9.325
		d (Å)	3.437	4.434	5.217		9.483
4	0	2θ (°)	26.143	20.626	16.252		8.875
		d (Å)	3.346	4.307	5.454		9.96
3	1	2θ (°)	21.613[a]	17.038	13.787		8.875
		d (Å)	~ 4.111	5.204	6.422		9.96
1	4	2θ (°)	24.788	20.675	15.725	11.688	9.25
		d (Å)	3.591	4.296	5.635	7.571	9.56

[a] Broad peak.

Table 9
Equilibrium water contents of segmented polyimides **I**, ethylene oxide contents (wt%) in parentheses

m \ n	0	1	2	3	4	5	6
0							11
	(0)	(0.085)	(0.157)	(0.218)	(0.271)	(0.317)	(0.358)
1				2.3		4.7	4.1
	(0.085)	(0.157)	(0.218)	(0.271)	(0.317)	(0.358)	(0.394)
2	3			4	3.1	3.1	4.5
	(0.157)	(0.218)	(0.271)	(0.317)	(0.358)	(0.394)	(0.426)
3			1.4	2.5	3	3.6	10
	(0.218)	(0.271)	(0.317)	(0.358)	(0.394)	(0.426)	(0.455)
4	13.2		6.2	4.6	6.3	7.8	12.3
	(0.271)	(0.317)	(0.358)	(0.394)	(0.426)	(0.455)	(0.481)
5				11.3	19	37	39
	(0.317)	(0.358)	(0.394)	(0.426)	(0.455)	(0.481)	(0.505)
6	17			50.7			
	(0.358)	(0.394)	(0.426)	(0.455)	(0.481)	(0.505)	(0.527)

there are some more subtle but consistent trends apparent. Polymers **I** which have two comparable, small EO sequences have lower water uptakes than polymers with the same overall EO content but a disparity in lengths of the EO sequences. Thus, **I**; $n = m = 3$ has a lower EWC than its isomers, as do **I**; $n = 4, m = 3$ or **I**; $n = 5, m = 4$. However, this trend is not absolute and symmetrical as polymers with longer EO sequences in the dianhydride moiety are more hydrophilic than their isomers with the longer sequence in the diamine moiety. Thus, EWC for **I**; $n = 2, m = 4$ is greater than for **I**; $n = 4, m = 2$, EWC for **I**; $n = 3, m = 5$ is greater than for **I**; $n = 5, m = 3$ and
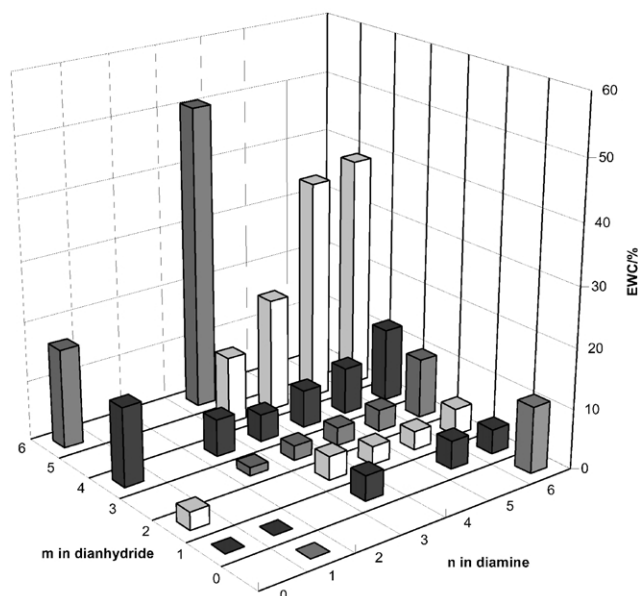
EWC for **I**; $n = 3, m = 6$ is greater than for **I**; $n = 6, m = 3$. The trend that polymers with two similar EO sequences has the lowest EWC of the isomers is also not completely upheld as, when long EO sequences are involved, the tendency for long EO sequences in the dianhydride moiety to have higher EWC tends to dominate; EWC for **I**; $n = m = 5$ is greater than for **I**; $n = 6, m = 4$. The origin of the unexpectedly high EWC for **I**; $n = 6, m = 0$, cf **I**; $n = 6, m = 1$ is not obvious and might be attributable to a difference in morphology.

