Gas Permselectivity Properties of High Free Volume Polymers Modified by a Low Molecular Weight Additive

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ABSTRACT: The permselectivity properties of mixtures of the highly substituted polymers tetramethylhexafluoro polysulfone (TMHFPSF) and tetramethylhexafluoro bisphenol A *t*-butyl isophthalate (TMHFBPA-tBIA) with a low molecular weight glassy additive Kenflex A (denoted here as KXA) were measured for different gases and compared with the permselectivity properties shown by the base, unsubstituted polymers polysulfone (PSF) and bisphenol A *t*-butyl isophthalate (BPA-tBIA). The results show that the selectivity-permeability balance of polymer membranes may be appropriately tailored by a combination of chemical and physical alterations of the base polymer. The addition of modest amounts of KXA (ca. 20 wt %) into TMHFPSF or TMHFBPA-tBIA leads to materials whose permeability/selectivity combination is better than that of the unsubstituted materials, PSF or BPA-tBIA. The polymer TMHFPSF responds more beneficially to the incorporation of KXA than TMHFBPA-tBIA. At the same level of permeability, mixtures based on TMHFPSF have higher selectivity factors for H_2/CH_4 and CO_2/CH_4 than those based on TMHFBPA-tBIA. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 403–415, 1998

Key words: membranes; gas seperations; permeability; antiplasticization; polysulfones; polyarylates

INTRODUCTION

The opportunities for expanded use of polymer membrane technology for gas separations hinge in part on identifying membrane materials with higher permeability and higher selectivity than those currently in use. Structure/property studies have identified some empirical rules for designing polymers with higher permeability with minimal sacrifice, if any, in selectivity or vice versa. Systematic changes in the bisphenol unit of polymers having the following molecular structure

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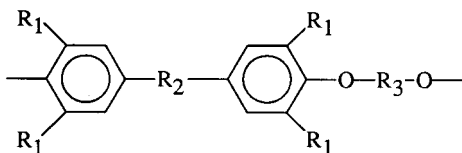
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such as polysulfones (R_3 = biphenyl sulfone),[1–6] polycarbonates (R_3 = carbonyl),[7,8] or polyarylates (R_3 = isophthalic or *t*-butyl isophthalic acid)[9–13] have led to materials with outstanding combinations of permeability and selectivity relative to commercially available polymers. Examples of such improvements include the incorporation of methyl groups or halogen atoms for R_1 instead of hydrogen and replacing the standard isopropylidene connector group, R_2, in the bisphenol with a hexafluoro isopropylidene or a fluorene connector group. The balance between inhibition of chain packing and chain mobility by such changes in structure has placed some of these polymers close to the "upper bound" proposed by Robeson,[14] above which no polymers seem to exist at the present time.

Prior work has shown that the physical incorporation of low molecular weight additives into glassy polymers generally reduce their permeability to gases but may increase their selectivity to transport of certain gas pairs. This response is consistent with the phenomenon referred to as

"antiplasticization"; generally, incorporation of such additives leads to a reduction in free volume that increases stiffness,[15,16] decreases permeability,[17-19] etc. The use of such additives has been examined as a route to tailoring the permeability-selectivity balance of gas separation membrane materials.[19-21] A recent study has shown that the incorporation of naphthalene-based additives into bisphenol A polysulfone (PSF) can lead to membranes with substantially higher selectivity but somewhat lower permeability relative to neat polysulfone.[19] An especially attractive additive for this purpose is the alkylated naphthalene oligomer with the following general structure
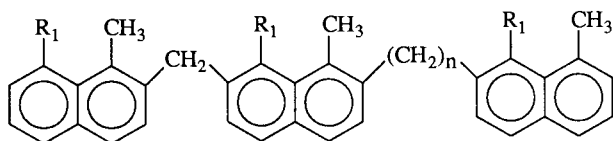
It is a mixture of compounds having values of n of 1 or 2 and where R_1 is a hydrogen or a methyl group. This glassy solid is commercially available under the trade designation of Kenflex A (or KXA as used herein).

The incorporation of such additives into high-performance polymers like those described previously may provide a simple and inexpensive route to improve their permselectivity characteristics, and this possibility is the focus of our current research. This article reports on the gas permselectivity properties of tetramethylhexafluoro polysulfone (TMHFPSF) and tetramethylhexafluoro bisphenol A t-butyl isophthalate (TMHFBPA-tBIA) modified with different concentrations of KXA as the permeation modifier. The goal is to determine the balance between permeability and selectivity of these KXA modified polymers.

Additive and Polymer Materials

The additive KXA (kindly donated by Kenrich Petrochemical, Inc., Bayonne, NJ) is an amber-colored, amorphous solid with a glass transition temperature of 32°C and a specific volume of approximately 0.917 cm^3 g^{-1} at room temperature. It is a condensation product of alkyl naphthalenes and formaldehyde that has a high content of methylnaphthalene units bridged by methylene or ethylene groups according to the chemical structure given in the previous section.[22] Thermal gravimetric analysis shows a 5 wt % loss of KXA

at 255°C when heated in air at a heating rate of 20°C min^{-1}. This compound was incorporated into the two polymers without any purification.
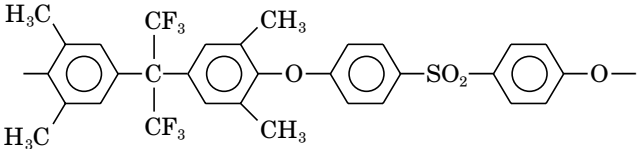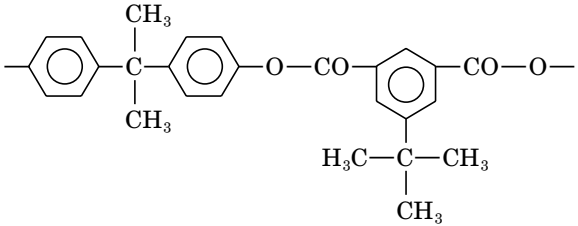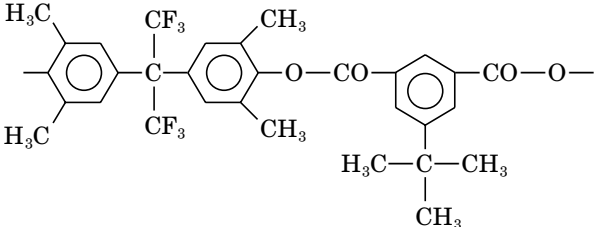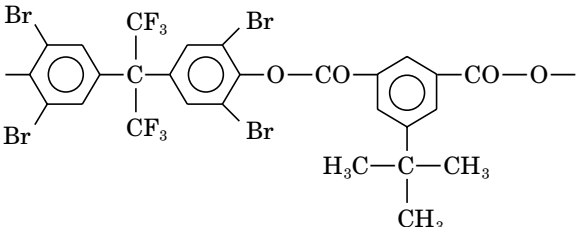
The pure polymers, TMHFPSF and TMHFBPA-tBIA, were synthesized in this laboratory. Table I gives the molecular structure of these and other related polymers that are used for comparison [e.g., bisphenol A t-butyl isophthalate (BPA-tBIA)[11] and tetrabromohexafluoro bisphenol A t-butyl isophthalate (TBHFBPA-tBIA)].[12] The polymer TMHFPSF, synthesized by McHattie,[6] was dissolved in dichloromethane, filtered to remove dust particles and precipitated into methanol, then Soxhlet extracted with ethanol for 2 days to remove residual 1-methyl-2-pyrrolidinone. TMHFPSF was selected because it contains substitutions that increase its fractional free volume and permeability to gases relative to PSF.[6] The other polymer used herein, TMHFBPA-tBIA (see structure in Table I), is a highly substituted polyarylate based on tetramethylhexafluoro bisphenol A and t-butyl isophthalic acid. This polymer was synthesized herein by interfacial polymerization according to a procedure outlined by Pixton and Paul[12] with minor modifications. Its transport properties have not been described previously. This molecular structure was selected, based on extensive structure/property studies of similar polyarylates, to give a polymer with a high fractional free volume and, hence, gas permeability.

