

Isomeric poly(ether imide)s: synthesis, thermal properties and permeabilities

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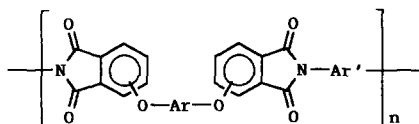
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This paper describes the synthesis of a novel series of poly(ether imide)s formed as isomeric pairs of polymers by interchanging the diol and diamine derived units. The polymers contained units having flexible and stiff hinges and groups to hinder segmental rotation. Most polymers were soluble in a variety of solvents, which allowed them to be characterized and cast into membranes. Permeabilities to carbon dioxide and methane and glass transition temperatures were determined. Consideration of structure–property relations showed the properties of the polymers to be sensitive to the position of the structural units within the polymer. The polymers showed a linear relationship between permeabilities to the two gases. There was a strong trend between high permeability and high glass transition temperature, suggesting that rigid polymers incapable of inefficient packing lead to highly permeable membranes and that such factors were enhanced by the presence of bulky substituents.

(Keywords: poly(ether imide); isomer; glass transition temperature; gas permeability; permselectivity)

INTRODUCTION

Poly(ether imide)s, with the general structure:



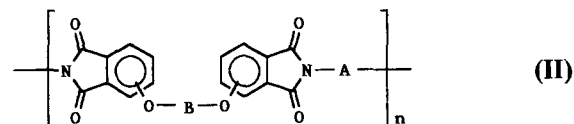
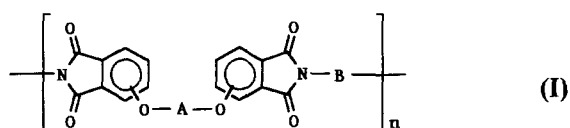
have found favour for potential applications such as membrane technology because they are more processable than polyimides. The large number of commercially available aromatic diols, the source of the Ar units, and diamines, the source of the Ar' moieties, means that hundreds of chemically different poly(ether imide)s may be synthesized.

There is, therefore, interest in developing algorithms based on group contributions for structural units (either in the main chain, such as isopropylidene or ether linkages, or in side chains, e.g. methyl, ethyl, etc.) to predict structure–property relationships¹. To develop such algorithms it is necessary to determine if a group's contribution to some property is sensitive to its location in the polymer. Thus, it is appropriate to study polymers that have identical groups organized differently within the polymer structure.

One approach is to produce polymers with different distributions of the same structural units through the synthesis of random and block copolymers. Our work in this direction will be described in a separate publication².

In this paper we consider an alternative approach, specifically applicable to poly(ether imide)s, which is based on the fact that the same aromatic moieties (Ar,

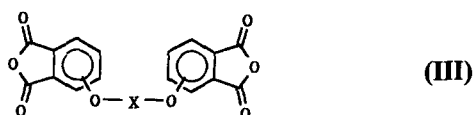
Ar') are often available as both diol and diamine. Consider two moieties A and B. Construction of the poly(ether imide) from the diol HO–A–OH and diamine H₂N–B–NH₂ gives polymer I; alternatively, diol HO–B–OH and diamine H₂N–A–NH₂ gives polymer II. Polymers I and II are isomeric. While it is possible to produce isomeric polymers in other ways, e.g. by having substituents in different locations or by interchanging *ortho*, *meta* and *para* isomers of monomers, this paper is concerned with isomeric pairs of polymers of types I and II.



We consider the properties of a limited selection of the available pairs of isomeric poly(ether imide)s. Figure 1 shows the structural moieties used in this study in the form of diols; the same moieties are available and were used as diamines. These species are a selection of rigid, flexible and hindered structures. To define the structures of specific polymers, we adopt the alphabetical notation used in Figure 1 to identify the structural units; the same symbol is used to identify diol and diamine. The diols were used in the synthesis of bis(ether anhydride)s, which were subsequently reacted with diamines to form the poly(ether imide)s; the symbol used to identify the diol is also applied to the corresponding bis(ether anhydride). To define a specific polymer we use the alphabetical

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symbol of the bis(ether anhydride) (and diol) first and diamine second. Thus, poly(ether imide) I, based on the bis(ether anhydride) derived from diol A and diamine B, is referred to as polymer A/B. The isomeric polymer II is B/A. In all cases in this study the bis(ether anhydrides) were derived from 4-substituted phthalic anhydrides, e.g. III is derived from HO-X-OH.



In this study we determined the glass transition temperatures of several isomeric pairs of poly(ether imide)s, of known molecular weight, based on structures in Figure 1. We determined the polymers' permeabilities to selected gases and monitored their long-range order. Thus, while considering the arrangements of structural units on properties, we take this opportunity to discuss the influence of hinged, rigid and hindered (bulky) units on selected properties. While synthesizing the polymers we examined the kinetics of poly(amic acid) formation, and the results of that study will be published separately².

EXPERIMENTAL

Materials

The diols, identified by symbols in Figure 1, were obtained from Fluka (A) or Kennedy and Klim Inc. (B, C, D, E), and were used without further purification. The diamines were obtained from British Petroleum (B), Kennedy and Klim Inc. (C, E) and Aldrich Chemical Co. (D). Bis(aniline-A) was prepared according to the procedure patented by Bayer³. 4-Nitrophthalic anhydride was obtained from Lancaster Synthesis. Aniline, *N,N*-dimethylacetamide (DMAC) and *N*-methylpyrrolidinone (NMP) were obtained from Aldrich. Acetic anhydride and pyridine, general reagents, were used as supplied.

Syntheses

Bis(aniline-A). Aniline hydrochloride was prepared, purified and then reacted (2 mol) in the melt with bisphenol-A (1 mol) at 180°C under nitrogen for 5 h. Phenol was distilled off, the reaction mixture was diluted with water, made alkaline with sodium hydroxide and extracted with toluene. Unreacted aniline was distilled off the extract. The bis(aniline) was distilled off (b.p. 100°C at 1 cmHg) and, after recrystallization from water, was in the form of pale pink crystals (m.p. 120–125°C). Elemental analysis gave: C 79.56 wt%, H 8.025 wt%, N 12.29 wt%; calculated values for C₁₅H₁₈N₂: C 79.6%, H 8.0%, N 12.4%.

