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A Comparison of Poly(ether imide)s with 3-Phthalimide and 4-Phthalimide Units: Synthesis, Characterization, and Physical Properties

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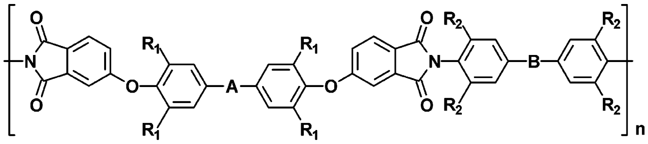
ABSTRACT: Bis(ether anhydride)s with 3- or 4-phthalimide moieties were prepared by reacting 3- or 4-nitrophthalodinitrile, respectively, with several diols and converting the resulting bis(ether dinitrile)s to bis(ether anhydride)s. Selected dianhydrides were converted into poly(ether imide)s in a two-stage solution polymerization and imidization process. It was found that, in most cases, the dianhydrides with 4-phthalic anhydride units gave high-molecular-weight polymers with any of several aromatic diamines. In contrast, dianhydrides with 3-phthalic anhydride units gave, primarily, low-molecular-weight products. Examination of several low-molecular-weight products by electrospray-ionization mass spectrometry demonstrated that the products consisted of small oligomers, cyclic or linear according to the structure of the diamine. A series of high-molecular-weight polymers were prepared from 4,4′-bis(4″-aminophenoxy)biphenyl (BAPB) and each of several bis(ether anhydride)s with 3- or 4-phthalic anhydride units; the anhydrides had isopropylidine or hexafluoroisopropylidine units or *ortho*-methyl or *ortho*-*tert*-butyl substituents in the diol residues. These polymers were characterized in terms of their molecular weights and glass-transition temperatures. The gas permeabilities, positron annihilation, and dielectric relaxation behaviors of the polymers were investigated and their properties related to their molecular structures. Dielectric relaxation spectroscopy measurements indicate that, in this group of polymers, the rates of the local chain mobility are comparable and are able to facilitate gas diffusion. An apparent linear correlation between the permeation coefficients and free volume as determined by positron annihilation lifetime spectroscopy was observed with certain gases. Comparison of polymers with similar molecular structures indicated that isomeric polymers with 3- and 4-linked phthalimide units have similar properties and that the introduction of branched chains or fluorinated groups leads to an increase in the free volume and consequently increased permeability.

Introduction

Over the past decade, many papers have reported investigations into relationships between the structures of polyimides and their processabilities, solubilities, glass-transition temperatures (T_g), and permeabilities to permanent gases. Studies have identified marked effects of varying aromatic substitution patterns, such as introducing *ortho*-substituents or main-chain *ortho*-linked units, on these properties. For example, in poly(ether imide)s significant effects arise by introducing methyl groups *ortho* to the ether or imide linkages.[1] Thus, in poly(ether imide)s **1**, replacing $R_1 = H$ or $R_2 = H$ by $R_1 = Me$ or $R_2 = Me$ simultaneously raises T_g and permeability coefficient (P). Replacing both $R_1, R_2 = H$ by $R_1, R_2 = Me$ has even greater effects. Increases in T_g and P were greater when $R_1 = Me$, $R_2 = H$ than when $R_1 = H$, $R_2 = Me$, an effect attributed to loss of conformational freedom (entropy) by restricting rotation about the ether linkage; $R_2 = Me$ simply restricts rotation about a rigid rotor. These trends occur with a variety of units A and B. Similar tendencies were recognized with *ortho*-*tert*-butyl and *tert*-amyl groups, especially when used in conjunction with *ortho*-methyl substituents.[2]

The effects produced by introducing bulky substituents, other than simply raising T_g, were attributed to the *ortho*-substituents hindering rotation about the ether or imide linkages and reducing the efficiency of chain packing.[1] Increases in P for these polymers correlated with increases in free volumes determined by positron annihilation lifetime spectroscopy (PALS).[3] More recently, Al-Masri et al. reported increases in P and T_g on introducing methyl groups *ortho* to imide linkages in polyimides based on *p*-terphenylenediamines and 2,2-bis(3′,4′-dicarboxyphenyl)hexafluoropropane (6FDA)[4] and similarly for other polyimides.[5] Nagel et al.[6] demonstrated that the effects of *ortho*-methyl groups in raising T_g, P, and free volume, as assessed by PALS, extended to related polymers. Liu et al. reported that, for polyimides based on methyl-substituted phenylenediamines, P increased with *ortho*-methyl group content.[7] Finally, Shimazu et al. recently demonstrated similar effects using propylene as penetrant.[8]



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Poly(ether imide) structures can also be varied by introducing main-chain *ortho*-linked units which influence chain flexibility. Previously, we reported the synthesis and properties of poly(ether imide)s with catechol and substituted catechol units in the bis(ether anhydride) components.[9,10] Recently, we prepared aromatic diamines with terminal 2-aminophenoxy groups, instead of the usual 4-aminophenoxy groups, and used these in

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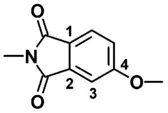
polyimide syntheses.[11] This paper explores the effects of introducing another variant of main-chain *ortho*-linkages. In bis(ether anhydride)s two structures are possible which lead to formation of 4-phthalimide or 3-phthalimide units in polyimides, as defined in structures **2** and **3**, respectively. In the latter the ether link is *ortho* to the imide ring; this variant has received very little attention. Ether linkages in bis(ether anhydride)s are formed by nucleophilic aromatic displacement reactions between a diol and a phthalic acid derivative.[12,13] Takekoshi et al.[14] described such displacement reactions from N-substituted 3- and 4-nitrophthalimides and used these reactions in the synthesis of poly(ether imide)s. They also described the synthesis of bis(ether anhydride)s from N-substituted 3- and 4-nitrophthalimides and bisphenols.[15] Williams and Donahue reported that, in nucleophilic aromatic displacement reactions in DMSO, phenoxide ions react with *N*-phenyl-3-nitrophthalimide 4 times faster than with the 4-nitro analogue.[13] Bis(ether anhydride)s so prepared were reacted with diamines to form poly(ether imide)s;[16] bis(ether diacid)s were also reacted with diamines.[17] An alternative route to poly(ether imide)s was to use the nitro-displacement reaction as the polymer-forming reaction between bis(nitrophthalimide)s and diols.[18] Poly(ether imide)s based on 3-phthalimide units have also been prepared by self-polycondensation of *N*-(3′-hydroxyphenyl)-3-nitrophthalimide to give polymer **4**.[19]



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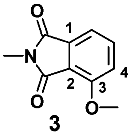

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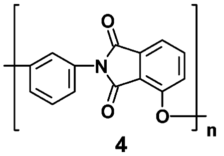

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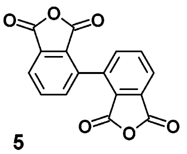
It has been shown that, within the limited number of isomeric pairs of poly(ether imide)s prepared with 3- and 4-linked phthalimide units, the T_gs and solubilities of the 3-isomers were greater than those of the 4-isomers;[16,20] these are trends normally considered favorable in developing new poly(ether imide)s. Thermal stabilities of the 3-isomers were slightly inferior to those of the 4-isomers, although in all cases decomposition started at or above 400 °C.[20]

Polyimides with 3-phthalimide units have also been based on the dianhydrides **5**−**8**[21−27] and the sulfide equivalents of **6** and **7**.[21] Unlike the planar 4-linked isomer, dianhydride **5** is nonplanar.[22,28] Polyimides were synthesized with several diamines. Molecular weights of soluble products were found to be generally low and the molecular weight distributions to be bimodal, and it was suggested that the low-molecular-weight fraction could be composed of cyclic oligomers; in some products from **6** and **8** Maldi-TOF mass spectrometry (MT-MS) identified the presence of cyclic oligomers.[25,26] Polymers from the 3-linked dianhydride were generally soluble and had higher T_gs and good thermal stability. Gerber et al. prepared polyimides from **6** and other isomers of oxydiphthalic anhydride.[29] In this case, polymers with 3,3′-linked phthalimide units had slightly lower T_gs than the 4,4′-linked isomers and had poorer thermooxidative stability but better solubility; polymers based on the 4,4′-linked unit were generally insoluble.

Apart from the above studies there are few, if any, reports of polyimides with 3-linked phthalimde units. Recent reviews of polyimide properties, e.g. of gas permeabilities,[30] contain no reference to polymers with 3-linked units, although it has been reported that polyimides prepared from **6**, or the equivalent sulfide, and bis(4-aminophenyl) ether had higher permeabilities for hydrogen and oxygen than their 4,4′-linked isomers but lower selectivity for gas separation with respect to nitrogen.[21] This general lack of information seems surprising in view of the facts that poly(ether imide)s with 3-phthalimide units tend to have higher T_gs and solubilities and that synthesis of bis(ether anhydride)s with ether links in the 3-position is more facile.[6,12] We therefore undertook a study of the synthesis of poly(ether imide)s with 3-phthalimde units, using a two-stage solution polymerization with chemical imidization and, where appropriate, to compare their physical properties and molecular packing with those of their 4-linked isomers.



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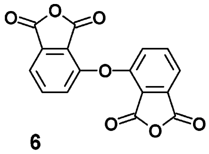

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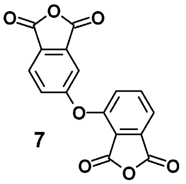

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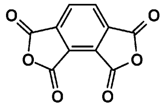

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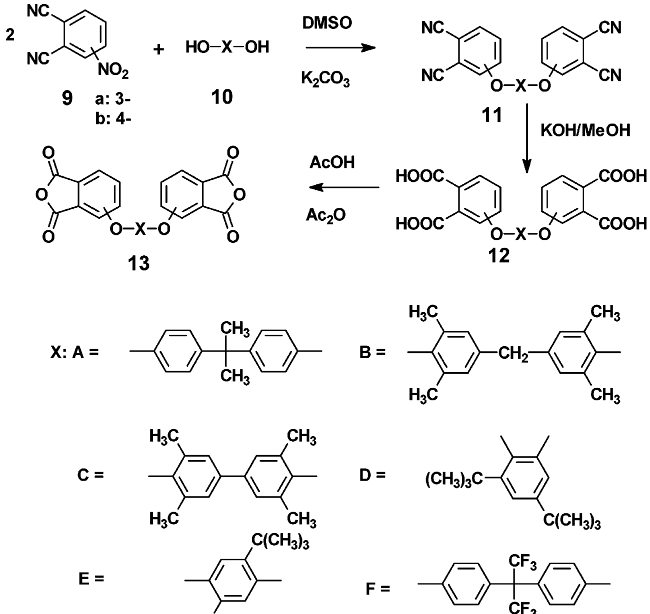
This paper therefore describes the synthesis of several new bis(ether anhydride)s with 3-linked phthalic anhydride units and the synthesis of isomeric poly(ether imide)s from dianhydrides with 3- and 4-phthalic anhydride units. Although several high-molecular-weight poly(etherimide)s with 3-phthalimide units have been prepared by high-temperature polymerization in *m*-cresol,[20] many such poly(ether imide)s prepared in this study were oligomeric, and only their T_gs could be compared with those of their 4-linked isomers. The oligomers were characterized by gel permeation chromatography and mass spectrometry. In the case of poly(etherimide)s based on a specific diamine that produced high-molecular-weight polymers, that could be cast as membranes, from 3-linked dianhydrides, the properties of pairs of isomeric polymers from different 3- and 4-linked anhydrides were compared. This study compared T_gs and gas permeation behavior, including determination of diffusion and

