Comparative Study on Polyimides from 3,3′- and 4,4′-Linked Diphthalic Anhydride

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SYNOPSIS

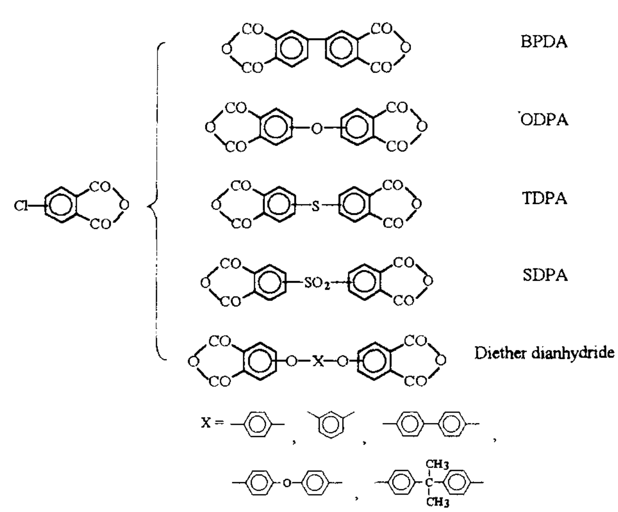
1,4-Bis(2,3-dicarboxyphenoxy)benzene dianhydride, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride, bis(2,3-dicarboxyphenoxy)sulfide dianhydride, bis(3,4-dicarboxyphenoxy)sulfide dianhydride, and 2,3,3′,4′-tetracarboxy diphenyl sulfide dianhydride were synthesized from 3-chlorophthalic anhydride and 4-chlorophthalic anhydride. Bis(2,3-dicarboxyphenyl)sulfone and bis(3,4-dicarboxyphenyl)sulfone were obtained by the oxidation of the corresponding bis(dicarboxyphenyl)sulfide by hydrogen peroxide. The polyimides from the dianhydrides mentioned above and 4,4′-oxydianiline were prepared. The properties, such as dynamic mechanical behavior, thermooxidative stability, stress–strain behavior, chemical resistance, and permeability to some gases have been in investigated for the isomeric polyimides. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Most aromatic polyimides from bridged dianhydride studied so far were prepared from 4,4′-linked diphthalic anhydride, such as 3,3′,4,4′-benzophenone dianhydride, 3,3′,4,4′-oxydiphthalic anhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, etc. Only a few works have dealt with 3,3′-linked diphthalic anhydride-based polyimides.[1-3]

Chlorophthalic anhydride was chosen as a common starting material in our laboratory for the preparation of a series dianhydride as shown in Scheme 1. Chlorophthalic anhydride was synthesized from *o*-xylene which was chlorinated first, followed by the oxidation catalyzed by vanadium oxide and the cocatalysts in the gas phase (see Scheme 2). In this case, the chlorophthalic anhydride was a mixture of isomers, i.e., 3-chlorophthalic anhydride and 4-chlorophthalic anhydride. The ratio of these two isomers was about 1 : 2.

In the present work, we report a comparative study on the polyimides based on the 3,3′-linked and 4,4′-linked diphthalic anhydride. The properties, such as dynamic mechanical behavior, glass transition temperature, thermooxidative stability, stress–strain behavior, chemical resistance, and permeability to some gases for these isomeric polyimides were investigated.



Scheme 1 Dianhydride from chlorophthalic anhydride.

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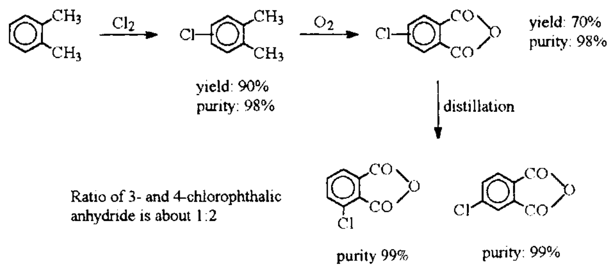


Scheme 2 Synthesis of chlorophthalic anhydride.

