Effect of Hexafluoro-2-propanol Substituents in Polymers on Gas Permeability and Fractional Free Volume[†]

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ABSTRACT: A series of polymers were synthesized containing hexafluoro-2-propanol (HFP) pendant groups by facile reaction of lithiated polymers with hexafluoroacetone (HFA). The purpose of the study was to evaluate the effect of the HFP group in potential membrane gas separation materials. Dibromobisphenol A polysulfone (PSf-Br_2), tetramethylbisphenol A polysulfone (TMPSf), dibromohexafluorobisphenol A polysulfone (6FPSf-Br_2), tetramethylhexafluorobisphenol A polysulfone (TM6FPSf), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were modified by using *n*-butyllithium to form lithiated intermediates and then treated with HFA to form the corresponding modified polymers PSf-HFP, TMPSf-HFP, 6FPSf-HFP, TM6FPSf-HFP, and PPO-HFP. Polymers with various degree of substitution per repeat unit of HFP were obtained, depending upon the extent of polymer lithiation and reactivity. PSf-HFP, TM6FPSf-HFP, and PPO-HFP were further derivatized at the hydroxyl group using iodomethane to obtain the respective methylated derivatives (HFM). The polymer structures were characterized by NMR spectroscopy, and thermal properties were investigated by differential scanning calorimetry and thermogravimetric analysis. The gas permeability coefficients of these polymers were measured for the gases He, O_2, CO_2, and N_2. The gas transport properties of PSf-HFP, PSf-HFM, and TMPSf-HFP for He/N_2, He/CO_2, O_2/N_2, and CO_2/N_2 gas pairs were all improved in comparison with PSf and TMPSf. The permeabilities for all gases increased 2−3-fold, while the permselectivities of the four gas pairs increased as well. All the HFP derivatives showed improvements of this magnitude only for the He/CO_2 gas pair.

Introduction

Membrane gas separation is a dynamic and rapidly growing field, wherein membranes are used commercially to separate gases from their mixtures by differential permeation of the components through them. Membrane separation processes offer a number of advantages in terms of low energy use and capital cost.[1] For more than two decades, an extensive body of experimental data on permeation of gases has been generated for a structurally wide array of glassy polymers. Much of this work has been done in an attempt to understand the principles that govern the relationship between gas permeability and polymer repeat unit structure because of an interest in developing improved gas separation membranes.[2] Increased performance requirements provide incentives to develop new membrane materials, since many studies have shown that an improvement in gas transport properties could be obtained by modifying or tailoring the polymer structure. The chemical structures coupled with subtle physical properties of the membrane material influence the permeability and selectivity. It is known that the response of a polymeric material to permeation is strongly influenced by the polarity and steric characteristics of the polymer and the permeant. The size and shape of bulky groups in both the polymer main chain and side chain strongly influence certain fundamental properties like packing density and rigidity. An absence of such pendant groups tends to increase structural regularity, which favors increased density.[1]

PSf is a thermoplastic that is widely used as a membrane material or membrane support for liquid separation processes such as ultrafiltration or reverse osmosis.[2,3] PSf was the material used for fabricating the first commercial gas separation membranes more than two decades ago. It is utilized in the form of hollow fiber membranes for commercial gas separations because of its overall combination of relatively high permselectivities and adequate permeabilities to various gases as well as its good mechanical properties and fiber spinning qualities.[4] PPO is another versatile and well-known commercial polymer having a high glass transition temperature (T_g)[5−8] exhibiting one of the highest permeabilities to gases, which is attributed to the absence of polar groups in the polymer backbone. However, PPO has a relatively low selectivity for gases and is insoluble in typical dipolar aprotic solvents.

The previous work most relevant and noteworthy to the present study for PSf is by the groups of Koros and Paul. Parallel families of polysulfones in which systematic structural modifications were introduced were correlated with their gas separation properties.[9−14] Guiver investigated the chemical modification of PSf in order to improve membrane separation properties. The modification of PSf by direct lithiation[15] or by bromination-lithiation[16] produced reactive intermediates that were converted by reaction with various electrophiles to yield carboxyl,[17] hydroxyl,[18] azide,[19] amine,[20] aldehyde,[21] trimethylsilyl (TMS),[22−27] and a number of other derivatives.[28−30]

PPO has also been modified to improve gas selectivity and solubility in dipolar solvents of this otherwise attractive membrane material. PPO was modified by various electrophilic substitutions including bromination,[31−35] carboxylation and methyl esterified car-

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boxylation,[32,35] sulfonylation and acylation,[32,34] and introduction of trialkylsilyl groups in the polymer backbone.[36] Sulfonated PPO was also studied as a potential material for gas separation membrane.[37−40]

Trifluoromethyl ($-CF_3$) groups in a polymer backbone are known to enhance polymer solubility (commonly referred to as the fluorine effect) without forfeiture of thermal stability. They also increase T_g with concomitant decrease of crystallinity. The $-CF_3$ group also serves to increase the fractional free volume of polymers and give materials with low dielectric constants and low water absorption, thereby improving various properties of polymers, including gas permeabilities and electrical insulating properties.[41] Considerable attention has been devoted to the preparation of new classes of partially fluorinated polymers because of their unusual properties. In previous work, we utilized simple chemistry to produce carbinol derivatives by reaction of aldehydes and ketones with lithiated polymers. Aryl and alkyl carbinol polysulfone derivatives were readily prepared[18,42] from acetone and other electrophiles. Hexafluoroacetone is also very reactive to lithiated polymers and cleanly produces derivatives with HFP pendant groups. Previously, polystyrene and polystyrene copolymers with pendant HFP, prepared either by polymer modification with HFA under Friedel−Crafts conditions or by polymerization of HFP-functionalized monomers, were studied by Hoechst researchers as a replacement for poly(4-hydroxystyrene) in 248 nm lithography.[43,44] In the present work, new modified polymers PSf, TMPSf, 6FPSf, TM6FPSf, and PPO with pendant HFP and their respective HPM derivatives were prepared for investigation of gas permeability properties.

Experimental Section

Materials. Dibromopolysulfone (PSf-Br_2),[16] tetramethylbisphenol A polysulfone (TMPSf),[25] dibromohexafluoropolysulfone (6FPSf-Br_2),[26] and tetramethylhexafluorobisphenol A polysulfone (TM6FPSf)[27] were prepared following previously published synthetic procedures. The above starting polymers and PPO (Polysciences Inc., Warrington, PA) were dried at 110 °C for at least 24 h. *n*-Butyllithium (10 M in hexane), iodomethane, hexafluoroacetone (HFA), and dimethyl sulfoxide (DMSO) were obtained from Aldrich Chemical Co. and were used as received. Analytical reagent toluene was obtained from BDH.

