

# Modification of Polysulfone Gas Separation Membranes by Additives

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**ABSTRACT:** The incorporation of additives into polymers like bisphenol A polysulfone (PSF) can provide an attractive alternative for modifying their permselective properties for gas separation, provided the additive is appropriately selected. In this work, three series of additives based on naphthalene, bisphenol A, and fluorene structures were incorporated into PSF and their effect on gas transport properties was measured. The results show that these additives increase selectivity and reduce permeability of PSF when incorporated at low concentrations. The largest increases in selectivity for the gas pairs He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub> are caused by those additives that cause the largest reductions in the glass transition temperature and fractional free volume, and typically, they are made up of planar molecules containing polar or small asymmetric protuberances. The productivity–selectivity balance response of the modified PSF membranes reveals that the naphthalene-based additives containing asymmetric groups of atoms lead to membranes with higher selectivity and with only small losses in permeability relative to the unmodified PSF membranes. The addition of 20 wt % of the glassy additive Kenflex A into PSF causes a fourfold increase in the selectivity of PSF to He/CH<sub>4</sub> at the expense of a 37% reduction in the permeability of helium. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1925–1941, 1997

## INTRODUCTION

Gas separation membranes with improved combinations of permeability and selectivity can be produced by systematic changes in polymer structure<sup>1,2</sup> or by chemical posttreatments.<sup>3,4</sup> The physical incorporation of additives into membranes made from readily available polymers represents an interesting alternative for modifying the gas permselectivity properties of membrane materials.<sup>5–7</sup>

The incorporation of certain types of additives at modest levels into glassy polymers leads to an increase in stiffness and has been termed “antiplasticization”; the additives which cause this phenomenon are called “antiplasticizers.”<sup>8</sup> In

the membrane area, antiplasticization has been shown to provide a possible way to trade selectivity at the expense of permeability via a reduction in polymer free volume and inhibition of short-scale segmental motions. The effect of various antiplasticizers on the gas permeability of polysulfone (PSF) and poly(2,6-dimethyl-1,4-phenylene oxide), (PPO), was studied in detail by Maeda and Paul.<sup>9–11</sup> The incorporation of antiplasticizers into PSF and PPO results in lower permeability values for all gases, while the corresponding selectivity for certain pairs of gases may increase. Because of the reduction in permeability, the increase in selectivity arising from antiplasticization does not always improve the selectivity/permeability trade-off characteristic relative to other pure polymers. Nevertheless, important increases in the selectivity for gas pairs like He/CH<sub>4</sub> were observed to occur when *N*-phenyl-2-naphthylamine (PNA) was used as an anti-

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plasticizer for PSF. From these results, it is clear that achieving an improved combination of selectivity and permeability hinges on the optimal selection of the antiplasticizer and the polymer to be modified.

This article examines the effect of the molecular structure of certain additives on the thermal, volumetric, and permselectivity properties of films based on bisphenol A polysulfone (PSF). The fundamental issue is the development of qualitative guidelines for optimizing additive molecular structure to obtain the best balance of thermal and permselectivity properties for PSF-based membranes.

## STRATEGY FOR ADDITIVE SELECTION

Table I shows the structure, name, acronym, and some physical properties of the additives that have been incorporated in PSF. Except for the glassy, alkylated naphthalene oligomer Kenflex A (KXA), suggested by R. P. Kambour (personal communication, 1993) and kindly donated by Kenrich Petrochemical, Inc., all of the other additives were crystalline solids of high purity, > 99%, purchased from various companies. The additives are divided into three series on the basis of naphthalene, bisphenol, and fluorene structures. The naphthalene-based additives were selected because prior work showed that phenyl naphthylamine (PNA), an antioxidant,<sup>12</sup> leads to significant increases in the selectivity for certain pairs of gases when added to PSF. The additives 1,1'-bi(2-naphthol) (BNAP) and KXA represent other more complex structures containing naphthalene units. The additive 7-bromo-3-hydroxy-2-*o*-anisole, also designated as Naphthol AZ BI but identified here as NAB (Table I), will be discussed later. The bisphenol-based additives are monomers which have been used to synthesize PSFs and polyarylates with high gas permeability and selectivity.<sup>13,14</sup> In this series, the main issue relates to the groups substituted on the two rings *ortho* to the hydroxyl groups. In the case of polymers synthesized from these monomers, the methyl groups in tetramethyl bisphenol-A (TMBPA) increase permeability by about fourfold while preserving selectivity relative to the structure without the methyl groups.<sup>15</sup> Replacing the methyl groups by bromine atoms (TBBPA), which are similar in size but increase polarity compared with methyl groups, leads to higher selectivity with relatively small losses in permeability rela-

tive to the polymers based on bisphenol A.<sup>14</sup> Addition of *t*-butyl groups to the phenylene rings of the monomer bisphenol-F (TBuBPF) would be expected to increase free volume and, thus, permeability, although no polymer based on this monomer has been examined as a membrane material. These additives were selected to learn whether their incorporation as physical additives to PSF has effects similar to those seen when they are part of the polymer repeat unit. Of course, an additional factor, when used as additives, is the effect of the hydroxyl groups which can interact strongly with the polymer and each other, for example, by hydrogen bonding. Finally, the additives based on the fluorene structure were selected because polymers synthesized from fluorene bisphenol (FBP) have high selectivity and permeability<sup>14,16</sup>; as in the previous series, the question is whether this structure can be similarly effective as an additive. This series includes fluorene, an additive that causes an increase in the yield strength of polycarbonate<sup>8</sup> (PC), and variants where the hydrogens of the carbon atom are systematically replaced with phenyl groups, that is, 9-phenyl fluorene (PF) and 9,9'-diphenyl fluorene (DPF). With this series, it is possible to learn how symmetric and asymmetric protuberances that disrupt the planarity of fluorene affect important physical properties of the polymer to which they are added. Moreover, the effect of the two hydroxyl groups in the monomer FBP on other properties can also be understood by comparison of DPF with FBP.

## FILM FORMATION AND CHARACTERIZATION

Pure PSF (Udel 1700) and each additive were mixed in the required ratio and then dissolved in dichloromethane to form a solution containing 5 wt % total solids. Films between 2 and 4 mil thick were solution cast on glass plates in a plastic bag to control the solvent evaporation rate and to avoid airborne dust particles from contaminating the films. For each additive, there was a maximum concentration (as low as 15 or as high as 40 wt %, depending on the additive) beyond which the formation of homogenous films was not possible; higher concentrations were not studied. Crystallization of some additives did not allow the formation of homogenous films having appropriate thickness for gas permeability measurements. The homogenous films were vacuum dried for a

period of 7 days, during which time the temperature was increased until the glass transition temperature ( $T_g$ ) was reached and then held there for 2 days. The films were then cooled slowly to room temperature under vacuum. All PSF films containing these additives produced a metallic sound when waved in the air. This sound is characteristic of antiplasticized polymers. These films generally had sufficient mechanical strength and toughness for gas permeability measurements, except for the FBP-based mixtures (20 and 30 wt %), where brittleness was a problem.

The glass transition temperature, defined by 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. Where possible, the glass transition temperature of the pure amorphous additive was determined from the onset of the transition during a first DSC scan at a heating rate of 20°C/min. Amorphous additives may be produced by quenching a melted sample of the pure compound in liquid nitrogen, as suggested by Garfield and Petrie.<sup>17</sup> Dynamic mechanical analysis via a Polymer Laboratories DMTA was used to determine the effect of selected additives on the magnitude of the sub- $T_g$  relaxations and the storage modulus of PSF. The measurements were made using laminated bars in a single cantilever mode at a frequency of 1 Hz and a heating rate of 3°C/min. The densities of the films were measured at 30°C in a density gradient column based on degassed, aqueous solutions of calcium nitrate and zinc chloride, depending on the additive incorporated. Gas permeability coefficients at 35°C were measured for six gases in a standard permeation cell described elsewhere.<sup>18</sup> The films for permeation were not conditioned with CO<sub>2</sub>. Exposure to high CO<sub>2</sub> concentrations for prolonged periods of times alters the properties of the films<sup>19</sup>; thus, the permeability measurement order always began with He and finished with CO<sub>2</sub>.

