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New Polyimides for Gas Separation. 1. Polyimides Derived from Substituted Terphenylenes and 4,4′-(Hexafluoroisopropylidene)diphthalic Anhydride

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ABSTRACT: Five new methyl-substituted diaminoterphenylenes were prepared by palladium-catalyzed coupling of bisboronic acids and bromoaromatics. The methyl groups are introduced to hinder rotations around the aromatic rings and to create a large free volume. These diamines were polycondensed with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and the imidization of the resulting polyamic acids was chemically completed by treating with acetic anhydride and triethylamine. The permeabilities and apparent diffusion coefficients of the pure gases He, H_2, N_2, O_2, CO_2, and CH_4 were measured in a time-lag apparatus at feed pressures below 1 bar. Apparent solubility coefficients and some selectivities for gases were calculated, and these data were discussed in the light of polyimides with comparable structures.

Introduction

Within several classes of membrane polymers, e.g., polysulfone, polycarbonate, and polyarylate, polyimides (PI) are particularly favored for nonporous (homogeneous) gas separation membranes. Their unique properties, such as excellent mechanical properties, low dielectric constants, high temperatures, long-term stability, good processability, and easy variability of the structure, can be adapted to that purpose. From 1962 to the present, a large variety of structures was synthesized and tested for their gas permeability/selectivity.[1−4] The gas permeability depends markedly on the structure. Even polyimides with the same dianhydride may differ in permeability by several orders of magnitude, e.g., from 0.7 to >100 Barrer for oxygen for 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)-based PIs. In general, increasing permeability is accompanied by decreasing selectivity. At a given permeability, however, polymers with different selectivity may be identified. PIs with the highest permeability detected so far are easily soluble in high and low boiling point solvents and consist of 6FDA polycondensated with durene diamine or mesitylene diamine. The methyl groups in these PIs hinders the rotation around the imide bond, resulting in stiffening of the polymer chain compared to PIs with no methyl groups in this position. In consequence, the chain packing density decreases, and therefore, the free volume of the polymer increases. Free volume, besides computation[4,5] or determination from WAXS measurements,[4] can directly be measured by positron annihilation.[6−8] However, both the amount of the free volume and its partition inside the dense polymer film influences the performance of the PI as gas separation material.[9] Computation of free volume by molecular modeling is improving fast, but in the case of stiff, large molecules, such as the most interesting PIs,[10] months of computation time are still necessary to get valid results for a singular structure. Other approaches to increasing understanding of permeability/selectivity relations in polymeric gas separation membranes are based empirically[11,12] or on a group-contribution method.[13,14]

When all of these pieces of information are taken into account, it is a challenge to design structures with the aim of improved separation properties for gases. Therefore, five structures of selected methyl-substituted diaminoterphenylenes were synthesized and polycondensated with 6FDA to PIs to contribute to information on structure−permeability−selectivity relationships of polymers.

Experimental Section

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride was purchased from Chriskew Co. (Leawood, KS) and purified by sublimation. 2,5-Dibromoxylene, 2,4-dibromomesitylene, 2-bromo-4-methylaniline 4-bromo-2,6-dimethylaniline, and 2-bromo-5-nitrotoluene were purchased from Aldrich Co.(Milwaukee, WI) and used as received. Trimethylborate was purchased from Merck KG (Darmstadt, FRG) and distilled prior to use. Pt catalyst (10% Pt on carbon) and trifluoroacetic acid were obtained from Aldrich and used as received. Tetrahydrofuran (THF) was refluxed and distilled over sodium wire. *N*-Methylpyrrolidone (NMP) and CH_2Cl_2 from Merck KG (Darmstadt, FRG) were used as received.

1,4-Xylene-2,5-diboronic Acid Bis(ethane diol ester) (7). Magnesium turnings (1 mol) were weighed into an 1 L three-necked flask (equipped with a mechanical stirrer) and activated with iodine. The solution of 2,5-dibromo-1,4-xylene (0.45 mol) in dry THF (600 mL) was added at a rate that kept the reaction mixture refluxing. Finally, the reaction mixture was refluxed for 24 h by heating with an oil bath. After being cooled to 0 °C, the Grignard solution was added dropwise to a solution of trimethylborate (2.7 mol) in dry diethyl ether cooled to −70 °C. After complete addition of the Grignard solution, the reaction mixture was stirred at −70 °C for 1 h and afterward for 20 h without any cooling. A 2 M aqueous HCl solution (700 mL) was then added, and the stirring was continued until the magnesium had completely dissolved. The precipitated boric acid was removed by filtration, and the liquid phases were separated. The aqueous phase was extracted eight times with 200 mL portions of diethyl ether. The