Film Formation and Characterization

Each polymer and the desired amount of KXA were dissolved in dichloromethane to give a solution containing 5 wt % total solids. Films between 2 and 4 mils thick were cast on glass plates in a plastic bag to control the solvent evaporation rate and to prevent air borne dust particles from contaminating the films. For each polymer, there was a maximum concentration of KXA (30 wt % for TMHFPSF and 20 wt % for TMHFBPA-tBIA), beyond which the films were too brittle for testing. The films were vacuum-dried for a period of 7 days, during which time the temperature was increased until 200°C and then held there for 2 days. The films were then cooled slowly to room temperature under vacuum. All polymer films containing KXA produced a metallic sound when waved in the air, and generally had sufficient mechanical strength and toughness for gas permeability measurements.

The glass transition temperature, defined by

Table I   Polymers Compared in This Work

Polymer Structure	Acronym	T_g (°C)	Density (g cm^{-3})	FFV
(structure: H_3C, CF_3, CH_3 … C … O—SO_2—O—, H_3C, CF_3, CH_3)	TMHFPSF[a]	242	1.286	0.196
(structure: CH_3, C, CH_3 … O—CO … CO—O—, H_3C—C—CH_3, CH_3)	BPA-tBIA[b]	218	1.126	0.174
(structure: H_3C, CF_3, CH_3 … C … O—CO … CO—O—, H_3C, CF_3, CH_3, H_3C—C—CH_3, CH_3)	TMHFBPA-tBIA[c]	242	1.189	0.219
(structure: Br, CF_3, Br … C … O—CO … CO—O—, Br, CF_3, Br, H_3C—C—CH_3, CH_3)	TBHFBPA-tBIA[d]	261	1.694	0.218

[a] Values from ref. 3.
[b] Values from ref. 11.
[c] This work. Synthesis conducted by Scott McCaig.
[d] Values from ref. 12.

the onset of the transition, for each film was measured by differential scanning calorimetry (DSC; Perkin–Elmer DSC7) during a second scan at a heating rate of 20°C min^{-1}. The densities of the films were measured at 30°C in a density gradient column based on degassed, aqueous calcium nitrate solutions. Gas permeability coefficients at 35°C were measured for six gases in a standard permeation cell described elsewhere.[23,24] The films for permeation were not conditioned with CO_2. Exposure to high CO_2 concentrations for prolonged periods of times may plasticize the films[25,26]; thus, the permeability measurement order always began with He and finished with CO_2.

Gas Transport Properties of Unmodified TMHFBPA-tBIA

Herein, we report the transport properties of the new polyarylate TMHFBPA-tBIA and compare its properties to some related polymers (*viz.* TMHFPSF and TBHFBPA-tBIA). The two tetramethyl substituted polymers in Table I (TMHFPSF and TMHFBPA-tBIA) have rather similar glass transition temperatures. The intrinsic viscosity of the TMHFBPA-tBIA sample (0.86 dL g^{-1} measured in chloroform at 25°C) is quite similar to that reported for the TMHFPSF synthesized by McHattie and coworkers.[6] It is important to note that TMHFBPA-tBIA has a 12% higher
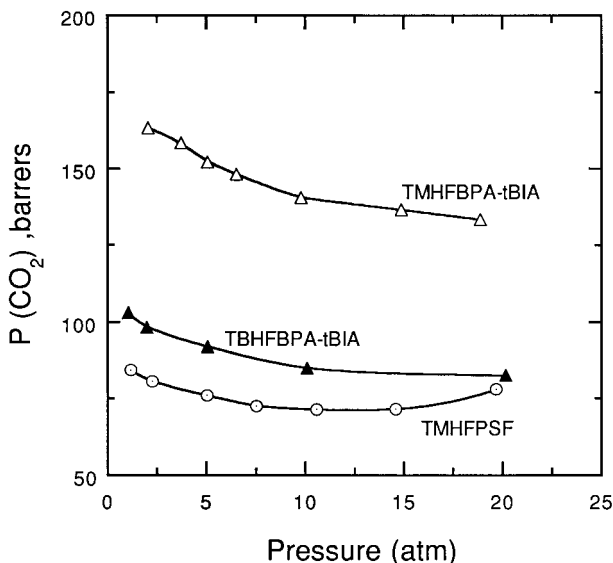
Figure 1 Effect of upstream pressure at 35°C on the CO_2 permeability coefficients of TMHFBPA-tBIA. Results for TMHFPSF and TBHFBPA-tBIA are shown for comparison.

fractional free volume (FFV) than TMHFPSF; thus, membranes based on TMHFBPA-tBIA have a more open structure and should exhibit higher gas permeation rates than membranes from TMHFPSF. Of course, replacement of the methyl groups in TMHFBPA-tBIA by bromine atoms, TBHFBPA-tBIA, increases the T_g because of the polarity introduced by this change. However, TMHFBPA-tBIA and TBHFBPA-tBIA have about the same FFV.

Figure 1 shows the effect of upstream pressure on the permeability of TMHFBPA-tBIA to CO_2; permeability coefficients for TBHFBPA-tBIA and TMHFPSF are also shown for comparison. The continuous decrease in the permeability coefficient with upstream pressure suggests that

TMHFBPA-tBIA is not plasticized by CO_2 up to 20 atm. This is in contrast to the plasticization effect shown by TMHFPSF. The permeability coefficients of TMHFBPA-tBIA to other gases show the normal behavior seen for glassy polymers. The permeability for the larger gases (CO_2 and CH_4) decreases with increasing upstream pressure, as predicted by the dual sorption model.[27] The permeability of TMHFBPA-tBIA to He, H_2, O_2, and N_2 does not show appreciable variations with upstream pressure.[28]

The permeability and ideal selectivity coefficients for TMHFBPA-tBIA are compared with those for TBHFBPA-tBIA and TMHFPSF in Table II. The permeability of TMHFBPA-tBIA to all gases is approximately twice that of TMHFPSF and TBHFBPA-tBIA, but the selectivity for all gas pairs is somewhat lower.