All lithiation reactions were conducted using anhydrous reagent grade tetrahydrofuran (THF) from Aldrich Chemical Co. which had been freshly distilled over lithium aluminum hydride and under a constant argon purge and with mechanical stirring. A dry ice/ethanol mixture was used for cooling reaction mixtures. *n*-Butyllithium was injected dropwise at a constant rate using a syringe pump.[15] All modified polymers were recovered by precipitation in an ice/ethanol mixture or ethanol using a Waring blender, washed thoroughly, and then dried in a vacuum oven at 55 °C.

The HFA gas cylinder was weighed prior to, and after use, to enable calculation of the amount of gas used. HFA (*caution: toxic*) was introduced into a dry receiver, cooled with dry ice/ethanol bath, by the use of a laboratory-made stainless steel $^1/_4$ in. diameter tubing condenser loop, and also cooled with dry ice/ethanol mixture. The equipment was designed to minimize exposure to the toxic gas which should be handled with caution.

Preparation of PSf-HFP. A solution of PSf-Br_2 (5.40 g, 9.00 mmol) in THF (2 wt %) was cooled −76 °C, and 2.15 mol equiv of *n*-butyllithium (1.93 mL, 19.3 mmol) was injected dropwise by syringe pump over a period of 15 min, during which time changes in the color and viscosity of the reaction solution were observed.[16,17] Following addition, the resulting solution of dilithiated polysulfone was stirred for 15 min. HFA (20 g, 25 mmol) gas was condensed at −40 °C and then poured promptly into the rapidly stirred reaction solution, which immediately developed a cloudy white color. There was also vapor in the reaction flask, which subsequently dispersed. The solution was stirred for 20 min, and then the polymer was recovered by precipitation from an ice/ethanol mixture and then washed and dried. The white product (4.80 g, yield 73% calculated from the formula PSf-$HFP_{1.75}$) had a degree of substitution (DS) of 1.75. The residual bromine content was 1.19% by elemental analysis.

Preparation of PSf-HFM. To a solution of PSf-HFP (0.5 g, 0.712 mmol) in THF (1.2 wt %) was added 35 mL of NaOH (0.02 g/mL of H_2O). The reaction mixture turned to cloudy white, and then the mixture was heated to 50 °C. 3 mL of CH_3I and 3 mL of DMSO were added to the mixture, and then it was heated to 60 °C. 10 min later the mixture became clear. The reaction mixture was stirred for an additional 35 min, and then the reaction was quenched by precipitating the polymer from ethanol. The recovered polymer was washed and dried, giving a white methyl ether derivative (0.32 g, yield 63%) which had a DS of 1.75.

Preparation of TMPSf-HFP. A colorless solution of TMPSf[25] (10.0 g, 20.0 mmol) in THF (1 wt %) was cooled to −60 °C. 2.2 mol equiv of *n*-butyllithium was injected dropwise over a period of 15 min. After stirring for an additional 15 min, HFA liquid (26 g, 156 mmol) which was condensed at −40 °C was poured promptly into the reaction solution at −60 °C. The solution was stirred with gradual warming to −5 °C and kept stirring for 1.5 h at −5 °C before being recovered. The polymer was recovered by precipitation from an ice/ethanol mixture, washed, and dried, giving a white product (13.3 g, yield 88%) which had a DS of 1.7.

Preparation of 6FPSf-HFP_2. To a colorless solution of 6FPSf[26] (6.0 g 10.90 mmol) in THF (1 wt %) at −40 °C was injected dropwise 3 mol equiv of *n*-butyllithium over a period of 15 min. After stirring for an additional 15 min at −40 °C, HFA (23.6 g, 142.2 mmol) was poured promptly into the reaction solution. The solution was stirred with gradual warming to −5 °C and kept stirring for 1.5 h at −5 °C before being recovered. The polymer was recovered by precipitation from an ice/ethanol mixture, washed, and dried, giving a white product (8.86 g, yield 92%) which had a DS of 1.8.

Preparation of 6FPSf-HFP_4. A colorless solution of 6FPSf-Br_2[26] (5.55 g, 7.84 mmol) in THF (1 wt %) was lithiated at −43 °C by the dropwise addition of 5 mol equiv of *n*-butyllithium over a period of 15 min. After stirring for an additional 15 min at −40 °C, HFA (12.2 g, 73.49 mmol) was poured promptly into the reaction solution. The solution was stirred with gradual warming to −5 °C and kept stirring for 1.5 h at −5 °C before being recovered. The polymer was recovered by precipitation from an ice/ethanol mixture, washed, and dried, giving a white product (6.98 g, yield 82%) which had a DS of 3.5.

Preparation of TM6FPSf-HFP. To a colorless solution of TM6FPSf[26] (5.0 g, 8.24 mmol) in THF (1 wt %) at −55 °C was added dropwise 3 mol equiv of *n*-butyllithium over a period of 15 min. After stirring for an additional 15 min at −40 °C, HFA (8 g, 48.13 mmol) at −40 °C was poured promptly into the reaction solution. The solution was stirred with gradual warming to −5 °C and kept stirring for 1.5 h at −5 °C before being recovered. The polymer was recovered by precipitation from ice−ethanol, washed, and dried, giving a white product (6.85 g, yield 80%) which had a DS of 1.5.

Preparation of TM6FPSf-HFM. To a yellow clear solution of TM6FPSf-HFA (5.0 g, 5.26 mmol) in THF (1 wt %) was added NaOH solution (1.1 g/35 mL of H_2O). The reaction mixture developed a white cloudy color, and then the mixture was heated to 50 °C. CH_3I (20 g) and DMSO (25 mL) were added to the mixture, and then it was heated to 68 °C. 10 min later the mixture turned clear. Following addition, the reaction mixture was stirred for an additional 35 min, and then the reaction was quenched by precipitating the polymer from ethanol, and the polymer product was washed and dried, giving a white product (4.65 g, yield 91%) which had a DS of 1.5.

