High performance polymers for membrane separation*

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Polymers have been recognized to exhibit selective permeation rates to gases for more than a century. The commercial reality of this characteristic, however, occurred in the late 1970s. There has been significant commercial activity in this area which has also brought about a rapid increase in the study of polymeric structural variations to optimize the combination of gas separation and permeability (permselectivity). It has been recently noted that upper bound limits exist for the separation of common gas pairs. These limitations will be discussed along with the structural features necessary to achieve the best combination of high permeability combined with high selectivity. One of the speciality polymers receiving significant attention in the past decade is poly(trimethylsilylpropyne) (PTMSP) primarily due to a permeability to common gases an order of magnitude higher than silicone rubber. Structural variations, solvent variations, non-solvent swelling effects and flux decline of PTMSP are discussed. Flux decline, which has been reported in detail in the literature, is believed to be due to two factors. Contamination can significantly decrease permeability which comprises the reason behind many literature citations. Another factor involves a slow collapse of the structure (as cast) which can depend on the casting solvent. Non-solvent swelling promotes an instantaneous increase in permeability which slowly decays back to original values. High glass transition temperature engineering polymers (e.g. polyimides, polyarylates, polycarbonates) yield permselectivity characteristics of interest for gas separation. Structural features and variations of these polymers to achieve high permeability combined with selectivity (e.g. upper bound properties) will be discussed. Surface modification techniques comprise another route to achieve high selectivity for permeable polymers. These methods (e.g. fluorination, plasma modification, u.v. exposure) offer an additional route towards meeting the requirements for separation of gases with polymeric membranes.

(Keywords: high performance polymers; membrane separation; permselectivity)

INTRODUCTION

The ability of polymeric membranes to separate common gases has been known for more than a century. The first serious attempts to propose polymeric membranes for gas separation involved investigation of helium recovery from natural gas[1]. The ability to produce ultra-thin membranes via coagulation of polymer solutions to yield asymmetric membranes was demonstrated in the 1960s[2]. This resulted in commercialization of cellulose-based polymers for reverse osmosis applications. Engineering approaches to maximize surface area/volume for membrane modules revolved around spiral wound and hollow fibre based systems. A review of methods to spin polymeric hollow fibres has been published by Puri[3].

Reverse osmosis and ultrafiltration applications were in large scale commercial use by the time of the initial commercial introduction by PERMEA of asymmetric polysulfone hollow fibres for H_2 separation from N_2 (ammonia production). The key to the PERMEA technology was the utility of silicone rubber as a thin permeable film to seal the pin-hole defects existing in the asymmetric hollow fibres[4]. Now membrane separation of gases is a recognized unit operation for separation of various gas mixtures. The specific gas mixtures commercially separated utilizing polymeric membranes include O_2/N_2 (nitrogen generation, medical oxygen), CO_2/CH_4 (landfill gas, natural gas enrichment), H_2/N_2 (ammonia purge gas), helium recovery, H_2O/air (air dehumidification), and H_2/hydrocarbon (refinery hydrogen recovery). Additional applications proposed for polymeric membrane separation include H_2/CO (synthesis gas adjustment), solvent vapour recovery pervaporation (e.g. alcohol/water), and CO_2/flue gas.

With the advent of polymeric membrane utility for gas separation, a significant amount of research has been conducted in the past decade to study the structure/permeability characteristics of polymers for gas separation. This paper will summarize the key developments and present relevant results generated in our laboratory programme. The subjects chosen for emphasis include discussion of the limits of polymeric membranes for gas separation (upper bound analysis), a summary of the gas separation capabilities of substituted polyacetylenics of which poly(trimethylsilylpropyne) (PTMSP) is of most interest due to the extremely high gas permeability, structure/property characteristics of high glass transition temperature (T_g), amorphous polymers which exhibit

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permselective properties of interest, and a review of surface modification techniques to maximize flux/separation.

Several books have been published discussing membrane separation[5,6]. There are also studies discussing polymer permeability in the literature[7–12].

Polymer permeability is characteristically referred to as a solution/diffusion process. The permeability coefficient (P) is the product of the diffusion coefficient (D) and the solubility constant (S):

$$P = D \times S \qquad (1)$$

where the units commonly employed are: $\mathrm{cm^3(STP)\,cm/(cm^2\,s\,cmHg)} \times 10^{-10} = 1$ Barrer.

For common gases (He, H_2, O_2, N_2), the diffusion coefficient and solubility constants are not a function of partial pressure over a wide range of temperature and pressure. For CH_4 and CO_2, this is also true at low partial pressure and modest temperatures. For more condensable gases (e.g. water, butane and higher hydrocarbons, organic vapours), the permeability coefficient can be highly concentration dependent. The separation factor for common gases can thus be expressed as the ratio of the pure component permeability coefficients of the gas pair:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} \qquad (2)$$

For the more condensable gases, α_{ij} can vary significantly as the feed ratio of the gas mixture is varied and thus pure component permeability values cannot be utilized to predict α_{ij}[13]. With glassy polymers and more condensable gases, the solubility constant is not a linear function of partial pressure and a dual mode sorption is observed. The dual mode sorption isotherm consists of a Henry's law 'dissolved' solubility and a Langmuir 'hole-filling' solubility:

$$C = C_k + C_H \qquad (3)$$

$$C = kp + \frac{C'_H bp}{1 + bp} \qquad (4)$$

where k is Henry's law constant, p is pressure, C'_H is the Langmuir capacity constant, and b is the Langmuir affinity constant. The value of C'_H has been shown[14] to be a linear function of the T_g with an intercept at zero at a temperature equal to the T_g.