The apparent diffusion coefficients reported herein were calculated from the diffusion time lag, θ, using the relation[29]

$$D = \frac{l^2}{6\theta} \tag{1}$$

where l is the thickness of the membrane. The solubility coefficient was then calculated from the permeability and diffusion coefficients by the relation[29]

$$P = DS \tag{2}$$

The apparent diffusion and solubility coefficients for O_2 and CO_2 in TMHFBPA-tBIA are given in Table III and compared with the corresponding values for TMHFPSF and TBHFBPA-tBIA. It is important to mention that the apparent solubility coefficients for TBHFBPA-tBIA, reported by Pixton and Paul,[12] were calculated from

Table II Permeability Coefficients and Ideal Separation Factors at 35°C

Polymer	Permeability, Barrers			Ideal Separation Factors			
	He[a]	O_2[b]	CO_2[a]	$\alpha_{CH_4}^{He}$	$\alpha_{H_2}^{He}$	$\alpha_{N_2}^{O_2}$	$\alpha_{CH_4}^{CO_2}$
TMHFPSF[c]	113	18	72	38	0.9	4.5	24
TMHFBPA-tBIA[d]	180	40	140	23	0.8	4.3	18
TBHFBPA-tBIA[e]	124	22	85	37	0.8	4.9	25

[a] Permeability of helium and carbon dioxide at 10 atm.
[b] Permeability of oxygen at 2 atm.
[c] From ref. 3.
[d] This work.
[e] From ref. 12.

Table III   Diffusivity and Solubility Contributions to O_2 (2 atm) and CO_2 (10 atm) Permselectivities at 35°C

Polymer	Diffusivity (10^{-8} cm^2/s^{-1})		Solubility (cm^3 (STP) cm^{-3} atm^{-1})		Ideal Diffusivity and Solubility Separation Factors			
	D_{O_2}	D_{CO_2}	S_{O_2}	S_{CO_2}	D_{O_2}/D_{N_2}	D_{CO_2}/D_{CH_4}	S_{O_2}/S_{N_2}	S_{CO_2}/S_{CH_4}
TMHFPSF[a]	15.0	8.9	0.91	6.1	3.3	7.1	1.4	3.4
TMHFBPA-tBIA[b]	36.9	19.2	0.82	5.5	3.1	5.5	1.4	3.2
TBHFBPA-tBIA[c,d]	18.1	16.3	0.93	4.0	4.4	9.3	1.1	2.7

[a] From ref. 3.
[b] This work.
[c] From ref. 12.
[d] Solubility calculated from the sorption isotherm, diffusivity from $P = DS$.

the secant slope of the sorption isotherm evaluated at the upstream condition, and then the apparent diffusivity coefficients were calculated from permeability coefficients via eq. (2). Thus, the comparison of the sorption coefficients for TBHFBPA-tBIA with those for the other two polymers appearing in Table III should be considered with caution because, typically, the solubility coefficients from time lag measurements are slightly larger than those measured from sorption experiments. The diffusivity and solubility selectivity coefficients for O_2/N_2 and CO_2/CH_4 are also reported in Table III. The higher permeability of TMHFBPA-tBIA to O_2 with respect to the other two polymers arises from its diffusivity for O_2,

which is approximately twice that for the other two polymers. The higher permeability of TMHFBPA-tBIA to CO_2 results from its larger diffusivity with respect to TMHFPSF and from larger diffusivity and solubility with respect to TBHFBPA-tBIA.

Thermal Properties of Polymers Modified with KXA

A combination of factors (including optical transparency), a single composition-dependent glass transition temperature, and the dependence of the glass transition temperature of the mixture on KXA concentration were used to confirm the
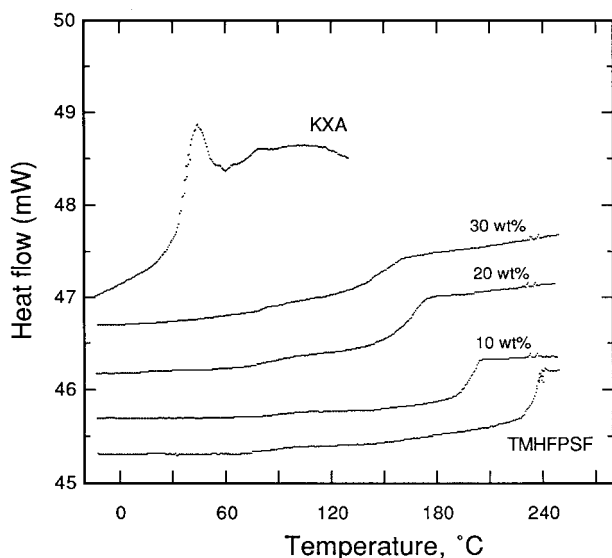

Figure 2   DSC scans (second heats) at 20°C min^{-1} for pure TMHFPSF and KXA and their mixtures at different weight concentrations of KXA.
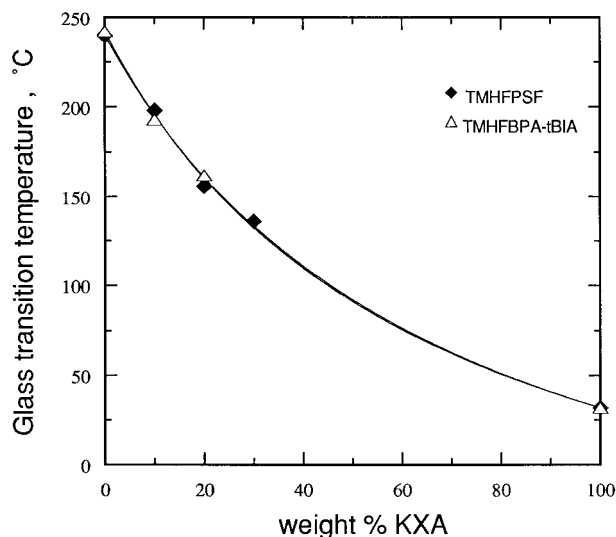