Bis(ether anhydride)s. Bis(ether anhydride)s are conveniently synthesized by a nucleophilic displacement reaction between a diol and a phthalic acid derivative. In this study we employed nitro-displacement from 4-nitrophthalic anhydride derivatives. During nitro-displacement the anhydride moieties require protection. In this study the anhydride, except for the synthesis of the bis(anhydride) D, was protected as the *N*-phenylphthalimide. Thus *N*-phenyl-4-nitrophthalimide was prepared by reacting 4-nitrophthalic anhydride (0.26 mol) with aniline (0.29 mol) in a mixture of glacial

acetic acid and cyclohexane. The reaction mixture was refluxed under nitrogen for 12 h; water was removed as its cyclohexane azeotrope. The product, which separated as a yellow solid, was recrystallized from toluene to give a product with a melting point of 189–190°C in 88.4% yield. The product was characterized by infra-red and nuclear magnetic resonance spectrometry and by elemental analysis (found: C 62.50 wt%, H 2.96 wt%, N 10.41 wt%; calculated for C₁₄H₈N₂O₄: C 62.69%, H 3.01%, N 10.44%).

To synthesize bis(*N*-phenylphthalimide ether)s, diols were converted to their sodium salts by reacting, typically, the bisphenol (0.105 mol) with aqueous sodium hydroxide (0.21 mol, 12.5 M). The mixture was added to dry toluene (276 cm³) and dimethylsulfoxide (DMSO) (92 cm³); water was removed azeotropically. After cooling the mixture to 50°C, *N*-phenyl-4-nitrophthalimide (0.21 mol) was added and the mixture was heated to about 80°C (70 to 100°C according to the nucleophilicity of the bisphenol salt) for 1.5 h under nitrogen. After cooling, the mixture was poured into water, upon which the bis(ether phthalimide) precipitated. The product was filtered and washed with methanol until white. Products were characterized by elemental analysis; data are given in Table 1.

Bis(*N*-phenylphthalimide ether)s were hydrolysed with aqueous sodium hydroxide; aniline was removed azeotropically. The resulting aqueous solutions were filtered and acidified; when the tetracarboxylic acids precipitated they were extracted with diethyl ether, washed with water and recovered using a rotary

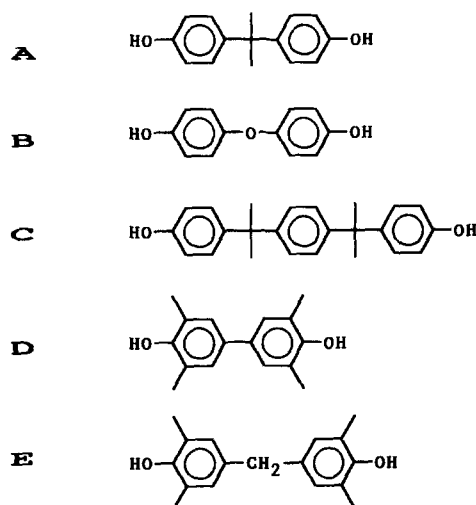


Figure 1 Aromatic units, depicted as diols, used in the synthesis of isomeric pairs of poly(ether imide)s

Table 1 Synthesis of bis(*N*-phenylphthalimide ether)s

Diol	Elemental analysis (wt%)			M.p. (°C)	Yield (%)	
	C	H	N			
A	Found	76.95	4.50	4.14	210–211	85
	Calc.	77.00	4.5	4.18		
B	Found	74.56	3.58	4.24	289	82
	Calc.	74.53	3.73	4.35		
C	Found	79.23	5.07	3.37	241–246	86
	Calc.	79.19	5.08	3.55		
E	Found	77.10	4.69	3.98	298	78
	Calc.	77.36	4.87	4.01		

Table 2 Synthesis of bis(ether anhydride)s

Diol	Elemental analysis (wt%)		M.p. (°C)	Yield (%)	
	C	H			
A	Found	71.47	3.82	182–184	95
	Calc.	71.54	3.87		
B	Found	68.01	2.69	235	89
	Calc.	68.02	2.83		
C	Found	74.98	4.68	190–192	87
	Calc.	75.24	4.70		
D				264–267	
E	Found	72.27	4.14	223–225	97
	Calc.	72.36	4.28		

evaporator. Yields of white solids were typically in excess of 95% and the solids had high melting points (> 300°C). The acids were dehydrated by refluxing with a mixture of acetic anhydride and glacial acetic acid. After cooling, pale yellow crystals of bis(ether anhydride) precipitated and were filtered off; yields were in excess of 90%, based on the phthalamide. Yields, melting points and analytical data for the bis(ether anhydride)s are presented in *Table 2*.

In the case of D, the nitro-displacement reaction was carried out with 4-nitrophthalonitrile; after nitro-displacement the nitrile groups were hydrolysed and the resulting tetraacid was converted to dianhydride. The synthetic procedure is described in ref. 4.

Poly(ether imide)s. Poly(ether imide)s were synthesized from bis(ether anhydride)s and diamines by first preparing the poly(amic acid) followed by chemical imidization in solution. To improve the uniformity of samples when comparing properties, single batches of bis(ether anhydride)s and diamines were used in preparing the several polymers. Equimolar mixtures of bis(ether anhydride) and diamine were reacted in DMAC at room temperature for up to 20 h, after which the poly(amic acid)s were imidized with an excess of acetic anhydride mixed with an equimolar amount of pyridine. Imidization reactions were allowed to proceed overnight. Polymers were isolated by precipitation into methanol, drying and reprecipitation from dichloromethane.

Characterization

Soluble poly(ether imide)s were characterized by gel permeation chromatography using *N,N*-dimethylformamide (DMF) with lithium chloride (1 M) as eluant. The chromatograph was calibrated using polystyrene standards.

In the absence of standards for poly(ether imide)s, molecular weights determined by g.p.c. are not accurate. To estimate corrections required to obtain absolute molecular weights, a Mechrolab membrane osmometer was used to determine number-average molecular weights of some polymers in chlorobenzene solution (35°C).

Sample preparation

While in practical gas separation systems polymers are used as asymmetric hollow-fibre membranes, the samples studied here were dense films prepared by slow solvent evaporation from polymer solutions (3 wt%) in dichloromethane in flat-bottomed Petri dishes (Anumbra). The transparent, yellow films, thickness 30 to 60 μm, were annealed for three days at 120°C under vacuum.