## THERMAL PROPERTIES

The miscibility of low-molecular-weight compounds in polymers has been the subject of numerous studies.<sup>20–24</sup> An important issue is how homogeneity at the molecular level can be assessed experimentally. In this work, a combination of optical appearance and thermal transition behavior were used to make this assessment. Optical transpar-

ency is consistent with a homogenous mixture, although this judgment is qualitative and can be influenced by factors that govern light scattering, for example, the size of dispersed domains and the difference in their refractive indices, by phase-separated mixtures. A single, composition-dependent glass transition temperature is a more objective criterion when applicable. Figure 1 shows typical DSC scans for PSF and its mixtures with KXA. Up to 30 wt % of KXA, there is a single glass transition. DSC scans for all transparent films showed single glass transition temperatures.

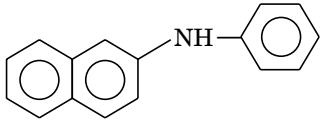
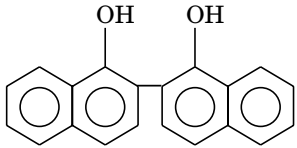
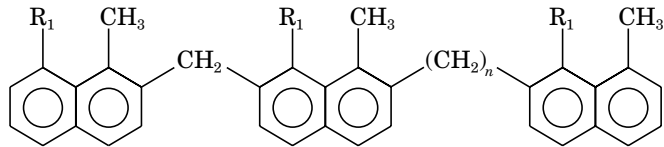
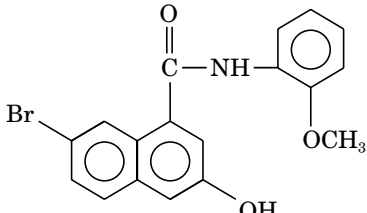
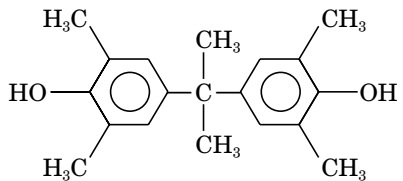
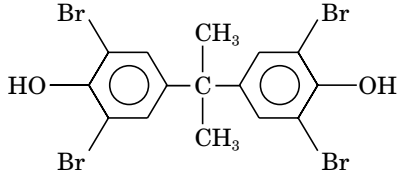
It is generally believed that, to some degree, cooperative motions between polymer chains and short-scale segmental motions define polymer membrane permselectivity characteristics. Both may be affected by the presence of additives.<sup>10,25</sup> Figure 2 shows the effect of the amount and type of additive on the glass transition temperature of PSF; the acronym for each additive is located adjacent to the maximum concentration studied. All additives depress the  $T_g$ , and the extent of the depression is determined by the  $T_g$  of the pure additive (Table I). The Gordon–Taylor equation<sup>26</sup>

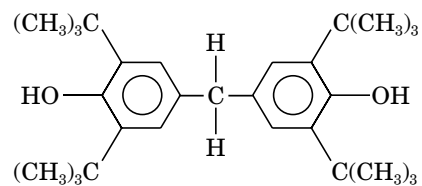
$$T_g = \frac{w_d T_{gd} + K w_p T_{gp}}{w_d + K w_p} \quad (1)$$

describes the behavior of the glass transition temperature of a mixture,  $T_g$ , with composition ( $T_{gi}$  and  $w_i$  are the glass transition temperature and weight fraction, respectively, for component  $i$  and  $K$  is an adjustable parameter) quite well as expected for miscible mixtures.<sup>27,28</sup> Typical values for  $K$  in mixtures of PSF with these additives are reported in Table III, where the effect of these additives on several physical properties of PSF is summarized.

Roughly speaking, the additives used in this study can be divided into three categories; a part of the identification of an additive with one of these categories may be seen by the influence of the additive on  $T_g$ . Additives in category C lead to PSF mixtures with the highest glass transition temperatures; FBP leads to the highest  $T_g$  in this category. Additives in category B lead to PSF mixtures with intermediate glass transition temperatures; these additives generally consist of molecules that are highly substituted with bulky atoms or groups, for example, TBBPA, TBuBPF, BNAP, KXA and DPF. Additives in category A consist of compact and planar structures, for ex-

**Table I Structure and Characteristics of Additives**

Additive Structure	Name	Acronym	State at 25°C	$T_m$ (°C)	$T_g^a$ (°C)	$V_o^b$ (cm <sup>3</sup> /g)
<b>Naphthalene series</b>						
	<i>N</i> -Phenyl naphthylamine	PNA	crystalline green	107	-11	0.743
	1,1'-Bi-(2-naphthol)	BNAP	crystalline yellowish	216	59	0.716
	$n = 1,2; R_1 = \text{H or } \text{CH}_3$ Alkylated naphthalene	KXA	glassy amber	> 100	32	0.778 <sup>c</sup> 0.811 <sup>d</sup>
	7-Bromo-3-hydroxy-2- <i>o</i> -aniside Naphthol AS BI	NAB	crystalline gold	186	55	0.598
<b>Bisphenol series</b>						
	Tetramethyl bisphenol A	TMBPA	crystalline white	165	19	0.814
	Tetrabromo bisphenol A	TBBPA	crystalline white	181	30	0.434



Tetra *t*-butyl bisphenol F

TBuBPF

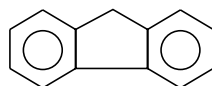
crystalline  
yellowish

156

20

0.854

Fluorene series



Fluorene

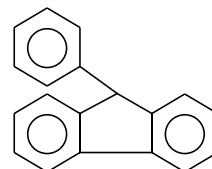
fluorene

crystalline  
white

115

< -30

0.756



9-Phenyl fluorene

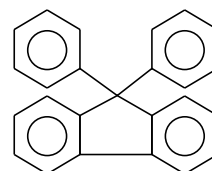
PF

crystalline  
white

145

< -30

0.746



9,9'-Diphenyl fluorene

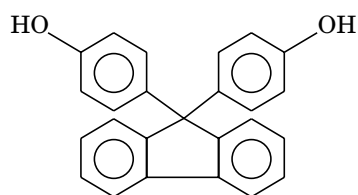
DPF

crystalline  
white

222

< -30

0.741



Fluorene bisphenol

FBP

crystalline  
white

226

96

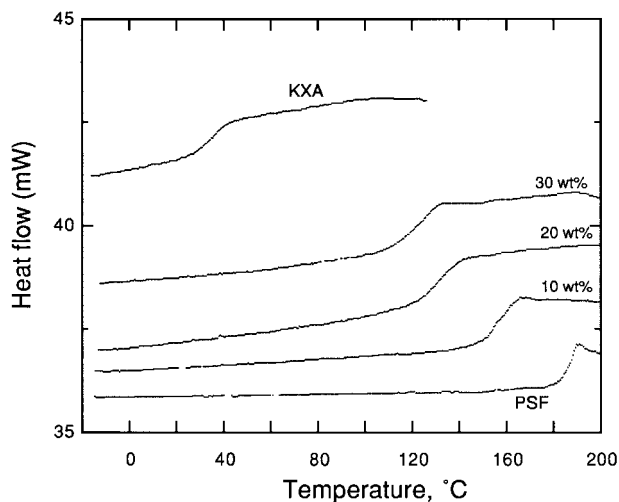
0.714

<sup>a</sup> Glass transition temperature of amorphous additive.

<sup>b</sup> Occupied volume calculated using Bondi's method

<sup>c</sup>  $n = 1$ ,  $R_1 = \text{H}$ .