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Table 1. Yields and Properties of Methyl-Substituted Diaminoterphenylenes

formula	yield (%)	mp (°C)	recrystal. from	mol. formula (mol. weight)	elemental analyses				^{1}H NMR chemical shifts ($CDCl_3$/TMS)
						C	H	N	
1	85^a	267−268	$CHCl_3$/ethyl acetate^b	$C_{22}H_{24}N_2$ (316.45)	calcd	83.50	7.67	8.85	1.94 (s, 6 H), 2.03 (s, 6 H),
					found	83.51	7.67	8.84	3.68 (s, 4H), 6.61−7.24 (m, 8 H)
2	81^a	173−175	$CHCl_3$/hexane (1:4)	$C_{22}H_{24}N_2$ (316.45)	calcd	83.50	7.67	8.85	1.93 (s, 6 H), 2,04 (s, 6 H),
					found	83.40	7.54	8.78	3,54 (s, 4 H), 6,63−7,24 (m, 8 H)
3	11	177−179	ethanol	$C_{22}H_{24}N_2$ (316.45)	calcd	83.50	7.64	8.85	2,22 (s, 6 H), 2,28 (s, 6 H),
					found	82.89	8.65	8.57	3,64 (s, 4 H), 68−7,10 (m, 8 H)
4	75^a	214−216	ethanol	$C_{22}H_{24}N_2$ (316.45)	calcd	83.50	7.67	8.85	2.02 (s, 12H), 3.44 (s, 4 H),
					found	83.51	7.67	8.85	6.52−7.22 (m, 8 H)
5	38	254−255	ethanol	$C_{24}H_{28}N_2$ (344.50)	calcd	83.68	8.19	8.13	2,24 (s, 12 H), 2,28 (s, 6 H),
					found	83.02	8.28	7.94	3,61 (s, 4 H), 6.98 (s, 4 H), 7.10 (s, 2 H)

[a] Product of the yield of the coupling and the hydrogenation step. [b] Purified by column chromatography.

combined organic phases were dried with Na_2SO_4 and evaporated. The residue was treated with hexane (200 mL), and the solid crude bisboronic acid was isolated by filtration (yield 97 g). The bisboronic acid and dry 1,2-ethanediol (1 mol) were refluxed in dry acetone for 8 h. The remaining overnight-precipitated boric acid was removed by filtration. The filtrate was concentrated in vacuo (finally, at >0.01 mbar), and the crude product **7** was recrystallized from ethanol. Yield: 41%. Mp: 169−170 °C. Anal. Calcd for $C_{12}H_{16}B_2O_4$ (245.88): C, 58.62; H, 6.56. Found: C, 58.36; H, 6.52%. ^{1}H NMR ($CDCl_3$/TMS): δ 2.49 (s, 6 H), 4.35 (s, 8 H), 7.61 (s, 2 H).

Mesitylene 2,4-Bisboronic Acid (bisethyl diol ester) (8). Starting from 2,4-dibromomesitylene (0.4 mol), the synthesis of **8** was conducted as that described for **7**. The crude product **8** was recrystallized from a toluene/hexane mixture (1:1 v/v). Yield: 3%. Mp: 136−138 °C. Anal. Calcd for $C_{13}H_{18}B_2O_4$ (259.90): C, 60.08; H, 6.98. Found: C, 59.73; H, 6.97%. ^{1}H NMR ($CDCl_3$/TMS): δ 2.33 (s, 6 H), 2.41 (s, 3 H), 4.36 (s, 8 H) 6.8 (s, 1 H).

4,4″-Diamino-2′, 3, 3″, 5, 5′, 5″-hexamethyl-*p*-terphenyl (3). The bisboronic acid ester **7** (0.03 mol), 4-bromo-2,6-dimethyl aniline (0.06 mol), and tetrakis(triphenylphosphine)-palladium(0) (1.4 mmol) were dissolved in dry THF (800 mL). A solution of 2 M deoxygenated sodium carbonate (400 mL) was added, and the mixture refluxed with stirring for 48 h in an atmosphere of argon. After being cooled, the organic phase was separated, and the water phase was extracted twice with 200 mL portions of CH_2Cl_2. The combined organic phases were washed twice with NaCl solutions and dried over Na_2SO_4. The solvent was evaporated, and the product was recrystallized from ethanol. The diamine **2** was prepared analogously. For yields and data, see Table 1.