EXPERIMENTAL

Materials

3-Chlorophthalic anhydride and 4-chlorophthalic anhydride were obtained by distillation of crude chlorophthalic anhydride. The purity of these two compounds was about 97% determined by gas chromatography. The boiling point of 3- and 4-chlorophthalic anhydride was determined at 750 mmHg

Table I Dianhydrides and Their Melting Points

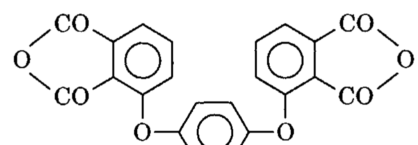
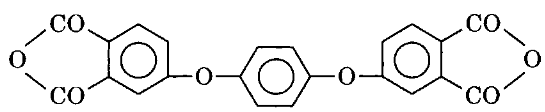
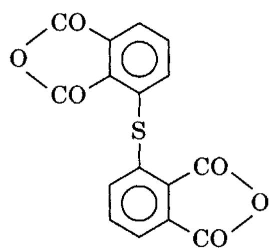
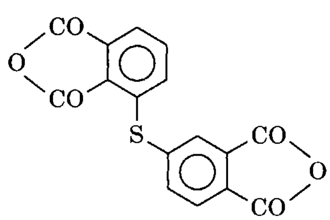
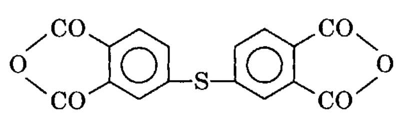
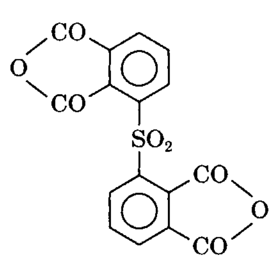
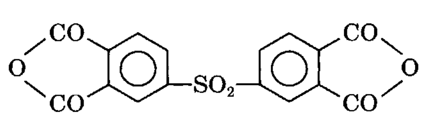
Dianhydrides	Abbreviation	Melting Point (°C)
	(3,3′)HQDPA	320
	(4,4′)HQDPA	264–265
	(3,3′)TDPA	245–247
	(3,4′)TDPA	207–209
	(4,4′)TDPA	202–203
	(3,3′)SDPA	384
	(4,4′)SDPA	275–277

Table II The Elemental Analysis of New Dianhydrides

	Elemental Analysis					
	Founded			Calculated		
Dianhydride	C	H	S	C	H	S
(3,3')HQDPA	65.70	2.62	—	65.67	2.49	—
(3,3')TDPA	59.00	1.87	10.15	58.89	1.84	9.82
(3,4')TDPA	59.46	1.75	10.57	58.89	1.84	9.82
(3,3')SDPA	53.41	1.52	8.83	53.63	1.67	8.93

for the samples in 99% purity to be 322 and 298°C, respectively.

1,4-Bis(3,4-dicarboxyphenoxy)benzene dianhydride [(4,4')HQDPA] and 1,4-bis(2,3-dicarboxyphenoxy)benzene dianhydride [(3,3')HQDPA] were prepared from the corresponding *N*-methyl chlorophthaliimide and hydroquinone in DMAc in the presence of potassium carbonate at 150°C for 8 h, followed by the hydrolysis of the diimide in aqueous sodium hydroxide under reflex for 8 h. After acidation with dilute sulfuric acid, the crude tetra-acid was filtered and boiled in 50% sulfuric acid for 30 min, washed with deionized water six times, and dehydrated at 250°C for 2 h to obtain the dianhydride. The total yield was about 75%.

Diphenylthioether dianhydrides (TDPA) were prepared from the corresponding *N*-methyl chlorophthaliimide, sulfur, and potassium carbonate in DMAc according to the procedure reported in Ref. 4. Diphenylsolfone dianhydrides (SDPA) were prepared by the oxidation of TDPA with hydrogen peroxide.[5]

Polymerization

Equivalent dianhydride and diamine was reacted in DMAc to make a solid content of 15% at room temperature. To the obtained viscous solution was added 2.5 equivalent acetic anhydride, the stirring was continued for 1 h, then 0.2 equivalent triethylamine was added as the catalyst for the imidization. The polyimide was formed as the powder in about 2 h; the equal volume ethanol was poured into the mixture. After stirring for 0.5 h, the polyimide powder was filtered and washed in hot ethanol three times, then dried and heated at 280°C. For the soluble polyimide, such as (3,3')TDPA/(4,4')-oxydianiline (ODA), the polymer solution was poured into ethanol; after washing and drying, the polymer was heated at 280°C for 1 h.