<sup>d</sup>  $n = 2$ ,  $R_1 = \text{CH}_3$



**Figure 1** DSC scans (second heats) at 20°C/min for pure PSF, pure KXA, and their mixtures at three different concentrations.

ample, fluorene, PF, and PNA, that lead to PSF mixtures with the lowest glass transition temperature. The additive TMBPA falls on the boundary between categories A and B, as seen in Figure 2.

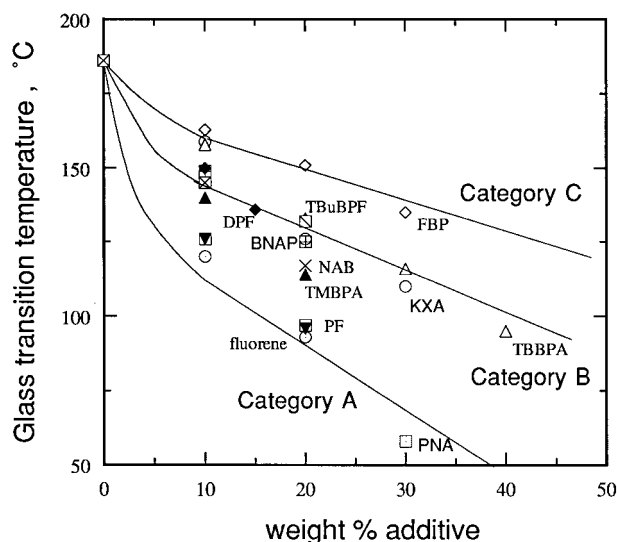
The effect on  $T_g$  by the bisphenol additives qualitatively follows the same trend observed for the polymers that contain these monomers in their repeat unit. For example, TBBPA leads to a PSF mixture with a higher  $T_g$  than does TMBPA, i.e., the symmetric replacement of methyl groups with the polar bromine atoms increases the  $T_g$ . The four bulky *t*-butyl groups of the additive TBuBPF also cause an increase in the  $T_g$  of PSF-based mixtures. The additives based on fluorene also show interesting responses, particularly for films containing FBP and DPF. The addition of the two hydroxyl groups, FBP, increases solubility in PSF by about twofold, and the materials have higher  $T_g$  values than those modified with DPF.

The permeation of gases in glassy polymer is defined by factors such as free volume, chain mobility, and gas-polymer interactions.<sup>29</sup> The interest in incorporating additives like those mentioned into glassy polymers stems from their ability to suppress segmental mobility in a way that effectively enhances the selectivity of the membrane for one gas species over another.

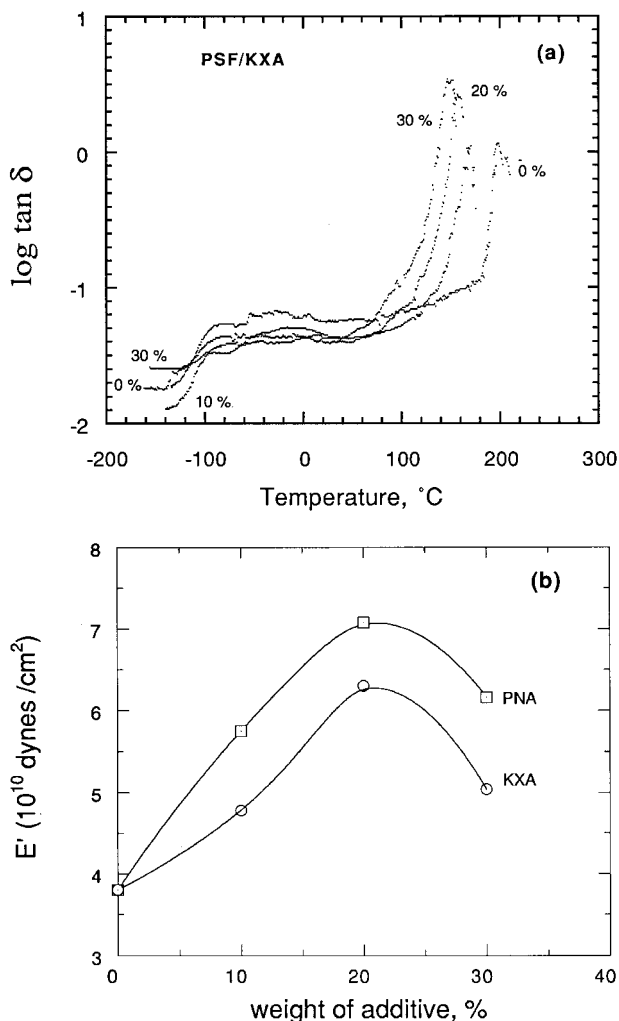
Figure 3(a) shows the sub- $T_g$  relaxation characteristics, as reflected by the dynamic mechanical parameter  $\tan \delta$ , as a function of temperature for PSF and its mixtures with KXA. The glass transition is shifted to lower temperatures as the concentration of KXA increases, as expected. The

other main feature of these data is the reduction in the magnitude of the  $\gamma$  peak, which for PSF is centered at approximately  $-80^\circ\text{C}$ , as KXA is added to PSF. Similar reductions in the magnitude of the sub- $T_g$  peak for other polymers caused by the presence of additives have been observed.<sup>30,31</sup> A reduction of the  $\gamma$  peak for PC caused by the addition of KXA has been recently reported.<sup>28</sup> A systematic study dealing with the effect of varying the bisphenol monomer for a series of PSF-based materials has revealed that the origin of the  $\gamma$  peak of bisphenol A PSF is primarily due to phenylene motions.<sup>32</sup> Modifications that directly involve the phenylene rings units, such as TMBPA, naphthalene, or *meta* or *para* isomers of bisphenol A, cause a significant bifurcation of the  $\gamma$  peak. The reduction in the magnitude of the sub- $T_g$  relaxation peak via incorporation of additives is generally believed to stem from the suppression of local modes of motions responsible for these peaks caused by the presence of such additives in glassy polymers. Most of the consequences of the phenomenon called “antiplasticization,” i.e., an increase in stiffness,<sup>8,28,33,34</sup> reduction in free volume,<sup>35,36</sup> reduction in permeability,<sup>9,10,37</sup> etc., may be qualitatively understood in terms of such losses of local chain motion.

Figure 3(b) shows the increase in the real part of the modulus of PSF, at 35°C, as PNA and KXA are added to PSF. Both additives cause an increase



**Figure 2** Glass transition temperatures of PSF mixtures with various additives (see Table I for definition of acronyms). The three lines have been arbitrarily drawn to define three categories of responses against which these additives are compared.



**Figure 3** (a) Dynamic mechanical  $\tan \delta$  curves for PSF/KXA mixtures at 1 Hz and a heating rate of 3  $^{\circ}\text{C}/\text{minute}$ . (b) Effect of addition of PNA and KXA to PSF on the storage modulus at 35  $^{\circ}\text{C}$  as measured at 1 Hz and 3  $^{\circ}\text{C}/\text{min}$ .

in the storage modulus until a maximum is reached at approximately 20 wt % concentration. On the basis of the mechanical responses, PNA is a slightly better antiplasticizer than KXA when added to PSF at concentrations up to 30 wt %.

## VOLUMETRIC PROPERTIES

Plasticizers are generally thought of as additives that increase chain motion and soften a glassy polymer because they increase the free volume of the mixture. On the other hand, antiplasticizers suppress certain chain motions and stiffen glassy polymers, presumably because they decrease free

volume. The incorporation of such additives into polymers can be a useful way of modifying properties. For example, a change in fractional free volume (FFV) is expected to alter the transport of small molecules and, thus, modify the selectivity for certain gas pairs.