3,3″-Dinitro-2,2′,2″,5′-tetramethyl-*p*-terphenyl (9). The bisboronic ester **7** (0.03 mol), 2-bromo-6-nitro toluene (0.06 mol), and tetrakis(triphenylphosphino)palladium(0) (0.04 mol) were reacted in a THF/sodium carbonate mixture as described above. The product **9** was recrystallized from toluene/ethanol (4:1 v/v). Yield: 95%. Mp: 240−242 °C. Anal. Calcd for $C_{22}H_{20}N_2O_4$ (376.41): C, 70.20; H, 5.35; N, 7.44. Found: C, 70.56; H, 5.54; N, 7.38%. ^{1}H NMR ($CDCl_3$/TMS) δ 2.04 (s, 6 H), 2.28 (s, 6 H), 7.02 (s, 2 H), 7.38−7.92 (m, 6 H).

3,3″-Dinitro-2,2′,5′,6,6″-tetramethyl-*p*-terphenyl (10). The synthesis of **10** was conducted as described for **9** with 2-bromo-4-nitrotoluene as starting material. The crude product was recrystallized from toluene. Yield: 90%. Mp: 237−239 °C. Anal. Calcd for $C_{22}H_{20}N_2O_4$ (376.41): C, 70.20; H, 5.35; N, 7.44. Found: C, 70.36; H, 5.43; N, 7.52%. ^{1}H NMR ($CDCl_3$/TMS): δ 2.04 (s, 6 H), 2.24 (s, 6 H), 7.02 (s, 2 H), 7.20−8.21 (m, 6 H).

4,4″-Dinitro-2,2′,2″,5′-tetramethyl-*p*-terphenyl (11). The synthesis of **11** was performed as that described for **9** using 2-bromo-5-nitrotoluene as starting material. The crude product was recrystallized from toluene. Yield: 86%. Mp: 250−252 °C. Anal. Calcd for $C_{22}H_{20}N_2O_4$ (376.41): C, 70.20; H, 5.35; N, 7.44. Found: C, 70.08; H, 5.37; N, 7.34%. ^{1}H NMR ($CDCl_3$/TMS): δ 2.03, (s, 6H), 2.23 (s, 6 H), 7.00 (s, 2 H) 7.30−7.17 (m, 6 H).

Diamines 1, 4, and 5 by Hydrogenation of 9−11. A solution of a dinitroterphenyl (0.1 mol) in dry THF (400 mL) was purged with nitrogen. To this was added 3 g of 10% Pt on carbon catalyst. Hydrogen gas was then introduced at 20 °C and normal pressure with permanent shaking until the calculated quantity was consumed. The remaining hydrogen was replaced with nitrogen, the catalyst was filtered off, and the filtrate was concentrated in vacuo. The crude products were recrystallized or purified by column chromatography (see Table 1).

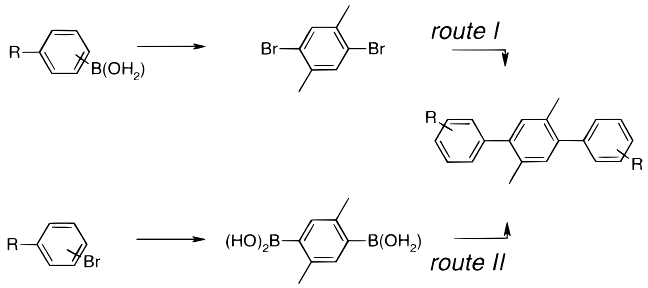
Polycondensation. Sublimated 6FDA (2.5 mmol) and a diaminoterphenyl (2.5 mmol) were dissolved in dry NMP (5 mL) under dry nitrogen and stirred for 24 h at 25 °C. After the addition of dry NMP (10 mL), distilled acetic anhydride (10 mmol), and triethylamine (10 mmol), stirring at 25 °C was continued for 24 h. The reaction mixture was poured into methanol (400 mL), and the precipitated polymer was filtered off. After being dried, the polyimide was dissolved in CH_2Cl_2 and reprecipitated into methanol. The isolated polyimide was dried at 100 °C in vacuo.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer at 20 °C. Differential scanning calorimetry (DSC) was conducted with a Perkin-Elmer DSC-7 at a heating rate of 20 °C/min. The infrared (IR) spectra were recorded with a Nicolet FT-IR spectrometer from KBr pellets. ^{1}H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in $CDCl_3$ using TMS as internal standard. The thermogravimetric analyses (TGA) were conducted with a Netzsch TG209 at a heating rate of 10 °C/min in an argon atmosphere. Gas permeation data were measured as follows. Solvent-free films about 30−90 μm in thickness were prepared (see Fritsch and Peinemann[5]). Pure gases were applied using a self-built vacuum time-lag apparatus.[15] Permeate pressure increase with time was recorded at 30 °C by two MKS Baratron pressure sensors (10 mbar max (permeate), 1 bar max (feed)) that were connected directly to a computer. Software developed in the Labview environment ensures automated measurements. Typically, the total time of measurement is set to four time-lags with an automatically adapting data sampling rate to yield 600 data points. For H_2 and He, usually only 200 data points measured at a speed of 20 data points per second are necessary to describe time-lag and steady-state gas transport completely. Time-lags below 1 s can be detected and reproduced precisely. Feed pressure was varied from 0.1 to 1 bar. Permeate pressure was $<10^{-4}$ mbar at the beginning of the experiment and was recorded up to 0.05−9 mbar, depending on the feed gas. Permeability was calculated from the slope of the permeate pressure versus time data in the steady-state region. Apparent diffusion coefficients, D_a, were estimated from the time-lag θ by $D_a = l^2/6\theta$ (l being the film thickness). Apparent solubility coefficients, S_a, were calculated from $S_a = P/D_a$.