Figure 3   Effect of KXA concentration on the glass transition temperature of mixtures with TMHFPSF and TMHFBPA-tBIA. Solid line was calculated using the Gordon–Taylor equation with $K = 0.4$.
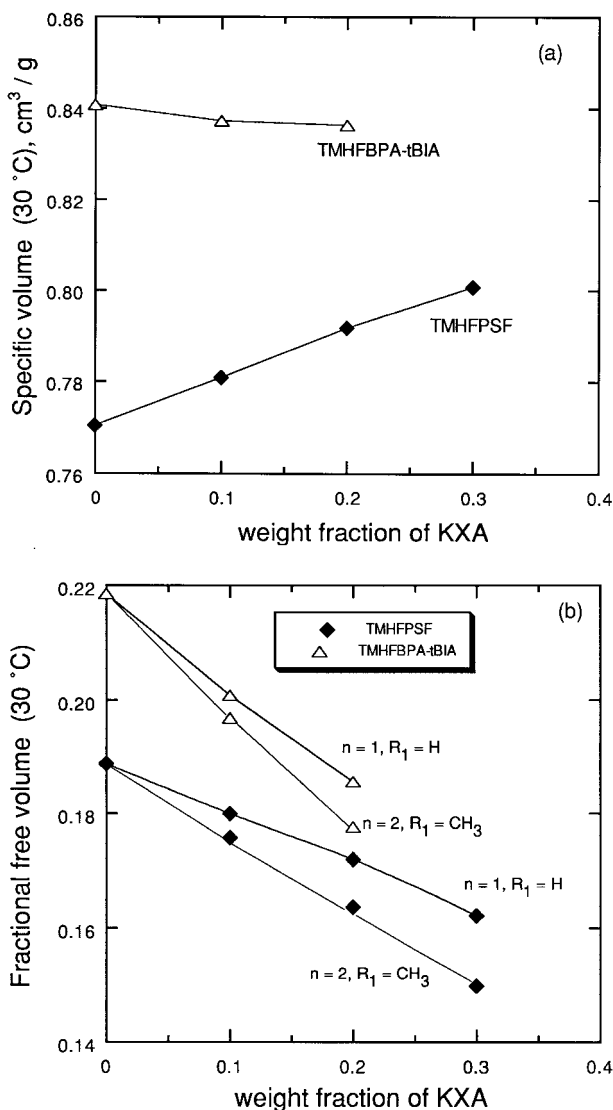
Figure 4   Effect of KXA concentration on the (a) specific volume and (b) the FFV of TMHFPSF and TMHFBPA-tBIA. The occupied volume of these mixtures has been calculated assuming two possible limits for n and R_1 (see structure in the text) to represent the molecular structure of KXA.

miscibility of KXA with these polymers. Permeation studies were limited to mixtures of KXA with TMHFPSF and with TMHFBPA-tBIA that formed optically transparent films. Figure 2 shows DSC scans for TMHFPSF, KXA, and their mixtures. Up to 30 wt % of KXA, there is a single glass transition; however, at higher KXA concentrations, there was evidence of phase separation. Mixtures with TMHFBPA-tBIA showed a single glass transition temperature up to 20 wt % KXA.

The effect of KXA addition on the glass transi-

tion temperature is similar for the two polymers (Fig. 3). The two pure polymers have the same T_g, and the depression of T_g by KXA is identified for each polymer. The solid line is the best fit of the data to the Gordon–Taylor equation[30]

$$T_g = \frac{w_d T_{gd} + K w_p T_{gp}}{w_d + K w_p} \qquad (3)$$

where w_i and T_{gi} are the weight fraction and glass transition temperature of component i, and K is an adjustable parameter set at 0.4.

Volumetric Properties of Polymers Modified with KXA

Figure 4 shows the experimental specific volume, V [Fig. 4(a)], and the calculated FFV [Fig. 4(b)] of the two polymers as a function of KXA content. The fractional free volume as used herein is defined by the relation

$$FFV = \frac{V - V_o}{V} \qquad (4)$$

where V_o is the occupied volume calculated from the van der Waals volume, V_w, using the following relation suggested by Bondi[31]

$$V_o = 1.3 V_w \qquad (5)$$

For polymer/KXA mixtures, V_o was calculated assuming volume additivity, i.e.,

$$V_o = w_d (V_o)_d + w_p (V_o)_p \qquad (6)$$

where w_i and $(V_o)_i$ are the weight fraction and occupied volume of pure component i. Because the structure of KXA is not fully defined, the occupied volume of KXA can have several values according to the structure selected (see structure in the Introduction). For the purpose of the present study, it is assumed that the value of V_o for KXA should lie on or between the limits set by the general structure with $n = 1$, $R_1 = H$ and $n = 2$, $R_1 = CH_3$.

The specific volume of KXA is higher than that of either polymer; however, the addition of KXA increases the specific volume of TMHFPSF, but decreases the specific volume of TMHFBPA-tBIA. Incorporation of KXA decreases the FFV for both polymers, as seen in Figure 4(b). From this point of view, it is clear that, regardless of which structure is used to calculate V_o (i.e., $n = 1$, $R_1 = H$ or

Table IV   Effect of KXA Concentration on Permeability Coefficients and Ideal Selectivity at 35°C

	Permeability Coefficient[a] Barrers				Ideal Separation Factors				
Material	He	H_2	O_2	CO_2	He/CH_4	H_2/CH_4	CO_2/CH_4	O_2/N_2	He/H_2
TMHFPSF	118	127.8	18.5	71.0	38	43	22.6	4.4	0.91
KXA 10%	44	38.5	3.3	11.0	129	114	32.6	5.9	1.13
KKA 20%	27	21.3	1.4	4.4	221	173	35.9	6.6	1.27
KXA 30%	17	12.7	0.7	1.9	320	234	35.4	7.2	1.36
TMHFBPA-tBIA	180	227.5	40	140	23	29	18	4.3	0.79
KXA 10%	90	93.9	11.7	37	52	55	21.5	5.0	0.95
KXA 20%	51	46.4	4.5	14	92	83	22.8	5.7	1.08

[a] Helium, hydrogen, carbon dioxide, and methane permeability at 10 atm; oxygen and nitrogen permeability at 2 atm.

$n = 2$, $R_1 = CH_3$), KXA acts as an antiplasticizer for both polymers. At all of the concentrations studied, the FFV of the TMHFBPA-tBIA mixtures is higher than that of TMHFPSF mixtures; however, the rate of decline of FFV with KXA addition is more rapid for TMHFBPA-tBIA than for TMHFPSF.

Gas Permeability and Selectivity for Selected Gas Pairs

Table IV summarizes the gas permeability and ideal separation factors at 35°C for each of the two polymers and their mixtures with KXA. As expected, the addition of KXA decreases the permeability to all gases, but important increases in the selectivity are observed, particularly in the case of TMHFPSF. The incorporation of 30 wt % of KXA to TMHFPSF causes impressive increases in its selectivity to He/CH_4 and H_2/CH_4.