Figure 4 illustrates how incorporating the additives shown in Table I changes the FFV of PSF. The quantity FFV as used here is defined by the relation

$$\text{FFV} = \frac{V - V_o}{V} \quad (2)$$

where  $V$  is the experimentally measured specific volume of the mixture at 30  $^{\circ}\text{C}$  and  $V_o$  is the occupied volume calculated from the van der Waals volume,  $V_w$ , using a method suggested by Bondi<sup>38</sup>

$$V_o = 1.3 V_w \quad (3)$$

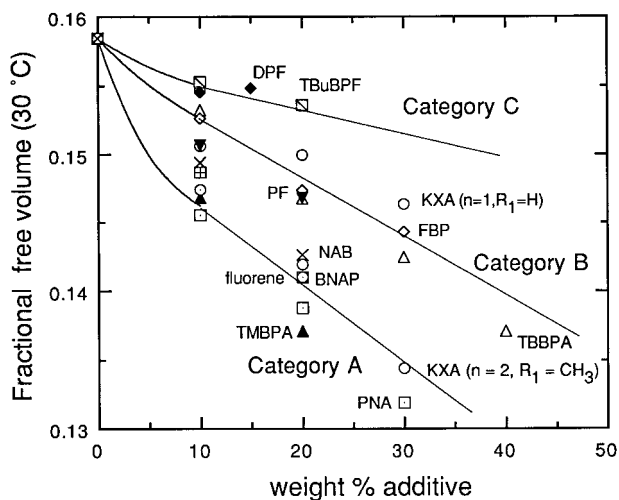
For mixtures of PSF with the various additives described in Table 1,  $V_o$  was calculated assuming volume additivity, i.e.,

$$V_o = w_d(V_o)_d + (1 - w_p)(V_o)_p \quad (4)$$

where  $w_i$  and  $V_{oi}$  are the weight fraction and occupied volume, respectively, of pure component  $i$ .

As suggested by the  $T_g$  behavior shown in Figure 2, the additives can also be roughly classified into three categories according to how they affect FFV. The additives in category C have very little effect on FFV, while those in categories B and A show progressively greater effect on FFV. The exact structure of KXA is not fully defined; thus, KXA can fall on or inbetween categories A or B, depending on the structure used to estimate  $V_o$ . As seen in Figure 4, KXA falls in category B if  $n$  is assumed to be 1 and  $R_1 = H$ , whereas, it falls in category A if  $n = 2$  and  $R_1 = \text{CH}_3$ . Other combinations of  $n$  and  $R_1$  will fall between categories A and B. In general, additives that fall in one of the arbitrarily defined categories based on the  $T_g$  response may fall in an entirely different category defined by the effect on FFV. The only additives that remain in the same categories for both effects ( $T_g$  and FFV) are fluorene and PNA (in category A) and TBBPA and KXA (with  $n = 1$ ,  $R_1 = H$ ) (in category B). All others change from one category to another because  $T_g$  and FFV are not uniquely correlated.

The effectiveness of the various additives within



**Figure 4** FFV of PSF mixtures with various additives (see Table I for definition of acronyms). The three lines have been arbitrarily drawn to define three categories of responses against which these additives are compared.

the three series of compounds listed in Table I for reducing FFV may be placed in the following order: naphthalene series: PNA > BNAP > KXA; bisphenol series: TMBPA > TBBPA > TBuBPF; fluorene series: Fluorene > PF  $\cong$  FBP > DPF. In every series, the additives with the smaller or more compact structures are generally more efficient in reducing the FFV of PSF. In the bisphenol series, the FFV of the mixtures based on PSF increase as bulky units are incorporated into the additive molecule. The physical addition of the monomers TMBPA and TBBPA to PSF show effects on FFV similar to those seen when these monomer units are incorporated in the polymer repeat unit, for example, polyarylates and PCs based on TBBPA have higher FFV than those based on TMBPA. No polymer based on TBuBPF has been reported so no similar comparison can be made in this case. In the fluorene series, the FFV of the mixtures also increases as more bulky additives are introduced into PSF. It is interesting to note that FBP more effectively reduces the FFV than does DPF. It has been observed that the volume of many compounds contracts when hydroxyl units are present, apparently as the result of strong hydrogen bonding interactions (i.e., compare  $V_o$  for DPF and FBP in Table I). Thus, the additive FBP in PSF is expected to have a stronger interaction with some of the chain segments of PSF than DPF because of the two hydroxyl groups. The additives FBP and PF are equally effective for reducing the FFV of PSF. The two phenol groups in FBP are not enough

to surpass the reduction of the FFV of PSF caused by the asymmetric PF additive.

## GAS PERMEABILITY AND SELECTIVITY FOR SELECTED GAS PAIRS

The gas permeability coefficients and ideal selectivity factors for PSF and its mixtures with the various additives are summarized in Table II. This table is organized according to the additive series shown in Table I. All additives considered cause a decrease in the gas permeability coefficient, but some cause quite large increases in the selectivity for certain gas pairs, e.g., He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub>, particularly those containing the naphthalene and bisphenol monomer structures. Especially impressive are the increases for He/CH<sub>4</sub> and H<sub>2</sub>/CH<sub>4</sub> caused by the addition of 30 and 40 wt % of PNA and TBBPA to PSF. The increases are about eightfold for He/CH<sub>4</sub> and sixfold for H<sub>2</sub>/CH<sub>4</sub>.

The effectiveness of the various additives for decreasing the permeability of PSF to He and N<sub>2</sub> is shown graphically in Figure 5, where the ordinate has been normalized by the permeability coefficient of pure PSF. Similar trends are observed for other gases.<sup>39</sup> Following the scheme suggested earlier, the additives can be roughly classified into three categories according to their effect on gas permeability. For helium, the category A additives cause the most drastic reduction in permeability and include PNA, BNAP, fluorene, PF, and TMBPA. Except for fluorene, the same additives also cause the most drastic reduction in the permeability of PSF to N<sub>2</sub>. For helium, category B additives cause intermediate reductions in gas permeability and include DPF, FBP, KXA, and TBBPA. The same additives plus fluorene are part of this category in the case of N<sub>2</sub>. Category C additives cause the least reduction in the permeability of both He and N<sub>2</sub>; the bulky TBuBPF falls in this category. With the exception of fluorene, all other additives remain in essentially the same category for all other gases, as can be seen in Table III, where the categorization of the additives by their effect on the physical properties of PSF has been summarized.

Using the series shown in Table I, the ability of these additives to decrease the gas permeability of PSF can be placed in the following order: naphthalene series: PNA > BNAP > KXA; bisphenol A series: TMBPA > TBBPA > TBuBPF; fluorene series: PF > fluorene > FBP  $\cong$  DPF. The rank in