Scheme 1



Scheme 2

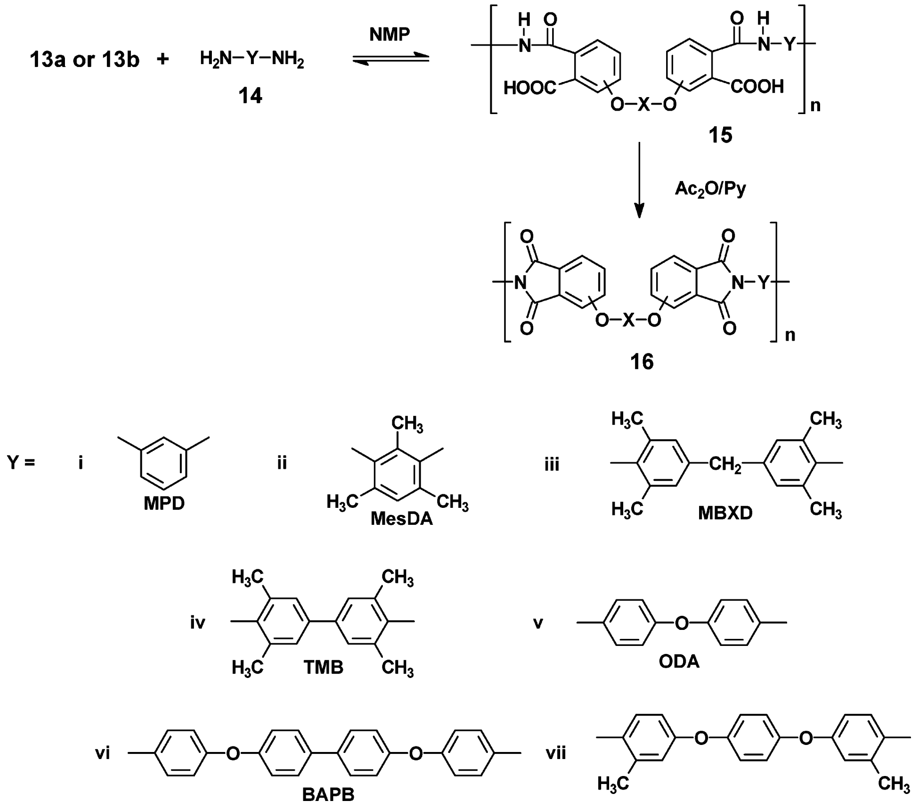


Table 1. Synthesis and Characterization of Bis(ether dinitrile)s 11a Derived from Various Diols 10

		elemental analysis					
diol		C	H	N	yield/%	crystallization solvent	mp/°C
10A	calcd	77.49	4.20	11.66	80	MeCN/MeOH	182.1−182.7
	found	77.18	4.11	11.66		1:10	179−180[a]
10B	calcd	77.94	4.76	11.01	95	MeCN/MeOH	238.3−239.7
	found	77.64	4.73	10.97		1:3	
10C	calcd	77.72	4.48	11.32	95	MeCN/MeOH	318.5−320.5
	found	77.57	4.47	11.35		1:1	
10D	calcd	75.93	5.52	11.80	93	MeOH	216.1−217.6
	found	75.81	5.49	11.77			
10E	calcd	75.93	5.52	11.80	87	MeCN	>300
	found	76.08	5.50	12.00			
10F	calcd	63.27	2.40	9.52	84	MeCN	255.0−255.7
	found	63.30	2.37	9.50			

[a] Reference 14.

Table 2. Synthesis and Characterization of Bis(ether anhydride)s 13a Derived from Various Diols 10

		elemental analysis/%			
diol		C	H	yield/%	mp/°C
10A	calcd	71.53	3.87	76	187.8−189.2
	found	71.44	3.84		186−187.5[a]186.5−187.5[b]
10B	calcd	72.25	4.41	84	245.7−247.5
	found	72.27	4.45		
10C	calcd	71.95	4.11	69	317.2−319.5
	found	71.74	4.09		
10D	calcd	70.03	5.09	80	208.7−215.0
	found	69.74	5.20		
10E	calcd	70.03	5.09	90	322 (DSC)
	found	69.63	5.11		
10F	calcd	59.25	2.25	88	208−209
	found	59.40	2.17		

[a] Reference 12. [b] Reference 15.

solubility coefficients. Permeability data were correlated with free volumes and dielectric relaxation behavior. The dielectric relaxation measurements were undertaken in order to assess the extent to which molecular mobility exits within the matrix at the temperature at which the gas permeation studies were performed.

Experimental Section

Materials. 3-Nitrophthalodinitrile was obtained from TCI, Tokyo, Japan. Other reagents were obtained from regular sources given in the references cited below.

Synthesis of Bis(ether dinitrile)s (11). The bis(ether dinitrile)s were synthesized by a nitro-displacement reaction between nitrophthalodinitrile (**9**) and a diol (**10**) in an aprotic solvent in the presence of potassium carbonate (Scheme 1). Details of the syntheses based on 4-nitrophthalodinitrile (**9b**) have been presented previously.[1,2,9] The same general procedure was adopted for the synthesis of bis(ether dinitrile)s from 3-nitrophthalodinitrile (**9a**). Thus, 20 mmol of **9a** was dissolved in 30 mL of dimethyl sulfoxide (DMSO), and while stirring under a nitrogen atmosphere, 10 mmol of **10** and 0.4 g of potassium carbonate were added. Mixtures were allowed to react at room temperature for 24 h. Reaction mixtures were then poured into iced water, and precipitates of crude product **11a** were filtered off. Bis(ether dinitrile)s were purified by crystallization. Details of their characterization are given in Table

Table 3. Poly(ether imide)s Prepared from Bis(ether anhydride)s and Various Diamines in Small-Scale Syntheses

dianhydride	substitution	diamine	polymer form	solubility	T_g/°C	M_p/kg mol^{-1}
13A	3-	**14v**	particulate		231	28
	4-			insol ClBz	215	90, 152
13A	3-	**14iv**	powder		265	2.6
	4-				280	60
13A	3-	**14iii**	powder		223	3.4
	4-			DCM, NMP, DMF, ClBz	249	120
13A	3-	**14i**	powder	insol DCM	219	7.7
	4-				215	commercial
13A	3-	**14ii**	powder		265	3.1
	4-					88
13A	3-	**14vi**	balls		236	106
	4-				220	130
13A	3-	**14vii**	particulate		222	29
13B	3-	**14v**	balls		270	54
	4-			insol	266	
13B	3-	**14iv**	powder	insol DMF	276	4.8
	4-			DCM, insol NMP, DMF	>420	
13B	3-	**14iii**	powder		243	6.1
	4-				264	7.0
13B	3-	**14i**	powder		269	11.8
	4-				245	66
13B	3-	**14ii**	powder		287	13.1
13B	3-	**14vi**	balls		259	94
	4-			insol	248	
13B	3-	**14vii**	particulate		238	68.6
13C	3-	**14v**	particulate	insol DCM, $CHCl_3$	298	7.4
	4-			sol	299	53
13C	3-	**14iv**	particulate		327	43.4
	4-				?	90
13C	3-	**14iii**	powder	sol DCM, $CHCl_3$	289	insol
	4-			sol	420	103
13C	3-	**14i**	particulate		311	45.3
	4-				295	40
13C	3-	**14ii**	powder		325	16.6
13C	3-	**14vi**	balls	insol DCM, $CHCl_3$	290	42.4
13D	3-	**14v**	powder		238	6.6
	4-			sol	228	123
13D	3-	**14vi**	powder		237	28.9

1. Melting points were determined with the aid of a polarizing microscope fitted with a Mettler hot stage, unless otherwise specified.

Synthesis of Bis(ether anhydride)s (13). Bis(ether dinitrile)s (**11a**) were converted to bis(ether anhydride)s (**13a**) by first hydrolyzing them to the bis(ether diacid)s (**12a**) and then dehydrating to form the bis(ether anhydride)s (Scheme 1). Details of the conversion, as used in the synthesis of 4-substituted bis(ether anhydride)s **13b**, have been presented previously.[1,2,9]

Approximately 3 g of **11a** (~10 mmol) was added to a solution of 6 g of potassium hydroxide dissolved in 6 mL of water, and the mixture was refluxed until the evolution of ammonia ceased. The reaction mixture was then diluted with water and the pH adjusted to ~1.1 by addition of concentrated hydrochloric acid. The resulting precipitate of **12a** was recovered by filtration, washed, and dried. Compounds **12a** were converted to **13a** by dissolving in glacial acetic acid (10 mL) and heating. After the acid had dissolved, acetic anhydride (10 mL) was added gradually. The mixture was cooled to −5 °C for 24 h, and the product **13a** was filtered off and recrystallized from glacial acetic acid. Details of the products prepared are given in Table 2.

Synthesis of Poly(ether imide)s. Poly(ether imide)s were prepared from each bis(ether anhydride) and each of several diamines using a standard two-stage synthesis involving chemical imidization, as depicted in Scheme 2. Details of syntheses involving the 4-substituted isomer bis(ether anhydride)s (**13b**) have been described in detail previously.[1,2,9] The same standard procedure was adopted with the 3-isomer bis(ether anhydride)s (**13**a). Thus, a diamine (**14**) (0.5 mmol) was dissolved in *N*-methylpyrrolidinone (NMP), and an exact stoichiometrically equivalent amount of bis(ether anhydride) **13a** or **13b**, as defined in Scheme 1, was added with stirring. Mixtures were left to react overnight to form a solution of poly(amic acid) (**15**); **15** was then imidized by addition of an equivolume mixture of acetic anhydride and pyridine to form the poly(ether imide) (**16a** or **16b**). Imidization was allowed to proceed overnight, and **16** was isolated by precipitation into methanol. The precipitated polymers were washed with hot methanol and dried.

Polymer Characterization. Polymer molecular weights were determined by gel permeation chromatography (GPC) using DMF/LiCl(0.1 M) as the mobile phase with a flow rate of 1 cm^3 min^{-1}, columns packed with 5 μm PL gel polystyrene (Polymer Laboratories), and a refractive index detector, and the instrument was calibrated with polystyrene standards (Polymer Laboratories).

Glass-transition temperatures (T_gs) were determined by differential scanning calorimetry (DSC) with the aid of a Perkin-Elmer DSC2 using a heating rate of 10 °C min^{-1}; T_gs were determined on the second or subsequent heating cycles.