Techniques

Gas permeability. Permeabilities were determined at BP International plc, by monitoring the permeation of individual pure gases through polymer films across a pressure gradient into vacuum. After clamping the membrane in the permeation cell, the cell was evacuated for 12 h and any leak rate was determined. One side of the cell was pressurized to 10 bar with gas and the steady-state permeation rate was determined by monitoring the accumulation of gas on the downstream side of the membrane. Other upstream pressures used were 7.5 and 5 bar. Between using different gases the rig was flushed with nitrogen and re-evacuated. Permeabilities *P* were calculated from:

$$P = Jl/A\phi_p$$

where *l* is the membrane thickness, *A* the membrane area and ϕ_p is the pressure difference across the membrane. The flux *J* is given by:

$$J = (dp/dt)(V/T)$$

where *dp/dt* is the rate of change of pressure in the downstream volume *V* and *T* is the temperature. Selectivities quoted are the ratios of individual gas permeabilities.

Glass transition temperature. Glass transition temperatures were determined by differential scanning calorimetry on a Hewlett-Packard DSCII. Heating rates were 20°C min⁻¹.

X-ray diffraction. Films were studied with the aid of a Huber four-circle wide-angle diffractometer using Cu K α radiation. Diffraction patterns were obtained from some films using a Weissenberg camera.

RESULTS

Polymer characterization

Polymer solubilities. All poly(amic acid) precursors and poly(ether imide)s were soluble in DMAC, in which the polymers were prepared. High-molecular-weight poly(ether imide)s have limited solubilities in many solvents; their solution behaviour often limits characterization and fabrication. The solubilities of the polymers synthesized in this study in various solvents at room temperature are recorded in *Table 3*.

Molecular-weight data, determined by g.p.c., were obtained for samples soluble in DMF. Values of \bar{M}_n determined by osmometry were only obtained for polymers soluble in chlorobenzene and of sufficiently high molecular weight that diffusion through the membrane was not a problem. Solubilities in dichloromethane, from which membranes were cast, limited gas permeation studies.

The solution properties of some isomeric pairs of poly(ether imide)s listed are different. These differences are probably real, but it is possible that some are only due to molecular-weight effects.

Molecular weights. Molecular weights of the several polymers determined by g.p.c. are given in *Table 4*. It is obvious that for relatively rigid poly(ether imide)s, especially those with hindered diol and diamine moieties, hydrodynamic volumes per unit weight of polymer chain will be different from that of polystyrene and

the procedure used will not give accurate molecular weights; molecular weights estimated will be too high. Table 4 presents the weight-average (\bar{M}_w) and peak (M_p) molecular weights; such values are more reproducible than number-average molecular weights, which are sensitive to errors in the low-molecular-weight tails of the chromatograms.

Number-average molecular weights ($\bar{M}_{n,o}$), determined by osmometry, of some of the polymers are also given in Table 4. For molecular weights of the order of magnitude found, the weight-average molecular weight ($\bar{M}_{w,est}$) should be almost twice the number-average

molecular weight and, hence, these two values may be compared: $\bar{M}_w = 2\bar{M}_n - M_0$, where M_0 is half the sum of the molecular weights of dianhydride and diamine. Thus, it is apparent that molecular weights determined by g.p.c. are generally too high by a factor ($\bar{M}_w/\bar{M}_{w,est}$) of about 2 or 3. It cannot be assumed that the same factor will apply at all molecular weights, as this implies parallel calibration curves for polystyrene and the poly(ether imide). More probably they are non-parallel and a further factor is required to obtain a true general correction; we do not have samples of high molecular weight and sufficient differences in molecular weight to establish these parameters. Nevertheless, the data provide a good estimate of actual molecular weights of samples used.

Table 3 Polymer solubilities, wide-angle X-ray scattering data

Polymer	Solvents ^a				<i>d</i> -spacing (Å)
	CH ₂ Cl ₂	ClBz	NMP	DMF	
A/B	Y	N	Y	Y	
A/C	Y	Y	Y	Y	
A/D	Y	Y	Y	Y	
A/E	Y	Y	Y	Y	5.8
B/A	Y	Y	Y	Y	
B/C	Y	N	Y	Y	
B/D	Y	N	N	N	
B/E	Y	Y	Y	Y	
C/A	Y	Y	Y	Y	
C/B	Y	Y	Y	Y	
C/D	Y	Y	Y	Y	5.7
C/E	Y	Y	Y	Y	5.6
D/A	Y	Y	Y	Y	
D/B	N	N	N	N	
D/C	Y	N	Y	Y	5.4 ^b
D/E	Y	Y	Y	Y	
E/A	Y	Y	Y	Y	5.5
E/B	N	N	N	N	
E/C	Y	Y	Y	Y	5.5
E/D	Y	N	N	N	

^a CH₂Cl₂, dichloromethane; ClBz, chlorobenzene

^b Minor peaks at 15.2, 12.3, semicrystalline

Infra-red spectra. Major characteristics of the infra-red spectra of isomeric pairs of polymers are virtually identical; only minor differences, presumably from differences in linkages, are apparent.

X-ray data. Wide-angle X-ray scattering (WAXS) data were obtained for some polymers: *d*-spacings for amorphous peaks are given in Table 3; traces for two polymers are shown in Figure 2. The polymers are pairs, of which one unit has *ortho*-methyl groups. The polymer pairs show a trend in that the isomer with the hindered unit derived from the diamine has the larger amorphous *d*-spacing; the *d*-spacing is 0.1 to 0.3 Å greater when the moiety is diamine rather than dianhydride derived.