**Table II** Effect of Additives on Gas Permeability and Selectivity at 35°C

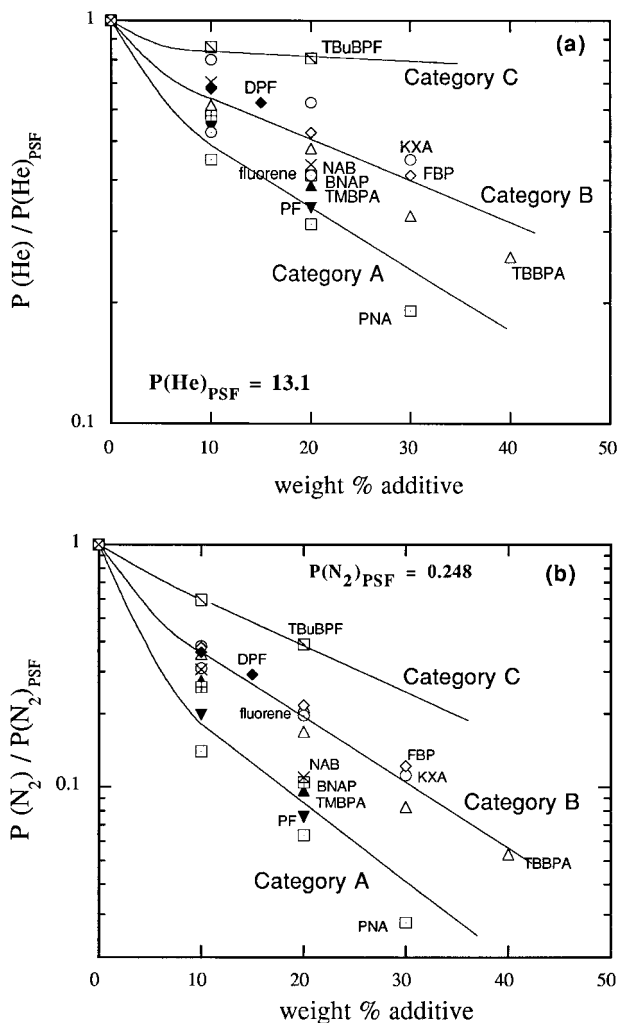
Additive (%)	P(He)	$\alpha_{\text{CH}_4}^{\text{He}}$	P(H <sub>2</sub> )	$\alpha_{\text{CH}_4}^{\text{H}_2}$	P(O <sub>2</sub> )	$\alpha_{\text{N}_2}^{\text{O}_2}$	P(CO <sub>2</sub> )	$\alpha_{\text{CH}_4}^{\text{CO}_2}$
No additive	13.1	51	13.8	55	1.39	5.60	5.69	22
PNA (10)	5.9	203	4.8	166	0.26	7.43	0.93	32
PNA (20)	4.1	315	3.0	231	0.13	8.13	0.41	31
PNA (30)	2.5	417	1.7	283	0.06	8.57	0.21	35
BNAP (10)	7.6	141	6.9	128	0.44	6.88	1.67	31
BNAP (20)	5.4	257	4.3	205	0.21	8.08	0.70	33
KXA (10)	10.5	131	10	125	0.66	6.95	2.35	29
KXA (20)	8.2	210	6.9	177	0.37	7.40	1.17	30
KXA (30)	5.9	281	4.9	233	0.21	7.50	0.66	31
NAB (10)	9.2	145	8.3	130	0.52	6.80	1.98	31
NAB (20)	5.8	282	4.6	225	0.22	8.20	0.76	37
TMBPA (10)	7.9	134	7.1	120	0.46	6.76	1.70	29
TMBPA (20)	5.1	255	4.0	200	0.18	7.50	0.61	31
TBBPA (10)	8.1	107	7.7	101	0.59	6.70	2.19	29
TBBPA (20)	6.3	185	5.3	156	0.31	7.38	1.05	31
TBBPA (30)	4.4	275	3.4	213	0.16	7.62	0.53	33
TBBPA (40)	3.4	425	2.5	313	0.09	6.92	0.27	34
TBuBPF (10)	11.3	82	11.1	80	0.92	6.22	3.37	24
TBuBPF (20)	10.6	116	9.2	101	0.62	6.39	2.34	26
Fluorene (10)	6.9	84	—	—	0.43	5.53	1.58	19
Fluorene (20)	5.4	98	—	—	0.33	6.88	1.19	22
PF (10)	7.1	165	—	—	0.36	7.35	1.29	30
PF (20)	4.49	281	3.5	208	0.15	7.89	0.48	30
DPF (10)	9.0	110	—	—	0.61	6.78	2.32	28
DPF (15)	8.2	117	7.4	111	0.49	6.81	1.85	26
FBP (10)	8.9	114	8.5	109	0.6	6.38	2.35	30
FBP (20)	6.9	222	5.9	191	0.38	7.04	1.06	34
FBP (30)	5.4	239	—	—	0.21	7.00	—	—

Permeability (barrers) of He, CH<sub>4</sub>, and CO<sub>2</sub> at 10 atm, O<sub>2</sub> and N<sub>2</sub> at 2 atm, and H<sub>2</sub> at 5 atm.

the ability of an additive to decrease permeability and FFV agrees well in the case of the naphthalene and the bisphenol series, as expected from the definition of effective antiplasticizers. The gas permeability of PSF-modified membranes increases as bulky naphthalene or bisphenol additives are incorporated. The physical addition of TMBPA and TBBPA monomers into PSF causes an effect on gas permeability opposite of that observed in the polymers containing these monomers in their repeat unit. TBBPA-based polymers have lower gas permeability than TMBPA-based polymers. The fluorene series contains systematic changes in which the planarity of fluorene is disrupted by the introduction of phenyl groups, PF and DPF, or by the addition of hydroxyl groups to the phenyl rings, FBP. If the effect of the additive fluorene on the permeability of PSF to gases is taken as a starting point, the incorporation of one phenyl group reduces permeability while symmetric substitution of two phenyl groups, DPF, or

phenol groups, FBP, causes an increase in the permeability. The PSF membranes modified with PF have higher FFV but lower permeability than the corresponding membranes modified with fluorene. The asymmetry introduced by one phenyl ring on fluorene, PF, and its effect on permeability and FFV resemble that seen with the asymmetry of the substituents in certain polyarylates based on isophthalic acid, i.e., the gas permeability is higher in polymers containing the symmetric TMBPA than in those containing the asymmetric dibromodimethyl bisphenol A, even though the FFV stands in an opposite order.<sup>14</sup> The additives PF and FBP cause the same reduction in FFV, but PF leads to PSF membranes with lower permeability. This behavior is similar to that observed when the connector group of some bisphenols used in the synthesis of polyarylates is replaced by other asymmetric connector groups.<sup>40</sup>

Figure 6 shows the effect of these additives on the ideal selectivity of PSF-based membranes for



**Figure 5** (a) Helium and (b) nitrogen permeability of PSF/additive mixtures at 35°C, normalized by the permeability of pure PSF (see Table I for definition of acronyms). The three lines have been arbitrarily drawn to define three categories of responses against which these additives are compared.

the gas pairs He/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub>. The ordinate has been normalized with the selectivity of a neat PSF membrane. The improvements in selectivity caused by these additives depend on the difference in size of the two gas molecules. For the pair He/CH<sub>4</sub>, where there is the largest difference in molecular size, a sixfold to eightfold increase in selectivity can be achieved by the introduction of some additives, while for the other gas pairs, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>, the same additives increase the selectivity by only 40 to 50%. Nevertheless, these increases are significant, considering that O<sub>2</sub> and N<sub>2</sub> are quite similar in size.

The effect of these additives on the selectivity

of PSF-based membranes has also been classified into three categories on the basis of data at 20 wt % concentration of each additive. As shown in Figure 6, for the gas pairs He/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub>, the three categories include the same additives; however, for the gas pair CO<sub>2</sub>/CH<sub>4</sub> the categorization is somewhat different as will be discussed later.

For He/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub>, category A additives cause the largest increase in the selectivity (at 20 wt %, 4- to 6-fold for He/CH<sub>4</sub> and 1.4-fold for O<sub>2</sub>/N<sub>2</sub>). The additives in this category include PF, PNA, BNAP, and TMBPA. Category B additives produce intermediate increases in selectivity (3- to 4-fold for He/CH<sub>4</sub> and 1.3-fold for O<sub>2</sub>/N<sub>2</sub>). This category is made up of KXA, TBBPA, and FBP. Category C additives include fluorene and TBuBPF, which lead to the smallest increase in selectivity (2-fold for He/CH<sub>4</sub> and 1.2-fold for O<sub>2</sub>/N<sub>2</sub>).