Chemical Resistance

Polyimide film about 20 μm thick was immersed in chemicals at room temperature for 30 days, then washed with ethanol and water and dried in air for testing.

Gas Permeability

For the apparatus and procedure for determining the permeability, see the literature.[6]

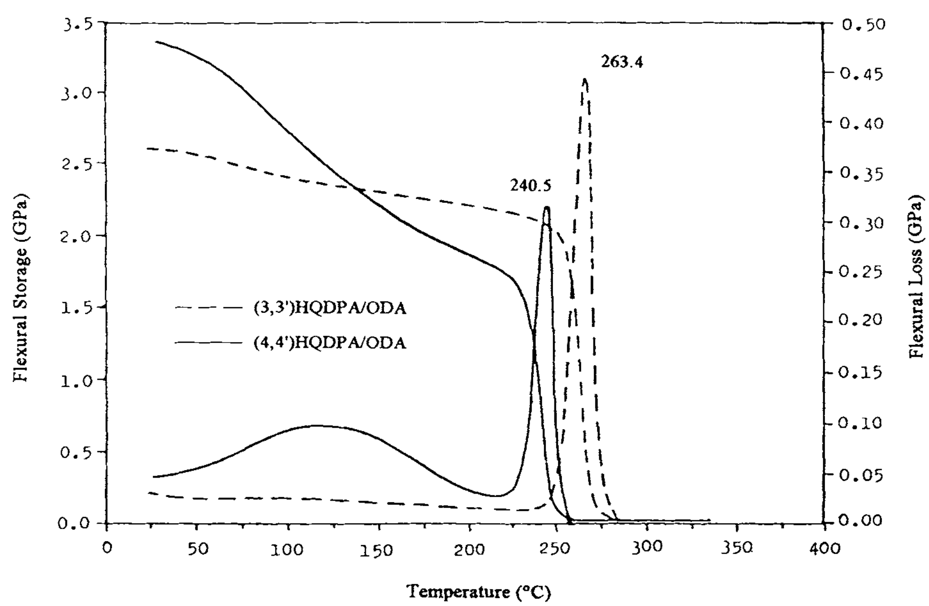


Figure 1 Dynamic mechanical analysis of polyimides based on HQDPA/ODA.

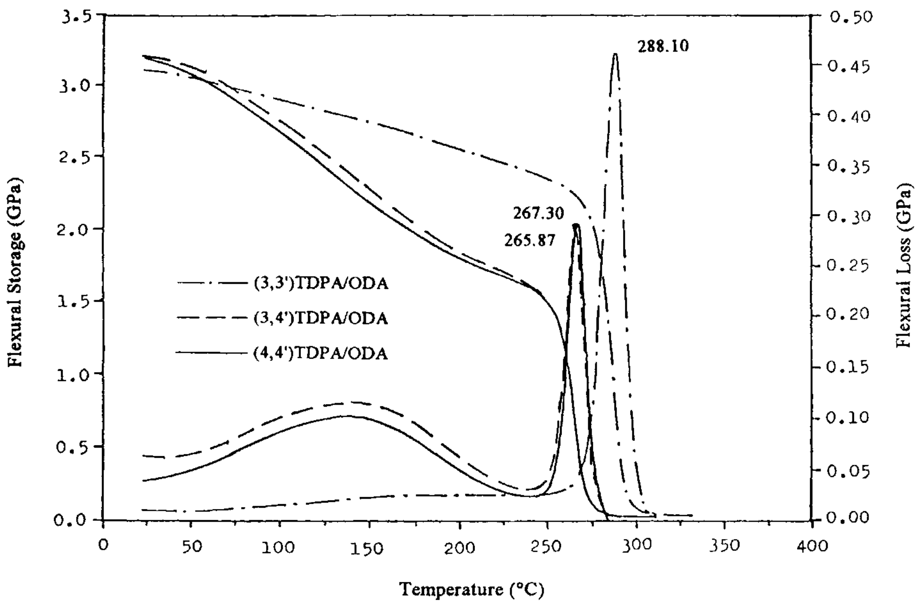


Figure 2 Dynamic mechanical analysis of polyimides based on TDPA/ODA.