All polymers were totally amorphous except for D/C, which showed some crystallinity. Polymer D/C films exhibit birefringence when viewed in a polarizing microscope and, with the film perpendicular to the X-ray beam in the Weissenberg camera, sharp diffraction peaks corresponding to 5.3, 6.3, 7.8, 14 and 18 Å repeat distances. When the film was tilted to 20° from the X-ray beam the rings at 6.3, 14 and 18 Å became arcs, indicating that the chains tend to lie parallel to the film surface; this observation is consistent with reflectance data from the Huber diffractometer. The 18 Å repeat corresponds to

Table 4 Molecular weights determined by gel permeation chromatography (\bar{M}_w , \bar{M}_n and M_p) and membrane osmometry ($\bar{M}_{n,o}$), extents of reaction (*p*), second virial coefficients (A_2) and number-average degree of polymerization (\bar{P}_n) derived from $M_{n,o}$

Sample	Molecular weights (kg mol ⁻¹)					$\bar{M}_w/\bar{M}_{w,est}$	<i>p</i>	A_2 (kg ⁻² m ³ mol)	\bar{P}_n
	\bar{M}_w	M_p	\bar{M}_n	$\bar{M}_{n,o}$	$\bar{M}_{w,est}$				
A/B	161.1	152.3	97.8						
A/C	164.8	157.2	92.8	28.0	54.8	3.0	0.985	3.55	67.6
A/D	59.6	56.4	34.4						
A/E	119.6	105.4	65.5	26.8	52.3	2.2	0.986	6.95	72.6
B/A	62.1	61.2	39.1						
B/C	173.3	167.9	106.4						
B/E	135.6	132.3	78.4	25.9	50.5	2.7	0.986	1.33	72.8
C/A	70.3	69.6	42.2	19.4	39.0	1.8	0.979	5.19	46.9
C/B	88.4	90.2	52.4	21.1	41.8	2.1	0.981	0.66	52.6
C/D	60.4	57.0	34.7						
C/E	64.7	64.8	41.5	17.4	33.8	1.9	0.975	7.81	40.7
D/A	52.8	50.1	30.8						
D/C	119.6	109.6	60.5	23.7	43.4	2.75	0.982	10.7	56.3
D/E	102.6	96.4	60.1						
E/A	50.8	46.9	29.7						
E/C	182.2	178.2	104.2	40.0	77.4	2.35	0.989	4.61	93.5

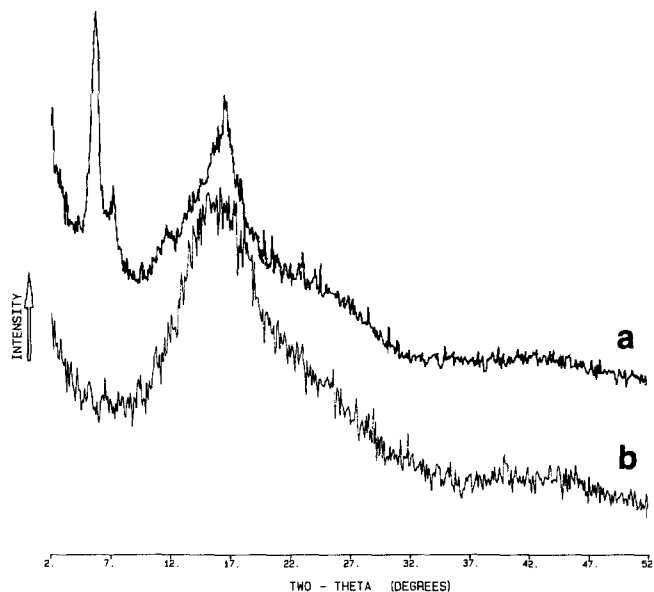


Figure 2 Wide-angle X-ray scattering traces for polymers (a) D/C and (b) C/D

Table 5 Properties of isomeric poly(ether imide)s, as described in text^a

Diol	Diamine					
	A	B	C	D	E	
A	(1)		0.045	0.134	0.174	
	(2)	225	215	212	280	249
	(3)		48.9	31.8		37.3
B	(1)	0.013		0.057	0.173	0.127
	(2)	219		221	300	256
	(3)	122.3		45.2	30.8	41.3
C	(1)	0.042	0.054		0.202	0.203
	(2)	210	194		252	230
	(3)	65.0	38.0		35.7	31.7
D	(1)	0.376		0.443		1.46
	(2)	299	292	296		>420
	(3)	35.4		34.3		27.3
E	(1)	0.172		0.300	0.755	
	(2)	250	266	253	>420	
	(3)	35.4		32.7	30.1	

^a Rows in each 'cell' are designated as follows:

- (1) CH₄ permeability (barrer)
- (2) Glass transition temperature (°C)
- (3) CO₂/CH₄ selectivity

one half of the length of the repeat unit measured using space-filling models.

Polymer properties

Data for several measurements on the various polymers are combined in Table 5. Each polymer is designated a 'cell' in the table identified by the letter codes of the aromatic residues used in its synthesis. The properties quoted in Table 5 are the glass transition temperature (T_g), the methane permeability (P_{CH_4}) and the permselectivity (α_{CO_2/CH_4}) for carbon dioxide relative to methane. In each 'cell' the properties are distinguished by location as indicated below the table.

Glass transition temperature (T_g). Glass transition temperatures (°C) for the several polymers are shown in Table 5. For polymers containing A, B or C residues only

(upper left-hand part of the table) T_g values are less than 250°C. In these polymers the aromatic units, derived from diol and diamine, do not have methyl groups *ortho* to the -O- or -N< linkages. There is nothing in these polymers to hinder rotation of either aromatic residue or to prevent the -O- linkages in the dianhydride units acting as hinges to permit conformational changes arising from main-chain motions.

Introducing hindering *ortho*-methyl residues into anhydride or diamine units (D, E) raises the polymers' T_g values to 250°C or greater. In D/E and E/D, in which both residues contain *ortho*-methyl residues, the T_g values are quoted as greater than 420°C, the limit of our d.s.c. experiments.

When identifying structural influences from comparisons of the properties of isomeric (or other) pairs of polymers, some caution should be exercised because of differences in molecular weight. Molecular weights of polymers may be in the region where properties start to vary with molecular weights⁵. However, all polymers had sufficiently high molecular weight to produce non-brittle films and to be in the region where T_g values were independent of molecular weight. We believe trends identified are real.

Structural units built into the polymers have different internal hinges. B and E have relatively unhindered hinges (-O-, -CH₂-), permitting internal rotation and conformational changes. A and C have isopropylidene residues, which constitute relatively stiff hinges. Unit D has no internal hinge and is rigid. Units D and E also have *ortho*-methyl substituents, which hinder rotation about their links to the phthalimide residues.

Fryd⁶ has suggested that charge-transfer interactions, which will enhance T_g values, exist in polyimides containing electron-accepting anhydrides and electron-donating diamines. To test this suggestion, we compare polymers in which A and B units, the units that are most similar in size, are interchanged, i.e. compare A anhydride with B anhydride (compare B/C with A/C, B/D with A/D, and B/E with A/E). Despite the expectation that the ether linkage in flexible B anhydrides might reduce T_g values of polymers with respect to those with stiffer hinges, we find that polymers with anhydride B have the higher T_g and Fryd's suggestion is supported. The same tendency does not exist to anything like the same extent when polymers with A and B diamine units are compared.