The rough classification of additives based on their effect on  $T_g$ , FFV, and selectivity of PSF for the gas pairs He/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> is generally quite consistent for the three categories. Except for fluorene and PF, the additives that cause the greatest reduction in  $T_g$  and FFV are the same additives that cause the greatest increase in selectivity (they are always category A). The additives BNAP and TMBPA have two hydroxyl groups that may interact with some segments of PSF and with each other via hydrogen bonds. The additive PNA has polar atoms that can strongly interact with some segments of the PSF chains. These interactions may bring the polymer chains closer together, reducing FFV and hindering short-scale segmental motions, thus restricting the diffusion of gases in the modified PSF membranes. Fluorene also causes drastic reductions in  $T_g$  and FFV but does not increase the selectivity as the other additives (TMBPA, BNAP, or PNA) do. The lack of polar atoms in fluorene seems to be an important issue for modifying gas selectivity properties. The additive PF drastically reduces  $T_g$  and leads to membranes with higher FFV than membranes modified with TMBPA, BNAP, and PNA; the incorporation of PF increases the selectivity for He/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> as the additives TMBPA, BNAP and PNA do. It is apparent from this observation that bulky asymmetric substituents which disrupt the planarity of fluorene play an important role.

It is now interesting to analyze how the changes in the molecular structure of an additive affect the selectivity of PSF-based membranes. By increasing the complexity of the naphthalene-based

additives, the selectivity is decreased, as expected from the corresponding increase in permeability. By replacing the methyl groups of the TMBPA with bromine, TBBPA, there is a reduction in the selectivity for the gas pairs He/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub>. Replacement of the bromines with *t*-butyl groups, TBuBPF, causes further reduction in selectivity. The PSF membranes modified with the fluorene-based additives show that asymmetric substitutions with phenyl groups, PF, lead to high selective membranes, whereas symmetric phenyl substitutions, DPF, cause relatively small increases in selectivity relative to the increases caused by fluorene. The additive FBP with two phenol groups causes greater increases in selectivity than that seen when fluorene or DPF is added to PSF. The two hydroxyl groups in FBP apparently lead to PSF membranes with higher selectivity to the gas pairs He/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub>.

The classification of additives by category based on their effect on the selectivity for the gas pair CO<sub>2</sub>/CH<sub>4</sub> is as follows. Category A additives increase selectivity by approximately 1.5-fold and include FBP and BNAP; these additives have the highest  $T_g$ , as seen in Table III. Category B additives lead to increases in selectivity of the order of 1.2- to 1.3-fold and include PNA, KXA, TMBPA, TBBPA, and PF. Category C additives, fluorene and TBuBPF, show no appreciable increase in selectivity for this gas pair. The reason why the additives change from one category to another based on their effect on selectivity for different gas pairs is not well understood. Changes in gas solubility by different additive molecular structures may play some role and perhaps explain the switch of additives in the qualitative categorization used in this work.

## SELECTIVITY-PRODUCTIVITY RELATIONSHIP

Figure 7 shows the effect of the various additives (at the 20 wt % level) on the selectivity-productivity relationship for the four gas pairs He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub>. Each additive increases the selectivity of PSF at the expense of a reduction in permeability for the various gas pairs shown.

In this section, the effect of additive structure on permeability and selectivity properties of PSF is analyzed in terms of the three series described in Table I. In Figure 7, the open circles, triangles, and diamonds represent the membranes modified

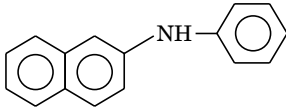
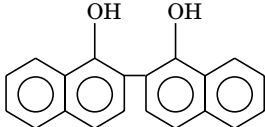
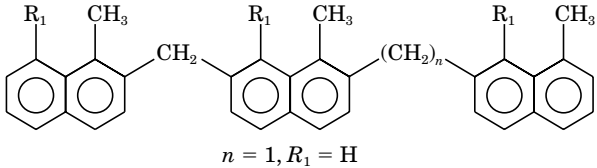
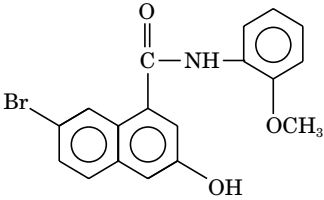
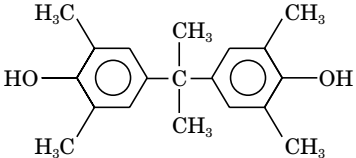
with naphthalene-, bisphenol-, and fluorene-based additives, respectively. For He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub>, the more bulky naphthalene or bisphenol additives lead to modified membranes with higher permeability at the expense of lower selectivity relative to their less bulky counterparts (PNA and TMBPA). The relative loss in selectivity is more dramatic in the membranes modified with the bisphenol additives, that is, TBuBPF and KXA lead to twofold increases in the permeability of He at the expense of 55 and 33% loss in selectivity to He/CH<sub>4</sub> with respect to the smaller and more compact TMBPA and PNA. No direct comparison between naphthalene and bisphenol additives is possible; however, it is apparent from these results that additives with more bulky connector groups, surrounded by small protuberances like methyl groups in KXA, lead to the formation of PSF membranes with a better combination in transport properties.

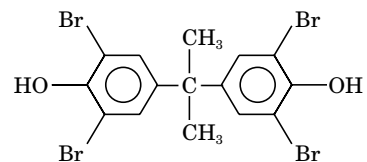
The permeability and selectivity combination shown by the membranes modified with fluorene-based additives is highly dependent on the structure of the additive. Except for CO<sub>2</sub>/CH<sub>4</sub>, the asymmetric PF leads to more selective but less permeable membranes than those modified with either the symmetric fluorene or FBP. The introduction of one phenyl ring into fluorene causes a 2.8-fold increase in the selectivity of PSF for He/CH<sub>4</sub> at the expense of a small reduction, 17%, in the permeability of helium relative to fluorene. The symmetric introduction of two phenols onto fluorene, FBP, increases both permeability and selectivity relative to the unsubstituted additive. The 30% increase in the permeability of helium is accompanied by a 2.3-fold increase in the selectivity for He/CH<sub>4</sub>.

The effect of additive structure on permeselectivity properties of PSF for the gas pair CO<sub>2</sub>/CH<sub>4</sub> is as follows: for the membranes modified with naphthalene-based additives, BNAP leads to higher permeability and selectivity, whereas KXA leads to higher permeability but lower selectivity than PNA. In the bisphenol series, the additive TBBPA increases permeability with no losses in selectivity, whereas TBuBPF causes large increases in permeability accompanied by large decreases in selectivity with respect to the additive TMBPA. In the fluorene series, the additive PF increases selectivity with a reduction in permeability, whereas FBP increases selectivity with no reduction in permeability relative to the unsubstituted fluorene.

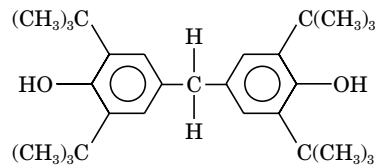
The additive NAB, the structure of which ap-

**Table III** Categorization of the Additives by Their Effect on the Physical Properties of PSF

Additive Structure	Additive				Mixture							
	Acronym	$T_m^a$ (°C)	$T_g^a$ (°C)	$V_o^b$ (cm <sup>3</sup> /g)	$K^c$	$T_g$	FFV <sup>d</sup>	P(He)	P(CO <sub>2</sub> )	P(CH <sub>4</sub> )	$\alpha_{CH_4}^{He}$	$\alpha_{CO_2}^{CO_2}$
Naphthalene series												
	PNA	107	-11	0.743	0.26	A	A	-A	-A	-A	+A	+B
	BNAP	216	59	0.716	0.27	B	+A	+A	+A	+A	-A	A
 $n = 1, R_1 = H$	KXA	> 100	32	0.778	0.43	B	+B	+B	B	B	B	B
	NAB	186	55	0.598	0.23	+A -B	+A	+A	+A	A	A	>A
Bisphenol series												
	TMBPA	165	19	0.814	0.31	+A -B	-A	+A	+A	+A	-A	B

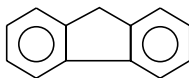


TBBPA	181	30	0.434	0.50	B	-B	-B	B	B	-B	B
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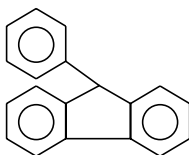


TBuBPF	156	20	0.854	0.45	B	C	C	C	C	C	+C
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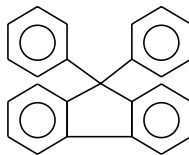
Fluorene series