Electrospray-ionization mass spectrometry (ES-MS) employed a Micromass LCT spectrometer using a cone voltage of 120 V and a variety solvents as required without added cationization agents.

Density Measurements. Densities of cast films of the polyimides were determined by a flotation method at 25 °C using a saturated aqueous solution of K_2CO_3. The density of the solution was calculated using the oscillating method by a PAAR DM60 digital density meter connected to a PAAR DM601 density measuring cell. Measurements were performed in triplicate.

The fractional free volume was calculated using eq 1.

$$V_f = \frac{V_T - V_0}{V_T} \qquad (1)$$

where V_T is the molar volume per repeat unit of polymer at temperature T calculated from the density. V_0 is the volume occupied by the molecules at 0 K per mole of the repeat unit and is estimated to be 1.3 times[31] the van der Waals volume calculated from the group contribution method of Bondi.[32]

Gas Permeabilities. Gas permeabilities for O_2, N_2, CO_2, and Ar were measured at 308 K using a vacuum time-lag apparatus that has been described previously.[33] The system was degassed for 24 h prior to each measurement, and the volumes of the downstream and upstream sides of the membrane were 200 cm^3. The polyimide membrane was a circular disk of 7 cm diameter. The polymer was held between the two halves of the stainless steel cell with two flat O-rings ensuring a good seal between the membrane and gas cell. With this system leak rates below 5 mTorr h^{-1} were obtained. The pressure change as a function of time was logged using a computer. The measurements allow the diffusion and solubility coefficients to be determined.

Dielectric Relaxation. Dielectric measurements were carried out using a Strathdow dielectric spectrometer operating between 0.1 × 10^4 and 6.5 × 10^4 Hz. To achieve maximum electrical contact, aluminum electrodes were coated onto the polymer films using an Edwards E306A coating system. The temperature was controlled by a Linkam CI93 computer interface and a Linkam LNP pump with a liquid nitrogen cooling system. Spectra were recorded at intervals of 10 °C from −140 to −60 °C. Cole−Cole plots were constructed from the dielectric data, and analysis was performed using a program based on the Havriliak−Negami eq 2 that allows calculation of the α and β distribution parameters;[34] ϵ^*, ϵ_s, and ϵ are respectively the complex and limiting low- and high-frequency permittivities, ω is the experimental frequency, τ is the dielectric relaxation time, and α and β are frequency-independent, dimensionless constants determined by the temperature and sample.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{(1 + (i\omega\tau)^{1-\alpha})^\beta} \qquad (2)$$

These data were used to calculate the characteristic relaxation times that were then used to calculate the activation energy according to the Arrhenius equation.

Positron Annihilation Lifetime Spectroscopy. Positron lifetime spectra were obtained by using a fast−slow system that has been described previously.[3] Measurements on benzophenone crystals were used to determine the equipment resolution of the equipment which was ~230 ps at full width half-maximum. POSITRONFIT[35] was used to analyze the decay curves. The intensities I_3 and I_1 were constrained at a ratio of 3:1. According to the pick-off model, the longest lived component of the positron lifetime spectra, τ_3, and the corresponding *o*-Ps intensity, I_3, may be correlated with the mean radius and the relative number of free volume cavities in the polymer matrix respectively according to eq 3.[36]

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_0}\right)^{-1} \qquad (3)$$

where τ_3 (*o*-Ps lifetime) and R (hole radius) are expressed in nanoseconds and angstrom units, respectively. R_0 equals $R + \Delta R$, where ΔR is the fitted empirical electron layer thickness and equals 1.66 Å.[37] Therefore, the mean free cavity volume can be expressed in Å^3 by eq 4.

$$V_{Ps} = \frac{4\pi R^3}{3} \qquad (4)$$

The positron source used was ^{22}NaCl encapsulated in polyimide foil and sealed with epoxy resin. The polymer films were cut into squares (15 × 15 mm) and stacked together in order to get a total thickness of ~4 mm. The ^{22}Na source was sandwiched between the two polymer stacks with a copper backing. The copper-sample-source-sample-copper sandwich was held together with PTFE tape. The assembly was placed in an evacuated Pyrex tube and inserted into an Oxford Instruments cryostat. Lifetime spectra were measured at 25 °C over a period of 8 h, giving approximately a million counts. Runs were conducted in triplicate.

Results and Discussion

Synthesis and Polymer Characterization. Nitro-displacement reactions between 3-nitrophthalodinitrile (**9a**) and each of several diols **10** (Scheme 1) proceeded with at least equal facility as those undertaken previously with 4-nitrophthalodinitrile (**9b**).[1,2,9] Thus, pure bis(ether dinitrile)s **11a** were readily prepared in good yields and were readily converted to bis(ether acid)s **12a** and, hence, to bis(ether anhydride)s **13a** (Table 2), thus providing a series of new 3-substituted monomers.

In a preliminary investigation of the 3-substituted dianhydrides, dianhydrides **13aA−D** were each reacted with a series of diamines **14** to prepare poly(ether imide)s **16a** in a standard two-stage process. Dianhydrides were added to solutions of individual diamines in DMF to form poly(amic acid)s **15a** (Scheme 2), and these were chemically imidized with acetic anhydride/pyridine mixtures to form polymers **16a**. This procedure was identical with that used in our previous studies to prepare the isomeric poly(ether imide)s from 4-substituted bis(ether anhydride)s, and the same diamines are those which produced high-molecular-weight polymers. Polymers **16a** were isolated from the imidization solutions by precipitation into methanol.

In earlier studies, using 4-substituted bis(ether anhydride)s, poly(ether imide)s **16b** gave dense coarse precipitates, frequently in the form of porous balls from individual drops of poly(ether imide) solution; such precipitates are indicative of high-molecular-weight polymers. When investigated by GPC the peak molecular weights of the chromatograms, measured against polystyrene standards, were almost always in excess of 60 kg mol^{-1} and frequently as high as 200 kg mol^{-1}; such polymers formed strong, tough, flexible, creasable films. In contrast, the precipitates of products **16a** were mainly powders, indicative of low-molecular-weight polymers (Table 3). GPC measurements on these polymers confirmed their low molecular weights in most cases. An exception was for polymers from **14vi** which were of high molecular weight. Chromatograms frequently showed the formation of a major polymer peak and individual peaks from oligomers; peak molecular weights for the highest molecular weight peak are given in Table 3.

These results are in marked contrast with those of Takekoshi et al., who demonstrated that similar high-molecular-weight poly(ether imide)s can be prepared from bis(ether anhydride)s with either 3- or 4-substituted phthalic anhydride units, with any of several diamines, using a high-temperature, one-pot synthesis in *m*-cresol;[20] inherent viscosities (IVs) were used as a measure of molecular weight. Indeed one such polymer was prepared from dianhydride **13aA** and diamine **14v**. Although that polymer had a lower IV (0.66 dL g^{-1}) than its 4-isomer from **13bA** (1.09 dL g^{-1}), the opposite trend was observed in several other cases. Thus, there is no fundamental reason why high-molecular-weight poly(ether imide)s cannot be prepared from the 3-isomer dianhydrides. So, it is interesting to enquire as to what other factors must hinders polymer growth processes under the conditions used in this study, viz. in the formation of poly(amic acid)s in solution.

Formation of high-molecular-weight poly(ether imide)s from each of several 4-linked dianhydrides with different diamines established the purity of the diamines used. Formation of low-molecular-weight poly(ether imide)s from pure diamines and 3-linked dianhydrides, with a stoichiometric equivalence of reactants, would conventionally be attributed to impure bis(ether anhydride)s or to low equilibrium constants for the first step in Scheme 2. Neither of these explanations is consistent with observations.

Although several diamines with each of the 3-linked dianhydrides gave poly(ether imide)s with low molecular weights, poly(ether imide)s prepared from the same dianhydrides and BAPB **(14vi)** gave poly(ether imide)s of high molecular weight.

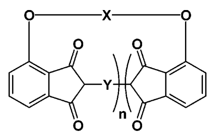
If **14vi** will give high molecular weight poly(ether imide)s, then dianhydrides **13a** must be pure. Therefore, impure monomers is not an explanation for the formation of low-molecular-weight poly(ether imide)s from **13a** and diamines other than **14vi**. Equally, if **14vi** forms poly(ether imide)s of high molecular weight, then there is no reason, based on dianhydride reactivity or low equilibrium constant, why **14v** (ODA) should not form high-molecular-weight polymers. There has to be an inherent tendency for the preferential formation of oligomers from 3-linked bis(ether anhydride)s under the reaction conditions used in this study that does not apply under the reaction conditions used by Takekoshi et al.[20]

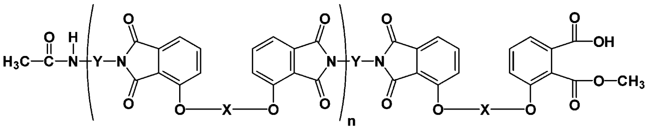
Gel permeation chromatograms for some typical products prepared from the 3-linked dianhydrides are presented in Figure 1; chromatograms a and b demonstrate that polymers formed from **14vi** with **13aA** and **13aB** are of high molecular weight, while those prepared from other diamines have overall low molecular weight. The latter chromatograms have specific features in chromatograms at high elution volumes that indicate the presence of large contents of oligomeric material. These chromatograms fall into two distinct categories. Chromatograms c and e , for products prepared from **13aB** and **13aC**, respectively, with mesitylene diamine **14ii**, and similarly for other products prepared from **14ii**, exhibit a single distinct peak at high elution volume. In contrast, chromatogram d, for the product from **13aB** with **14iii**, and other chromatograms for products prepared from the hindered two-ring diamines **14iii** and **14iv**, exhibit a series of oligomeric peaks extending to very low molecular weights and beyond the calibration limits of the instrument. The distinctive features of these chromatograms are discussed later in relation to mass spectrometry data.

Nature of Low-Molecular-Weight Polymers from 3-Linked Bis(ether anhydride)s. In an attempt to understand the reason for the formation of the low-molecular-weight products from the 3-linked dianhydrides with various diamines, the reaction products for representative systems were examined by ESI-MS. To provide useful information on the molecular species present, it was appropriate to vary the solvent used to extract samples for analysis. All the samples exhibited related patterns of similar oligomers, with some differences as detailed below.

The main signals observed were from $[n + n]$ cyclic oligomers (**17**) and/or from linear oligomers with different combinations of end groups, as depicted in structures **18**−**20**, all associated with one of various adventitious cations (H$^+$, Na$^+$, or K$^+$) and, in some cases, adducts with small molecules. Signals from other related oligomers were also observed, as specified in the text. The main adduct molecules observed were DMF, when used as solvent, or methanol, when used as solvent or when retained after isolating the sample by precipitation into methanol.