The permeability coefficients of mixtures of these polymers with KXA are shown in Figure 5 for H_2 [Fig. 5(a)] and CH_4 [Fig. 5(b)] as a function of KXA concentration. Note that the ordinate has been normalized by the corresponding permeability coefficient of the pure polymer. At any concentration, KXA reduces the permeability of TMHFPSF more than for TMHFBPA-tBIA. This effect is even greater in the case of CH_4. The fact that the extent of permeability change depends
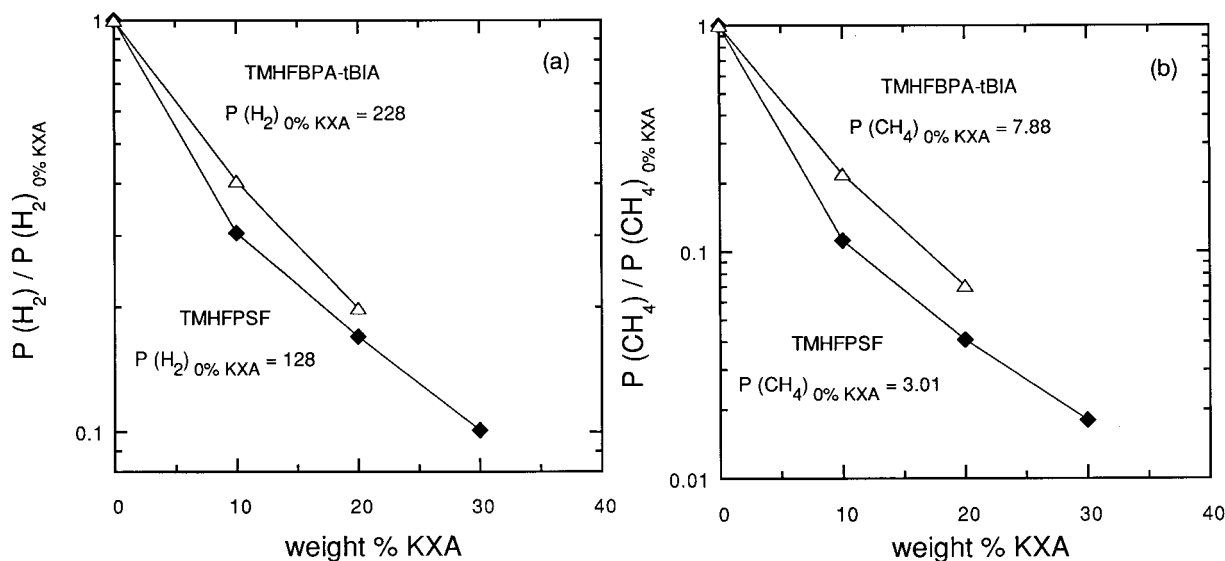

Figure 5   Effect of KXA concentration on the (a) H_2 and (b) CH_4 permeability coefficients of TMHFPSF and TMHFBPA-tBIA, normalized by the permeability of the unmodified polymer.
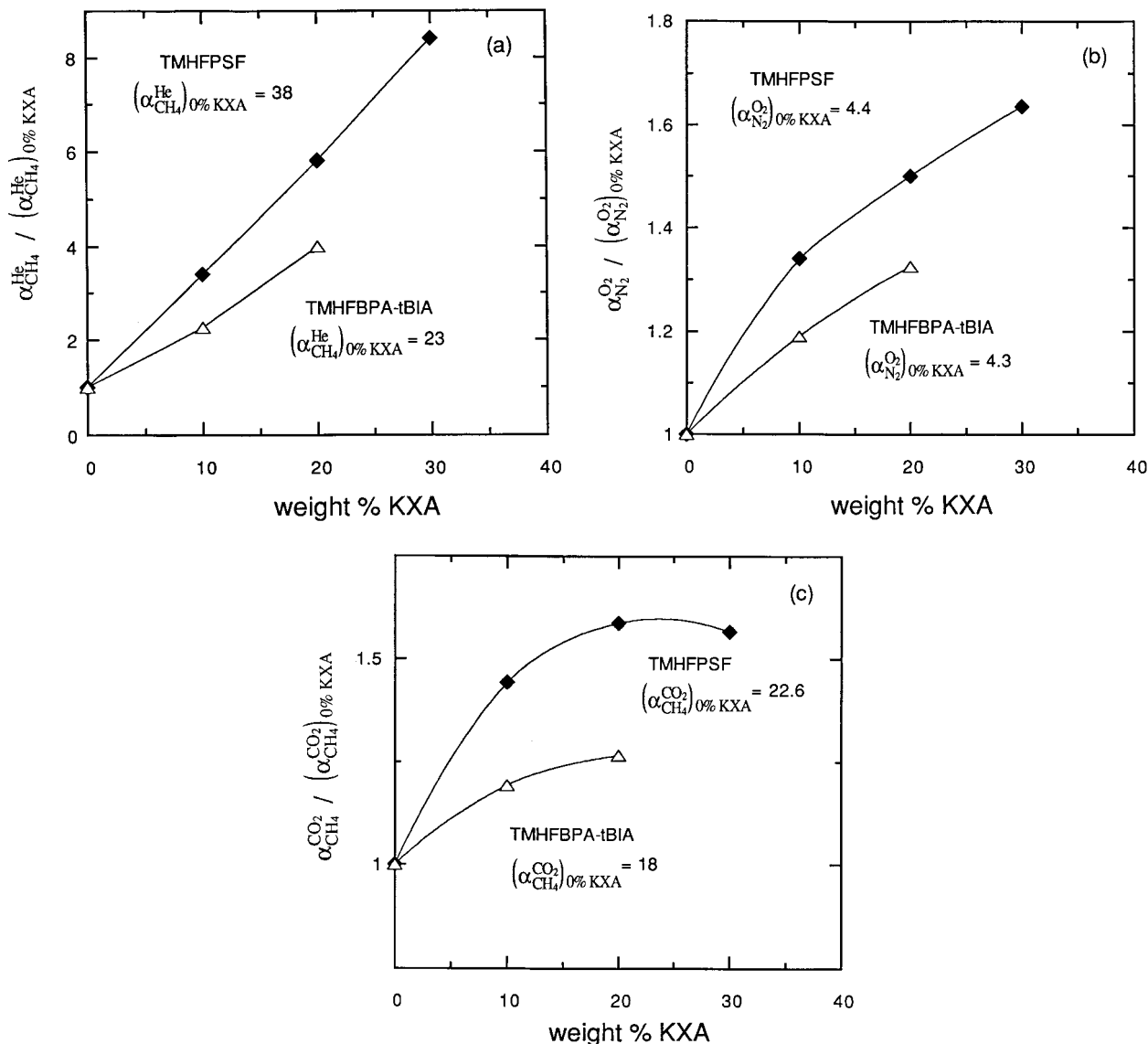
Figure 6 Effect of KXA concentration on the ideal (a) He/CH_4, (b) O_2/N_2, and (c) CO_2/CH_4 separation factors of TMHFPSF and TMHFBPA-tBIA, normalized by the ideal separation factor of the unmodified polymer.

on the gas molecules is reflected in the separation characteristics of these modified materials.