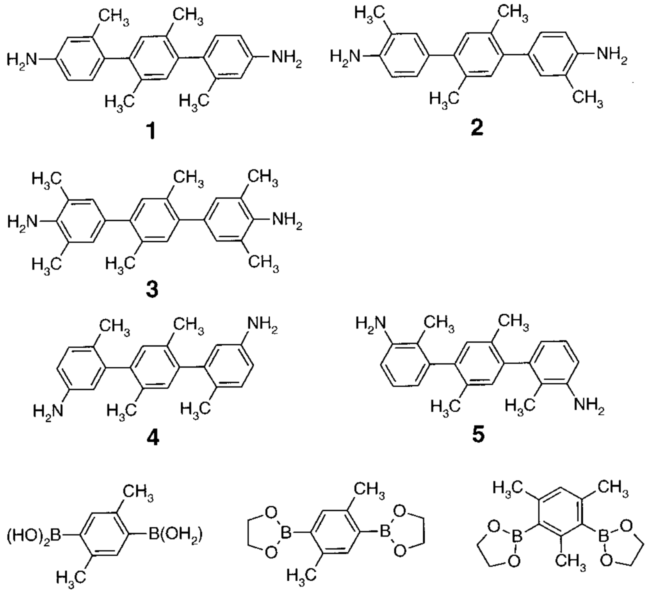
Results and Discussion

Syntheses. Coupling of boronic acids to built up aromatic ring systems has been used successfully by several groups.[16−18] The first goal of the present work was the synthesis of the five diamino-terphenylenes **1**−**5**. By the application of boronic acid chemistry, two alternative synthetic routes can be envisaged to achieve

Scheme 1. Routes to Methyl-Substituted Terphenylene Diamines



Scheme 2. Compounds 1−8



this goal (see Scheme 1 for routes and Scheme 2 for structures). Either amino or nitrophenylboronic acids can be synthesized and coupled with 2,5-dibromoxylene (route I) or the *p*-xylene-2,5-bisboronic acid **6** is prepared and coupled with suitable amino or nitrobromoaromatics (route II). 2,5-Dibromoxylene is a commercial product, and route I looks more promising at first glance. However, all attempts to prepare methyl-substituted amino- or nitrobenzeneboronic acids in satisfactory purity and yield failed. Therefore, resort was taken to route II. By starting with 2,5-dibromoxylene, several attempts were made to prepare **6** by means of butyllithium and trimethylborate in analogy to other alkyl-substituted phenylene bisboronic acids.[16,17] However, in all of our experiments, only the monoboronic acid was obtained. After a report by Nielsen[19] was taken in account, butyllithium was replaced by magnesium, and in this way, the double substitution was successful. Nevertheless, a satisfactory purification required the transformation of **6** into its bisethylene glycol ester **7**. The bisboronic acid ester **8** was prepared analogously, but due to its low yield (3%), it was not used for further syntheses.