Products from Two-Ringed, Unhindered Diamines. The methanol extract of the polymer from **13aA** with the short, two-ring, unhindered diamine **14v** gave a simple ESI-MS spectrum totally dominated by the signal for the cyclic dimer **17,*n*=2** with weaker signals from similar cyclic oligomers with $n = 3$ and 4 with intensities, relative to the $n = 2$ dimer, of 8 and 2%, respectively (Figure 2). In Figure 2, groups of signals for the cyclic dimer ($n = 2$) and trimer ($n = 3$) species are designated **C,*n***, and the signal for the cyclic tetramer is **[M$_4$+Na]**$^+$, where **M*$_n$*** represents an oligomer with n repeat units of structure **M**. The main signals for each cyclic were for the oligomers with Na$^+$, together with small signals for the same oligomers with K$^+$ and for adducts with one ($n = 2$, 3) or two ($n = 2$) molecules of methanol. The detailed signals from the cyclic dimer **17,*n*=2**, except for the large signal from $[M_2+Na]^+$, are displayed in the inset to Figure 2 and annotated. There are two extra small signals possibly corresponding to the cyclic dimer associated with two Na$^+$ (one with methanol as adduct), but with loss of H$^+$, relevant peaks are marked with these attributions and a question mark. In the case of the species with methanol as adduct, H$^+$ could readily have been lost from methanol, but we have no explanation for the loss of H$^+$ for the cyclic dimer without adduct as there is no obviously replaceable proton in the structure; nevertheless, the accurate mass for that signal is consistent with the tentative attribution to within −5.8 ppm. The only other signal observed from the sample that could be attributed to any relevant species was for the linear, amine-ended species **19** (with Na$^+$) with both ends monoacetylated; this small signal, designated **L,2** in Figure 2, was about 1% of the intensity of the main peak for the cyclic dimer.


17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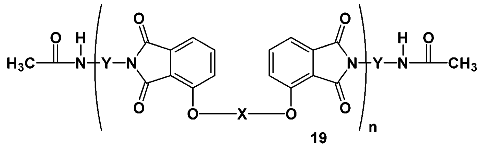
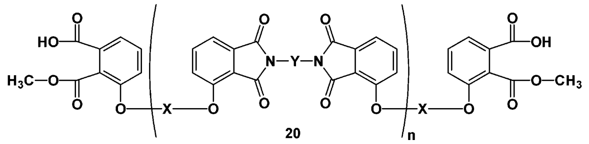

19


20

Products from Mesitylene Diamine. Spectra for the two polymers prepared from mesitylene diamine (**14ii**) and either **13aB** or **13aC** and extracted with DMF were very similar to each other and again totally dominated by strong signals from the cyclic dimers **17,*n*=2**. The total spectrum obtained from **13aC** with **14ii** is shown in the inset to Figure 3, where a combined group of peaks from the cyclic dimer, designated **C,2**, and overlapping peaks from $[2 + 2]$ linear oligomers, designated **L,2**, are identified. The primary signal in the group **C,2**+**L,2** was from the cyclic dimer $[M_2 + Na]^+$. There was a small signal at slightly lower mass from $[M_2 + H]^+$ with a series of signals at higher masses; the latter are shown in more detail in the small inset to Figure 3. These smaller signals from the cyclic dimer are for $[M_2 + K]^+$ and for various adducts with one or two molecules of methanol and/or DMF, as indicated. Overlapping with the peaks for the adducts are peaks labeled **L,2** in the small inset. One, at lower mass, is attributed to the linear oligomer **18,*n*=2** and the other, probably, to its methanol adduct. In addition to the major group of signals, the total spectrum for the mass range 1500−3000 Da, in the inset to Figure 3, shows a series of very low-intensity peaks that, although extremely small, can be attributed to other typical oligomers. These peaks, in groups, are designated **C,*n*** for cyclic oligomers **17,*n***, **L,*n*** for linear oligomers **18,*n***, **Am,*n*** for oligomers **19,*n***, and **An,*n*** for oligomers **20,*n*** in Figure 3. The peak designated **Am,1** in the full spectrum is for **18,*n*=1** with Na$^+$ and an expansion

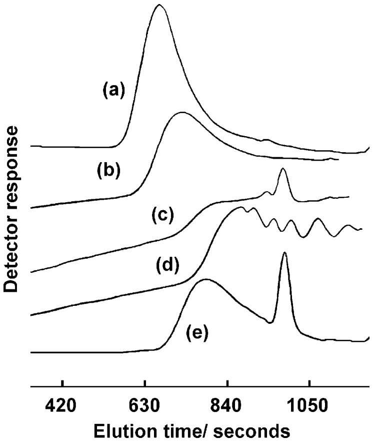


Figure 1. Gel permeation chromatograms for products formed from: (a) **13aA** with **14vi**; (b) **13aB** with **14vi**; (c) **13aB** with **14ii**; (d) **13aB** with **14iii**; (e) **13aC** with **14ii**.

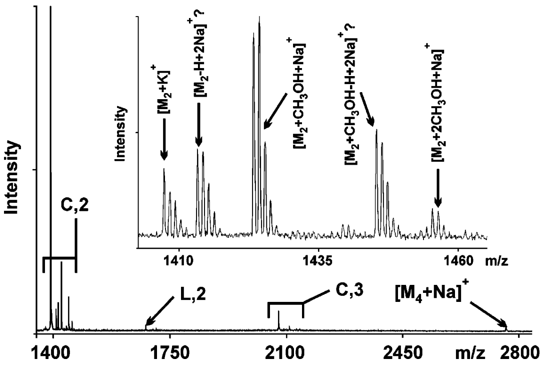


Figure 2. ESI-MS spectra for the product prepared from **13aA** and **14v**.

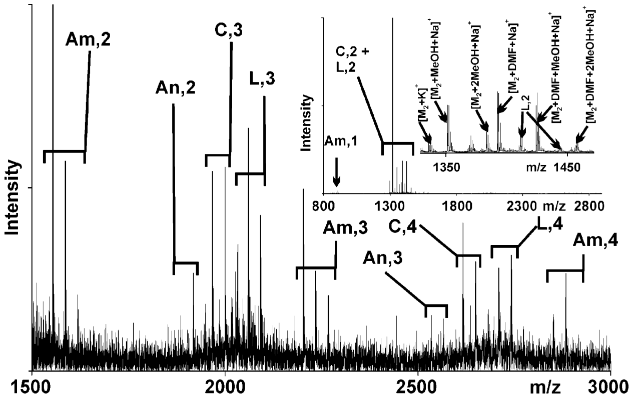


Figure 3. ESI-MS spectra for the product prepared from **13aC** and **14ii**.

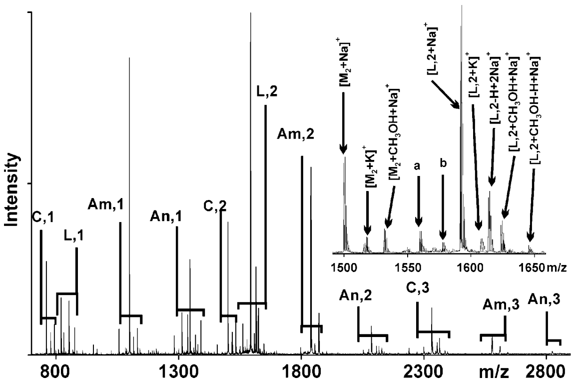


Figure 4. ESI-MS spectra for the product prepared from **13aA** and **14iii**.

allowed adjacent peaks attributable to its adducts with 1 and 2 molecules of methanol to be identified. The peaks at higher masses are depicted in the expansion which forms the major part of Figure 3. The groups designated **C,*n***, **L,4**, and **Am,4** in Figure 3 are pairs of peaks for the oligomer indicated with Na^+ and the same species with methanol as adduct. In the case of species **Am,3** and **Am,4** there are additionally signals from adducts with two molecules of methanol. The group **L,3** also contains a signal for the oligomer with H^+. The groups **An,*n*** are for species **20,*n*** with Na^+ and, at lower masses, for similar species in which only one terminal unit is esterified, and the other is the unhydrolyzed anhydride. Although several of the peaks attributed are very small, these attributions are considered to be correct and significant because corresponding peaks are observed in spectra of all other samples with related structures.

The product from **13aB** and **14ii**, examined as its methanol and its DMF extracts, gave similar spectra which were again totally dominated by signals from cyclic dimer species (peaks included species associated with K^+ and adducts), with weak signals from other cyclics, up to $n = 4$, and linear oligomers. The main distinction in this case was that, in addition to peaks for cyclics being relatively a little stronger, there were weak signals from the cyclic with $n = 1$, associated with Na^+. Relatively prominent signals from linear oligomers were for oligomers **19** with both ends monoacetylated for $n = 1-3$ in the methanol extract and up to $n = 4$ in the DMF extract. There were smaller peaks for species with only one end acetylated for $n = 1$ and 2 and with neither end reacted for $n = 1$. There were signals attributable to oligomers similar to **18**, the most prominent of which was for $n = 1$ in DMF, where the amine end was monoacetylated and the other was unhydrolyzed anhydride, with a weaker signal for a similar species in which the anhydride end was hydrolyzed to diacid. Additional weak peaks observed could be attributed to oligomers **20** where the anhydride ends were unhydrolyzed or esterified. In addition, among the peaks associated with adducts of the [2 + 2] cyclic dimers was a very small peak which could be attributed to other oligomers. The mass corresponded to cyclic dimer plus water, especially in the DMF extract. This mass could be attributed to a [2 + 2] linear oligomer with one unacetylated amine end and one unhydrolyzed anhydride end. Probably, and more likely, the signal should be attributed to an isomeric cyclic dimer in which one amic acid residue remained unimidized. An example of a similar species has been observed elsewhere where a very constrained cyclic oligomer was involved.[11]

Products from Two-Ring, Hindered Diamines. Three other products, prepared from 3-linked dianhydrides with two-ring, hindered diamines, were examined by ESI-MS. These were all prepared from either the rigid, 3,3′,5,5′-tetramethylbenzidine (TMB, **14iv**) or the more flexible bis(3,5-dimethyl-4-aminophenyl)methane (MBXD, **14iii**) diamine with either the stiff dianhydride **13aA** or the more flexible dianhydride **13aB**. The three products all gave very similar ESI-MS spectra to each other, but with very different patterns of signal intensities from those already described. For all these products, using various solvents to prepare solutions for analysis, the spectra were dominated by signals from a variety of linear oligomers, with little and, in some cases, no overall contribution from cyclic oligomers. These products are exemplified in Figure 4 where a spectrum for the product from **13aA** and **14iii** in acetonitrile solution is shown. Almost all significant peaks above noise level in Figure 4 are in distinct groups and can be reliably attributed to various oligomers. The groups of peaks designated **C,*n*** are attributed to [$n + n$] cyclic oligomers **17**, those designated **L,*n*** to the linear [$n + n$] oligomers **18**, those designated **Am,*n*** to linear oligomers **19** formed from *n* dianhydride units and ($n + 1$) diamine units, and those as **An,*n*** to oligomers **20** formed from *n* diamine and ($n + 1$) dianhydride units. Thus, almost all significant peaks are within those groups and can be attributed to the above species with various adventitious cationization agents and adduct molecules or to closely related species.