Another interesting comparison is between polymers containing A and C anhydrides. These polymers contain the same structural features. Replacement of A by C incorporates an additional stiff hinge per repeat and reduces the overall content of phthalimide units. It is difficult to separate these factors that are likely to influence T_g in opposite directions; dilution of phthalimide residues is likely to reduce interchain interactions. In each case the replacement reduces the T_g of the polymer by 15 to 30°C, approximately. All polymers with C anhydrides have the lowest T_g for polymers prepared with a given diamine. In contrast, C diamines do not give comparable reductions in T_g with respect to polymers containing A diamine; differences in T_g are too small to be considered significant. In this case, even though the imide content is reduced in the presence of C units, any effect is reversed by the presence of a relatively stiff hinge. Again, this is an example where interchange of anhydride and amine moieties does not have an equivalent influence on properties.

Other useful comparisons involve D and E units with *ortho*-methyl substituents, which hinder rotation about their links to the phthalimide residue; D is internally rigid, E has a $-\text{CH}_2-$ hinge. For polymers D/E and E/D, which contain both moieties, no glass transition was observed. This result is consistent with their expected rigid nature despite their solubility.

Whenever D and E residues are used in conjunction with other aromatic moieties, whether anhydride or amine, the polymer containing rigid D units has the higher T_g , as might be expected.

A D unit in a diamine renders two phthalimide units and the intermediate D unit a single rigid entity with very limited possibility for the two phthalimide units to change their orientations with respect to each other. Where the D unit is in the dianhydride unit, two phthalimide units, the intermediate D unit and the aromatic rings of the diamine units attached to the phthalimide units will be a single rigid unit with very little possibility for internal reorientation (Figure 3); the rings of the diamine units may be able to rotate, but this does not cause conformational changes. Thus, in these circumstances very large rigid units are built up, which will severely restrict conformational changes and molecular packing. E units will bring about the same type of restrictions to conformational changes, through similar restriction to molecular rotations. However, E units have an internal $-\text{CH}_2-$ hinge unit, which allows rotation and conformational changes within the E units and, hence, within diamine or dianhydride units.

In almost all cases, polymers with D or E moieties in the anhydride have higher T_g values than the corresponding polymers in which D or E are diamine residues. Exceptions are A/E, where T_g is similar to that for E/A, and D/B, where T_g is a little lower than for B/D. The general observation is consistent with hindering rotations about the ether link to the phthalimide residue raising T_g more than does hindering rotation about the C–N bond between diamine and imide ring. This effect is entirely reasonable because rotation of the aromatic residue around the C–N linkage does not change the chain conformations as does rotation about the $-\text{O}-$ link to the phthalimide, which is a hinge unit, as is apparent from Figure 3. It is not clear if the exceptions to this last generalization are significant in terms of molecular structure or if molecular-weight differences are responsible; polymers D/B and B/D were insoluble in the g.p.c. eluant.

More detailed comparisons of T_g values of isomeric pairs of polymers, to identify influences of structural features on T_g , are probably not useful at this stage.

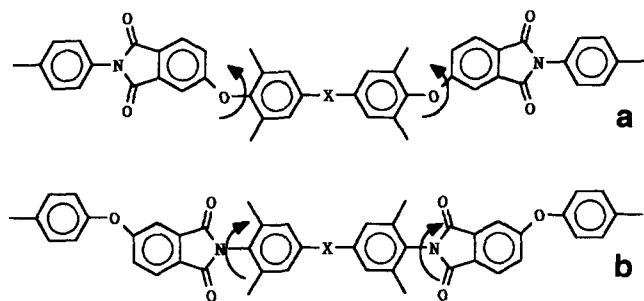


Figure 3 Restrictions to group rotations and conformational changes for polymers having hindered D units in (a) anhydride and (b) amine units

Gas permeabilities and selectivities. Values of methane permeabilities (P_{CH_4}) and carbon dioxide/methane selectivities ($\alpha_{\text{CO}_2/\text{CH}_4}$), from which carbon dioxide permeabilities are calculable, at 10 bar are given in Table 5, together with T_g values of the polymers.

Permeabilities (P_i) are often given as the products of diffusivity (D_i) and solubility (S_i) parameters and permselectivities (α_{ij}) as the ratios of permeabilities^{7,8}. However, permeation through glassy polymers is non-simple. According to the dual-mode theory⁹ the apparent solubility coefficient at gas pressure p is given by:

$$S_i = k_{D,i} + C_{H,i} b_i p / (1 + b_i p)$$

where the first term arises from Henry's law and the second is a Langmuir adsorption term; k_D is the solubility constant in dense material, C_H is a concentration of holes and b is an affinity constant. The permeability P_i is given by:

$$P_i = k_{D,i} D_{D,i} + D_{H,i} C_{H,i} b_i p / (1 + b_i p) \quad (1)$$

where $D_{D,i}$ and $D_{H,i}$ are diffusion coefficients for molecules dissolved in dense material and adsorbed molecules, respectively. Selectivities are then the ratios of the permeabilities:

$$\alpha_{ij} = P_i / P_j$$

Methane (kinetic diameter 3.8 Å) and carbon dioxide (kinetic diameter 3.3 Å) permeabilities through the various isomeric poly(ether imide)s were determined at gas pressures of 10, 7.5 and 5 bar. Equation (1) predicts that P_i decreases as p increases, in accord with data for P_{CO_2} (above) although not necessarily for P_{CH_4} . Carbon dioxide permeabilities decreased slightly with increasing gas pressure and are best represented by an equation of the form $P = kp^a$ with values of a between -0.17 and -0.24 ; for B/A $a = -0.30$. No pattern was discerned in values of a . No trend in methane permeability, outside experimental error, was apparent; this would be consistent with a low value of b . Data were obtained at 21–22°C except for polymer A/B, for which data were determined at 35°C; the temperature dependence of poly(ether imide) permeabilities is normally small and this difference in temperature does not compromise the following discussion. Any difference in activation energies for permeation of carbon dioxide and methane is unlikely to reduce the permselectivity $\alpha_{\text{CO}_2/\text{CH}_4}$ at the higher temperature. Thus the data are consistent with the dual-mode theory.

In the absence of additional and non-stationary-state data, we cannot determine values of parameters in equation (1). We can, however, discuss overall permeabilities.