To synthesize the diamine **2**, the bisboronic acid ester **7** was coupled with 4-bromo-2-methyl aniline in THF/aqueous Na_2CO_3 mixtures, whereby tetrakis(triphenylphosphine)palladium(0) served as a catalyst.[17,20,21] An analogous condensation was performed by replacing THF with toluene, but the yield of **2** was low. This behavior was observed for all coupling reactions. Significantly higher yields reported in Table 1 and in the Experimental Section are all based on THF as a reaction medium. The synthesis of diamine **3** was performed analogously to **2**. Commercial 4-bromo-2-methylaniline served as a reaction partner for the coupling with the bisboronate **7**. The bromoanilines required for the syntheses of the diamines **1**, **4,** and **5** were not commercially available, but the corresponding bromonitroaromates were available. Therefore, these nitrocompounds were used as coupling partners of **7,** and the bisnitroterphenylenes **9−11** were isolated. Their yields were somewhat higher than those of the diamines **2** and **3**. We conclude that the route using by nitro-group-protected amines is generally more efficient despite the additional hydrogenation step (compare with yields of **1−3** of the 4,4″ diamino-*p*-terphenylenes). The hydrogenation of the three bisnitroterphenylenes was successfully executed with hydrogen and a palladium/carbon catalyst at 25 °C in THF. The yields of this step were above 90%. The overall yields of coupling and hydrogenation are from 75 to 85%. Table 1 summarizes some results of the monomer syntheses.

All polycondensations were performed in the same way. A diaminoterphenylene and recrystallized 6FDA were reacted in dry NMP for 24 h at 25 °C and chemically imidized overnight by an excess of acetic anhydride plus triethylamine. The yields and some properties of the isolated polyimides **PI1−5** were summarized in Table 2 (numbering of these polyimides parallels the numbering of the diamines **1−5**).

Polymer Properties. All polymers are accessible in high yields (83−98%) and are soluble in high boiling point solvents such as NMP, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), as well as in low boiling point solvents, e.g., THF, CH_2Cl_2, and $CHCl_3$. The molar masses are sufficiently high (M_w's by GPC relative to polystyrene standards from 37 000 to 85 000) to form clear, flexible, and transparent films from either high or low boiling point solvents, thus proving to be suitable as gas separation polymers. Thermogravimetric analyses verified a high thermal stability in nonoxidizing Ar atmosphere (values of 10% weight loss are above 500 °C; see Table 2) although methyl groups are present. Long-term durability up to 300 °C is expected; however, glass-transition temperatures (T_g) were not detected by DSC. Dynamic mechanical thermoanalyses (DMTA) were carried out ($z = 1.6$ s^{-1} and $T = 2$ K min^{-1})[22] with **PI-3** resulting in T_a = 370 °C corresponding to T_g. Because all the structures are similar and sterical hindrance of the methyl groups causes a rigid structure, T_g's above 300 °C are expected for the other PIs as well.

Gas Separation Properties. In polyimides, the steric effect of methyl groups ortho to the imide nitrogen effects both overall polymer chain rigidity and subsequently packing density and gas permeability/selectivity.[3,5,23,24] Scheme 3 gives an overview of related structures of increasingly substituted mono-,[23] bi-,[10,24] and terphenylenes (this work). The monophenylenes are meta or para diamines with increasing numbers of *o*-methyl substituents (m0, m1, m3; p0, p2, p4). The biphenylenes are only para (B2, B4;[24] B2Ar[10]). The central ring of the *p*-terphenylenes (**PI-1−5**) is 2,5-dimethyl-substituted to hinder ring rotation and contribute to free volume by sterical hindrance. The 4,4″-terphenylenes (**PI-1−3**) are not (**PI-1**), mono- (**PI-2**), or dimethyl- (**PI-3**) substituted ortho to the imide nitrogen,

Table 2. Yields and Properties of the Polyimides

PI	yield (%)	inh. visc.[a] (dL/g)	M_w[b] (GPC)	TGA[c] (−10%)	mol. formula (mol. weight)	elemental analyses	C	H	N
PI-1	85	0.51	38 000	-	$(C_{41}H_{26}F_6N_2O_4)_n$ (724.67)	calcd	67.96	3.62	3.87
						found	67.25	3.18	3.88
PI-2	83	0.47	37 000	516	$(C_{41}H_{26}F_6N_2O_4)_n$ (724.67)	calcd	67.96	3.62	3.87
						found	66.80	4.07	4.77
PI-3	98	0.88	85 000	525	$(C_{43}H_{30}F_6N_2O_4)_n$ (752.72)	calcd	68.60	4.02	3.72
						found	67.87	3.99	3.33
PI-4	90	0.55	42 000	500	$(C_{41}H_{26}F_6N_2O_4)_n$ (724.67)	calcd	67.96	3.62	3.87
						found	66.91	3.80	3.81
PI-5	91	0.64	74 000	530	$(C_{41}H_{26}F_6N_2O_4)_n$ (724.67)	calcd	67.96	3.62	3.87
						found	67.03	3.77	3.85

[a] Inherent viscosity at 20 °C in CH_2Cl_2/TFA (4:1 v/v). [b] Relative to polystyrene. [c] Thermogravimetric analyses recorded at 10 °C/min in Ar at 10% weight loss.