For the product from **13aA** and **14iii** in acetonitrile solution (Figure 4), the groups of peaks labeled **C,*n*** include signals from $[M_n + Na]^+$ (the major signal) and $[M_n + K]^+$ and for $[M_n + CH_3OH + Na]^+$; for the group **C,2** these are shown more clearly in the inset to Figure 4. The groups designated **L,*n*** include signals attributed to oligomers **18** with Na^+ and the major signal for **L,2** with smaller signals for the same species with K^+; for **L,1** there is a signal for the same species with H^+ and for **L,2** with methanol as adduct. The group of peaks associated with **L,2** is also shown in the inset to Figure 4. In addition, there are signals for the related oligomers in which the anhydride-derived end is unhydrolyzed anhydride with Na^+ which is the largest signal in the group for **L,1**. This peak for **L,2** is identified as **a** in the inset to Figure 4, while a signal for the similar oligomer in which the anhydride-derived end is hydrolyzed, but unesterified, diacid is marked **b**. For both **L,1** and **L,2** there are also signals at 22 Da higher mass than for **18** with Na^+ which are tentatively attributed to the same oligomer with an additional Na^+ and loss of H^+, possibly lost from the acid group of the monoesterified phthalic acid moiety. In the groups labeled **Am,*n*** the major signals are for oligomers **19** with Na^+ with smaller signals from the same species with methanol as adduct and for the same oligomer with K^+ and for related oligomers in which one end is unreacted amine; this latter signal is very small for **Am,2**. For **Am,3** there are just small signals for oligomer **19,*n*=3** with Na^+ and for its methanol adduct. Finally, for the groups **An,*n*** the major signals are for oligomers **20** with Na^+. For **An,1** there are also signals for related species with one end monoesterified. In one case, the other anhydride end is unreacted anhydride and, in the other case, is diacid. There are small signals for corresponding species in **An,2**. Also associated within the group **An,1** are two signals 22 and 44 Da higher than the main signal form the oligomer **20** which are consistent with species with one additional Na^+ and loss of one H^+ and with two additional Na^+ and two H^+, respectively; the H^+ of the unesterified acid groups could have been replaced by Na^+, and the signals are tentatively assigned to such species. Thus, almost all observable signals are attributable to likely oligomers. There are a few tiny peaks that do not appear to be attributable to any species consistent with the relevant known chemistry; these extraneous peaks do not fall into any consistent pattern either within an individual spectrum or between spectra for similar reaction products, allowing for mass differences. These peaks are therefore attributed to impurities or unrecognized adducts.

The spectrum from the same product obtained using a DMF solution was virtually identical to the above except for a few additional peaks, attributed to DMF adducts, and modified relative peaks intensities, thus supporting the validity of the assignments described above.

The other two products prepared from the two-ring, hindered diamines both gave very similar spectra to those from the above product. The only differences were some changes in relative intensities of the major peaks and minor differences in adducts observed. In both the product from **13aB** with **14iii** and that from **13aA** with **14iv** the major signals were from oligomers **18,*n*=2** with signals from **19,*n*=2** the next most intense. For the product from **13aB**/**14iii** signals from cyclic oligomers **17** were relatively less intense, but extended with very weak signals up $[M_3 + H]^+$ and $[M_3 + Na]^+$, while for the product from **13aA**/**14iv** no signals for cyclic oligomers were observed.

To summarize, in the spectra described above, most peaks, even the very small ones, could be attributed to a consistent series of oligomeric species. Most spectra contained a few additional signals, mostly extremely weak, which could not be attributed to any oligomer of realistic structure and sensible end groups. Furthermore, these extra peaks did not fall into any recognizable pattern, either within a spectrum or between spectra, allowing for compositional differences, and such peaks are assumed to arise from impurities or unrecognized adducts.

Comparison of Gel Permeation Chromatography and Mass Spectrometry Data. The relative intensities of peaks observed cannot be considered to provide definitive information on the populations of species present in the sample. Different solvents used to provide solutions for analysis gave rise to signals of different relative strengths from the same sample, even though the same species must have been present prior to dissolution. These differences reflect different solubilities of species in the reaction product. However, the spectra presented show that, in different samples, both cyclic and linear oligomers are readily observed. This contrasts with some other investigations of oligomeric polyimides where only cyclic species were observed, unless stoichiometric imbalances of reactants were used to minimize the content of cyclics in the products,[11] which might cast doubt on the ability to detect linear species. The observation of both types of species, and at different relative intensities, in the present work suggests that, to a first approximation, the spectra provide a reasonable representation of the species present in the reaction products. This view is reinforced from a comparison of mass spectrometric and gel permeation chromatographic data.

Gel permeation chromatograms and mass spectrometric data show interesting correlations. As already remarked, chromatograms for the higher-molecular-weight products derived from **14vi** show no sign of any oligomeric material at high elution volumes, Figure 1, traces **a** and **b**; all the product is contained within the high-molecular-weight envelope. In contrast, chromatograms for the lower-molecular-weight products exhibit distinct peaks for oligomeric species at high elution volumes, and the main undifferentiated peak is shifted to greater elution volumes.

Two types of such chromatograms are identified in Figure 1. First, the products from **13aB** with **14ii** and **13aC** with **14ii** (traces **c** and **e**) exhibit a single intense peak at very low molecular weight. These peaks correlate well with the corresponding mass spectrometric data that are dominated, in each case, by a single oligomeric species, namely the cyclic dimer (Figures 2 and 3). The mass spectra show only weak peaks for other oligomers, and there are no distinct peaks to correlate with such species in the chromatograms.

Second, the chromatogram for the polymer from **13aB** and **14iii** (Figure 1, trace **d)** and also for related products prepared from two-ring, hindered diamines **14iii** and **14iv** show a series of distinct, overlapping peaks at high elution volumes, extending beyond the normal calibration range of the GPC instrument to very low molecular weight. The mass spectra for these products all exhibit peaks for a series of oligomers, with no especially dominant peak, as observed in the previous examples. Although it is not possible, at this stage, to correlate individual peaks in the chromatograms with those in the ESI-MS spectra, it is clear that there is a strong correlation between the two sets of data, supporting the view that mass spectrometric data give a reasonable description of the populations of species present in the products isolated, especially at low molecular weights; the solvents used for samples preparation for ESI-MS were non-solvents for high-molecular-weight polymers.

Discussion of Results from Low-Molecular-Weight Products. Having established the nature of the products formed from 3-linked bis(ether anhydride)s and given the consistency of the correlations with GPC data, it is interesting to consider the origins of the different oligomers present in various products. It is also interesting to enquire why the products prepared from the 3-isomer bis(ether anhydride)s in this study are so different from those prepared from the 4-isomer dianhydrides and also from the high-molecular-weight products previously prepared by Takekoshi et al., using a high-temperature synthesis in *m*-cresol.[20]

We have already demonstrated precedents for the formation of cyclic oligomeric products from monomers with specific *ortho*-linked units. A previous communication described a poly(ether imide) obtained from a bis(ether anhydride) **13b** derived from catechol with 1,2-bis(2′-aminophenoxy)benzene, a combination which incorporated four *ortho*-linked phenylene rings in the repeat unit of the polymer structure.[38] The product obtained was of low molecular weight (although the gel permeation chromatogram did exhibit a peak at 38 kg mol^{-1}) and MT-MS established that the product contained a very high proportion of cyclic oligomers. Also, a more recent study of polyimides based on other dianhydrides with various three- and four-ringed aromatic diamines with 2-aminophenoxy groups, giving polymers with two or three *ortho*-linked phenylene groups per repeat unit, all gave low-molecular-weight polymers with high contents of cyclic oligomers; a characteristic only avoided if stoichiometric imbalances of monomers were used to force the presence of specific end groups and reduce the probability of macrocycle formation.[11] The current observation of cyclic and linear oligomers in polymers derived from bis(ether anhydride)s with the ether linkages *ortho* to the anhydride is an interesting variant to those previous studies.

Although the initial treatments of step polymerization assumed formation of linear species only,[40] it was soon realized that cyclic species must be formed concurrently.[41] Subsequent work established that high extents of reaction inevitably correspond to the formation of cyclic species.[42] Those conclusions do not determine the nature of the products. Whether the products at high conversion are oligomers or high-molecular-weight polymers must depend on the relative rate coefficients for cyclization and growth at each stage. Jacobson−Stockmeyer theory predicts that the population of cyclics should decrease with ring size as $n^{-1.5}$, where n is the degree of polymerization;[41] this dependence is based on the assumption of a Gaussian distribution of end-to-end distances of the growing species. Kricheldorf et al. recently suggested introducing a parameter to quantify the propensity for cyclization.[43] We recently reported a situation exemplifying this distinction where poly(ether imide)s, prepared using the same procedure as that employed here and with several dianhydrides, at high conversion produced high-molecular-weight polymers from bis(4-aminophenoxy) diamines but cyclic oligomers from bis(2-aminophenoxy) diamines.[11] The distinction between these scenarios had little to do with the intrinsic reactivity of the diamines but to the disposition of the amine groups *ortho* to the phenoxy linkage.

The first step in the solution polymerization process used here (Scheme 1) is a reversible, exothermic, addition reaction, favored at lower temperatures, to form amic acid units and, if the growth process continues, poly(amic acid). It is our experience, and that of many others, that for reaction between a wide variety of diamines and bis(ether anhydride)s with 4-linked phthalic anhydride units the equilibrium constants for this process are normally very high, and reaction leads to viscous solutions of high-molecular-weight poly(amic acid)s. Subsequent chemical imidization, by addition of acetic anhydride/acetic acid mixture, converts the distribution of poly(amic acid) species to poly(etherimide); it is presumed that imidization essentially quenches the equilibrium process. Thus, the final product molecular weight distribution reflects the distribution of poly(amic acid) species. That is, extents of reaction are very high, and there is little formation of cyclic oligomers. The only major exception that we are aware of is where bis(2-aminophenoxy) diamines are used when, with a stoichiometric equivalence of reagents, the products are almost exclusively cyclic oligomers.[11] The amine groups situated *ortho* to the ether linkages are reactive and lead to high extents of reaction but predispose the poly(amic acid) oligomers to cyclize rather than grow to high-molecular-weight species.

The procedure adopted by Takekoshi et al., to produce high-molecular weight poly(etherimide)s from 3-linked bis(ether anhydride)s, is rather different.[20] At the high temperatures used, any preformed poly(amic acid) would tend to depolymerize. However, thermal dehydration to convert amic acid to imide, with continuous removal of water liberated, would eventually and inevitably achieve high extents of reaction. In practice, the polymers formed were of moderately high molecular weight, but in principle, with other monomer combinations, high-molecular-weight cyclic polymers or oligomers could be produced.