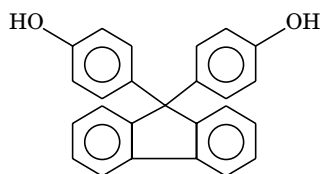
Fluorene	115	< -30	0.756		A	+A	+A	B	B	C	-C
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PF	145	< -30	0.746		A	-B	-A	-A	A	A	-B
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DPF	222	< -30	0.741		B	C	B	+B	+B	+A -B	B
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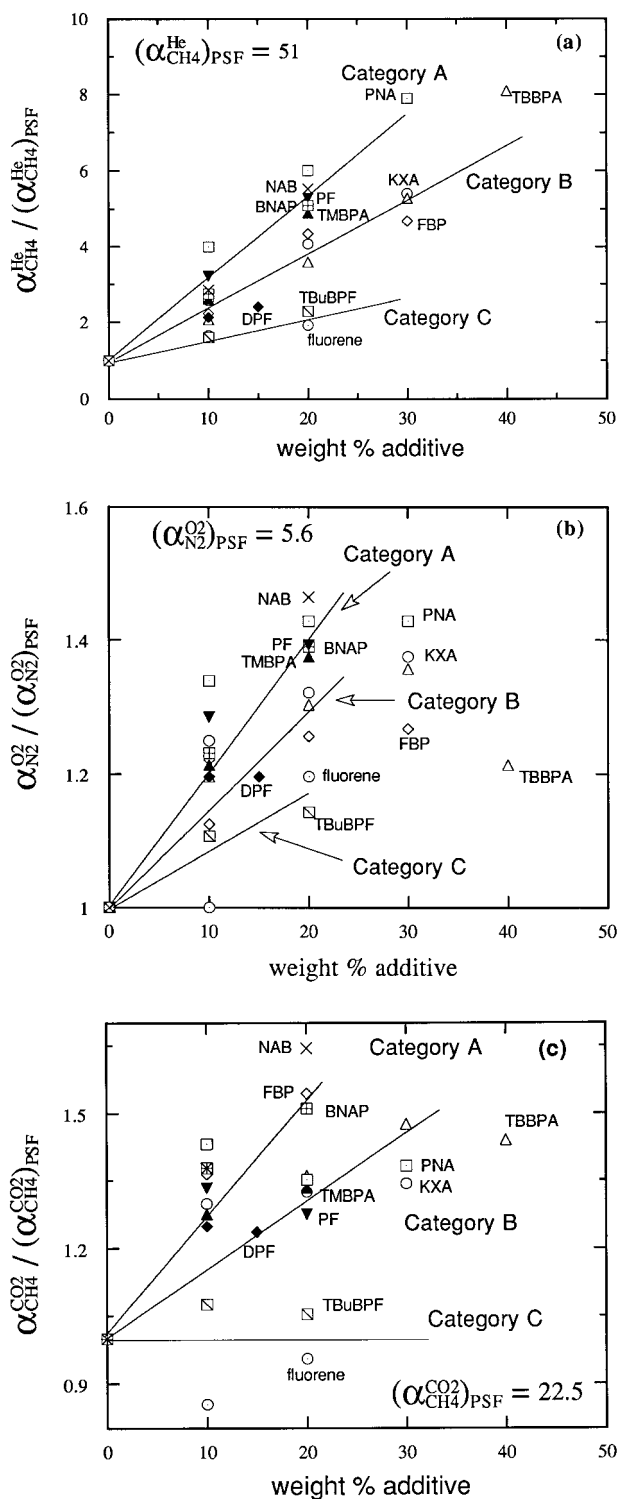
FBP	226	96	0.741	0.35	C	-B	B	B	B	+B	A
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<sup>a</sup> Glass transition temperature of amorphous additive.

<sup>b</sup> Occupied volume calculated using Bondi's method.

<sup>c</sup> Fitting parameter in Gordon-Taylor equation given by eq. (1).

<sup>d</sup> FFV =  $(V - V_0)/V$ .



**Figure 6** Effect of additives on the ideal (a) He/CH<sub>4</sub>, (b) O<sub>2</sub>/N<sub>2</sub>, and (c) CO<sub>2</sub>/CH<sub>4</sub> separation factor of PSF, normalized by that of pure PSF (see Table I for definition of acronyms). The three lines have been arbitrarily drawn to define three categories of responses against which these additives are compared.

appears in Table I, has been incorporated in the list of naphthalene-based additives to verify some of the qualitative observations related to their effect on the permselectivity properties of PSF. The transport properties of the membranes modified with NAB can be found in Table II. The effect of NAB on  $T_g$ , FFV, permeability, and selectivity of PSF is shown in Figures 2, 4, 5, and 6, respectively, while its categorization according to these effects is summarized in Table III. The results of incorporating 20 wt % of NAB into PSF on the productivity-selectivity properties are shown in Figure 7. As seen in Table I, the additive NAB is somewhat similar to PNA in molecular architecture but contains polar substituents on the rings. As Figure 7 shows, PSF modified with 20 wt % of NAB has higher permeability for all gases while preserving selectivity relative to PSF modified with the same amount of PNA. The increases in selectivity for H<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> are of the same order of magnitude for NAB and PNA, whereas the increase for CO<sub>2</sub>/CH<sub>4</sub> caused by NAB is larger than that caused by PNA. This comparison of NAB to PNA indicates that polar substitutions on this naphthalene-based additive cause substantial increases in selectivity with only relatively small losses in permeability when incorporated into PSF.

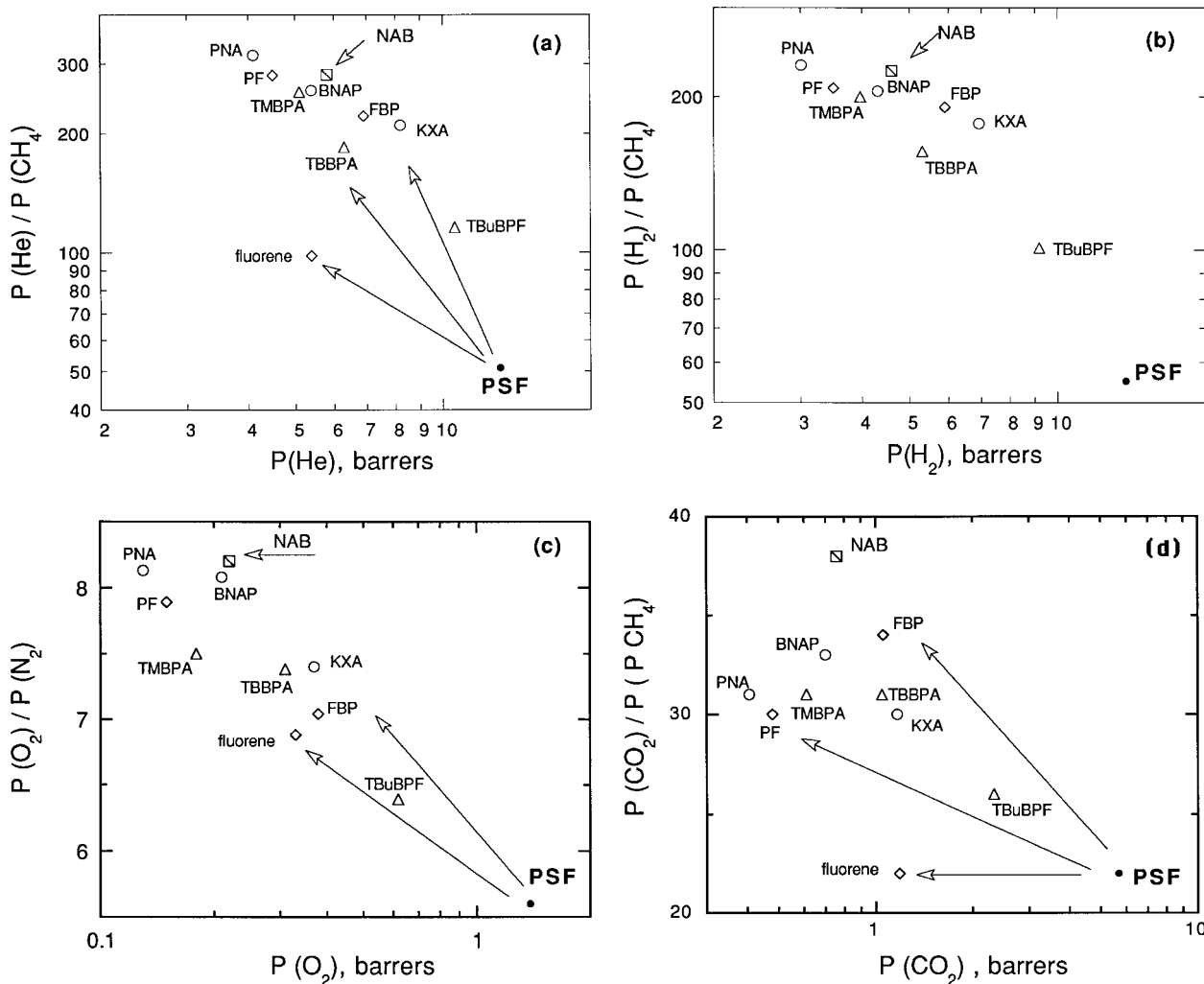
## PERMEABILITY-FREE VOLUME RELATIONSHIP