As most of the data discussed in this paper are for common gases, the separation factor for mixtures can be estimated from pure component permeability data.

LIMITS OF POLYMER PERMEABILITY/SELECTIVITY

It has been recognized that an inverse relationship exists for permeability and selectivity for common gases. Several references[15–17] note an 'upper bound' relationship for specific gas pairs and have plotted α_{ij} *versus* log P_i (i = fast gas). More recently, a correlation of separation factor *versus* permeability for polymeric membranes has been published[18]. It was shown that an upper bound relationship (linear) was observed when the multitude of literature data was plotted as log α_{ij} *versus* log P_i. Above this linear line on the log–log plot virtually no data exist. This relationship was shown to be valid for O_2/N_2, H_2/N_2, He/N_2, H_2/CH_4, He/CH_4, CO_2/CH_4, and He/H_2. The slope of this line (n) determined from the equation ($P_i = k\alpha_{ij}^n$) was found to correlate with the Lennard/Jones kinetic diameter difference between the gas pair ($d_j - d_i$). A plot of $-1/n$ *versus* ($d_j - d_i$) resulted in a linear relationship. This analysis clearly demonstrated that the gas separation capabilities of polymers (for common gases) is controlled by the diffusion coefficient. With decreasing molecular spacing, permeability decreases and the separation capability increases. Thus, polymer membrane separation for common gases is a molecular sieving mechanism with the efficiency determined by the average pore size and the distribution of pore sizes of the polymer membrane. It is of interest to note that many polymers which exhibited 'upper bound' characteristics for one gas pair also exhibited this behaviour for other gas pairs.

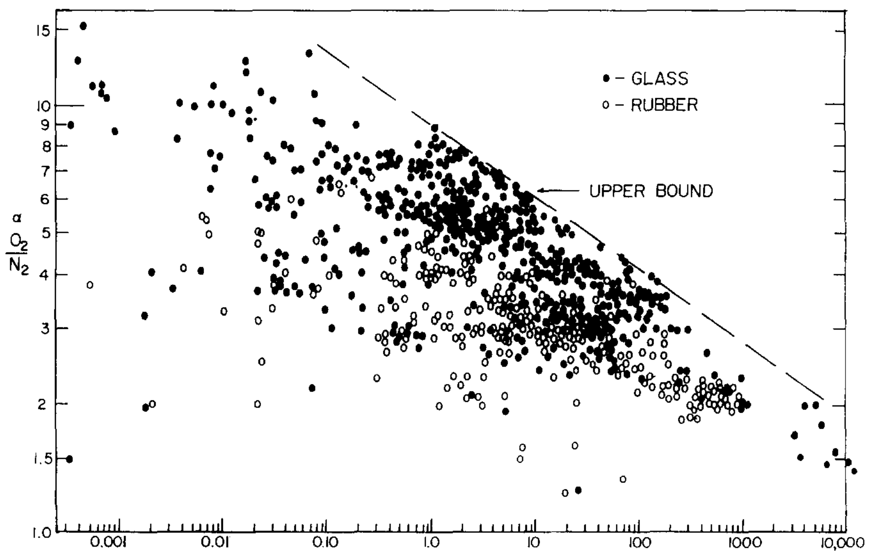


Figure 1 Permselectivity of polymeric membranes for O_2/N_2 separation (update of upper bound curve from ref. 18)