In our recent study of bis(2-aminophenoxy) diamines, of different rigidities and with different numbers of aromatic rings, we established that reaction with any of a variety of 4-linked dianhydrides almost always resulted in the formation of cyclic oligomers. Only when a stoichiometric excess of one or other reagent was used were linear oligomers formed; the exception was the product from pyromellitic dianhydride and 4,4′-bis(2-aminophenoxy)biphenyl, both of which had rigid elements and had disparate lengths, where a mixture of cyclic and linear oligomers was formed.[11]

Those observations have parallels in this study. Analysis of the product prepared from **13aA** and **14v**, the short, flexible, unhindered diamine, exhibited strong evidence for macrocycle formation, albeit for the cyclic dimer only (Figure 2); the gel permeation chromatogram was weak and showed no distinctive features. In contrast, the longer diamine **14vi** with any dianhydride gave high-molecular-weight polymers. It is difficult to perceive, on the grounds of chemical reactivity, why, with several bis(ether anhydride)s with 4-linked phthalic anhydride units, diamines **14v** and **14vi** both give high-molecular-weight poly(ether imide)s, but with the isomeric 3-linked dianhydrides only **14vi** gives high-molecular-weight poly(ether imide)s while **14v** gives cyclic oligomers. We can only attribute this distinction to the conformations preferentially adopted by the poly(amic acid) oligomers from 3-linked dianhydrides with **14v**. We assume that the ends of such [$n + n$] oligomers have a high tendency to come into close proximity and cyclize, whereas the end groups of the equivalent species based on **14vi**, with their rigid central biphenyl units, tend to be forced apart and react by further polymer growth.

The other products examined here were all prepared from diamines with hindering methyl groups *ortho* to the amine groups, i.e., from **14ii**, **14iii**, or **14iv**. These methyl groups restrict the approach of anhydride and amine units. Other studies have demonstrated that the rate coefficient for propagation in such situations is more than an order of magnitude lower than in the absence of methyl groups;[39] the methyl groups must also restrict rotation in the final substituted *N*-phenylphthalimde units. However, this fact alone in insufficient to explain all the observations. First, all these diamines produced similar high-molecular-weight polymers from the 4-linked dianhydrides, as did the unhindered diamines under the reaction conditions employed. Second, mesitylene diamine, **14ii**, produced cyclic oligomers only, indicating a high extent of reaction, with various dianhydrides, while **14iii** or **14iv** gave primarily or exclusively linear oligomers, corresponding to low extents of reaction.

In the case of the products prepared from **14ii**, the absence of rotational isomerism within the diamine forces adjacent groups to an angle of 120° to each other. We suggest that this constraint forces the terminal reactive end groups of the [$n + n$] poly(amic acid)s closer than in many other situations and consequently enhances macrocycle formation. Space-filling models show that, with some flexibility in the diamine moiety, it is relatively easy to form the cyclic dimer, identified as the main oligomeric species formed. ES-MS spectra show a large content of cyclics (e.g., Figure 3), and chromatograms show a single distinct peak (e.g., Figure 2c,e) which is likely to correspond to the cyclic dimer.

Within the series of 2-ring aromatic diamines there is a clear distinction between the behavior of species derived from hindered and unhindered diamines. The unhindered diamine **14v**, with its flexible central ether linkage, gave rise to mainly cyclic products. In contrast, diamine **14iii**, a diamine with a central flexible methylene linkage but with hindering *ortho*-methyl groups, gave primarily linear oligomers, with some cyclic species, while the diamine **14iv** having a rigid biphenyl unit, also with hindering methyl groups, gave almost exclusively linear oligomers. It appears that the methyl groups, *ortho* to the amine and, ultimately, to the phthalimide unit, reduce both the formation of cyclic amic acid species and the overall rate of reaction. The hindering methyl groups, when reacted with the anhydride units of the bis(ether anhydride), occupy space above and below the amide linkage in the poly(amic acid) intermediate and might well restrict the local conformations adoptable at the ether linkage in the dianhydride moiety, forcing neighboring units away from each other and leaving the oligomers less able to form cyclic products, reducing the rate of cyclization. This tendency, it is expected, would be enhanced in the case of the rigid diamine **14iv** where phthalic residues at either end of the diamine are forced away from each other and where no cyclic products were observed. Poly(ether imide)s derived from **14iv** have large, linear, rigid units consisting of two phthalimide groups and a biphenyl group that could hinder cyclization.

These considerations, however, do not immediately explain the low extents of reaction achieved, resulting in linear oligomers with reactive end groups, in the case of the hindered diamines with 3-linked dianhydrides. At this stage we can only presume that conformations of active species are such as to massively retard reaction over and above that which might be expected on the grounds of intrinsic reactivity of the end groups and that the difference in flexibility between **14iii** and **14iv** gives a higher proportion of cyclic oligomers in the former case.

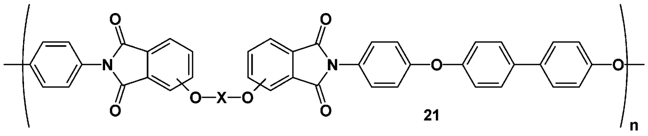
The several results presented here, and their potential interpretation, suggest that the reaction mechanism for the synthesis of poly(ether imide)s by the solution polymerization route is more subtle than has so far been recognized. To validate the suggested interpretation or to establish alternative explanations for the observations reported will require substantial further research.

Table 4. Characterization of Polyimide Films Used in Studies of Physical Properties

polyimide	M_p [kg mol^{-1}]	T_g [°C]	thickness [μm]	density [g cm^{-3}]	V_f
21aA	105	236	32	1.248	0.162
21bA	130	220	56	1.242	0.166
21aB	68	259	48	1.226	0.169
21bB	64	248			
21aE	51	275	51	1.182	0.184
21bE	394	262	49	1.180	0.185
21aF	114	234	45	1.348	0.172
21bF	71	217	44	1.355	0.168

Attempts to extract oligomers from the precipitated high-molecular-weight poly(ether imide)s formed from 4-linked dianhydrides to provide analytical samples failed to give any identifiable signals. It is possible that either a very low content of oligomers formed were trapped in the precipitate or were lost on polymer isolation

Physical Property Studies of High-Molecular-Weight Polymers. To determine the physical properties of polymers and to correlate dielectric relaxation and free volume data with permeability data, it is necessary to use materials that have truly polymeric properties and can be cast into free-standing, creasable films. This requires polymers that are soluble and have high molecular weights (>60 kg mol^{-1}). The 3-linked poly(ether imide)s prepared by solution polymerization and chemical imidization from one- and two-ring diamines gave oligomers that were unsuitable for investigation. However, simply extending the length of the diamine to four aromatic rings, with some in-built flexibility, allowed formation of high-molecular-weight polymers **21** from diamine **14vi**. We, therefore, compared the properties of 3- and 4-linked poly(ether imide)s **21** with diol residues **10X** (**X = A, B, E** and **F**), as defined in Scheme 1. These polymers were prepared on a larger scale, and their molecular weights and T_gs are presented in Table 4. Polyimide **21bB** was not soluble in organic solvents suitable for casting membranes and, after initial characterization, the polymer was excluded from further studies. Other characteristics of the polymers and films used are presented in Table 4.



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The high-molecular-weight polymers (Table 4) exhibit consistently higher T_gs for the 3-linked poly(ether imide)s **21aX** than for their 4-linked isomers **21bX**; this observation is in accord with data reported previously for related 3- and 4-linked poly(ether imide)s.[16,20] T_gs of other 3-linked polymers, recorded in Table 3, were too low to allow a valid comparison with their 4-linked isomers, but where moderate molecular weights were obtained, the data are consistent with the above observation.

Theories of gas permeability differentiate the diffusion process according to the extent to which the diffusing species can move relative to the mobility of the matrix. Large-scale motion is characterized by T_g, which for the polyimides is relatively high. It would therefore appear appropriate to consider these polymers as being glasses. However, the possibility exists that within these polymers, a significant amount of molecular motion can occur below T_g. A dielectric study was carried out to determine the extent to which such molecular motions can occur and to explore

Table 5. Havriliak−Negami Parameters, Loss Maximum, and Dipole Strength at − 100 °C

polyimide	α	β	loss (max)	$\epsilon_s - \epsilon_\infty$	E_a (kJ/mol)
21aA	0.47	0.31	0.0446	0.385	31.8 + 0.8
21bA	0.52	0.28	0.0140	0.115	31.1 ± 0.9
21aF	0.48	0.59	0.0311	0.202	34.7 ± 1.3
21bF	0.49	0.32	0.0268	0.225	28.4 ± 1.6
21aB	0.47	0.38	0.0483	0.38	29.6 ± 1.7
21bB	−	−	−	−	
21aE	0.49	0.32	0.0426	0.344	31.4 ± 0.8
21bE	0.50	0.44	0.0311	0.215	30.9 ± 0.9

whether any significant differences exist between the molecular mobility of the chains within this series of polymers.

Dielectric Characterization. Detailed isothermal spectra for the several polymers were determined at intervals of 10 °C from −140 to −60 °C over the frequency range 0.1−65 kHz, and data are given in Table 5. Example data for polymer **21bF** are in shown in Figure 5. Combining the variations in dielectric permittivity (ϵ') (Figure 5a) and dielectric loss (ϵ'') (Figure 5b) with log frequency allowed Cole−Cole plots to be created (Figure 5c). Using the result of the analysis, the characteristic frequency was calculated and used to compute the activation energies for dipole relaxation (Figure 5d). The dielectric plots for this group of polymers are characterized by a single dipole relaxation process as indicated by a single relaxation process (Figure 5c). The Arrhenius plots indicate a thermally activated process, and relevant values are presented in Table 5. The activation energies do not differ significantly between the several polyimides. The Cole−Cole plots shown in Figure 5d were fitted in agreement with the Havriliak−Negami equation;[34] values of α, β, the dielectric loss maximum, and the oscillator strength, ($\epsilon_s - \epsilon_\infty$), at −100 °C are displayed in Table 5.

In general, the β-relaxation processes in all the polyimides studied were broad due to the nonuniformity of the glassy state and the variety of local environments around the dipoles. The coincidence of the Cole−Cole plots obtained at different temperatures indicates that the nature of the process associated with the dipole relaxation does not change over the temperature range studied. The activation energies all have similar values, implying that the barrier to reorientation is similar for all the polymers studied. Inspection of Figure 5 indicates that the common element for all the polymers would be the diphenyl ether unit. Changes in the nature of the linking bridge unit (**X**) would influence the chain−chain interactions but will not dramatically influence the form of the barrier. The differences in the magnitude of $\epsilon_s - \epsilon_\infty$ would arise from changes in the distribution of dipoles involved in the relaxation process which would be sensitive to the distribution in the ground state. Comparison of the 3- and 4-isomers indicates that certain systems, i.e **21aA** and **21bA**, exhibit significant differences whereas the values for **21aF** and **21bF** are relatively close. The difference between these structures is the presence of the fluorine atoms in the bridge methylene structure between the two phenyl groups in **21aF** and **21bF**. The differences in the ability to pack chains in this central section as influenced by the 3- or 4-linkage influences the energy difference between states accessed during the dipole rotation and change the observed strength of the process.