The permeation of small gas molecules in glassy polymers has been correlated with good success using the notions of free volume theory and the empirical relationship<sup>2</sup>

$$P_i = A_i e^{(-B_i/FFV)} \quad (5)$$

where  $P_i$  is the permeability of gas  $i$  and  $A_i$  and  $B_i$  are characteristic parameters for each gas which may also depend to some degree on the polymer family, that is, PSFs, polyarylates, and polyimides.

Figure 8 shows an attempt to relate the effect of the various additives on the permeability of He, O<sub>2</sub>, and CH<sub>4</sub> in PSF-based membranes in terms of FFV, based on the suggestion by Maeda and Paul.<sup>11</sup> The solid line represents the best fit of eq. (5) to the data (solid circles) for the various PSF structures described in previous studies.<sup>41</sup> The data points for PSF containing various amounts of additives are represented by the same symbols used throughout this work. The data for the addi-



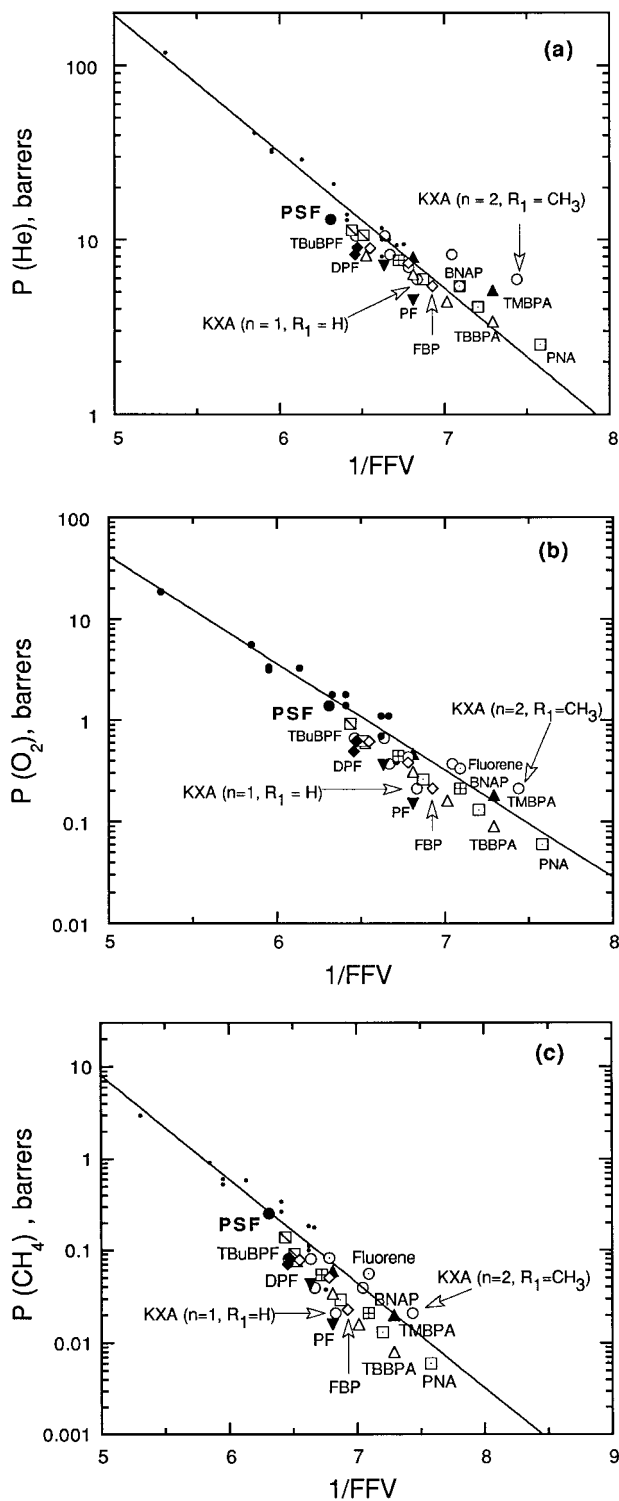
**Figure 7** Effect of incorporation of 20 wt % of various additives in PSF on the selectivity-permeability balance for the gas pairs (a) He/CH<sub>4</sub>, (b) H<sub>2</sub>/CH<sub>4</sub>, (c) O<sub>2</sub>/N<sub>2</sub>, and (d) CO<sub>2</sub>/CH<sub>4</sub>. Circles, triangles, and diamonds represent additives belonging to the same series of additives as described in Table I.

tive-modified materials appear to fall systematically below the solid correlation line drawn for the neat PSF materials. However, it should be noted that the neat PSF materials which form the basis for this line generally have a higher FFV than PSF, while the additive-modified PSF materials have a lower FFV. It is possible that a somewhat different correlation line may have resulted if the series of neat PSFs had included materials with lower values of FFV. Thus, it is premature to conclude that mixtures do or do not follow the same relationship as the neat PSFs.

## SUMMARY

The physical incorporation of various naphthalene-, bisphenol-, and fluorene-based additives

to PSF membranes significantly increases the permselectivity for the gas pairs He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub>. In general, additives containing naphthalene units with various substituents lead to PSF-based membranes with higher selectivity at the expense of relatively small losses in permeability compared with the unmodified PSF membrane. For the gas pairs He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub>, the additive KXA produces PSF-based membranes with higher permeability than the membranes modified with BNAP and PNA. The incorporation of bisphenol-based additives containing small groups symmetrically substituted on the ring, for example, TMBPA, increases selectivity at the expense of drastic reductions in permeability relative to unmodified PSF. Replacing the methyl groups in TMBPA by more



**Figure 8** Gas permeability versus FFV for (a) He, (b)  $O_2$ , and (c)  $CH_4$  in PSF-based polymers (small solid circles) and PSF modified with various concentrations of additives. The solid line represents the best fit of eq. (5) using some glassy PSFs reported previously. The other symbols are PSF-modified membranes with the various additives shown in Table I.

polar or by more bulky units, TBBPA or TBuBPF, leads to more permeable but much less selective membranes relative to the unsubstituted additive. The incorporation of fluorene-based additives into PSF shows that asymmetry and polarity can have a strong effect on the transport properties of the host PSF. The membranes modified with PF have higher selectivity and slightly lower permeability than when modified with fluorene. The additive FBP leads to membranes with both higher permeability and higher selectivity than fluorene.

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