What is not immediately apparent from the presentation in Table 5 is the general relationship between permeability and selectivity for this series of polymers. The variation in carbon dioxide permeability with $\alpha_{\text{CO}_2/\text{CH}_4}$ is shown in Figure 4; polymer identities are omitted for clarity. As usual, high CO_2 permeability (P_{CO_2}) is coupled with low selectivity. This presentation hides the fact that high selectivity for CO_2 (low selectivity for methane) is not necessarily coupled with low permeability for CH_4 . Generally, the data show much higher permeabilities for CO_2 than for CH_4 , in line with the smaller molecular dimensions of CO_2 , especially if CO_2 is considered as a rod.

The variation in P_{CO_2} with P_{CH_4} is almost linear, with

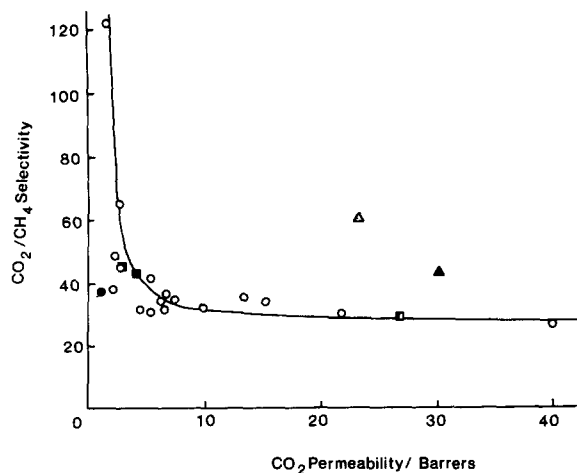


Figure 4 Variation in permselectivity for carbon dioxide and methane separations ($\alpha_{\text{CO}_2/\text{CH}_4}$) with carbon dioxide permeability for the series of isomeric pairs of poly(ether imide)s listed in Table 5 (○); identities of individual polymers are not given for clarity. The curve is calculated from equation (1). Data points for other polyimides are indicated: (●) Ultem, (□) PMDA-ODA, (■) PMDA-MDA, (▣) PMDA-IPDA, (△) 6FDA-ODA and (▲) 6FDA-IPDA. PMDA = pyromellitic dianhydride; 6FDA = hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride); ODA = bis(4-aminophenyl)ether (see B in Figure 1); MDA = *m*-phenylenediamine; IPDA = 2,2-bis(4-aminophenyl)propane (see A in Figure 1); data taken from references indicated in text

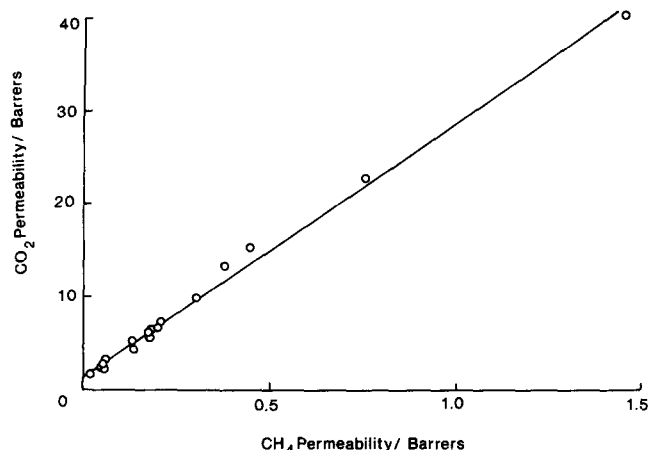


Figure 5 Variation in carbon dioxide permeability with methane permeability for the poly(ether imide)s described in Table 5; individual polymers are not identified for clarity

the best straight line passing almost through the origin (Figure 5); the equation for the best overall straight line is:

$$P_{\text{CO}_2} = (27.13 \pm 0.60)P_{\text{CH}_4} + (1.46 \pm 0.26) \quad (2)$$

If this linear dependence passed through the origin, then the selectivities for all polymers would be the same. Differences in selectivity, therefore, reflect the small intercept and the deviations from that straight line. The line is dominated by high permeabilities of polymers containing D and E moieties, anhydride or diamine. Taking those polymers alone, the best straight line is:

$$P_{\text{CO}_2} = (26.58 \pm 0.74)P_{\text{CH}_4} + (1.93 \pm 0.41)$$

For polymers excluding D and E moieties, the data are slightly more scattered and the dependence is:

$$P_{\text{CO}_2} = (21.46 \pm 3.71)P_{\text{CH}_4} + (1.33 \pm 0.25)$$

It is not certain if the two groups of polymers are better

considered separately, but the line taking all points into consideration gives smaller standard deviations for slope and intercept. The curve in Figure 4 is calculated from equation (2).

The approximate proportionality of P_{CO_2} and P_{CH_4} gives rise to the bunching of selectivities between 27.3 and about 38. The very high selectivity for B/A and, to lesser extents, those of other polymers of low permeability is a consequence of the lack of proportionality between the two permeabilities at low permeability, without which data it would be difficult to argue against all the polymers having the same selectivity, almost independent of molecular structure.

The good linear dependence between CO_2 and CH_4 permeabilities, and detailed examination of data points in terms of molecular structure, suggests that variations in relative solubilities of the gases, due to groups A–E, do not cause a variation in selectivity. There is no pattern of one or other structural moiety enhancing the permeability for either gas. We therefore propose that the membranes act primarily as simple molecular sieves and that differences in permeability are a consequence of the concentrations of suitable pores for gas diffusion.

By far the dominant feature of these data is the high permeabilities for polymers with D and E moieties, i.e. with methyl groups *ortho* to the linkages joining the aromatic units, from diol or diamine, to the general polymer structure. This trend is reinforced by the very high permeabilities for polymers D/E and E/D, which contain both units. We consider this general feature again later.

Detailed examination of data for polymers having D and E moieties reveals further trends. Internally rigid D moieties, whether in dianhydride or diamine, generally give rise to higher permeabilities than do E moieties in the corresponding location. In addition, these hindered moieties give rise to higher permeabilities if they are in the anhydride unit rather than in the diamine derived unit. These trends are reinforced by the observation that polymers with both D and E units have the highest permeabilities and that, of these two, polymer D/E has by far the highest permeability.