Measurement

Dynamic mechanical analysis was taken in a DuPont 982 instrument with a heating rate of 5°C/min. The specimens were about 2 mm thick and compression-molded from the resin powder at 370°C under 10 MPa.

The tensile measurements were carried out on an Instron Model 1122 testing machine at room temperature. Crosshead speed was 2.0 cm/min, corresponding to the relative strain rate of 1.0/min. Thermal analysis was taken in a DELTA TGA 7 thermogravimetric system in air under the heating rate of 10°C/min.

RESULTS AND DISCUSSION

Synthesis

The melting points of the dianhydride used in this work are listed in Table I. The elemental analysis of the newly prepared dianhydrides are listed in Table II.

(3,3′)TDPA, (3,4′)TDPA, and (3,3′)SDPA were quite soluble in water compared with the corresponding 4,4′-linked analogs, so that the extraction of ether from the aqueous solution of the tetraacid may be necessary for recovering the product. The polyimide from (3,3′)SDPA was too brittle to be cast as a film and has too high a softening temperature to be compression-molded, so, unfortunately, there was no mechanical property that could be measured in this work.

Dynamic Mechanical Behavior

As can be seen in Figures 1 and 2, the (4,4′) polyimides have a broad T_β transition, but one very weak for (3,3′)polymers. The T_β might be a common characteristic for the (4,4′)polyimides that we investigated, such as (4,4′)ODPA/ODA,

Table III T_g **and** T_β **of Polyimides**

Polyimide	T_g K (°C)	T_β (K)	T_β (K)/T_g (K)
(3,3′)TDPA/ODA	561 (288)	—	—
(4,4′)TDPA/ODA	540 (267)	411	0.76
(3,4′)TDPA/ODA	539 (266)	412	0.76
(3,3′)HQDPA/ODA	542 (269)	—	—
(4,4′)HQDPA/ODA	518 (245)	390	0.75
(4,4′)SDPA/ODA	608 (335)	444	0.73
(4,4′)TDPA/MDA	545 (272)	401	0.74
(4,4′)HQDPA/MDA	544 (271)	405	0.75
(4,4′)ODPA/MDA	552 (279)	404	0.73

(4,4′)ODPA/(4,4′)-methylenedianiline (MDA), and (4,4′)HQDPA/MDA as well, except the polyimide from 3,3′,4,4′-biphenyl dianhydride, which will be reported elsewhere.

Furthermore, the glass transition temperature for (3,3′)TDPA/ODA and (3,3′)HQDPA/ODA is about 20°C higher than that for the corresponding 4,4′-linked polymers. Nevertheless, the (3,4′)TDAP/ODA has a similar behavior as that for (4,4′)TDPA/ODA. The absence of T_β for (3,3′)-linked polyimides may result from the steric hindrance of the rotation around the bond to the imide group vicinally located.[7]

The T_g and T_β of the polyimides studied are shown in Table III. The ratio of T_β to T_g in Kelvin scale are constant around 0.75.

Thermooxidative Stability

From Table IV, we can see that the thermooxidative stability of polyimides is independent of the isomerism. The polymers from TDPA/ODA have the highest stability, but that from SDPA/ODA, the lowest among the studied polyimides.

Stress-Strain Curves

The polyimide from (3,3′)TDPA/ODA appears brittle, but the (4,4′) analog is strong and tough (Fig. 3). Both polymers from (3,3′)HQDPA/ODA and (4,4′)HQDPA/ODA are strong and tough (Fig. 4).

This behavior may be caused by the rigidity of the polymer chain. As mentioned above, in (3,3′)TDPA-based polyimide, the rotation of imide was restricted by the adjacent S—C bond to the imide group, whereas in the (3,3′)HQDPA-based polymer, the —OC_6H_4O— linkage acts as a buffer for the restriction of the rotation of the imide ring, so that the rigidity of the chain is decreased.