Preparation of PPO-HFP. PPO (5.0 g, 41.53 mmol) was added to a mixed-solvent system of THF and toluene (4:1 by volume) (1.2 wt %). The mixture was refluxed to until all the solids had dissolved and then cooled to room temperature. *n*-Butyllithium (4.9 g, 1.2 equiv) was added dropwise, and the resulting mixture was stirred at room temperature for 15 min and then cooled to −30 °C. A large excess of HFA (37.6 g, 223 mmol) was condensed to −40 °C and then added to the reaction mixture quickly, and the solution was stirred for 15 min at −30 °C. The resulting polymer was precipitated from water/ethanol (2:1) and washed with water twice. The polymer was dried, resulting in a white product (7.4 g, yield 87%) which had a DS of 0.6.

Preparation of PPO-HFM. To a yellow clear solution of PPO-HFP (7.0 g, 35.5 mmol) in THF (1.6 wt %) was added NaOH (5 g/50 mL of H_2O). The solution developed a yellow cloudy color, and then the mixture was heated to 30 °C. CH_3I (23 g) and DMSO (40 mL) were added to the mixture, and then it was heated to 60 °C. 10 min later the mixture turned to clear. Following addition the reaction mixture was stirred for an additional 30 min, and then the reaction was cooled to room temperature. The solution was evaporated to a 300 mL volume, and then the polymer was precipitated from ethanol, washed with ethanol, and dried, giving a white product (7.4 g, yield 87%) which had a DS of 0.6.

Characterization Methods. Nuclear magnetic resonance spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^1H and 100.579 MHz for ^{13}C. Polymer samples were prepared using $CDCl_3$ or CD_3OD as the NMR solvents, and the solvent signals were used as the chemical shift reference (^1H $C\mathit{H}Cl_3$ 7.25 ppm, $C\mathit{H}_3$-OD 3.31 ppm). The intrinsic viscosities of polymers in NMP at 35 °C were determined using an Ubbelohde viscometer. The DS of modified polymers were readily determined using ^1H NMR by comparative integration of selected signals (described later). Polymer thermal degradation curves were obtained from thermogravimetric analysis (TGA) (TA Instruments model 2950). Polymer samples for TGA were preheated to 60 °C for 2 h inside the TGA furnace for moisture removal under nitrogen gas and then heated to 600 °C at 10 °C/min for degradation temperature measurement. Glass transition temperatures (T_g) were obtained from differential scanning calorimetry (DSC) (TA Instruments model 2920), and samples for DSC were heated initially to at least 30 °C above T_g at 10 °C/min under a flow of 50 mL/min of nitrogen gas, quenched with liquid nitrogen, and reheated at 10 °C/min for the T_g measurement.

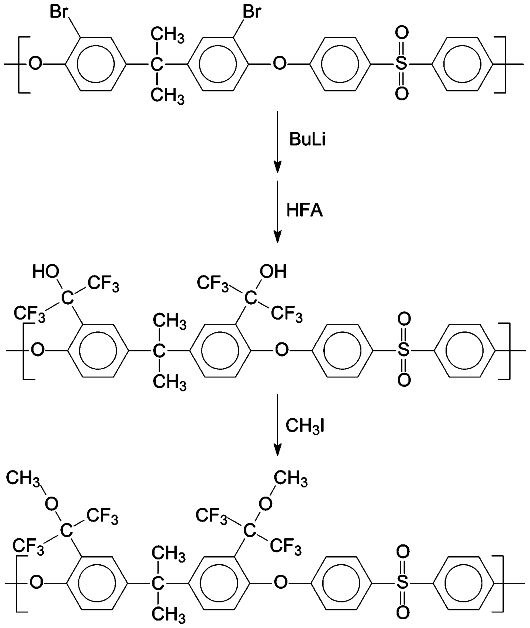
Wide-angle X-ray diffraction (WAXD) was used to investigate *d*-spacings. A MacScience model M18XHF22 was utilized with Cu Kα radiation of wavelength (λ) 1.54 Å, and the scanning speed was 5 °C/min. The value of the *d*-spacing was calculated by means of Bragg's law ($d = \lambda/2 \sin \theta$), using θ of the broad peak maximum. Polymer density was determined by the displacement method using a Mettler density kit with anhydrous ethanol at 23 ± 0.1 °C.

Dense polymer films for gas permeability measurements were prepared from 5 wt % polymer solutions in anhydrous THF that were filtered through 1 μm poly(tetrafluoroethylene) filters and then poured into flat-glass dishes and dried slowly under a nitrogen atmosphere at room temperature. The detached films were further dried for 3 days in a vacuum oven at 40 °C to remove the residual solvent and then annealed at 130 °C for 4 h. Optically clear films were obtained with a thickness of about 40 μm in all cases. The absence of residual solvent in the films was confirmed by observing T_g using DSC. Permeability coefficients (P) of helium, carbon dioxide, oxygen, and nitrogen were measured by the constant volume method at 35 °C with an upstream pressure of 760 and 4000 Torr.

Results and Discussion

Preparation of Polymers. A bromination−lithiation reaction was used to difunctionalize PSf-Br_2 ortho to the ether linkage, as described previously.[16] The PSf-Br_2 polymer was first reacted with 2.15 mol equiv of n-C_4H_9Li followed by reaction with electrophile HFA to produce a HFP derivative with DS 2.0, as outlined in Scheme 1. Under these conditions, lithium−bromine exchange at the ortho ether (-*o*-) site is by far the predominant reaction over direct lithiation at the ortho sulfone (-*s*-) site. Elemental analysis of the HFP product for bromine (1.19%) indicated that only ~1.2% of bromine remained unexchanged. Minimal amounts of lithium substitution occurred at the (-*s*-) site because the bromine on the bisphenol portion of the polymer chain assists in deactivating the (-*s*-) site.

Scheme 1. Synthesis of PSf-HFP and PSf-HFM



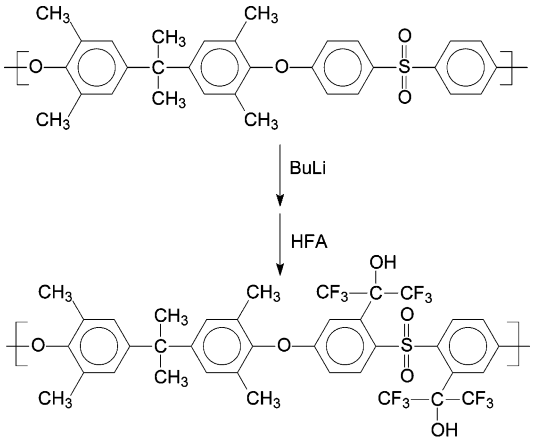
Since the Ar-HFP group has a similar acid constant to that of Ar-OH,[43] the −OH group can be further converted to other functional groups such as −OCl and $-OCH_3$. The conversion of −OH to $-OCH_3$ is shown in Scheme 1, which was done to compare the effect of H-bonding (HFP) and non-H-bonded (HFM) substituents. The $-CF_3$ group has been shown by numerous studies to be effective for improving performance for gas separation.