Scheme 3. Overview on Comparable Structures from Literature and This Work

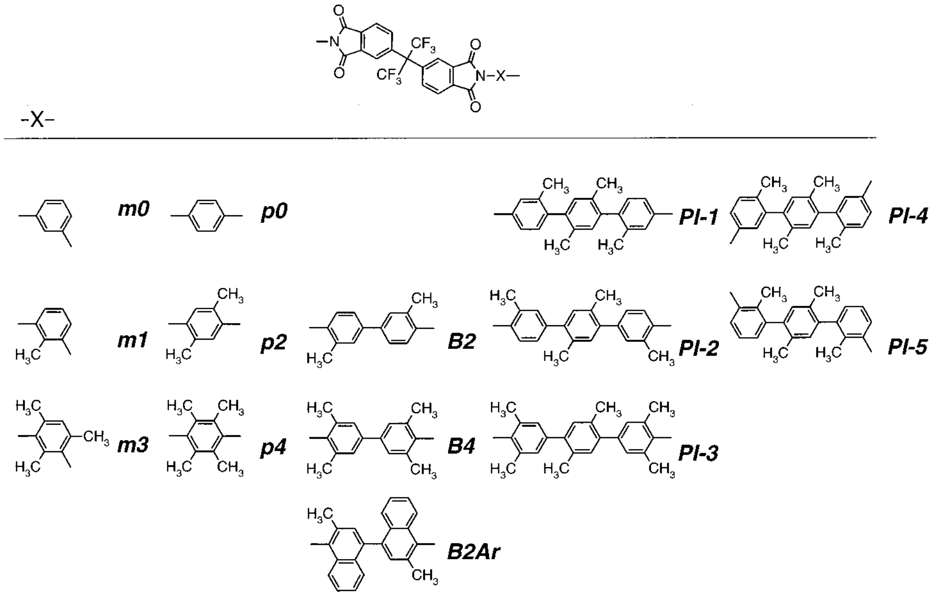


Table 3. Permeabilities[a] of the Polyimides to Pure Gases

PI	P_{He}	P_{H_2}	P_{CO_2}	P_{O_2}	P_{N_2}	P_{CH_4}
PI-3	230	350	360	67.0	16.5	15.00
PI-5	160	210	190	32.0	7.3	5.60
PI-4	84	100	62	12.0	2.4	1.90
PI-2	47	51	n.m.[b]	8.6	1.6	1.10
PI-1	71	72	32	7.2	1.4	0.88

[a] Permeability (*P*) in cubic centimeters (STP) centimeter/cubic centimeter second centimeter Hg × 10^{-10} (Barrer). [b] n.m. = not measured.

whereas the 3,3″-terphenylenes are not (**PI-4**) or mono- (**PI-5**) substituted. Terphenylenes with no *o*-methyl substitution are additionally monomethyl-substituted ortho to the central ring (**PI-1**, **PI-4**). Table 3 reports permeability data of the gases He, H_2, CO_2, O_2, N_2, and CH_4 for **PI-1**−**5** ordered by decreasing oxygen permeability. (The following tables are within the same order). This order is similar for the gases CO_2, N_2, and CH_4, but in the row of He and H_2, **PI-1** changed place with **PI-2**. This may be explained by a different sensitivity of the substitution pattern (*o*-methyl, **PI-2,** or *m*-methyl, **PI-1**) to gases with smallest (He and H_2) and largest (CO_2, O_2, N_2, and CH_4) sizes. In Table 4 are summarized some selectivites of the gases. The O_2/N_2, N_2/CH_4, He/H_2, and H_2/CH_4 selectivity increases with decreasing O_2, N_2, or H_2 permeability (see Tables 3 and 4). The apparent diffusion coefficients reported in Table 5 decreases in order of decreasing gas permeability. The same behavior is seen in the apparent solubility coefficients reported in Table 6. The dependence of O_2 permeability on O_2/ N_2 selectivity is further illustrated in Figure 1. For comparison are included data of the mono-[24] and biphenylenes[10,23] (see Scheme 3). In the terphenylene series, the permeability decreases from **PI-3** to **PI-2** to **PI-1** following the decrease in methyl substitution in the ortho position. The same order is found for the series m3 to m0, p4 to p0, B2Ar to B4 to B2, and **PI-5** to **PI-4**. The 3,3″-linked **PI-5** and the 4,4″-linked **PI-2** both are methyl-substituted in the ortho position to the imide bond; however, the 4,4″-linked **PI-2** has O_2 permeability reduced by a factor of about 4 (**PI-5** = 32, **PI-2** = 8.6 Barrer). This marked decrease in permeability is found also for the other gases. The following are the structural considerations in the series of the terphenylenes: the hindrance of the rotation around the imide bond in the 4,4″-linked **PI-1**−**3s** and the 3,3″-linked **PI-4** and **PI-5** results for the 3,3″-linked PIs in a cis or a trans conformation (see Scheme 4 and Fritsch[25] for similar effects with poly(amide imide)s). The 4,4″-linked PIs cannot obtain cis/trans symmetry. We assume the inflexible cis and trans conformers are present in equal amounts statistically partitioned in the polymer chains, thus creating a larger free volume than that for similarly 4,4“-linked terphenylene PIs. The hypothetical 4,4”-linked meta terphenylene PI from diboronic acid **8** (Scheme 4) is considered to increase free volume further and be even more permeable to