There are many possibilities for synthesizing polyimides incorporating aromatic and aliphatic units and polymers of several different structures have been studied. It is appropriate to discuss results obtained for those polymers most closely related to those prepared in this study. Several such polymers have been found to exhibit liquid crystalline behaviour but most of these incorporate both phthalimide and ester units; this work has recently been reviewed [27]. Few studies have been made on segmented polyimides not incorporating ester groups and relevant polymers have variations on structure **IX**. Koning et al. [28] and Kricheldorf and Linzer [26] both investigated polyimides **IX** in which **Z** = **A**, i.e. polymers based on biphenyltetracarboxylic acid dianhydride, and **Y** = **a**, $n = 4, 9, 10$. Both groups reported that these polymers were crystalline but not liquid crystalline; polymers in which **Z** = **B** and **C** were also crystalline but not liquid crystalline. Replacing the simple alkane sequence **Y** = **a** with **Y** = **b** introduces a phenoxy group and converts the phthalimide to a longer rigid N-phenylphthalimide. In no case where **Z** = **B**, **C** or **D** and **Y** = **b** did polymers exhibit liquid crystallinity but such polymers with **Y** = **b** and $n = 10$ were reported to be crystalline [26]. Only in polymers **IXAb**(R = H); $n = 7$–12 was liquid crystallinity observed; i.e. where the rigid mesogen is bis(*N*-phenylphthalimide). Even then the phenyl groups linking the alkane sequences to the phthalimide unit had to be *para*-substituted; *ortho*- and *meta*-substitution did not give liquid crystallinity. In addition, if a methyl group (R = –CH_3) was introduced *ortho* to the imide ring, to twist the phenyl ring out of planarity with the phthalimide unit, liquid crystallinity was destroyed [26]. Thus, these several studies show that in polymers with alkane sequences liquid crystallinity is limited to very specific structures and only bis(*N-para*-phenylphthalimide) units will act as mesogens and long alkane spacers are required.

In other studies Cheng et al. [7] and Heberer et al. [8] studied polymers **IX** in which **Z** = **B** and **Y** = **c**; $n = 1$–3. These polymers are similar to **I** with $n = 1$–$3, m = 0$ except that in polymers **IXBc** one of the phenylene units at the termini of the ethylene oxide sequences is *para*- and the other is *meta*-substituted. These workers examined the thermal properties of **IXBc**; $n = 1$–3 and their crystallization behaviours in considerable detail. Polymers with $n = 1$ and $n = 2$ showed conventional T_gs, crystallization exotherms (on heating quenched samples) and single melting endotherms. However, **IXBc**; $n = 3$ showed more

Fig. 3. Variations in equilibrium water contents of segmented polyimides **I** with the numbers of ethylene oxide units in diamine (n) and dianhydride (m) moieties.

complex behaviour with two melting peaks separated by ~50 °C and a pronounced sharp intermediate exotherm. It was established that this polymer, unlike the others, exhibited polymorphism and the intermediate exotherm arose from recystallization of crystals melting at the temperature of the lower endotherm into a new structure.

With this background it is interesting to compare results obtained previously with data from polymers prepared in the current study. Comparing polymers $\mathbf{I}; m = 0$ with $\mathbf{IX}$, polymers $\mathbf{I}$ with $n = 0$ and $n = 1$ were not found to have crystal melting behaviour below 400 °C. However, $\mathbf{I}; n = 3, m = 0$ was found to exhibit two melting endotherms, separated by ~20 °C, as with $\mathbf{IXBc}; n = 3$. Polymer $\mathbf{I}; n = 6, m = 0$ showed similar behaviour, while $\mathbf{I}; n = 4, 5, m = 0$ only showed single melting peaks. Therefore, similar behaviours were observed if the two phenylenes were both *para*-substituted or if one was *meta*-substituted; the former gives higher T_ms than the latter. It is noticeable that none of the polymers, with an $-\mathbf{O}-$ spacer between the phthalimide units, so far has shown any evidence of liquid crystallinity.

Turning the structures round to the isomers $\mathbf{I}; n = 0$, where the $-\mathbf{O}-$ link is between the phenylenes of the phthalimides the polymers also showed no evidence for crystallinity on first or second heating cycles.

Introducing one short spacer into either the dianhydride ($m = 1$) or diamine ($n = 1$) moiety (except $\mathbf{I}; n = 1, m = 1$) produced a series of crystalline polymers, several with multiple melting endotherms, Table 6; $\mathbf{I}; n = m = 1$ was totally amorphous. Longer spacers in both units have only produced amorphous polymers to date, except for $\mathbf{I}; n = 4, m = 2$ and $\mathbf{I}; n = 6, m = 2$. Of the partially crystalline polymers, $\mathbf{I}; n = 2, m = 1$ and $\mathbf{I}; n = 1, m = 3$ did not exhibit positive evidence for polymorphism in the form of an exotherm between the two endotherms on heating; the lower melting peaks were possibly a consequence of premelting of poor crystallites. It is hoped that current SAXS/WAXS studies will clarify this situation. Polymers $\mathbf{I}; n = 1, m = 5$, $\mathbf{I}; n = 1, m = 6$ both showed strong exotherms between the melting endotherms on heating, consistent with polymorphism, but not liquid crystallinity; the two T_cs recorded for $\mathbf{I}; n = 1, m = 5$ were obtained individually on first (160 °C) and second (144 °C) coolings.