In general, for all polymer functionalization by the direct lithiation route, dilithiated intermediates were prepared for conversion to HFP derivatives to give the highest DS. Direct lithiation of TMPSf resulted in a lithiated intermediate at the (-*s*-) site,[25] leading to a HFP derivative with DS of 1.7, as shown in Scheme 2.

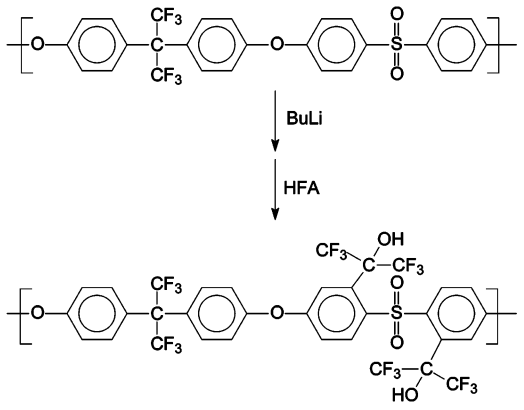
Scheme 3 shows the chemical modification pathway in which 6FPSf was lithiated directly by 2.9 mol equiv of n-C_4H_9Li (0.9 mol equiv excess) to afford a THF-soluble intermediate with lithiation occurring at the (-*s*-) site.[26] For the direct lithiation of 6FPSf, an additional ~1 mol equiv of n-C_4H_9Li is required since it appears that the lithiation reaction competes with a complex formed between n-C_4H_9Li and the 6F moiety. The electrophile HFA was subsequently reacted under the right temperature conditions with the dilithiated intermediate to yield the corresponding highly substituted 6FPSf-HFP with a DS of 1.8.

When excess *n*-butyllithium is reacted with dibrominated polymers, two types of reactions occur: bromine−lithium exchange and direct lithiation. This methodology generally results in derivatives with the highest achievable DS. Scheme 4 shows the chemical modifica-

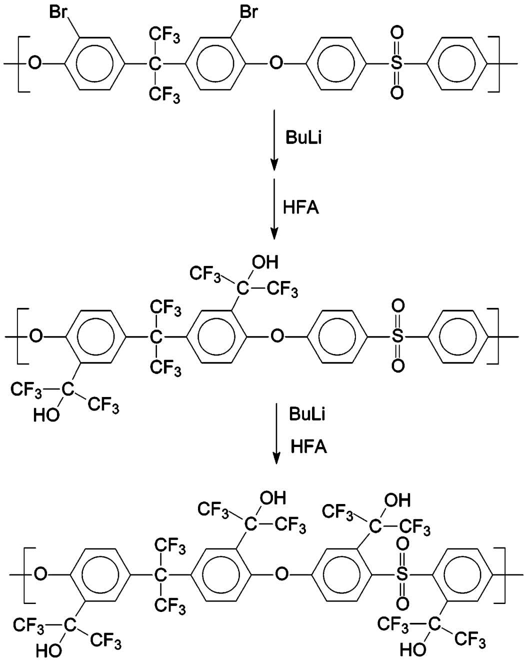
Scheme 2. Synthesis of TMPSf-HFP



Scheme 3. Synthesis of 6FPSf-HFP$_2$

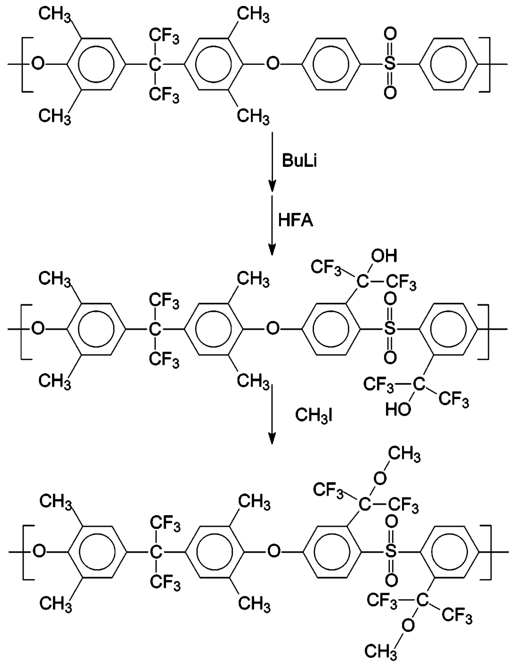


Scheme 4. Synthesis of 6FPSf-HFP$_4$

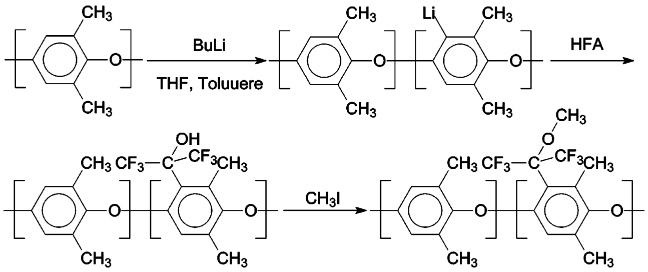


tion pathway in which 6FPSf-Br$_2$ was lithiated using an excess of n-C_4H_9Li (5 mol equiv) to afford a THF-soluble intermediate in which lithiation occurs around both the (-*o*-) and (-*s*-) site, thereby achieving the maximum DS of 3.5. However, the 6FPSf-HFP polymer membranes were brittle and were not further converted to HFM derivatives.

Scheme 5. Synthesis of TM6FPSf-HFP and TM6FPSf-HFM



Scheme 6. Synthesis of PPO-HFP$_{0.5}$ and PPO-HFM$_{0.5}$



Scheme 5 shows the chemical modification pathway in which TM6FPSf was lithiated directly by 3.1 mol equiv of n-C_4H_9Li to afford a THF-soluble intermediate lithiated at the (-*s*-) site. A polymer with a lower DS of 1.6 was obtained that was likely the result of the presence of the tetramethyl groups. This would make the polymer less reactive due to the electron-donating properties and also increase the steric hindrance. In earlier work, TMPSf and TM6FPSf were brominated.[26] In the first case, aromatic bromination occurred on the unoccupied sites of the tetramethylbisphenol ring. However, in the latter case where the 6F was also present, steric and electronic effects combined to prevent bromination occurring in this ring. Instead, dibromination occurred unusually on the ortho ether site on the diphenyl sulfone rings. Thus, a HFP-modified polymer derived from TM6FPSf-Br$_2$ was not prepared.