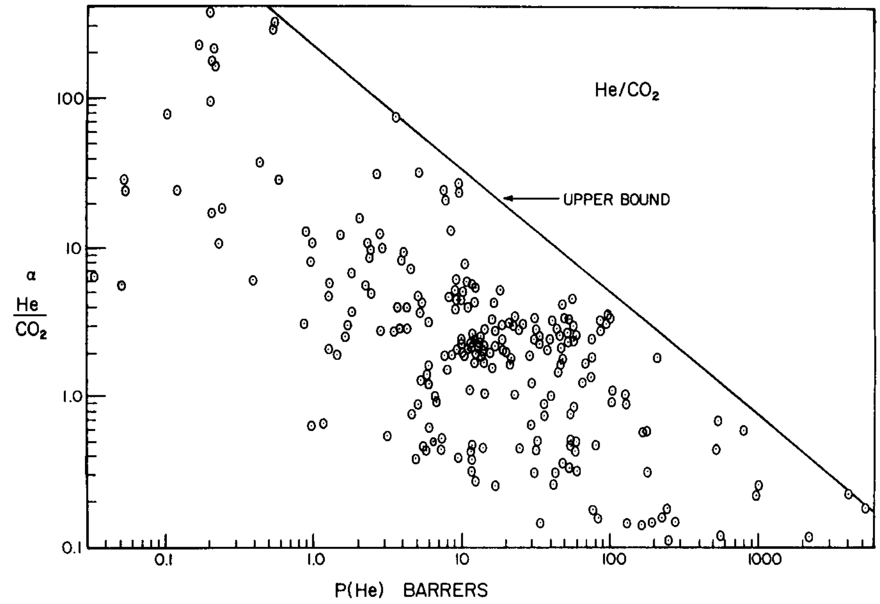


Figure 2 Upper bound analysis for He/CO$_2$ separation with polymeric membranes

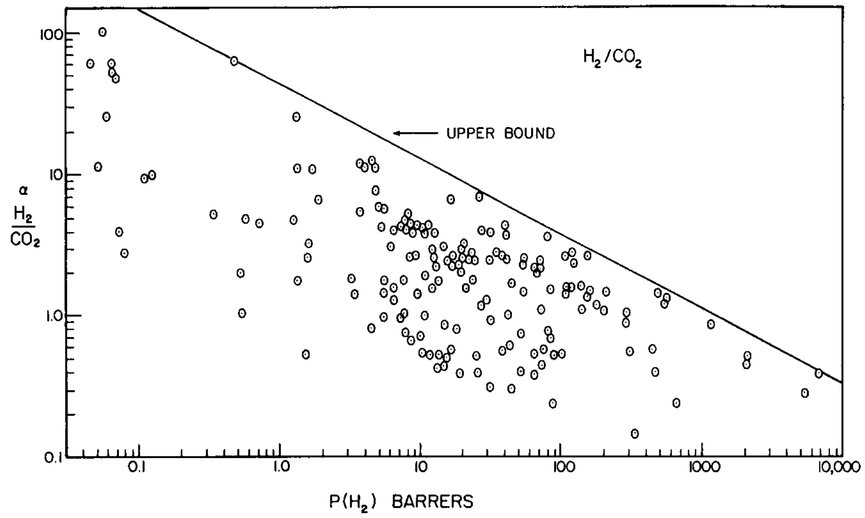


Figure 3 Upper bound analysis for H$_2$/CO$_2$ separation with polymeric membranes

One of the key gas pairs of interest is O$_2$/N$_2$. This is illustrated in *Figure 1* on an updated version of the data for O$_2$/N$_2$ taken from reference 18. Additional literature data added since submission has not changed the position of the 'state-of-the-art' upper bound. Literature data compiled from the survey utilized in reference 18 and updated were utilized to evaluate the upper bound for He/CO$_2$ and H$_2$/CO$_2$. The results illustrated in *Figure 2* (He/CO$_2$) and *Figure 3* (H$_2$/CO$_2$) also demonstrate an upper bound relationship for these two gas pairs. The addition of the slope (n) data from these curves to previously published values illustrate continued agreement (*Figure 4*) for the linear relationship of $-1/n$ *versus* the kinetic diameter difference (Δd_{ji}) for common gas pairs. The values of k and n for He/CO$_2$ are 705 Barrers and -1.220, respectively, and 1200 Barrers and -1.9363 for H$_2$/CO$_2$. No upper bound correlation was noted where the CO$_2$/N$_2$ data were applied to the above analysis.

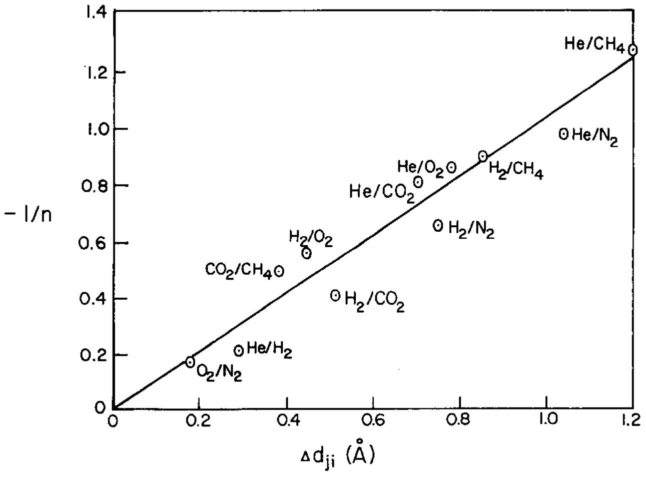


Figure 4 Correlation of upper bound slope (n) with kinetic diameter difference (Δd_{ij}) of gas mixture (additional data plotted on figure from ref. 18)