Figure 6 shows the increases in the ideal selectivity for He/CH_4 [Fig. 6(a)], O_2/N_2 [Fig. 6(b)], and CO_2/CH_4 [Fig. 6(c)] that result from the incorporation of KXA into these polymers. The observed values have been normalized by the ideal selectivity of the corresponding pure polymer. At all KXA concentrations, the glassy mixtures based on the polysulfone, TMHFPSF, are more selective than those based on the polyarylate, TMHFBPA-tBIA. As stated earlier, the increase in selectivity to He/CH_4 is quite impressive (up

to 8-fold), compared with the improvements observed for the other two gas pairs O_2/N_2 and CO_2/CH_4. In contrast to the apparent linear increase in selectivity to He/CH_4 (up to 30 wt % for TMHFPSF), there seems to be a maximum increase in selectivity for O_2/N_2 and CO_2/CH_4 at about 20 wt % KXA.

Permeability-Selectivity Balance in Modified Polymers

As shown previously, addition of KXA to the substituted, high free volume polysulfone (TMHFPSF)
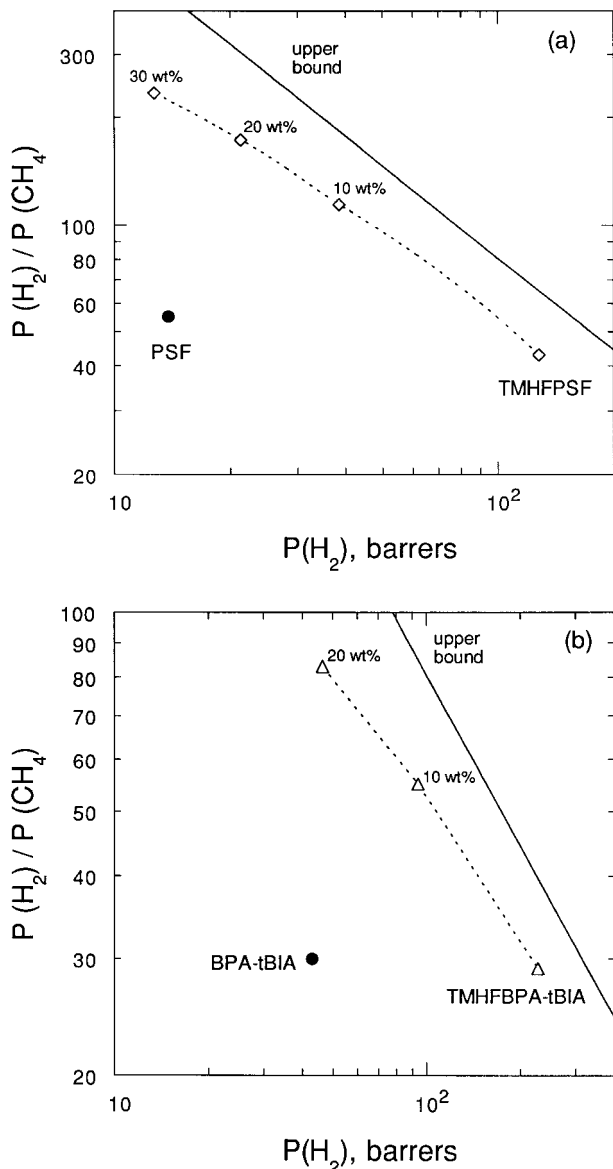
ted vs. the absolute permeability of the fast gas for three gas pairs: H_2/CH_4 in Figure 7, O_2/N_2 in Figure 8, and CO_2/CH_4 in Figure 9. Part a of each of these figures shows data for the unsubstituted polysulfone, PSF; the substituted polysulfone, TMHFPSF; mixtures of TMHFPSF with KXA; and the "upper bound" relationship proposed by Robeson. Part b of each figure shows analogous results for the polyarylates BPA-tBIA and TMHFBPA-tBIA. As discussed in previous arti-
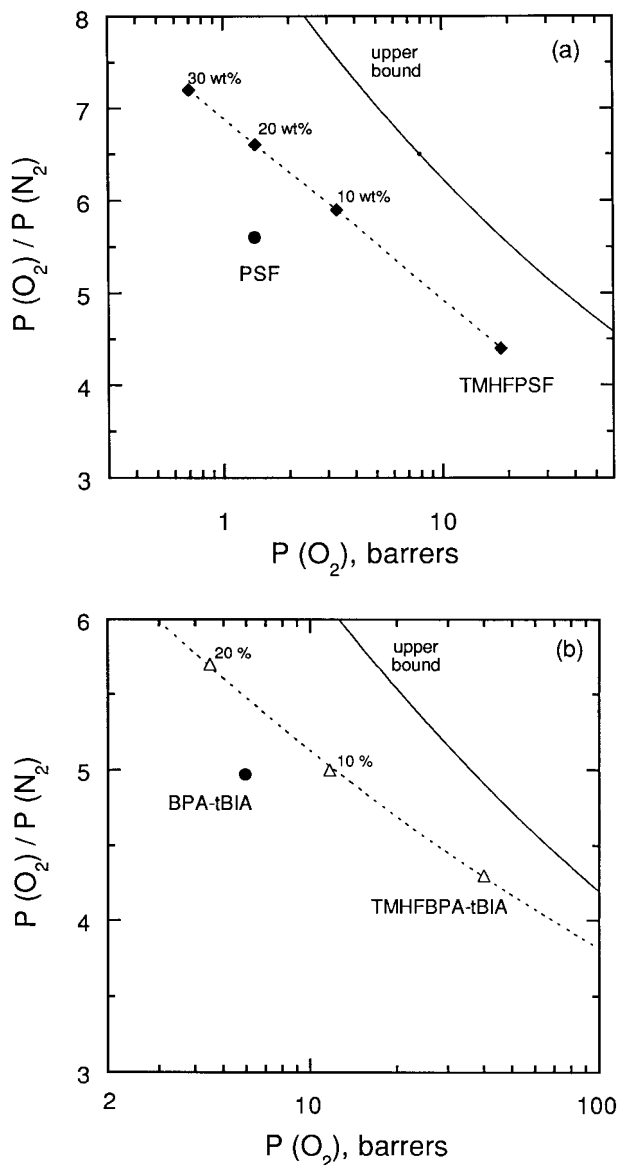
Figure 7 Effect of incorporation of KXA in (a) TMHFPSF and (b) TMHFBPA-tBIA on the selectivity-permeability balance for the gas pair H_2/CH_4. The properties of the unmodified polymer are identified by the polymer acronym, whereas the mixtures are identified by the weight percent of KXA they contain.

and polyarylate (TMHFBPA-tBIA) materials increases their selectivity for all gas pairs, but reduces their absolute permeability. Analogous trade-offs are qualitatively observed in most attempts to generate materials with improved permselectivity, so it is important to compare the trade-off in a more quantitative way to understand the merits of one approach over another. This is conveniently illustrated graphically in Figures 7–9, where the ideal separation factor is plot-

Figure 8 Effect of incorporation of KXA in (a) TMHFPSF and (b) TMHFBPA-tBIA on the selectivity-permeability balance for the gas pair O_2/N_2. The properties of the unmodified polymer are identified by the polymer acronym, whereas the mixtures are identified by the weight percent of KXA they contain.