Scheme 6 shows the chemical modification pathway in which PPO was lithiated directly by 1 mol equiv of n-C_4H_9Li to afford a lithiated intermediate. A polymer with a lower DS of 0.5 was obtained since the presence of the dimethyl group made the polymer less reactive due to the electron-donating properties and steric hindrance of the symmetrically placed methyl groups. The methylated derivative of HFA was too brittle to fabricate free-standing films. It is also possible that the chemical stability of PPO is not adequate for the methylation reaction.

Structural Characterization. The ^1H NMR spectra of Figures 1−4 display the aromatic regions of the

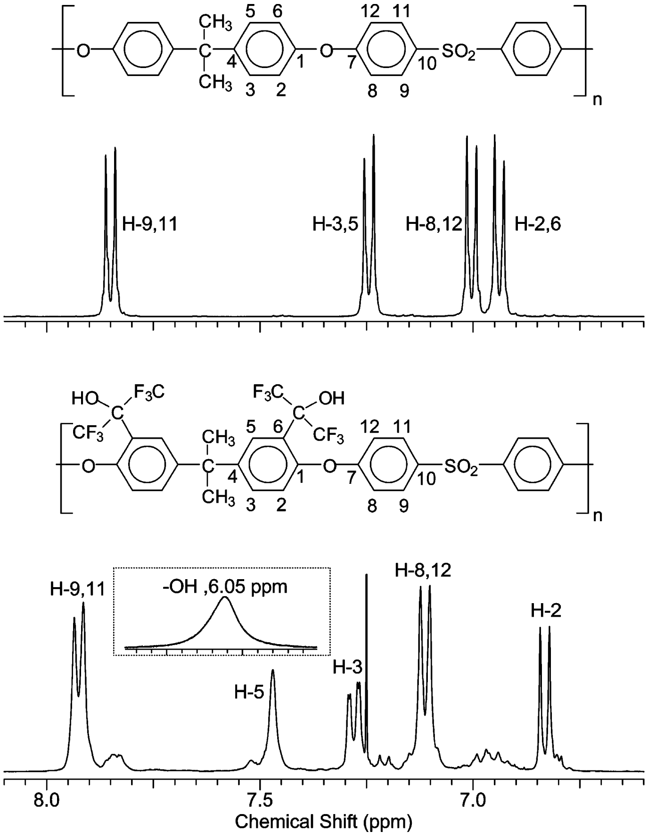


Figure 1. ^{1}H NMR spectra of unmodified and HFP-functionalized PSf ($CDCl_3$).

polymers before and after addition of the HFA groups. All of the spectra show well-defined signals which were all readily assigned using simple homonuclear decoupling or 2D COSY experiments. The simplicity of the ^{1}H spectra is due to structural symmetry of highly substituted, nominally DS 2 and DS 4 polymers. A polymer of DS 2 renders all repeat units (RU) in the polymer identical, whereas a polymer with lower DS would result in a mixture of un-, mono-, and disubstituted RU, hence giving more complex spectra. The polymer derivatives were also investigated by ^{19}F and ^{13}C NMR which confirmed the structures displayed in the ^{1}H NMR figures. These results are not reported since we believe the ^{1}H NMR data alone clearly provide sufficient unambiguous structural support. Furthermore, the site of lithiation on various polysulfone structures is well established in previous publications.[29,30] The DSs of polymers were assessed by using different calculation methods. In the case of polymers having methyl groups, PSf and TMPSf, the intensities of the low-frequency signals were set to 6H and 12H, respectively. The DS of polymers were then directly obtained by reading the integral values of any of the well-resolved aromatic signals located on the substituted rings or by reading the integral value of the hydroxyl group. In the case of the 6F polymer derivatives, where low-frequency signals are absent, the DS values could only be accurately measured by ^{19}F NMR where the polymer chain 6F fluorine signal intensity was compared with that of the pendant HFP groups. Finally, the smaller signals labeled “m” and “u” in the TM6F-PSf HFA derivative of Figure 3 are due to ortho sulfonyl hydrogen atoms mono- and unsubstituted repeat units resulting from incomplete disubstitution reaction.

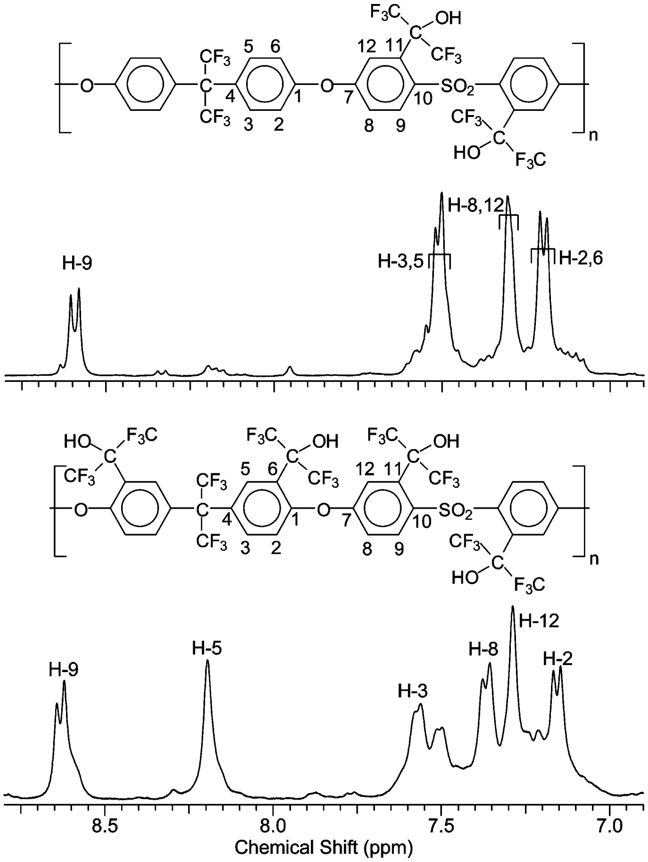


Figure 2. ^{1}H NMR spectra of unmodified and HFP-functionalized 6FPSf (CD_3OD).