POLY(TRIMETHYLSILYLPROPYNE) AND VARIANTS

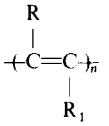
About a decade ago, permeability data on PTMSP were initially published[19]. They were surprisingly high (an order of magnitude higher than silicone rubber — previously the most permeable polymer) and altered the commonly held belief that flexible, rubbery polymers were more permeable than rigid, high T_g polymers. PTMSP is a glassy polymer with a T_g higher than its decomposition temperature (335°C in N_2: t.g.a.)[20]. Structure permeability studies on variants of PTMSP and polyacetylene have been reported[21–26] by Masuda and Higashimura and others at Kyoto University. Work in our laboratories related to variants of PTMSP has been covered in several papers[27,28]. Additionally, the gas permeability of poly(trimethylgermylpropyne) has been reported[29]. The O_2 permeability results along with O_2/N_2 separation data on these variants are listed in *Table 1*. The data clearly demonstrate that even minor variations of the structure of PTMSP lead to dramatic reductions in permeability. The details of the structure–permeability relationships for these polymers, and the rationale for the high permeability of PTMSP are discussed elsewhere[27,28] and will be only summarized here. In essence, PTMSP is unique due to the non-rotating units along the main chain, the low cohesive energy density, and the poor packing efficiency, all of which in combination leads to a very low density (0.78–0.81 g cm^{-3}) and thus high free volume. The only variant of PTMSP which retains a similar high permeability is poly(trimethylgermylpropyne). The O_2 permeability and O_2/N_2 separation factor data on a log–log plot for all the variants in our studies as well as in the published literature for substituted propynes and acetylenic polymers are compared with the O_2/N_2 upper bound relationship in *Figure 5*.

Additional studies in our laboratories involving PTMSP included a study on the ageing characteristics of PTMSP[20] where it was shown that the oxidative stability could be improved by the incorporation of higher molecular weight hindered phenolic antioxidants. The estimate of void volume fraction of PTMSP[30] from vapour solubility constants was determined to be 0.25; much larger than typical glassy polymers. The solubility constants are noted to be in the range of other glassy polymers thus demonstrating the high permeability is due to rapid diffusion. The permeability of PTMSP was shown to increase with decreasing temperature (quite unlike all other polymers) (as also noted by Masuda *et al.*[24]). This is due to the very low activation energy of diffusion, E_d, being of absolute magnitude lower than the heat of solution thus yielding a negative value of the activation energy of permeation (E_p). That is:

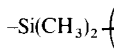
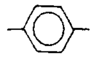
$$P_0 e^{-E_P/RT} = D_0 e^{-E_D/RT} \times S_0 e^{-\Delta H_S/RT} \qquad (5)$$

Thorogood and Hsu[31] investigated the permselectivity of PTMSP down to cryogenic temperatures (90 K). Selective surface flow was observed as the more condensable gas obstructed the flow of the light gas. While He permeability was invariant from room

Table 1 Oxygen permeability and O_2/N_2 separation factor data on substituted polypropynes (25°C)



$$\left[\overset{\overset{\large R}{|}}{C} = \underset{\underset{\large R_1}{|}}{C} \right]_n$$

R	R_1	O_2 permeability (Barrers)	$\alpha(O_2/N_2)$
CH_3	$-Si(CH_3)_3$	10 000	1.4
CH_3	$-Ge(CH_3)_3$	4000	1.5
CH_3	$-Ge(CH_3)_2(n\text{-}C_4H_9)$	20	–
CH_3	$-Si(CH_3)_2(C_2H_5)$	968	1.99
CH_3	$-Si(CH_3)_2(C_3H_7)$	70	3.3
CH_3	$-Si(CH_3)_2(CH(CH_3)_2)$	455	2.7
CH_3	$-Si(CH_3)_2(n\text{-}C_4H_9)$	28.6	3.5
CH_3	$-Si(CH_3)_2(n\text{-}C_8H_{17})$	23.4	1.21
CH_3	$-Si(CH_3)_2$ 	4.43	3.7
CH_3	$-Si(CH_3)(C_2H_5)_2$	437	2.1
$-CH_3$	$-Si(C_2H_5)_3$	635	2.2
$-CH_3$	$-CH_2-CH_2-CH_2-Si(CH_3)_3$	128	2.4
$-CH_3$	 $Si(CH_3)_3$	241	2.4

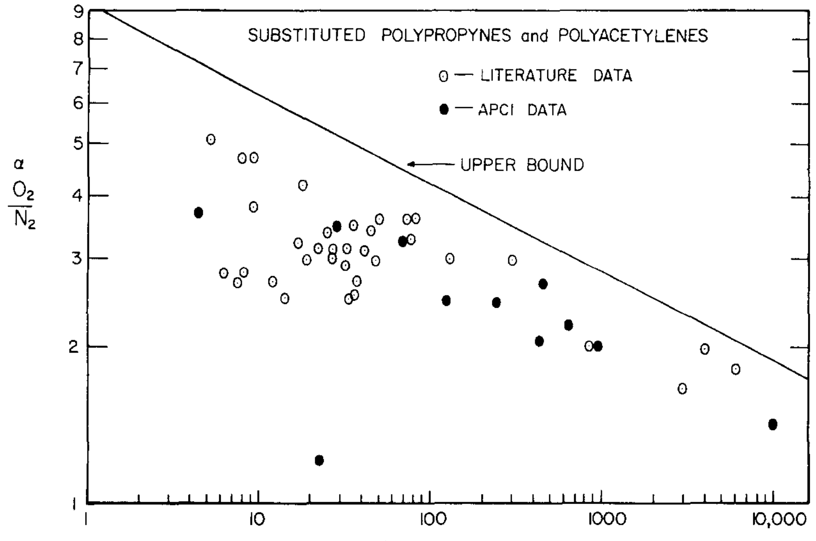


Figure 5 Comparison of permselectivity data for substituted polypropynes and polyacetylenics *versus* upper bound curve (O_2/N_2)

temperature to 220 K, the addition of CO_2 in the permeating gas significantly reduced the He permeability as the temperature was decreased.