Table IV The Thermooxidative Stability of Polyimides

Polyimide	T_c (°C)	$T_{5\%}$ (°C)
(3,3′)TDPA/ODA	530	556
(4,4′)TDPA/ODA	535	559
(3,4′)TDPA/ODA	526	571
(3,3′)HQDPA/ODA	505	531
(4,4′)HQDPA/ODA	503	536
(3,3′)SDPA/ODA	483	521
(4,4′)SDPA/ODA	448	522
(4,4′)ODPA/ODA	480	546

T_c: Commence temperature of the weight loss (°C). $T_{5\%}$: The temperature for 5% weight loss (°C).

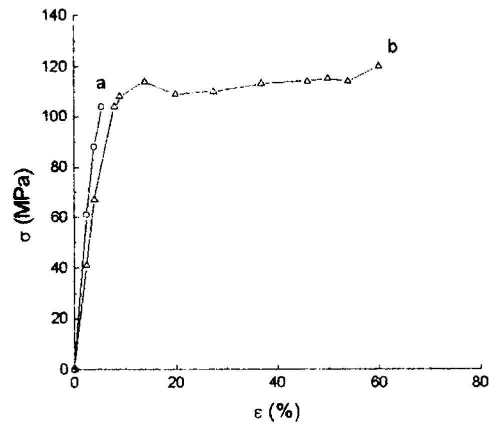


Figure 3 Stress-strain curves of polythioether-imides (a) (3,3′)TDPA/ODA; (b) (4,4′)TDAP/ODA

Chemical Resistance (Tables V and VI)

Ignoring the ±5% change from the value of block samples for the experimental error which may caused by the determination and/or the preparation of the sample, we can see from the results that

1. Polyimides based on HQDPA/ODA have better chemical resistance than those based on TDPA/ODA. The latter lost the yield point in most chemicals.
2. (4,4′)Polyimides are quite resistant to chloroform, but the (3,3′)counterpart became swollen or even dissolved in that. Compared with Kapton, the polyimide from pyromellitic dianhydride and ODA, these polymers, especially the HQDPA-based ones, are quite stable in 10% aqueous sodium hydroxide.

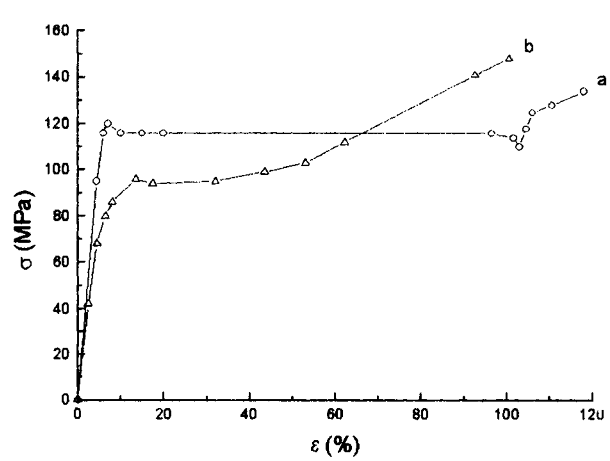


Figure 4 Stress-strain curves of polyetherimides: (a) (3,3′)HQDPA/ODA; (b) (4,4′)HQDPA/ODA.

Table V Chemical Resistance of Polyetherimides[a]