The trends in permeability with molecular structure are easily reconciled. Polymers with low permeability have only A, B or C units in both dianhydride and diamine. These units are essentially flexible within themselves, having either isopropylidene (A, C) or ether (B) linkages. These flexible linkages allow conformational changes to occur readily and we can envisage the molecules being able to adjust their conformations in order to fill space efficiently and leave few pores for molecular diffusion to take place.

In contrast, units D and E have *ortho*-methyl groups, which, in addition to hindering rotation, introduce bulky side groups. As we have already discussed (preceding section), the restrictions to rotation produce large rigid segments that are bent rather than linear. D units produce larger segments than do E units. The bulky groups will further hinder packing of these structural units and it is easy to envisage how such polymers will pack irregularly to generate relatively large pores.

Thus, by recognizing restrictions to internal rotations and restrictions on chain packing, we can rationalize all the observed variations in permeability. In summary, D or E units, which hinder rotation about linkages with phthalimide residues and molecular packing, enhance

permeability. D units, by having no possibility of internal conformational changes, enhance this effect. D or E units in anhydride moieties enhance permeabilities to a greater extent by creating larger stiff units and further hindering conformational changes.

The above simple generalizations account for the following differences in permeability: D/E > E/D; D/A > E/A; D/C > E/C; D/C > C/D; E/C > C/E. The only relevant pair for which this generalization does not hold is E/A and A/E, which have very similar permeabilities.

Within the non-hindered units used, comparisons are somewhat limited by polymer solubilities in the casting solvents, despite greater intrinsic flexibilities of the molecules. However, we can identify that C units, with two stiff hinges per moiety, give higher permeabilities than A units: D/C > D/A; E/C > E/A; C/E > A/E; B/C > B/A; C/B is approximately the same as A/B. Polymers with the least hindered B moiety generally have lower permeabilities than those with other units: B/A < C/A; B/C < A/C; B/E < A/E, C/E; B/D < C/D; C/B is approximately the same as C/A. C units dilute the phthalimide unit concentration.

All the above observations, with very little in the way of exception, can be rationalized in the single statement that: 'Restrictions to chain flexibility and conformational changes give rise to higher permeabilities.'

Comparison with other polymers

Koros *et al.*¹⁰ recently reviewed factors that influence permeabilities and selectivities in a variety of materials. They pointed out that the low solubilities of gases in glassy membranes cause little change in inherent membrane properties and solubility differences are of secondary importance in explaining general trends. This observation is probably consistent with our failure to identify variations in permeability, attributable to changes in solubility, with molecular structure. Thus, in this study, selectivity differences appear to be determined primarily by the ratio of diffusivities, which Koros *et al.*¹⁰ state is 'based on the inherent ability of polymer matrices to function as molecular size and shape media', which is 'governed primarily by such factors as chain backbone rigidity and intersegmental packing'.

The general aim in designing membranes for gas separation is to increase permeability and selectivity simultaneously. While contrary to general experience, Koros *et al.*¹⁰ point out that this aim can be achieved, to some extent, within a family of polymers by 'suppression of interchain packing by addition of bulky groups and/or "kinks" in the backbone which also cause simultaneous inhibition of interchain motion around flexible hinge points [and] tends to increase permeability without unacceptable loss in permselectivity'. This statement is in line with our observations on the isomeric poly(ether imide)s. They go on to state¹⁰: 'These segments must disrupt the interchain packing of the polymer while also increasing the distance between consecutive appearances along the chain of the most mobile linkage. Any such added spacer segments should have at least equivalent inhibitions to rotational mobility and interchain packing as the less mobile segments in the original repeat unit. This effectively "dilutes" out the more mobile linkage.'

The introduction of hindered units in this work does not necessarily increase the distance between hinge units, e.g. the use of diamine E, or, because the methyl group

Table 6 CO₂ permeabilities (P_{CO_2}) for several polyimides at 35°C and 10 atm pressure, permselectivities for CO₂ and CH₄ separation (α), and d -spacings from X-ray scattering

Polymer ^a	P_{CO_2} (barrer)	α	d (Å)	Ref.
PMDA-ODA	2.71	45.9	4.6	11
PMDA-MDA	4.03	42.9	4.9	11
PMDA-IPDA	26.79	29.7	5.5	11
Kapton ^R	0.22	688		12
Ultem ^R	1.33	36.9		13
6FDA-ODA	23.0	60.5	5.6	14
6FDA-IPDA	30.0	42.5	5.7	14

^a Abbreviations are explained in caption to Figure 4

is relatively small, dilute the system much. Hindering rotation will, however, affect packing of chains. Diol E and D units increase the distance between effective hinges, especially by removing the hinge at the ether link to the phthalimide residues.

Considered alongside permeability data for other commercial glassy polymers¹⁰, polymers prepared in this study compare favourably. The bulk of our polymers, having selectivities of 30–40 and P_{CO_2} of 5–10 barrer, fall around the general trend line identified by Koros *et al.*¹⁰ for glassy polymers. Polymers to the right of that trend line (high permeability and high selectivity) are favoured. Excluding fluorinated materials, favoured polymers are based on pyromellitic dianhydride; relevant data are summarized in Table 6.

Kapton^R is a commercial film chemically the same as PMDA-ODA but, because of its processing, has low permeability. Ultem^R is a commercial poly(ether imide). Of these materials, perhaps the most favoured is PMDA-IPDA. Polymers E/D and, especially, D/E are at least as good.

At the other extreme, polymer B/A has only low permeability but has very high selectivity, and it has a higher permeability than other known polymers of high selectivity. Polymer C/A also shows better properties than the trend line identified by Koros *et al.*¹⁰.

According to Koros *et al.*¹⁰, only by introducing fluorinated units, i.e. hexafluoroisopropylidene units in 6FDA, are better combinations of properties achieved. This improvement was attributed to dilution of ether linkages (hinges) and incorporation of a group that disrupts packing but allows some flexibility between phthalimide units (within the dianhydride moiety).

Koros *et al.*¹⁰ conclude that bulky groups aid permeability, especially if bulkiness is not associated with polar groups. Incorporation of methyl substituents onto main-chain aromatic residues improves permeabilities without loss in selectivity for polycarbonate⁸. Aryl bromination produces a similar effect in poly(2,6-dimethylphenylene oxide) (PPO)¹⁵ but reduces permeability in polycarbonate⁸. In PPO the effect was attributed to a reduction in packing density, while the reverse effect in polycarbonate was attributed to polar intermolecular interactions. Very bulky trimethylsilyl groups are known to increase permeability in rubbery polymers^{16,17}. We have also demonstrated that *t*-butyl groups aid permeability in glassy polyimides; these data will be discussed separately¹⁸.