One of the basic problems noted in the literature is the failure of PTMSP to maintain a high initial permeability[21,22,32–34]. This problem generally referred to as flux decline has been attributed to several causes. Initially, it was widely speculated that the high free volume of PTMSP collapsed with time yielding the expected flux decline. Indeed, experimental data from the references cited showed flux decline up to several orders of magnitude within days. After the initial observations, it was also noted that PTMSP is particularly sensitive to contamination and the sources noted included compressor oil, migrating oil from rubber gaskets in permeability apparatus[33], and storage conditions between permeability measurements (e.g. vacuum oven). In fact, it has been noted that storage of PTMSP in vacuum oven leads to weight gain presumably from aerosoled oil from the vacuum source[20] and weight gains of up to 20 wt% were reported[35].

A discussion of the effect of contaminants and flux decline has been covered in a patent by Langsam *et al.*[36]. This patent covers the addition of various low molecular weight compounds to modify the permselectivity of PTMSP. Additives noted include silicone oil, hydrocarbon oils, phosphate esters, brominated aromatic flame retardants, natural oils, PVC stabilizers, aromatic nitrogen-containing compounds, epoxides, and non-ionic surfactants.

In our studies, there appear to be two modes of flux decline. The first mode (and the major cause noted in the literature) can be attributed to contamination whereas the second mode appears to be a slow, gradual permeability decline yielding a decrease in permeability of 25% over a 6 month period for thin (~5 μm) films. This is illustrated in *Figure 6* for literature data[32,33] compared to thin (~5 μm) and thick (~50 μm) films of PTMSP where extreme care was taken to eliminate sources of contamination. Ultrapure oxygen (zero grade) was utilized for the continuous testing in a permeability cell. In one case the oxygen was passed through an adsorbent bed of PTMSP powder and a bed of activated carbon. This yielded a lower level of flux decline compared to similar thickness PTMSP film where the oxygen source was not further purified. It would be expected that thin films would be more affected by contamination than thicker films as was noted. Note that the contamination problem is magnified as the surface of PTMSP is modified (relative to the bulk film) and the pore structure of PTMSP is sealed. As would be predicted from the series resistance model, the permeability would drop faster for thinner films. Thus, even minor levels of contamination at the surface can have a major influence on the permeability.

Table 2 Effect of non-solvent immersion of PTMSP permeability (Barrers) (25°C)

Gas	Control	DMSO[a]	DMF[a]	Ethylene glycol	Ethanol
He	6750	20600	9460	11400	32100
H_2	17600	38400	24000	29300	59300
CO_2	37000	57700	45900	57800	51000
Ar	9140	19100	12700	15200	20800
O_2	9710	21500	13600	16500	21900
N_2	6890	17600	10100	11500	20800
CO	8520	20700	12500	14400	22100
CH_4	18400	39200	26400	29600	40000

[a] DMSO, dimethylsulfoxide; DMF, dimethylformamide

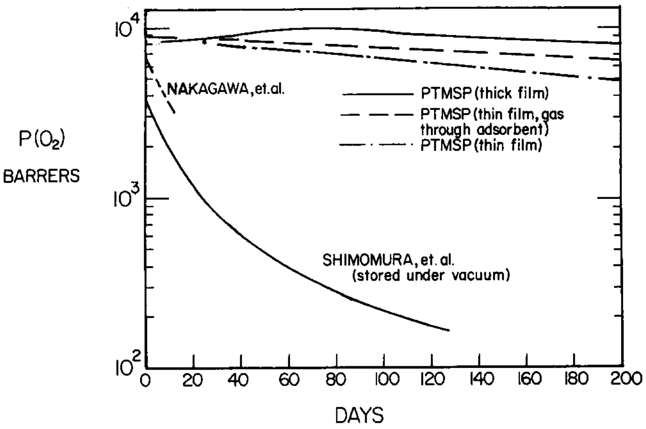


Figure 6 Experimental flux decline data (O_2) *versus* literature observations

An example has been found whereby major flux decline in PTMSP has been observed due to structural changes with time. With immersion of PTMSP in non-solvents, major dimensional changes occur in the film and sorption of up to 100 wt% is observed. Upon removal of the film from ethanol, methanol, or other non-solvents, devolatilization rapidly occurs (in minutes) and the measured permeability is initially very high but rapidly decreases with time approaching the original value after 1 month.