Physical Properties. Solubility was observed during the day of sample preparation and then 14 days later to determine whether the solutions were stable. All the HFP and HFM polymers dissolved in $CHCl_3$, THF, DMAc, and DMSO, except 6FPSf-HFP$_2$ and 6FPSf-HFP$_4$, which dissolved in DMSO and methanol. The samples were protected under an inert atmosphere and from light to eliminate the possibility of any environmental reaction. It is known that 6F groups in the polymer backbone enhance polymer solubility (commonly referred to as the “fluorine effect”). In the case of HFP derivatives, the presence of OH group also influences the polymer solubility.

The thermal stabilities of PSf and PPO derivatives were measured by TGA and actual onset temperatures of degradation (for 1% weight loss) are shown in Table 1. All polymer derivatives were thermally less stable than their respective parent polymers. The curves of all the modified polymers exhibited a three-step degradation profile. This suggests that during the heating process the pendant HFP was lost initially. For example, the initial degradation for TM6FPSf-HFA (DS 1.6) is a weight loss of 3.0%, which is believed to be the loss of $-OH$, since the weight loss corresponds with the theoretical weight loss of this polymer with DS 1.6. The second degradation for TM6FPSf-HFA is believed to be the overall loss of $-C(CF_3)_2$ since the weight loss is close to the theoretical weight loss of 30% from the polymer with DS = 1.6. The initial degradation for TM6FPSf-HFM (DS 1.6) is believed to be the loss of $-OMe$ since the weight loss is close to the theoretical loss of 5.5%. These initial degradation step results correspond almost exactly with the DS values obtained by NMR spectroscopy. TM6FPSf-HFP has a higher thermal stability than

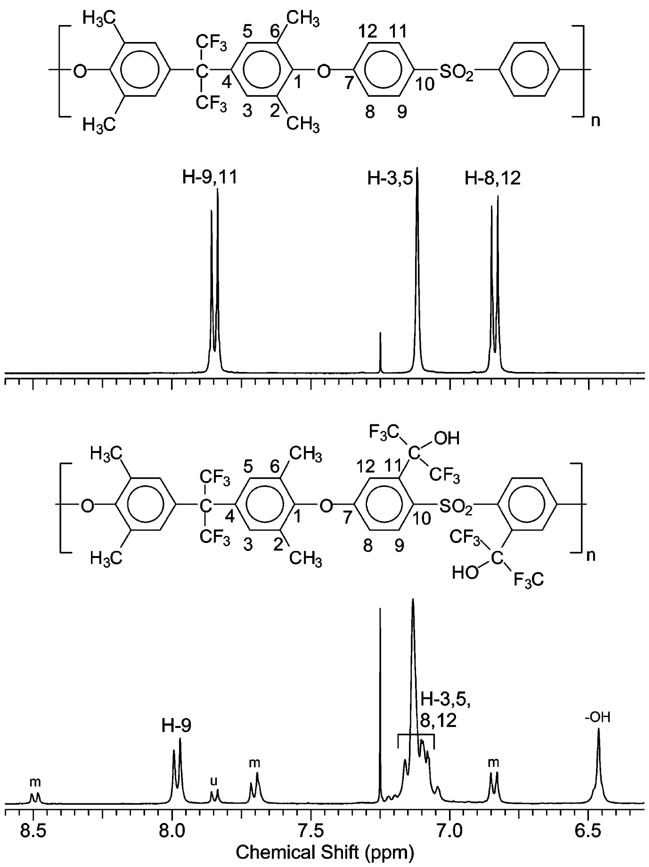


Figure 3. ^{1}H NMR spectra of unmodified and HFP-functionalized TM6FPSf ($CDCl_3$).

the TM6FPSf-HFM. The reason for the higher stability is probably that the HFP groups are more polarized and not as readily removed due to the strong electron-withdrawing effect of the sulfone linkages.

All HFP and HFM derivatives had lower T_gs than their starting polymer. For example, compared with PSf having a T_g of 188 °C, both PSf-HFP and PSf-HFM polymers had lower T_gs of 167 and 163 °C, respectively. Usually the presence of 6F in the polymer main chain increases the T_g, as shown by the T_g of 199 °C for 6FPSf. In the case of polymers with pendant HFP substituents, the T_g reduction suggests that this was possibly due to a loss in symmetry of the phenylene ring by the introduction of HFP. For the 6FPSf-substituted polymers, increasing DS led to increased T_g because of the addition in symmetry of the phenylene ring.

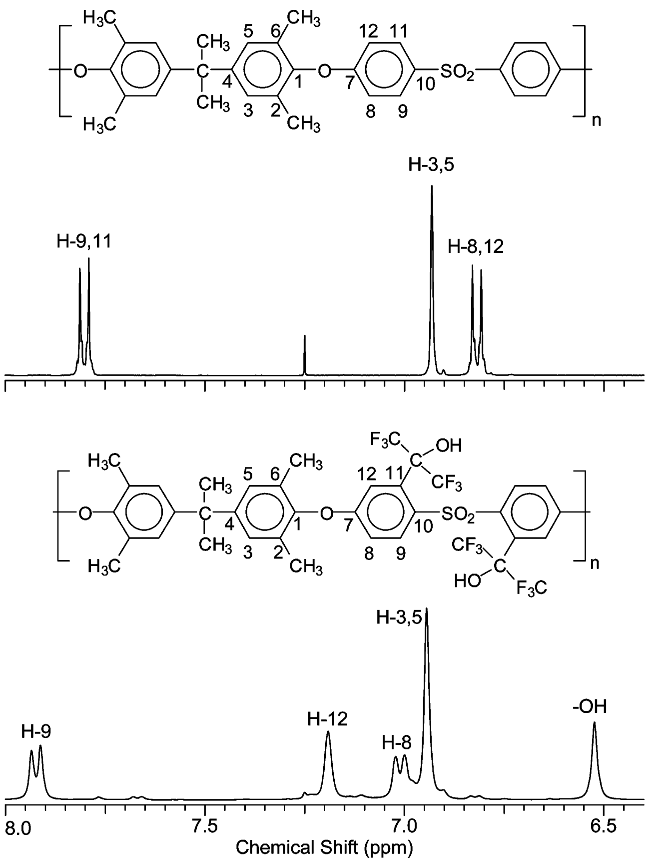


Figure 4. ^{1}H NMR spectra of unmodified and HFP-functionalized TMPSf ($CDCl_3$).