Correlation of properties

For several of the polymers synthesized we can compare their thermal transition behaviours and gas

permeabilities; the different structural units involved many influence T_g values and permeabilities in various ways. However, the parameter $C_{H,i}$ in equation (1), and hence P_i , has been correlated with non-equilibrium free volume in glassy polymers¹⁹, which has, in turn, been correlated with $(T_g - T_m)$ (T_g is the glass transition temperature, T_m is the measuring temperature)²⁰, i.e. with T_g for the same T_m . These correlations seem to be widely applicable²¹.

For polymers prepared in this study, there is no simple correlation between gas permeability and T_g . However, a plot of data from Table 5 shows a general trend with an increase in T_g associated with an increase in permeability. This is exemplified by polymers D/E and E/D, which have the highest permeabilities and no T_g below 420°C. The trend is observed especially for polymers containing hindered units D or E.

Polymers without D or E units, i.e. having no hindered units, have the lowest permeabilities and T_g values, consistent with the above correlation. However, amongst those polymers there is no specific trend between permeability and T_g . What is apparent from a plot of permeability against T_g is that polymers containing B units have low permeabilities irrespective of T_g (cf. C/B with B/C, and A/B with B/A). In contrast, polymers A/C and C/A have almost identical T_g values but different permeabilities.

Thus, it is essentially only for polymers having D or E units that permeabilities increase with T_g . Specifically, the trend is seen in the isomeric pairs C/D, D/C and C/E, E/C. The general trend, however, is not obvious within the group of polymers C/D, A/E, E/A and B/E. In the pair of polymers B/D and B/E, B/D has a much greater T_g although the permeabilities are very similar. Despite the general trend of increased permeability with T_g , the reverse trend is apparent between some pairs of polymers. Specifically, polymers with C anhydrides have higher permeabilities and lower T_g values than do the corresponding polymers with B anhydrides, irrespective of the diamine. Thus, although the increased length of the C anhydride might dilute interchain interactions and T_g values, presumably the B units allow more efficient chain packing and reduce permeabilities.

Rubbery polymers, i.e. polymers with high segmental mobility and free volume, have high permeabilities. However, all polymers used in this study were glassy and it is relevant to discuss the above trends in relation to other glassy polymers. In the polymer literature there are statements that correlate permeability with chain mobility²². For polysulfones a correlation has recently been drawn between gas permeability and γ relaxation behaviour: polymers with lower-temperature γ relaxations have higher permeability⁷. Although it remains to study secondary relaxations in the isomeric poly(ether imide)s described here, such correlations hardly seem sustainable amongst these polymers. Unless certain rocking motions of the hindered residues, which would have to occur more readily in polymers of higher T_g , are responsible for gas permeation, it is hard to see how molecular mobility is associated with gas permeability in these materials. On the evidence available it seems more reasonable to correlate high permeability with chain rigidity and low mobility in polymers having hindered sub-units. This correlation is more consistent with views expressed by Koros *et al.*¹⁰.

It might then be expected that high permeability is

associated with a large number of suitable pores, a large free-volume fraction and large d -spacing. On the basis of the few data available on d -spacings in pairs of polymers containing D and E units, it seems that it is polymers with the hindered units in the diamine derived moieties that have the larger d -spacings. Thus, while hindered diamines result in larger d -spacings in the polymers, this does not correlate with high permeability, which is presumably associated with a larger number of suitably sized pores caused by some subtlety in chain packing. Further evidence from additional polymers and techniques is required to establish the exact factors involved in controlling T_g values and permeabilities.

CONCLUSIONS

A series of isomeric poly(ether imide)s have been synthesized in which units derived from diols and diamines are interchanged within the polymer structure. The structural units that have been incorporated into the polymer structures are hinged, rigid and hindered moieties. Carbon dioxide and methane permeabilities of the poly(ether imide)s have been determined as well as their T_g values and, in some cases, their wide-angle X-ray scattering data. Correlations have been drawn between these various parameters.

Clearly, within limits of the molecular-weight dependences of T_g , while in some isomeric pairs there is little change in properties on interchanging the diol and diamine moieties (e.g. C/A and A/C), in most cases there are large changes in properties, especially where one unit hinders rotation about the linkages between those moieties and the phthalimide units. Thus, in general, the properties of isomeric pairs of poly(ether imide)s are sensitive to the arrangement of structural units in the chain but in some cases they do not differ. In constructing algorithms to relate molecular structure to properties, therefore, the position of structural units within the polymer must be taken into account.

For the several polymers involved in this study having structural units that hinder segmental rotation and reduce possibilities for conformational changes, there is a general correlation that high permeability is associated with high glass transition temperature. This correlation does not apply to the few polymers with no hindered moieties, whether hinged or rigid. We conclude that moieties that hinder rotation and changes in chain conformation enhance both the glass transition temperature and gas permeability of the polymer and that this effect is more pronounced when that hindered moiety is rigid. We suggest that the enhanced glass transition temperatures and permeabilities are a result of inefficiencies in chain packing in polymers having long rigid segments and that these give rise to a higher concentration of pores of suitable size for gas permeation.

For polymers with hindered moieties there is little difference in permselectivity, and we suggest that changes in molecular structure are more important in controlling the concentration of pores suitable for gas permeation rather than changing the distribution of pore sizes that influence selectivity.

Rigid hindered units enhance permeability and glass transition temperature of a polymer to a greater extent if they form part of the anhydride moiety rather than the diamine moiety of the polymer; possibilities of conformational changes in the chain are thereby reduced.

Increased permeability is not necessarily correlated with a lower density, as indicated by an increased *d*-spacing determined by wide-angle X-ray scattering.

Polymers that have flexible units that do not hinder conformational changes have relatively low T_g values and low permeabilities. We attribute the low permeabilities to more efficient chain packing of the more flexible molecules; permeability is not generally aided by greater chain mobility.

Polymers with electron-accepting anhydrides and electron-donating diamines have higher T_g values, as suggested by Fryd⁶. The reverse is not true.

Polymers with hindered units have higher T_g values if the hindered moiety is in the anhydride unit rather than in the diamine; the effect is associated with removal of effective hinges in the chain.

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