Polymer $\mathbf{I}; n = 6, m = 1$ was unique amongst the polymers studied so far in exhibiting liquid crystallinity; DSC thermograms showed two overlapping endotherms with no evidence of an intermediate exotherm. The polymer exhibited liquid crystallinity over a small temperature range, as judged by the ability to shear the birefringent melt when observed in the optical microscope and which existed at temperatures between the endotherms observed by DSC. Thus, this sample establishes that it is not necessary to have long bis(*N*-phenylphthalimide) units to induce liquid crystallinity; just one *N*-phenylphthalimide unit will suffice if adjacent *N*-phenylphthalimide units are not too close together but are separated by a suitable, short, flexible spacer, equivalent to one ethylene oxide unit. Increasing the length of the spacer in polymer $\mathbf{I}; n = 6, m = 2$ gave a polymer which showed a very similar DSC thermogram of two overlapping endotherms. However, this sample has shown no evidence of liquid crystallinity. These several observations and conclusions are supported by other preliminary optical microscopy and SAXS observations [25] further studies are in progress and a more detailed discussion of the thermal and morphological data of these and related materials will be published in the future. Clearly, the data obtained so far, and in conjunction with data of other workers, show that the segmented polyimides are capable of exhibiting a range of features and that the features associated with molecular organisation are very structure sensitive and specific; many more data are required to obtain a full understanding of these and related materials.

3. Conclusions

It has been demonstrated that the previously established route to bis(4-nitrophenoxy)-terminated PEO oligomers and hence to bis(4-aminophenoxy)-terminated PEO oligomers, by fluorodisplacement between poly(ethyleneglycol)s and 4-fluoronitrobenzene can be extended to glycols with six ethylene oxide units to give products in high yield.

It was also established that poly(ethyleneglycol)s will undergo cyano-activated nitrodisplacement with 4-nitrophthalodinitrile at room temperature in the presence of potassium carbonate, but with lower yields than for corresponding displacement reactions with aromatic bisphenols. Replacement of potassium carbonate with caesium carbonate does not improve yields. Improved yields could be obtained by reacting potassium salts of the glycols in hexamethylphosphoramide solution at 4 °C. The resulting tetranitriles $\mathbf{V}$ are readily converted to tetraacids and, hence, to dianhydrides, in high yield. Dianhydrides with up to six EO units have been prepared.

The diamines and dianhydrides with specific EO sequences were shown to be usable in different combinations to yield new segmented polyimides consisting of sequences from zero to six EO units separated by *N*-phenylphthalimide units; a series of 49 such polymers were available from the monomers prepared. Properties of the polymers vary with molecular structure, from those of a conventional aromatic polyimide to highly flexible PEO-like polymers reinforced by *N*-phenylphthalimide units. Solubilities and film-forming properties of the polymers varied greatly according to molecular structure; polymers with low EO contents were shown to be soluble only in aprotic solvents, others with higher EO contents were shown to be soluble in chloroform.

Polymers were shown to be thermally stable up to about 400 °C and it was concluded that the EO sequences do not

constitute thermally weak links in the polymers. It was established that the glass-transition temperatures of the polymers varied systematically with composition from 270 °C to sub-ambient; there was good agreement between experimentally determined T_gs and values calculated from the Fox equation [16].

Most polymers prepared were found to be amorphous. However, it was established that, especially after thermal cycling or annealing, that several polymers were crystallizable. It was concluded that crystallizable polymers contained either zero or one EO unit in the diamine moiety and from two to six EO units in the dianhydride moiety, or one EO unit in the dianhydride moiety and two to six EO units in the diamine moiety. On the basis of DSC data it was concluded that a few of these polymers exhibit polymorphism and, in conjunction with optical microscope observations, it was concluded that one polymer **I**; $n = 6, m = 1$ (with one EO unit in the dianhydride moiety and six EO units in the diamine moiety) was liquid crystalline over a small temperature range; further work to clarify molecular arrangements in the polymers by SAXS and optical microscopy is in progress. It was also concluded that ratios of T_g/T_m are in accord with previously established values for other types of partially crystalline polymers.

The polymers, having combinations of hydrophobic, aromatic *N*-phenylphthalimide units and hydrophilic, aliphatic EO units (from 0 to 57 wt% EO units), exhibited considerable differences in hydrophilicity. The equilibrium water contents of film-forming polymers were determined and were found to vary from about 1% to more than 50% as EO contents vary from 0 to 50 wt%; equilibrium water contents of polymers with the highest EO contents were not determined as they formed extremely friable hydrogels, but were not water soluble. It was therefore conluded that *N*-phenylphthalimide units provide physical crosslinks which prevent dissolution of the polymers. Equilibrium water contents generally varied systematically with composition. However, it was concluded, symmetrical polymers had lower hydrophilicity and that EO sequences in the dianhydride moiety impart greater hydrophilicity than the same sequences in the diamine moiety.

From a comparison of data established in this paper and data on other segmented polyimides, it was concluded that current data are in accord with trends previously established, but trends in behaviour with composition have been extended considerably by the new structures. It was also concluded that possibilities for producing liquid crystalline polyimides have been extended to include structures which have short spacers (one EO unit) in the dianhydride moiety of polyimides.

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