Table 1. Glass Transition Temperatures and Thermal Stabilities of the Polymers

polymer	DS	T_g, °C	actual onset, °C	extrapolated onset, °C
PSf		188	455	521
PSf-HFP	1.75	167	235	366
PSf-HFM	1.75	163	364	448
TMPSf		231	396	432
TMPSf-HFP	1.7	187	349	377
6FPSf		199	489	511
6FPSf-HFP	1.8	148	226	354
6FPSf-HFM	~3.5	167	242	285
TM6FPSf		236	424	430
TM6FPSf-HFP	1.6	196	284	366
TM6FPSf-HFM	1.6	163	202	237
PPO		218	409	423
PPO−HFP	0.6	174	254	306
PPO−HFM	0.6	162	241	284

Gas Transport Properties. The *d*-spacing of two series of polymers PSf and TMPSf were calculated from WAXS spectra by Bragg's law and are listed in Table 2. The *d*-spacings of all the HFP and HFM derivatives are greater than their respective starting polymers, suggesting that the HFA and HFM substituent increased polymer *d*-spacing. The disrupted chain packing is also validated by the fractional free volume (*FFV*) and the packing density (*PD*). *FFV* was calculated using the following relationship:[45]

$$V_f = (V_{sp} - 1.3V_w)$$

$$FFV = V_f/V_{sp}$$

where V_f is the free volume, V_{sp} is the specific volume, and V_w is the specific van der Waals volume, calculated using the group contribution method of Bondi.[46,47] *PD* was calculated[33] using

$$PD = V_{sp}/(V_{sp} - V_w)$$

PD and *FFV* data are also listed in Table 2. The results are consistent with those of the *d*-spacing. In other words, the larger the *d*-spacing is, the larger *FFV* and the smaller *PD* are, and vice versa. Therefore, it is apparent that the HFP and HFM groups are effective in disrupting chain packing, which is directly correlated with gas permeability. Larger *d*-spacing and *FFV* and lower *PD* result in higher gas permeabilities.

A tradeoff relationship is usually observed between permeability (P) and ideal permselectivity (α) for common gases in glassy or rubbery polymers. That is, higher permeability is gained at the cost of lower permselec-

Table 2. Physical Properties of the Polymers

polymer	*d*-space, Å	ρ, g/cm^3	V_{sp}, cm^3/g	*M*, g/mol	V_w, cm^3/mol	V_f, cm^3/g	*PD*	*FFV*
PSf	5.0	1.25	0.8	442.5	235.6	0.108	2.99	0.135
PSf-HFP	6.0	1.46	0.68	734.8	329.9	0.101	2.90	0.148
PSf-HFM	6.1	1.39	0.72	759.4	349.5	0.121	2.78	0.168
TMPSf	5.2	1.18	0.85	498.6	279.9	0.118	2.96	0.139
TMPSf-HFP	7.3	1.32	0.76	782.6	371.5	0.140	2.68	0.185

Table 3. Gas Permeabilities and Ideal Permselectivities of the Polymers

	P				α				$\delta \times 10^3$			
polymer	He	CO_2	O_2	N_2	O_2/N_2	CO_2/N_2	He/CO_2	He/N_2	O_2/N_2	CO_2/N_2	He/CO_2	He/N_2
PSf	11	6.3	1.1	0.19	5.8	33	1.8	58	213	387	966	809
PSf-HFP	20	5.4	1.5	0.22	6.8	25	3.7	91	124	355	550	486
PSf-HFM	24	7.7	2.0	0.26	7.7	26	3.6	92	50	305	516	424
TMPSf	41	21	5.6	1.1	5.3	20	2.2	44	132	253	599	519
TMPSf-HFP	66	30	8.5	1.5	5.7	16	2.5	40	70	199	438	331
TM6FPSf	113	72	18	4.0	4.5	18	1.6	28	110	120	424	296
TM6FPSf-HFP	151	81	19	5.92	3.2	14	1.9	25	256	214	236	292
PPO	82	66	14.6	3.5	4.2	19	1.3	24	159	117	582	450
PPO-HFP	108	89	23	11.3	2.0	7.9	1.2	9.6	429	430	524	633

tivity and vice versa. Upper bound performance lines for the relationship between gas permeability and permselectivity have been proposed by Robeson et al.[3] A basic principle for overcoming this tradeoff behavior so as to achieve simultaneously higher permeability and permselectivity is that the polymer chain stiffness should be maintained while increasing the interchain separation. On this basis, a series of HFP groups were introduced onto the polymer chains.

Single gas permeability coefficients (*P*) were measured on polymer dense films for He, CO_2, O_2, and N_2 and a summary of these *P* values, and ideal permselectivities for various gas pairs are shown in Table 3. The distance (δ) from the permeability point (P_i vs α_{ij}, where permselectivity $\alpha_{ij} = P_i/P_j$) to the upper bound line which was generated from the data of Park et al. was calculated by the method developed previously,[26] and the values are also shown in Table 3. The gas permeation improvement trends are shown in Figures 5 and 6, where the dashed lines are Robeson upper bound lines and the real lines are the generated upper bound lines. The marks on the upper bound line show poly(tetrabromofluorene tetrabutyl isophthalate) in Park's data for both O_2/N_2 and CO_2/N_2 gas pairs.

The *P* values decrease in the following order: He > CO_2 > O_2 > N_2, which is also the order of increasing kinetic diameters of the gases. All the polymers containing the HFP substituent were significantly more permeable to all gases than their parent polymers PSf, TMPSf, TM6FPSf, and PPO. For the PSf series, P(He), $P(CO_2)$, and $P(O_2)$ increased 2−3-fold with the introduction of HFP and HFM groups. Although there were some decreases in ideal permselectivity, the distances δ to the upper bound line were shorter: O_2/N_2 from 0.213 to 0.124 and 0.050, respectively, indicating an overall improvement. The *d*-spacing and *FFV* increased from 5.0 to 6.0 Å and from 0.135 to 0.148 and 0.168 by introducing HFP and HFM group on PSf, as shown in Table 2. The *FFV* is closely correlated to the diffusion coefficients in a strict sense according to the free volume theory. However, it has been experimentally found that the permeability can also be similarly correlated with *FFV* as follows:[10]

$$P = A \exp(-B/FFV)$$

where *A* and *B* are parameters. Figure 7 shows that a fairly linear relationship exists between log(P) vs 1/*FFV* for the PSf, PSF-HFP, and PSF-HFM polymer for all four gases.