	(3,3′)HQDPA/ODA					(4,4′)HQDPA/ODA				
	Yield			Break		Yield			Break	
Medium	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)
Control	1891	114	7.5	116	128.5	1484	104	12.2	128	84.1
10% H_2SO_4	1697			99	7.6	1512	94	14.1	124	84.3
	(−10.3)			(−15.1)	(−94.1)	(2.0)				
10% HCl	1807	99	6.7	111	126	1626	97	13.7	123	80.1
	(−4.0)	(−13.0)	(−10.4)	(−4.2)	(−2.1)	(9.4)	(−6.6)	(12.3)	(−4.4)	(−0.2)
10% HNO_3	1816	103	7.4	94	10.0	1594	98	13.7	130	81.2
	(−4.0)	(−9.8)	(−1.3)	(−19.4)	(−92.2)	(7.4)	(−6.5)	(12.3)	(1.3)	(−3.4)
10% HF	1752			100	7.7	1855			124	12.4
	(−7.4)			(−14.0)	(−94.0)	(25.0)			(−3.7)	(−85.3)
10% NaOH	1795	99.7	6.9	84	15.9	1652	95	14.0	125	85
	(−5.1)	(−12.3)	(−8.0)	(−27.7)	(−87.6)	(11.4)	(−8.9)	(14.5)	(−2.4)	(0.6)
30% H_2O_2	1748	101	7.7	96	45.3	1629	93	13.7	130	88.9
	(−7.6)	(−11.2)	(2.7)	(−17.3)	(−64.7)	(9.8)	(−10.6)	(12.3)	(1.1)	(5.7)
Ethanol	1680	76.5	9.4	98	117	1733	91	15.0	137	94.1
	(−11.2)	(−32.7)	(25.3)	(−15.8)	(−8.0)	(16.8)	(−12.5)	(23.0)	(6.5)	(11.8)
Acetone	1608	65.9	4.5	89	131	1545	83	6.3	120	85.2
	(−15.0)	(−42.0)	(−40.0)	(−23.0)	(2.2)	(4.1)	(−19.7)	(−48.4)	(−6.9)	(2.5)
Chloroform						1689	96	13.7	140	88.9
						(13.8)	(−7.5)	(12.3)	(8.9)	(5.8)
Toluene	1846	97.7	6.8	92.5	43.6	1665	105	11.9	140	88.1
	(−2.4)	(−14.1)	(−9.3)	(−20.3)	(−66.1)	(12.2)	(1.0)	(−2.5)	(9.1)	(4.8)
Glacial acetic	1613	64	6.5	80.7	95.7	1936	103	10.9	155	72.3
acid	(−14.7)	(−43.6)	(−13.3)	(−30.5)	(−25.5)	(30.5)	(−1.2)	(−10.7)	(20.6)	(−14.0)
Ethyl acetate	1591	61	3.5	77.2	98.2	1645	90	14.2	127	76.3
	(−15.9)	(−46.1)	(−53.3)	(−33.5)	(−23.6)	(10.8)	(−13.6)	(16.4)	(−1.3)	(−9.3)
Petroleum	1672	92	4.5	112	130.9	1793	113	14.4	139	71.6
ether	(−11.6)	(−18.8)	(−40.0)	(−3.7)	(1.9)	(20.8)	(9.1)	(18.0)	(8.2)	(−14.9)
Mineral oil	1624	96	7.2	93	42.1	2000	103	12.4	137	84.9
	(−14.1)	(−15.6)	(−4.0)	(−20.0)	(−67.2)	(34.8)	(−1.2)	(1.6)	(6.7)	(1.0)

[a] Films about 20 μm thick were immersed at room temperature for 30 days.

Table VI Chemical Resistance of Polythioetherimides[a]

	(3,3′)TDPA/ODA					(4,4′)TDPA/ODA				
	Yield			Break		Yield			Break	
Medium	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)
Control	1999			107	6.5	1776	121	15.0	129	64.7
10% H_2SO_4	1840			81.2	5.1	1549			100	10.0
	(−7.9)			(−24.3)	(−21.5)	(−12.8)			(−22.7)	(−84.5)
10% HCl	1845	102	6.4	99	6.8	1714	106	12.5	102	28.3
	(−7.7)			(−7.3)	(4.6)	(−3.4)	(−12.7)	(−16.7)	(−21.1)	(−56.3)
10% HNO_3	1945			104	6.3	1637			105	28.5
	(−2.7)			(−2.6)	(−3.1)	(−7.8)			(−18.8)	(−56.4)
10% HF	1712			92	5.2	1898			117	10.4
	(−14.3)			(−14.6)	(−20.0)	(6.8)			(−9.5)	(−84.2)
10% NaOH						1581			98.7	12.0
						(−11.0)			(−23.7)	(−81.5)
30% H_2O_2	1810	96	6.6	92	29.0	1670			111	13.6
	(−9.4)			(−13.8)	(346.2)	(−6.0)			(−13.9)	(−79.0)
Ethanol	1712	82	7.9	85	26.1	1666			102	10.2
	(−14.3)			(−20.7)	(301.5)	(−6.3)			(−21.2)	(−84.2)
Acetone	1646	73	7.5	82	122.6	1784	91	8.6	108	49.5
	(−17.6)			(−23.2)	(1786)	(0.5)	(−24.8)	(−42.7)	(−16.2)	(−23.5)
Chloroform						1700	111	13.9	108	40.0
						(−4.3)	(−7.9)	(−6.7)	(−16.2)	(−38.5)
Toluene	1781			98	7.4	1734			124	12.4
	(−10.9)			(−8.4)	(13.8)	(0.5)			(−4.9)	(−80.8)
Glacial acetic	1700	77	6.2	71	57.2	1918			117	12.6
acid	(−14.9)			(−33.8)	(780)	(8.0)			(−9.8)	(−80.5)
Ethyl acetate	1617	74	5.8	71	13.1	2043			123	13.2
	(−19.1)			(−33.6)	(101.5)	(15.0)			(−4.9)	(−79.6)
Petroleum	1920			108	6.6	1860	126	15.2	134	60.0
ether	(−3.9)			(0.7)	(1.5)	(4.7)	(4.2)	(1.2)	(3.9)	(−7.2)
Mineral oil	1898			109	7.2	2373			145	12.1
	(−5.1)			(1.9)	(10.8)	(33.6)			(12.0)	(81.3)