The effect of non-solvent immersion followed by devolatilization on the permeability of PTMSP is noted in *Table 2*. During these experiments it was found that the permeability decreased with time, thus the values are transient and dependent upon the order of measurement. The transient permeability results are illustrated in *Figure 7* for a PTMSP film soaked in methanol for 30 min. The data show that measurements taken at shorter time intervals (<2 days) could be significantly higher. At any

Table 3 PTMSP permeability as a function of casting solvent (25°C)

Casting solvent	Hexane	Toluene	THF[a]	$CHCl_3$	$CHCl_3/CH_3CN$
P(He) (Barrers)	4100	5510	6330	6940	12710
P(O_2) (Barrers)	5790	8520	9540	10550	20640
P(N_2) (Barrers)	3920	6200	6670	8050	14770
δp ($cal^{1/2}\ cm^{-3/2}$)	7.3	8.9	9.1	9.3	9.9
$\alpha(O_2/N_2)$	1.48	1.37	1.43	1.31	1.40

[a] THF, tetrahydrofuran

rate, after 1 month the data are approaching original values. This example is a true case of free volume collapse of PTMSP resulting in flux decline. Cast films (from good solvents) do not show this behaviour unless contamination problems exist. However, a trend was observed in the permeability of PTMSP as a function of the solubility parameter of the casting solvent (*Table 3*), and this behaviour may be related to the non-solvent swelling noted above. The poorer solvents (higher δp) result in higher permeability. During the solvent evaporation, the gel point (phase separation) is reached at a higher residual solvent level for poor solvents thus leaving a more open structure for PTMSP. This more open structure is presumably able to collapse similar to that observed with non-solvent swelling. The solvent differences possibly explain the range of PTMSP permeability values noted in the literature.

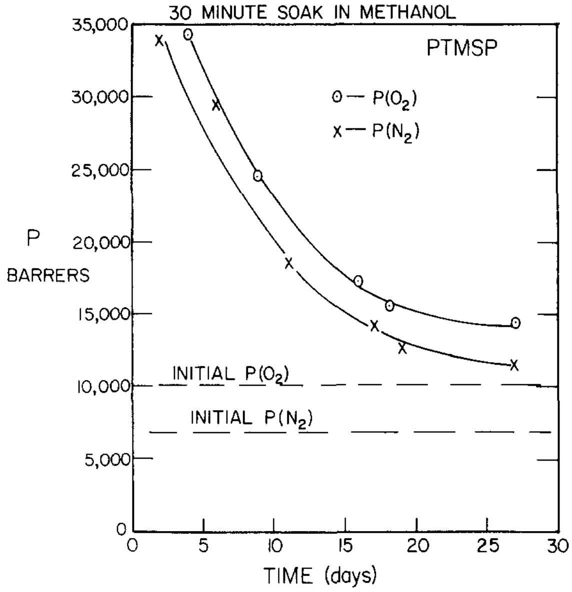


Figure 7 Permeability decline for PTMSP films after methanol immersion

It is of interest to note that one of the earlier references on the 'instability' of PTMSP investigated the isobutane permeability after films had been immersed in methanol to remove casting solvent (benzene)[32]. This treatment, in essence, caused the observed flux decline and led to the conclusions involving the stability of PTMSP.

PTMSP has also exhibited unique properties in separation areas involving liquids. The preferential permeation of ethanol through PTMSP from ethanol/water mixtures has been observed[37]. It has also been observed that PTMSP exhibits absorbent properties for the removal of trace organics from air and water sources[38]. PTMSP approaches activated carbon efficiency for organics removal and was found to be much closer than other polymeric materials. Although not as effective as activated carbon, PTMSP offered an advantage in simple regeneration from a fixed bed by employing air sweep or vacuum.

PERMSELECTIVITY CHARACTERISTICS OF POLYIMIDES

One of the most investigated classes of polymers for membrane separation is polyimides. This is at least partly due to the structure/permeability studies noted by Koros and co-workers[39–41]. Specific polyimides have been noted to exhibit upper bound characteristics for a number of different gas pairs (O_2/N_2; He/N_2; He/CH_4; H_2/CH_4; and CO_2/CH_4)[18]. O'Brien *et al.*[39] showed a correlation between the X-ray diffraction *d*-spacing (amorphous halo) of polyimides and permeability to gases. Kim *et al.*[40] noted a relationship between polyimide permeability with intrasegmental mobility and intersegmental packing. High permeabilities for polyimides were observed with a fluorinated dianhydride (5,5′-[1,1,1-trifluoro-1-(trifluoromethyl) ethylidiene] bis-1,3-isobenzofurandione (6FDA)[40,41]. Tanaka *et al.*[42] studied polyimides based on 6FDA and methyl substituted phenylenediamines. Very high permeabilities were noted for 6FDA polyimides using 2,3,5,6-tetramethyl-1,4-phenylenediamine or 2,4,6-trimethyl-