The HFP substituent contains both $-CF_3$ groups and H-bonded hydroxyl groups. The 6F group significantly improves permeability and permselectivity by increasing chain stiffness, forcing chain segments apart, while reducing intersegmental chain packing and reducing interchain interactions such as charge-transfer complexes (CTC), since $-CF_3$ groups are electron-withdrawing and reduce CTC formation. PSf-HFM has better permeability and permselectivity because the methyl

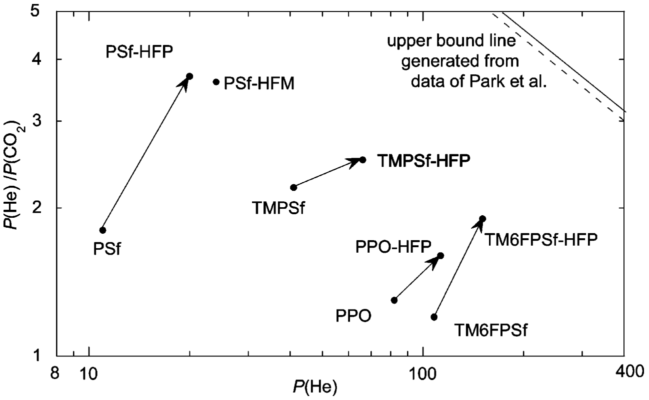


Figure 5. Polymer gas permeabilities and permselectivities for the He/CO_2 gas pair.

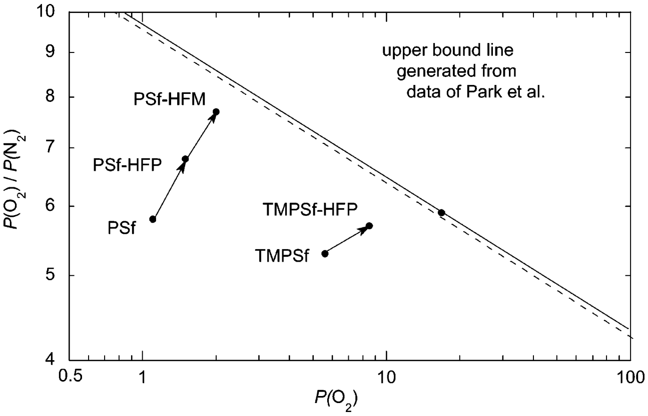


Figure 6. Polymer gas permeabilities and permselectivities for the O_2/N_2 gas pair.

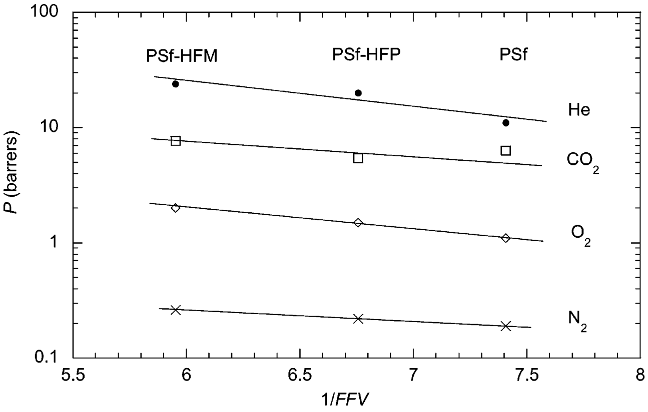


Figure 7. Logarithmic *P* of PSf, PSf-HFP, and PSf-HFM as a function of reciprocal *FFV* at 35 °C and 4000 Torr upstream pressure.

group is larger than OH and there is no H-bonding. As expected, the evidence for this is larger *d*-space, *FFV*, and *P*.

Both TMPSf and TM6FPSf have significantly higher *P* than PSf because of steric bulkiness of the tetramethyl segment and the nature of the 6F group. Thus, the incremental increases in *P* observed with the introduction of the HFP substituent were less than those for PSf. The observed increases in *P* for TMPSf-HFP were 1−2-fold in comparison with TMPSf, and the overall performance increased. For the O_2/N_2 gas pair, the distance to the upper bound line is 0.070. However, TM6FPSf-HFP and PPO-HFP did not show good overall performance, as shown by a larger distance δ for both the CO_2/N_2 and O_2/N_2 gas pairs, with the exception of He/N_2. Structurally, TMPSf-HFP, TM6FPSf-HFP, and PPO-HFP contain both the bismethylphenol segment as well as the HFP substituent, both of which increase the interchain distance. However, the HFP substituent is considerably larger than methyl and further increases chain stiffening. This may explain why TM6FPSf-HFP and PPO-HFP exhibit only slightly increased permeability and reduced ideal permselectivity for both the CO_2/N_2 and O_2/N_2 gas pairs compared with PSf-HFP.

Conclusions

Novel modified PSf, TMPSf, 6FPSf, TM6FPSf, and PPO with HFP functional group were readily synthesized by using *n*-butyllithium to form soluble lithiated intermediates followed by treatment with hexafluoroacetone. They have lower T_g and degradation temperatures than the starting polymers. Depending upon the extent of lithiation and polymer reactions PSf-HFP hydroxyl derivation was further methylated using iodomethane to obtain PSf-HFM. PSf-HFP, TMPSf-HFP, and PSf-HFM have better overall permeability/permselectivity performance for the CO_2/N_2 and O_2/N_2 gas pairs than their starting polymers. Increases about 2−3-fold with some drops in permselectivity with N_2 in both CO_2 and O_2 permeabilities were observed. The $P(O_2)$ of PSf-HFP and PSf-HFM were 1.5 and 2.0 and $\alpha(O_2/N_2)$ were 6.8 and 7.7, respectively. The distances δ to the upper bound line for PSf-HFP and PSf-HFM were reduced for O_2/N_2 from 0.213 to 0.124 and 0.050, respectively, compared to PSf. TMPSf-HFP has good overall performance as well. The $P(O_2)$ of TMPSf-HFP was 8.5 and $\alpha(O_2/N_2)$ was 5.7. The distance δ to the upper bound line for TMPSf-HFP was reduced for O_2/N_2 from 0.132 to 0.070 compared with TMPSf. The incorporation of HFP and HFM into PSf and TMPSf led to marked improvements in performance. All modified polymers exhibited improved He/CO_2 permeability/permselectivity performance.

Although two of the new polymer derivatives showed markedly improved performance, they clearly fall below the "upper bound" performance limit. However, the present work seeks to correlate the effect of this particular type of side substituent on gas permeability and *FFV*. The fact that these purely polymeric membrane materials fall below the performance limit does not preclude their use as components in mixed-matrix or cross-linked membranes, which may well exceed the "upper bound". Indeed, the HFP derivatives contain hydroxyl groups, which may be utilized for cross-linking or for attachment to an inorganic dispersed phase within the polymer.

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