Figure 9 Effect of incorporation of KXA in (a) TMHFPSF and (b) TMHFBPA-tBIA on the selectivity-permeability balance for the gas pair CO_2/CH_4. The properties of the unmodified polymer are identified by the polymer acronym, whereas the mixtures are identified by the weight percent of KXA they contain.
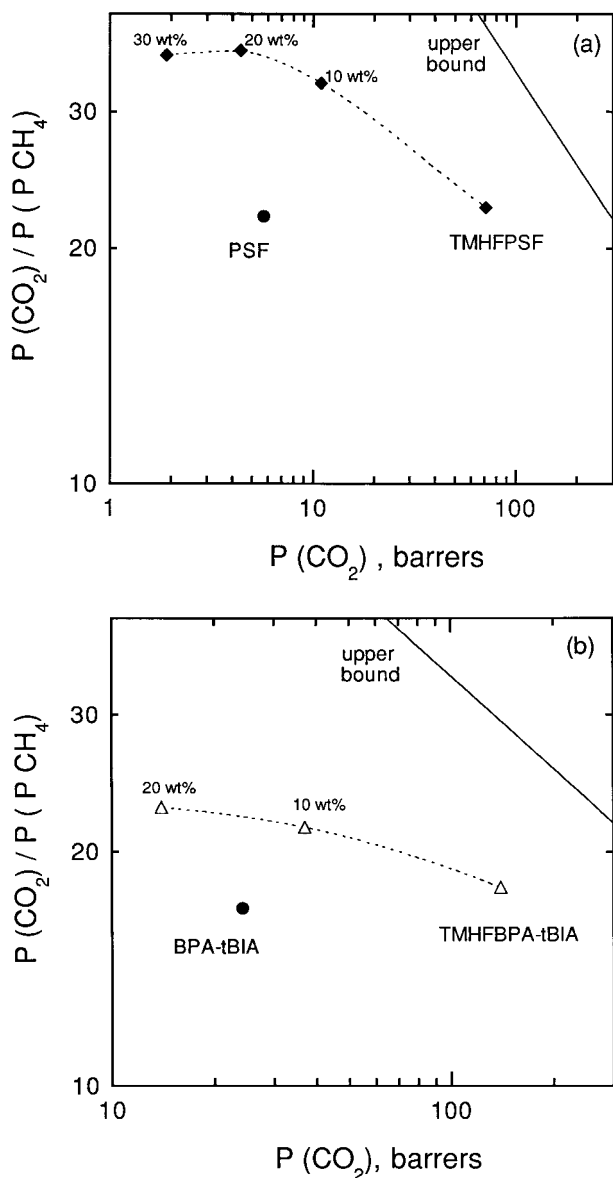
cles, repeat unit substitutions that increase the FFV of a base polymer (in the present case, addition of methyl groups to the phenyl ring and the substitution of fluorine atoms in the isopropylidene connector group of the bisphenol) causes a large increase in absolute permeability. As may be seen in Figures 7–9, this generally is accompanied by a slight decrease in selectivity; but, in some cases, the selectivity may actually increase

slightly for gas pairs like CO_2/CH_4. By the addition of modest amounts of KXA (less than 20 wt %) to the substituted polymers TMHFPSF or TMHFBPA-tBIA leads to materials with considerably improved combinations of selectivity and permeability than the unsubstituted polysulfone (PSF) or polyarylate (BPA-tBIA), as may be seen in Figures 7–9. Addition of KXA results in materials that lie above and to the right of the properties of the base polysulfone or polyarylate. To illustrate quantitatively the benefits that can be achieved, it is instructive to consider the selectivity of a TMHFPSF/KXA mixture that has the same permeability as PSF. The appropriate mixture is more selective than PSF by the following factors: 4.3-fold for H_2/CH_4, 1.18-fold for O_2/N_2, and 1.6-fold for CO_2/CH_4. Similarly, the TMHFBPA-tBIA/KXA mixture with equal permeability as BPA-tBIA is more selective than BPA-tBIA by the following factors: 2.8-fold for H_2/CH_4, 1.1-fold for O_2/N_2, and 1.3-fold for CO_2/CH_4.

It is also instructive to compare the selectivity characteristics of mixtures of the two substituted polymers with KXA at the same level of permeability. A mixture of TMHFPSF containing 10 wt % of KXA has approximately the same permeability as a mixture of TMHFBPA-tBIA containing about 20–22 wt % (by extrapolation) of KXA. This TMHFPSF mixture is more selective than the TMHFBPA-tBIA mixture by the following factors: 1.3-fold for H_2/CH_4, 1.4-fold for CO_2/CH_4, and equally selective for O_2/N_2. Thus, for the separation of H_2 and CO_2 from CH_4, the highly substituted polysulfone (TMHFPSF), responds more beneficially to the addition of KXA than the corresponding polyarylate, TMHFBPA-tBIA.

It is interesting to note, however, that addition of KXA to either TMHFPSF or TMHFBPA-tBIA does not lead to materials that exceed or are even closer to the "upper bound" relationship. As shown in Figures 7–9, addition of KXA results in materials whose selectivity-permeability balance moves parallel to the upper bound in the best case where the molecular size difference of the gases is large (e.g., H_2/CH_4). For CO_2/CH_4, the selectivity-permeability balance moves further away from the upper bound as KXA is added.