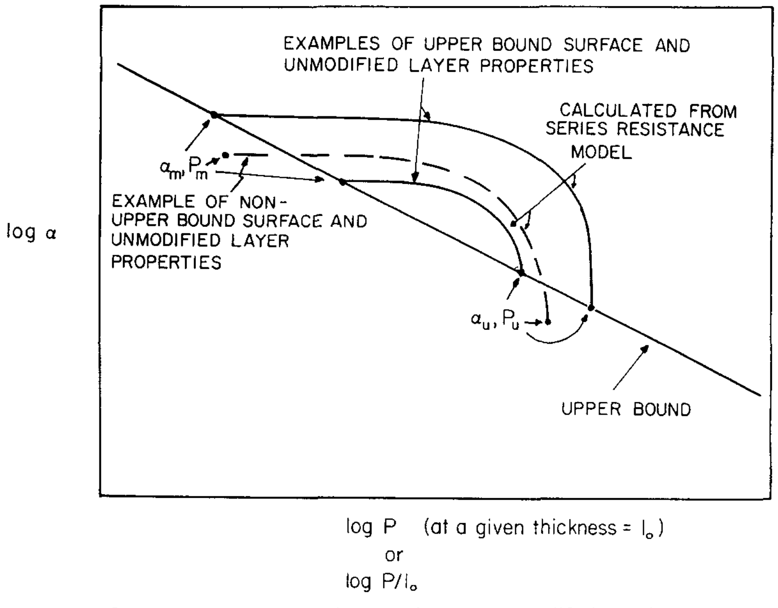
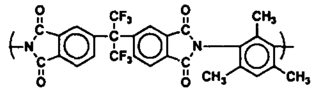
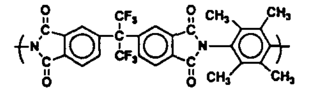


Figure 8 Generalized permselectivity data for surface modified membranes

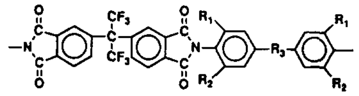
1,3-phenylenediamine:

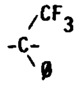
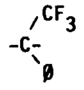
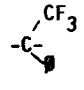
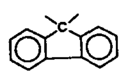
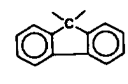
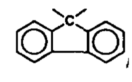
Structure	$P(O_2)$ (Barrers)	$P(N_2)$ (Barrers)
	109	32
	122	36

This confirms the data reported earlier by Hayes[43,44] in the patent literature.

Tanaka *et al.*[45,46] reported on the gas permeabilities of polyimides based on 3,3′, 4,4′-biphenyl tetracarboxylic dianhydride. Okamoto *et al.*[47] reported on the permselective properties of polyimides based on 4,4′-diaminotriphenylamine. The CO_2 diffusion coefficient was found to be correlated with free volume. Yamamoto *et al.*[48] reported on the structure/permeability of 6FDA based polyimides.

Table 4 Permselectivity of substituted polyimides[58]



Polymer			$P(O_2)$ (Barrers)	$\alpha(O_2/N_2)$
R1	R2	R3		
H	H	$-CH_2-$	2.8	5.7
H	$CH(CH_3)_2$	$-CH_2-$	8.2	5.9
H	$C(CH_3)_3$	$-CH_2-$	19.0	4.7
CH_3	CH_3	$-CH_2-$	11.0	4.2
$CH(CH_3)_2$	$CH(CH_3)_2$	$-CH_2-$	47.1	3.8
H	H	 $-\underset{\phi}{\overset{CF_3}{C}}-$	3.8	4.2
CH_3	CH_3	 $-\underset{\phi}{\overset{CF_3}{C}}-$	25.5	3.0
$CH(CH_3)_2$	$CH(CH_3)_2$	 $-\underset{\phi}{\overset{CF_3}{C}}-$	80.0	3.2
H	H		11.7	3.9
CH_3	CH_3		60.1	3.6
CH_3	$CH(CH_3)_2$		84.4	4.2

Stern *et al.*[49] reported on the structure/permeability of silicon-containing polyimides and observed that silicone–polyimides block copolymers gave much lower selectivity than polyimides employing dianhydrides containing a dimethylsilane linking group. Additional data on the O_2, CO_2 and H_2O permeability of 16 different polyimides was reported by Sykes and St. Clair[50]. These references in combination note interesting results of permeability and selectivity of common gases for polyimides.

Studies in our laboratories on polyimides have been noted in a number of patents[51–57] and in a recent publication summarizing these results[58]. The effect of the diamine monomer structure on the gas permeability of polyimides based on 6F dianhydride is tabulated in *Table 4*. *Ortho* substitution on the diamine monomers is shown to have a major effect on the O_2 permeability. In fact, a correlation was shown between the Van der Waal's volume of the substituent *ortho* groups and O_2 permeability (linear for $\log P(O_2)$ and van der Waal's volume of the *ortho* substituents). The positions of the relationship varied with diamine bridging group as would be expected, but the slope was invariant. Correlations between density and *d*-spacing and the van der Waal's volume of the substituent *ortho* groups were also observed. The prior observations of Koros *et al.*[39–41] and Hoehn[59] that substituents reducing interchain packing and increasing intrachain segmental rigidity increase permeability were further confirmed in this work.