[a] Films about 20 μm thick were immersed at room temperature for 30 days.

Table VII Permeability and Permselectivity of Polyimide

	P_{H_2}			α_{H_2/N_2}		
Polyimide	30°C	100°C	150°C	30°C	100°C	150°C
(3,3')HQDPA/ODA	6.99	16.7 (2.39)	26.1 (3.73)	108	69.4 (0.64)	55.3 (0.51)
(4,4')HQDPA/ODA	4.00	11.5 (2.87)	19.8 (4.95)	118	73.0 (0.62)	61.9 (0.52)
(3,3')TDPA/ODA	6.91	16.3 (2.36)	24.6 (3.56)	149	89.6 (0.60)	70.3 (0.47)
(4,4')TDPA/ODA	4.68	13.2 (2.82)	22.4 (4.79)	221	111 (0.50)	79.3 (0.36)
	P_{O_2}			α_{O_2/N_2}		
(3,3')HQDPA/ODA	0.416	1.22 (2.92)	2.18 (5.19)	6.3	5.1 (0.81)	4.5 (0.71)
(4,4')HQDPA/ODA	0.216	0.777 (3.55)	1.50 (6.82)	6.4	5.0 (0.78)	4.7 (0.73)
(3,3')TDPA/ODA	0.346	0.988 (2.83)	1.68 (4.80)	7.5	5.5 (0.73)	4.8 (0.64)
(4,4')TDPA/ODA	0.198	0.661 (3.30)	1.24 (6.26)	10.1	6.3 (0.62)	5.0 (0.50)

P: 10^{-10} cm^3 (STP) cm/cm^2 S cmHg. The data in parentheses are the ratios to the values determined at 30°C.

The Permeability and Permselectivity for Gases

Polyimide homogeneous membranes have been tested for hydrogen, oxygen, and nitrogen. The results are compiled in Table VII. 4,4′-Linked polyimides have higher permeability but lower permselectivity than have 3,3′-linked polyimides. This phenomenon may be caused by the difference in the free volume (see Table VIII), which was estimated according to the report by Lee.[8] The temperature dependence of the permeability and permselectivity for 3,3′-linked polyimides is smaller than that for 4,4′-linked ones, except that the permselectivity for HQDPA-based polyimides is almost independent of temperature. On balance, the 3,3′-linked polyimide may be the more promising membrane material for gas separation.

Table VIII The Free Volume of Polyimides

Polyimide	V_f (cm^3/mol)
(3,3')HQDPA/ODA	0.093
(4,4')HQDPA/ODA	0.088
(3,3')TDPA/ODA	0.097
(4,4')TDPA/ODA	0.092

CONCLUSION

Isomeric polyimides can be synthesized by a similar procedure using 3-chlorophthalic anhydride and 4-chlorophthalic anhydride as the starting material. But the properties for these isomers are quite different. The 3,3′-linked polyimides may be developed as novel materials for various applications.

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