Table 4. Ideal Selectivities of the Polyimides to Some Gases

PI	P(O_2/N_2)	P(CO_2/N_2)	P(N_2/CH_4)	P(He/H_2)	P(H_2/CH_4)	P(CO_2/CH_4)
PI-3	4.0	21	1.1	0.66	24	23
PI-5	4.4	26	1.3	0.76	38	34
PI-4	5.1	26	1.3	0.84	53	33
PI-2	5.2	n.m.[a]	1.5	0.92	45	n.m.[a]
PI-1	5.2	23	1.6	0.99	82	37

[a] n.m. = not measured.

Table 5. Apparent Diffusivities[a] of the Polyimides to Pure Gases

PI	$D_{\text{a He}}$	$D_{\text{a H}_2}$	$D_{\text{a CO}_2}$	$D_{\text{a O}_2}$	$D_{\text{a N}_2}$	$D_{\text{a CH}_2}$
PI-3	1400	740	9.1	28.0	8.3	1.90
PI-5	1200	560	4.1	15.0	4.1	0.79
PI-4	920	340	1.9	7.6	1.9	0.35
PI-2	830	290	n.m.[b]	5.5	1.2	0.21
PI-1	940	310	1.3	4.9	1.2	0.23

[a] Apparent diffusion coefficient (D_a) in cubic centimeters × 10^{-8}. [b] n.m. = not measured.

Table 6. Apparent Solubilities[a] of the Polymers to Pure Gases

PI	$S_{\text{a He}}$	$S_{\text{a H}_2}$	$S_{\text{a CO}_2}$	$S_{\text{a O}_2}$	$S_{\text{a N}_2}$	$S_{\text{a CH}_4}$
PI-3	1.70	4.8	390	23	20	79
PI-5	1.40	3.8	460	21	18	71
PI-4	0.92	2.9	330	16	13	54
PI-2	0.56	1.7	n.m.[b]	16	14	53
PI-1	0.76	2.3	250	15	12	38

[a] Apparent solubility coefficient (S_a) in cubic centimeters (STP)/cubic centimeters centimeters Hg × 10^{-3}. [b] n.m. = not measured.

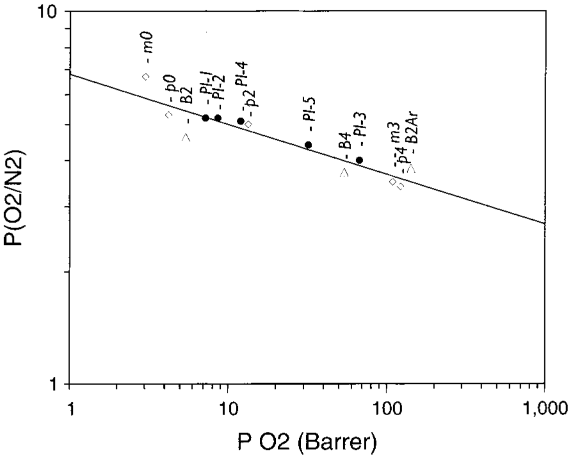


Figure 1. Correlation between oxygen permeability and oxygen/nitrogen selectivity of *p*-terphenylenes and related structures.