Inspection of Figure 5d indicates that the dipole motion at room temperature occurs with a relaxation time less than 10^{-10} s. For all of the polymers studied, the dipoles are labile at room temperature and indicate that, despite the high glass transition of the polymer, localized motions of the polymer backbone are possible and will aid gas diffusion through the membrane.

Positron Annihilation Lifetime Spectroscopy. In previous studies, [3] the ability to demonstrate a correlation between the average void structure (i.e., free volume) and the permeability of a gas through the matrix was shown. Subsequently, a number of papers illustrating the validity of this approach have appeared.[4,44,45]

The positron annihilation process can be influenced by the chemistry of the matrix, but within a series of closely-related structures such as the polymers measured in this paper, it can be assumed that the observed changes are directly related to the relative changes in free volume. The lifetime of the positron annihilation provides a measurement of the average void size, whereas the intensity is directly proportional to the number of voids in the matrix capable of trapping positronium. The dielectric studies indicate that the cavities change at a rate greater than the positron lifetime, indicating that the quantity measured is a truly averaged value for the free volume radius. The results of the positron studies are presented in Table 6. The mean values for *o*-Ps lifetimes, τ_3, intensities I_3, hole radii R, and free volumes V_{Ps} as calculated by the described τ_3−hole radius relationship.[46] The free volumes probed by *o*-Ps showed that for the polyimides which do not contain fluorine atoms the lifetimes and intensities were higher for the 4-isomers than for the 3-isomers. The total free volumes, calculated as $\tau_3{}^3I_3$, probed by PALS were therefore higher for the 4-isomers in comparison to the values for the 3-isomers. A closer inspection of the data indicates that in certain cases the mean radius and the total number of the cavities do not follow this simple correlation.

For the fluorine-containing polyimides, the free volume of the 4-isomer presented a higher concentration of “voids”, as probed by the intensity of the long lifetime component, but of smaller size than those observed for the 3-isomer. The high values for the product observed with **21aE** and **21bE** are indicative of the effects of steric hindrance of bulky *tert*-butyl groups in the bridge group opening up the matrix that aids the diffusion process. The close packing possible with the dimethyl-substituted bridge group in **21aA** leads to both a smaller radius for the voids and a lower intensity. The *ortho*-methyl substituents in **21aB** inhibit favorable packing leading to an increased void radius and a slight increase in the number density of voids. The bigger microvoids available in the 3-isomer polyimide would allow a higher probability of diffusion jumps of the gas molecules and promote permeability. However, the free volume probed by PALS defined as $\tau_3{}^3I_3$ in this case is higher for the 4-isomer-containing polyimide which implies that on average there is more space for diffusion. This begs the question of whether it is the size of the void or its frequency that is the governing factor for diffusion in the membrane.

Gas Permeability. The permeabilities and diffusion and solubility coefficients of the polyimides were determined at 298 K and 4 atm pressure for oxygen, carbon dioxide, nitrogen, and argon gases. Permeabilities for the several gases for each polymer are recorded in Table 7.

For systems investigated here the permeability coefficients (P) vary by more than a factor of 3 depending on the structure of the polyimide and gas used. Values of P for polymers with 4-phthalimide units (designated **21b**) show the same tendencies between structure and properties as those reported previously.[3] The same tendencies are maintained for the new polymers with 3-phthalimide units, designated **21a**. Thus, it has long been recognized that fluorine-containing polymers have higher permeabilities than their hydrogenated equivalents.[44] Data in Table 7 are generally consistent with this observation where fluorinated poly(ether imide)s **21aF** and **21bF** have higher permeabilities than **21aA** and **21bA**, except when argon is the permeant where values for **21bA** and **21bF** are very similar. Methyl and *tert*-

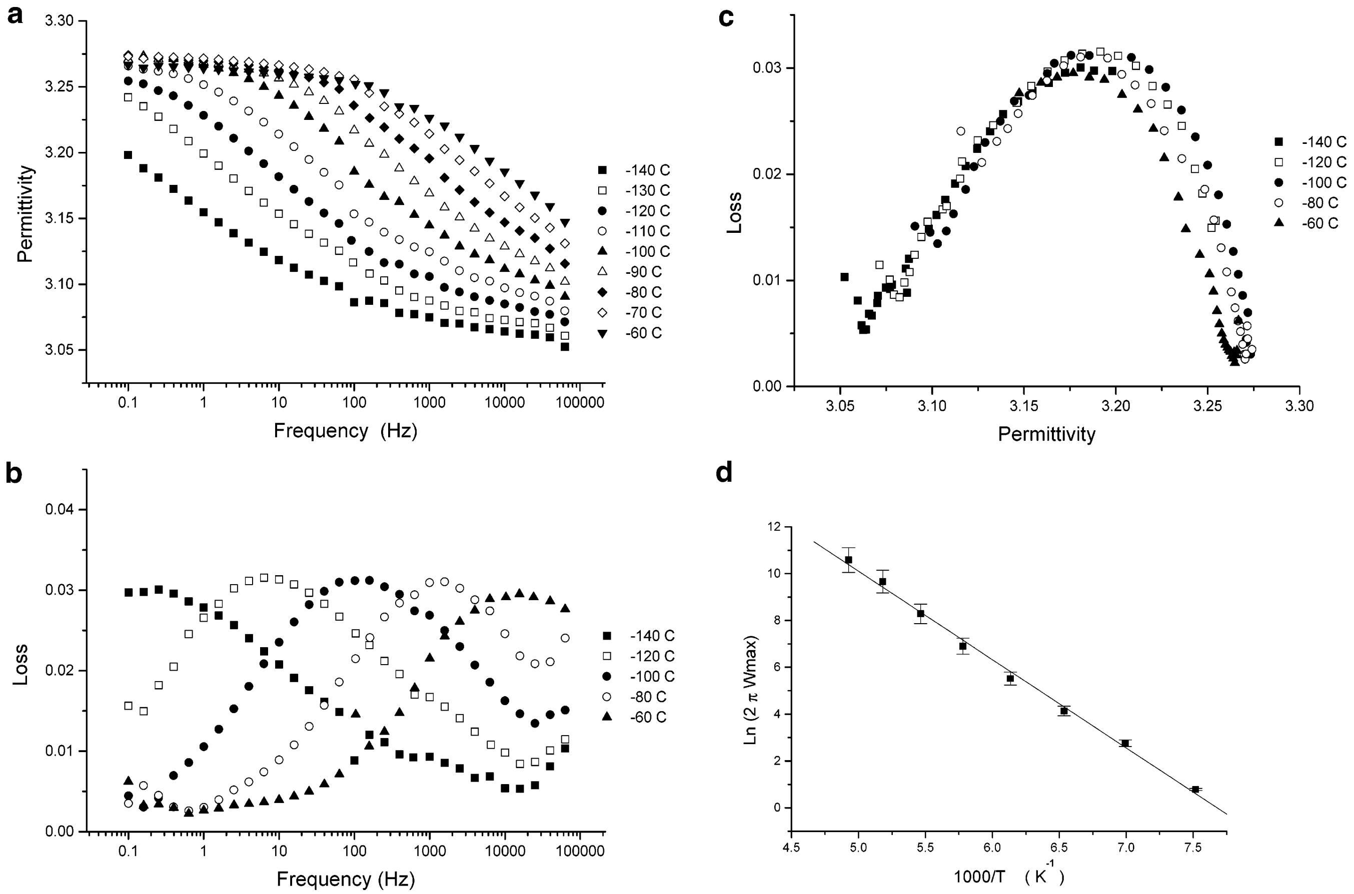

Figure 5. (a) Dielectric permittivity spectra for **21bF** polyimide. (b) Dielectric loss spectra for **21bF** polyimide. (c) Cole−Cole plot for **21bF** polyimide. (d) Arrhenius activation energy plot for **21bF** polyimide.

Table 6. Lifetime, Intensity, and Spherical Cavity Model Results for the Polyimides at 298 K

polyimide	τ_3 (ns)	I_3(%)	R (nm)	V_{Ps} (nm^3)	$\tau_3{}^3 I_3$ [(ns^3%)]
21aA	1.53 ± 0.02	10.2 ± 0.6	0.238 ± 0.003	0.056 ± 0.001	36.5 ± 2.5
21bA	1.75 ± 0.03	12.9 ± 0.2	0.261 ± 0.004	0.074 ± 0.002	69.1 ± 2.9
21aF	2.01 ± 0.01	12.1 ± 0.8	0.286 ± 0.001	0.098 ± 0.001	98.2 ± 3.8
21bF	1.95 ± 0.02	14.4 ± 0.1	0.282 ± 0.003	0.094 ± 0.002	106.7± 3.9
21aB	1.87 ± 0.02	12.3 ± 0.7	0.273 ± 0.003	0.085 ± 0.002	80.4 ± 3.0
21aE	2.11 ± 0.02	17.6 ± 0.4	0.295 ± 0.003	0.108 ± 0.002	165.3± 2.9
21bE	2.14 ± 0.02	22.3 ± 0.2	0.298 ± 0.003	0.111 ± 0.002	218.5 ± 3.1

Table 7. Permeability Coefficients for Oxygen, Carbon Dioxide, Nitrogen, and Argon in Polyimides, Based on Diamine 14vi, at 298 K and 4 atm[a]

polyimide	$P_{O_2}{}^{b}$	$P_{CO_2}{}^{b}$	$P_{N_2}{}^{b}$	$P_{Ar}{}^{b}$
21aA	0.45	2.22	0.08	0.35
21bA	0.79	2.26	0.08	0.45
21aB	1.64	4.26	0.33	0.65
21aE	2.75	7.02	0.69	1.45
21bE	3.37	13.47	0.56	1.41
21aF	1.56	5.09	0.29	0.64
21bF	0.99	3.27	0.21	0.40

[a] Values of P are in 10^{-10} cm^3 (STP) cm^{-1} s^{-1} cmHg^{-1}. [b] ± 3% error.

butyl substituents on the diol moiety *ortho* to the ether linkages to the phthalimide unit have also been reported to increase permeability,[1,2] and this tendency is maintained here as illustrated with **21aB**, **21aE**, and especially **21bE**.

Distinctions between the overall permeabilities of poly(ether imide)s based on 3- and 4-linked phthalimide units are not consistent. In some cases, permeabilities of gases through poly(ether imide)s with 3-linked phthalimide units are lower than, or similar to, those for the 4-linked isomer. This situation applies to polymers based on diol **10A** for all gases and for those based on **10E** for oxygen and carbon dioxide. However, for the fluorinated poly(ether imide)s based on **10F**, for all gases, and for the polymers based on **10E** for nitrogen and argon diffusion, the polymers with 3-phthalimide units have the higher permeabilities.