Permeability-FFV Correlation for Modified Polymers

Penetrant diffusion and solubility both depend on polymer free volume.[6] The permeability coeffi-
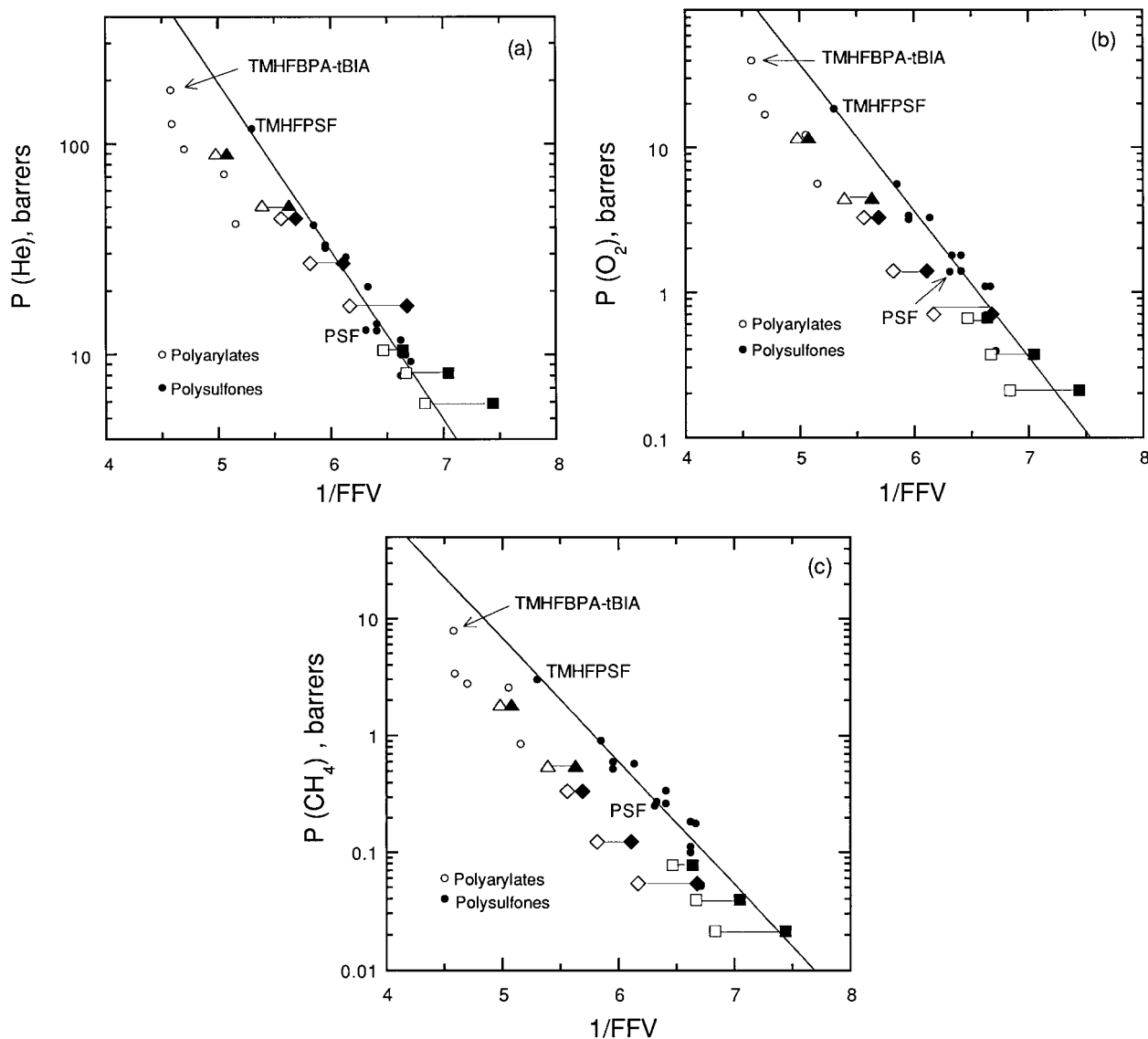
Figure 10 Gas permeability vs. inverse of FFV for (a) He, (b) O_2, and (c) CH_4 in some polysulfones (small solid circles), some polyarylates (small open circles), plus mixtures of TMHFPSF (diamonds), TMHFBPA-tBIA (triangles), and bisphenol A PSF (squares) with different amounts of KXA. The permeability-selectivity combination shown by the unmodified polymers are labeled by the acronym of each polymer. The FFV for the mixtures can fall on or between the FFV calculated assuming KXA has the structure with $n = 1$, R_1 = H (open symbols) and $n = 2$, R_1 = CH_3 (solid symbols). Solid line represents the best fit of eq. (6) using some glassy polysulfones described previously.

cients of gases can also generally be fairly well described by the empirical equation[6]

$$P_i = A_i e^{(-B_i/\text{FFV})} \qquad (7)$$

where P_i is the permeability coefficient of gas i, and A_i and B_i are characteristic parameters for each gas. To some degree, the values of A_i and

B_i may also depend on the polymer family (i.e., polysulfones, polyarylates, polyimides, etc.).

A previous article attempted to extend the correlation of permeability coefficients defined by a family of pure polysulfones to include mixtures of PSF with various additives.[19] To expand this effort, Figure 10 includes results for mixtures of KXA with TMHFPSF and with TMHFBPA-tBIA

for He [Fig. 10(a)], O_2 [Fig. 10(b)], and CH_4 [Fig. 10(c)], along with data for PSF membranes modified with KXA (squares) described previously.[19] Note that the values of FFV of mixtures containing KXA (triangles for TMHFBPA-tBIA, diamonds for TMHFPSF, and squares for PSF) can lie on or between the values calculated with $n = 1$, $R_1 = H$ (open symbols) and $n = 2$, $R_1 = CH_3$ (solid symbols) as described previously. The solid line represents the best fit of eq. (6) to the data (solid small circles) for the various polysulfone structures described in previous studies.[2] Some of the polyarylates (open small circles) studied by Pixton and Paul are also shown for comparison.[32] Pure TMHFBPA-tBIA falls within the expected trend for polyarylates. The relationship for the polyarylate family is shifted to the left, but parallel to that shown by the PSF family. Because B_i is apparently the same for these two families of polymers, the shift may be associated with other factors not taken into account by FFV that are reflected in the preexponential parameter A_i.

In broad terms, the permeability coefficient for each gas is correlated with the observed FFV, regardless of whether this parameter is varied by changing the repeat unit structure of the polymer or by incorporation of an additive into a given polymer. However, on a finer scale, there are systematic differences. Adding KXA to PSF and TMHFPSF seems to result in a lower permeability coefficient at the same FFV than would be expected, based on the trend established by varying the molecular structure within the polysulfone family, especially for the larger gas molecules like O_2 and CH_4. However, the effects of addition of KXA to TMHFBPA-tBIA seem to better follow the trend established for the polyarylate family; although, there seems to be a greater deviation toward higher permeability for the mixtures, especially for He. However, it is premature to conclude that the mixtures of these polymers with KXA do or do not follow the same relationship as the PSF or polyarylate family.

CONCLUSIONS

The permeability coefficients for all gases in TMHFBPA-tBIA are approximately twice as large as those for TMHFPSF and TBHFBPA-tBIA. The combination of permeability and selectivity properties shown by TMHFBPA-tBIA places this polymer close to the empirical "upper bound" limit proposed by Robeson.

Incorporation of the alkylated naphthalene oligomer, KXA, into highly substituted polysulfones, like TMHFPSF, and polyarylates, like TMHFBPA-tBIA, reduces their FFV and gas permeability coefficients, but significant increases in the selectivity for some gas pairs like He/CH_4 and H_2/CH_4 are observed.

The permselectivity balance of polymeric gas separation membrane materials may be tailored by combinations of chemical and physical changes in the base polymer. Addition of modest amounts of KXA (*ca.* 20 wt %) to highly substituted polymers like TMHFPSF or TMHFBPA-tBIA leads to materials with a combination of selectivity and permeability that is superior to the combination shown by the unsubstituted polymer PSF or BPA-tBIA.

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