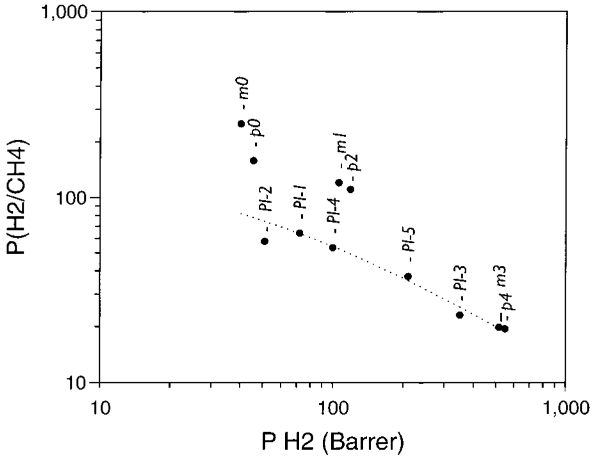


Figure 2. Correlation between hydrogen permeability and hydrogen/methane selectivity of *p*-terphenylenes and related meta and para phenylenes.

Scheme 4. Sterical Views of Different *p*-Terphenylenes

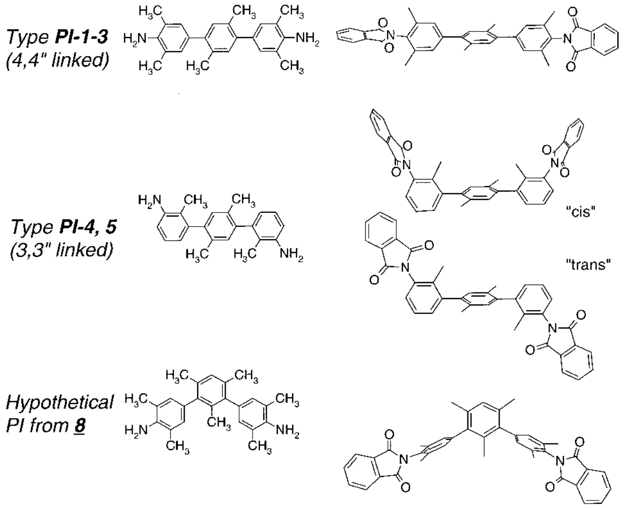


Table 7. Comparison of Permselectivity and Diffusion Selectivity of He/H₂

PI[a]	P(He/H_2)	D_a(He/H_2)	S_a(He/H_2)
PI-3	0.66	1.85	0.36
PI-5	0.76	2.13	0.35
PI-4	0.84	2.70	0.31
PI-2	0.92	2.86	0.32
PI-1	0.99	3.03	0.33

[a] The order of the PIs decreases with their O_2 permeability (diffusivity).

gases than is **PI-3**. By comparing with the permeability/selectivity relationship in this series of PI, the terphenylenes are fitting into the results of the monophenylenes (see trend line in Figure 1). The biphenylene derivatives are less selective in respect to their permeability except the Ar-substituted B2Ar, which fits to the terphenylenes. Figure 2 compares the hydrogen permeability with the H_2/CH_4 selectivity. The highly methyl-substituted terphenylenes **PI-1**−**5** are fitting into a line with the most substituted monophenylenes, p4 and m3. Lower substituted p2 and m1 showed an increased selectivity by a factor of about 2 (compare to **PI-4** in Figure 2). Because the level of H_2 permeability is similar, the overall structure is not shape selective enough to increase the selectivity to an optimum. Perm-, diffusion- and solubility selectivity of the gases with the smallest size (He and H_2) are reported in Table 7. The permselectivity as well as the diffusion selectivity of He/H_2 increases with decreasing order of O_2 permeability (or diffusivity). The solubility selectivity is constant within the experimental errors. Therefore, these changes are due to increasing diffusivity as a result of increasing polymer matrix void dimensions.

Conclusions

Three 4,4″ and two 3,3″-amino-*p*-terphenylenes with different methyl-substitution patterns were synthesized and polymerized with 6FDA to PIs. The completely characterized polymers form clear, flexible, and tough films and are soluble in low and high boiling point solvents, thus being suitable as membrane polymers. The gas permeability, diffusivity, and solubility increases in general with increasing numbers of methyl substituents ortho to the imide nitrogen. However, 3,3″-linked *p*-terphenylenes are superior compared to the 4,4″-linked ones. This is explained by the appearance of cis/trans conformers in the case of 3,3″ links and the subsequently higher free volume.

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