Within this series of polymers, there is a strong correlation between gas permeabilities and both the positron annihilation data and calculated free volume fractions V_f recorded in Table 4. For all gases, values of P increase with values of V_f calculated from the polymer densities with the aid of eq 1, although the permeability of **21aE,** with *tert*-butyl groups, toward carbon dioxide is relatively high.

Solubility coefficients S, determined from nonstationary permeability data and recorded in Table 8, exhibit high values for carbon dioxide for all polymers. The other main feature of the data is that solubility coefficients are higher for polymers with *ortho*-methyl or *tert*-butyl groups. In most cases introduction of trifluoromethyl groups (in **21aF** and **21bF**) enhance solubility coefficients over those of **21aA** and **21bA**, except that for **21aF** the solubility coefficients for carbon dioxide and argon are lower, as is that for nitrogen in the case of **21bF**.

Table 8. Solubility Coefficients for Oxygen, Carbon Dioxide, Nitrogen, and Argon in Polyimides at 298 K and 4 atm[a]

polyimide	S_{O_2}[b]	S_{CO_2}[b]	S_{N_2}[b]	S_{Ar}[b]
21aA	7.2	75.1	4.5	9.8
21bA	4.2	50.4	2.8	7.3
21aB	11.4	74.5	6.5	10.7
21aE	13.7	75.9	9.2	13.8
21bE	7.8	79.9	6.9	11.2
21aF	7.5	56.1	5.6	8.8
21bF	5.7	69.8	2.2	8.2

[a] Values of S are in 10^{-3} cm^3 (STP) cm^{-3} $cmHg^{-1}$. [b] ± 3% error.

Table 9. Diffusion Coefficients for Oxygen, Carbon Dioxide, Nitrogen, and Argon in Polyimides at 298 K and 4 atm[a]

polyimide	D_{O_2}[b]	D_{CO_2}[b]	D_{N_2}[b]	D_{Ar}[b]
21aA	6.2	3.0	1.8	3.6
21bA	18.8	4.5	3.0	6.2
21aB	14.4	5.7	5.0	6.1
21aE	20.0	9.2	7.5	10.5
21bE	43.1	16.9	8.0	12.6
21aF	20.9	9.1	5.2	7.3
21bF	17.4	4.7	9.6	4.9

[a] D is in 10^{-9} cm^2 s^{-1}. [b] ± 3% error.

Table 10. Selectivity Ratios for Polyimides at 298 K and 4 atm

polyimide	P_{CO_2}/P_{O_2}	P_{CO_2}/P_{N_2}	P_{O_2}/P_{N_2}	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
21aA	4.9	27.4	5.5	3.5	1.6
21bA	2.9	26.9	9.3	6.3	1.5
21aB	2.6	13.0	5.0	2.9	1.7
21aE	2.6	10.2	4.0	2.7	1.5
21bE	4.0	24.3	6.1	5.4	1.1
21aF	3.2	17.5	5.4	4.0	1.3
21bF	3.3	15.8	4.8	2.8	1.7

Diffusion coefficients D were determined from permeabilities P and solubility coefficients S, assuming that P is the product of D and S (Table 9). Again, the fluorinated polymers **21aF** and **21bF** have higher values of D than their hydrogenated equivalents, **21aA** and **21bA**, except for values of D for oxygen and argon for **21bF**, where lower values of D were found. Polymers with *ortho*-methyl (**21aB**) and *tert*-butyl (**21aE**, **21bE**) groups also have high values of D. For the nonfluorinated polymers, values of D for the 4-linked polymers were higher than for the 3-linked polymers. For the fluorinated polymers the reverse trend was observed, except for nitrogen diffusion where again D for the 4-linked polymer was higher. Apart from the low values of D for **21aF**, for diffusion of oxygen, and **21aE**, for diffusion of carbon dioxide, and the high value of D for **21bF**, for diffusion of nitrogen, values of D are almost proportional to V_f.

Comparison of the values of P, D, and S shows that the high permeabilities of some poly(ether imide)s are primarily a result of high solubility coefficients, although fluorinated polymers often have been reported to have high permeabilities. However, as in our previous studies,[1,2] it is polymers with *ortho*-methyl groups in the diamine moiety and especially with *ortho*-*tert*-butyl groups which have the highest permeabilities. These tendencies were attributed to the alkyl substituents hindering chain packing to leave voids that enhanced gas permeability. This proposition is supported by the positron annihilation lifetime data.

Table 10 presents permselectivities for several pairs of gases for each polymer. It is generally perceived that there is a tradeoff between permselectivity, calculated from single gas permeabilities, and permeabilities of the permeants, so that high permeability is often associated with low selectivity, and vice versa.[47,48] This tendency, based on the data in Table 10 and other combinations of permeabilities for gas separations, is generally consistent with most data determined in our broader studies but, within the limitations of this study, is not strictly adhered to within the small series of polyimides having either 3- or 4-linked dianhydride moieties. The main exceptions to the general trend are that polymer **21bE** exhibits the best combination of permeability and permselectivity for carbon dioxide/nitrogen, carbon dioxide/oxygen, oxygen/nitrogen, oxygen/argon, and carbon dioxide/argon separations and good permselectivity for oxygen/argon separations. High overall properties for gas separation, especially for oxygen/nitrogen separation, for polymers based on the dianhydride **13bE** have been reported previously.[2] The related polymer **21aE** also has relatively high permselectivities with good permeabilities for argon/nitrogen and oxygen/argon separations.

Ding et al. reported relatively high permselectivities for hydrogen/nitrogen and oxygen/nitrogen separations for two specific polyimides based on 3,3′-linked phthalimides and **14**, but associated with lower permeabilities than their 4,4′-linked isomers.[21] Based on the data in the current study, this tendency is not general. For single gas permeabilities determined here, in some cases permeabilities for polymers based on 3-linked dianhydrides are higher and in some cases lower than those of their 4-linked isomers. Although there is some tendency for the polymers based on 3-linked dianhydrides to exhibit lower diffusion and higher solubility coefficients, these tendencies are not consistently upheld; the fluorinated polymers tend to exhibit the opposite trend. Similarly, there is no overriding tendency in permselectivity among the polymers with 3- or 4-linked dianhydride moieties.

Plots of diffusion coefficients and permeabilities indicate that, for the gases studied, these parameters are almost proportional to $\tau_3{}^3 I_3$. However, closer inspection indicates that significant deviations for the apparent linear correlation do occur in the case of the diffusion coefficient and reflect the effects of local interactions which are reflected in the solubility coefficients. Because the cavities are dynamic entities, it is also possible that subtle effects of shape and the distribution can be influencing the values and lead to apparent deviations from a simple linear behavior.

Conclusions

By performing aromatic nucleophilic displacement reactions between various diols and 3-nitrophthalodinitrile, in the presence of potassium carbonate in anhydrous dimethyl sulfoxide, it was concluded that the reaction proceeds with equal facility as the well-established reaction with 4-nitrophthalodinitrile. The bis(ether dinitrile)s so formed were readily converted to bis(ether anhydride)s.

From the results of polymerization reactions between bis(ether anhydride)s and 4,4′-bis(4″-aminophenoxy)biphenyl, it was concluded that bis(ether anhydride)s with 3-phthalic anhydride units react with at least equal facility as bis(ether anhydride)s with 4-phthalic anhydride units.

Bis(ether anhydride)s with either 3- or 4-phthalic anhydride units were polymerized in solution (10 wt % solids) with a variety of aromatic diamines and imidized. The reaction products were characterized. While it was demonstrated that the bis(ether anhydride)s with 4-phthalic anhydride units, as observed in other studies, gave high-molecular-weight polymers, it was concluded that bis(ether anhydride)s with 3-phthalic anhydride units prepared in this way, in most cases, yield only low-molecular-weight products. These low-molecular-weight products were examined by electrospray-ionization mass spectrometry, and from an analysis of the results it was concluded that the products were small oligomers, either cyclic or linear. It was further concluded that products from bis(4-aminophenoxy) ether (ODA) as diamine were almost exclusively cyclic oligomers, with domination by the cyclic dimer. Products prepared from mesitylene diamine were also dominated by cyclic dimer, but with low contents of other cyclics and several linear species. In contrast, products from other diamines with hindering *ortho*-methyl groups were dominated by various linear oligomers. From these data it was concluded that oligomers with ODA and mesitylenediamine as diamines favor macrocycle formation but that oligomers from other diamines with hindering diamines adopt conformations which favor neither polymer growth nor cyclization.

A series of high-molecular-weight poly(ether imide)s were prepared from BAPB and each of several bis(ether anhydride)s with 3- or 4-phthalic anhydride units and were characterized with respect to molecular weight and glass-transition temperature. By comparing data from groups of polymers, it was concluded that polymers with 3-linked phthalimide units had T_gs 10−20 °C higher than their isomers with 4-linked phthalimide units; this extends data previously reported for other pairs of such polymers.[16,20] This effect presumably arises from restrictions to rotation about the ether linkage in the ether anhydride moiety. Interactions between the associated phenyl group of the diol and the phthalimide rings will enhance the energy barrier to rotation and/or the magnitude of the smallest unit able to undergo the large-scale reorientations associated with T_g. In contrast, from the dielectric study it was concluded that all the polymers contain a backbone segment capable of undergoing rapid, small-scale molecular motions at room temperature and aiding gas diffusion. Because the polymers are characterized by a single dipole-relaxation process, it is further concluded that the same structural unit is responsible for this motion in all cases.

From the analysis of gas permeation data for diffusion of single gases, it was concluded that polymers having 3- or 4-phthalimide units exhibited similar properties with no systematic differences between them. However, it was concluded that high permeabilities to carbon dioxide for both groups of polymers is primarily a consequence of high solubilities of carbon dioxide. The higher values of D found for nonfluorinated, 4-linked polymers were reversed for 3-linked polymers, except for nitrogen diffusion From permeation and PALS studies it was also concluded that *tert*-butyl groups *ortho* to the ether linkage in the polymers with 3-phthalimide units open the structure and enhance free volume, as shown in this study and previously for polymers with 4-phthalimide ether units.[3] It was also shown that there is a good general correlation between both P and D and free volumes as determined by PALS, and the data implied that the size of voids and their distribution controls the ability of gas molecules to diffuse through the membrane. These studies also indicated that, to a first approximation, the polymers with 4-linked phthalimide units have the higher free volume. It was also concluded that, while for the nonfluorinated polymers, values of τ_3 and I_3 are generated for the 4-linked polymer, for the fluorinated polymers the 4-linked polymer had more voids, but of smaller size.

A graphical comparison of permeability and permselectivity data clearly shows that, while both the 3- and 4-linked poly(ether imide)s with *ortho*-*tert*-butyl substituents **21aE** and **21bE**, respectively, have relatively high permeabilities for all gases studied, the 4-linked polymer **21bE** is far superior in terms of permselectivity and has the best overall properties for gas separation. This conclusion extends a similar observation for other poly(ether imide)s based on the same dianhydride.[2]

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