ADDITIONAL AROMATIC POLYMERS

Studies of polysulfone, poly(ether ketone) and polycarbonate variants have been reported in many studies[15,60–63], most of which are from the University of Texas. One of the polymers which generated interest was tetrabromobisphenol A polycarbonate[60]. At the time it was reported, the $P(O_2)$ and $\alpha(O_2/N_2)$ combination made it one of the most promising polymers available. More recently a polytriazole was noted to have even better O_2/N_2 permselectivity[64]. Another polymer offering O_2/N_2 permselectivity on the upper bound line is a polypyrrolone[63]. These and other aromatic polymers of interest are noted in *Table 5*.

A series of aromatic polyamides derived from dicarboxylic acid chlorides and cardodiamines with *ortho* substitution on the diamine were noted to have permselectivities approaching upper bound properties by Tien *et al.*[65]. Polyarylates based on tetrabromobisphenol where the bisphenol bridging group was fluorene, norbornylidene, or t-butyl cyclohexyl were shown to also exhibit upper bound properties for O_2/N_2 permselectivity[66–68].

The hexafluoroisopropylidene bridging group has been shown in various polymers to exhibit a positive effect on the O_2 permeability. A series of polyarylates have been synthesized and the results are shown in *Table 6*. The trends are in accordance with the *ortho* substituents noted with other polymer systems.

SURFACE MODIFICATION

Various surface modification procedures have been reported to yield modifications in the permselectivity of polymers. One of the earlier references[69] noted electron beam treatment of polymers yielded improved selectivity with modest decreases in permeability. Kawakami *et al.*[70]

Table 5 Permselectivity of selected aromatic polymers

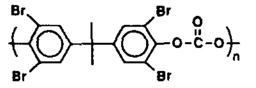
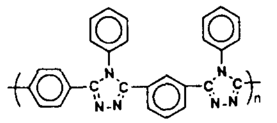
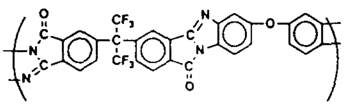
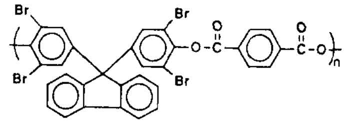
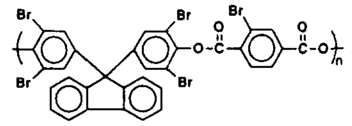
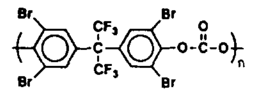
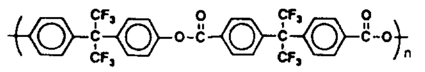
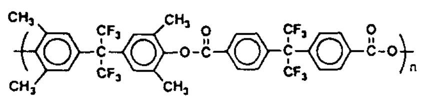
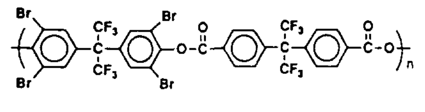
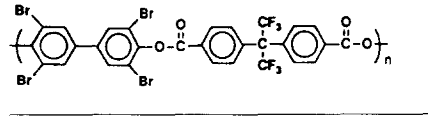
Structure	$P(O_2)$ (Barrers)	$\alpha(O_2/N_2)$	Ref.
	1.36	7.5	60
	1.2	9.0	64
	7.9	6.5	63
	9.0	6.1	68
	4.0	6.8	68
	9.7	5.2	78

Table 6 Permselectivity of 6F based polyarylates

Structure	$P(O_2)$ (25°C)	$\alpha(O_2/N_2)$ (25°C)
	15.6	4.0
	47.8	4.1
	38.4	5.0
	8.97	5.1

demonstrated dramatic improvements in the selectivity (O_2/N_2) for plasma polymerization of 4-vinylpyridine and 2-vinylpyridine on silicone rubber and natural rubber. Anand *et al.*[71] noted selectivity enhancement of PTMSP upon plasma polymerization with nitrogen heterocycles (e.g. vinylpyrazine, 4-vinylpyridine, vinylimidazole). Plasma polymerization yielded $\alpha(O_2/N_2)$ increases of PTMSP from 1.4 to >8.0 with a marked decrease in the flux ($P(O_2)/l$). Fluorination of PTMSP[72] was shown to yield a very thin selective layer backed by a permeable substrate of unmodified PTMSP. Fluorooxidation of poly(4-methyl-1-pentene) was shown to yield improved selectivity over fluorination in the absence of oxygen by Anand *et al.*[73]. U.v. exposure of PTMSP films was also noted to yield improved selectivity by Puri[74]. U.v. treatment of permeable polyimides to yield improved selectivity has been noted in several patents[75–77].

The reason for the interest in surface modification is illustrated by the upper bound curve. If a highly permeable polymer is surface modified such that the surface modification creates an impermeable layer (both positions on the upper bound), the series resistance model can be employed to show how the α, P relationship changes with the thickness of the surface layer (*Figure 8*). The results can clearly lie above the upper bound. Note that this analysis relative to the upper bound is only valid at a specific thickness. This approach is significant (relative to P/l) at membrane thicknesses approaching that commonly employed for homogeneous membranes (~1000 Å). With the extremely high permeability of PTMSP, surface modification techniques have shown promising values where the modifying layer is less than several thousand angstroms.

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