

Functional Ethynyl-Substituted Polysulfones by Bromination-Alkynylation Suitable as Gas Permselective Membranes

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ABSTRACT: Poly(arylene ether sulfone) has been successfully modified by a process of bromination followed by displacement of bromine with substituted acetylenes using a palladium catalyst. The degree of bromination and alkynylation, determined by ¹H-NMR, was in the range of 98–50% and 92–45%, respectively. FT-IR and ¹³C-NMR confirmed the structure of the polymers. The final aim was to obtain a new material employable as a membrane for gas separation. Permeation properties of substituted poly(arylene ether sulfone) to carbon dioxide, methane, oxygen, and nitrogen were evaluated. Asymmetric membranes of alkynylated polymer were prepared by phase inversion technique. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1987–1997, 1997

Key words: poly(arylene ether sulfone); chemical modification; bromination; alkynylation; membrane; gas separation

INTRODUCTION

Aromatic polysulfones (PSf) are known to be important engineering thermoplastics with high thermostability and excellent mechanical properties. Chemical modification of PSf by sulfonation,¹ bromination,² lithiation,³ halomethylation,⁴ and aminomethylation,⁵ have been described in literature. Considerable attention has also been directed towards acetylenic terminated oligomers in order to obtain cured resins with attractive properties⁶ and, recently, a work reports a series of PSf containing pendant ethynyl groups prepared starting from novel bisphenols.⁷

In a previous article⁸ we reported that chemical modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by bromination-alkynylation provides a general and powerful way for the introduction of side chain on different aromatic polymers; therefore, we used this method to introduce bulky

substituents in the phenylene ring of PPO to increase its gas permeability.

Such a chemical modification has been proved to be effective in increasing PPO permeability up to 10 times,⁹ but solubility characteristics of the polymer remain unchanged, preventing its use in asymmetric membrane formation by means of those phase inversion processes using water as coagulant.

PSf, on the contrary, is commonly formed into asymmetric hollow fibers by spinning into aqueous baths its solution in dipolar aprotic water miscible solvents, such as dimethyl formamide, dimethyl acetamide, *N*-methyl pyrrolidone or formyl piperidine.¹⁰ Herein we report the chemical modification of PSf by a process of bromination of bisphenolic aromatic rings, followed by displacement of bromine with substituted acetylenes using a palladium catalyst, outlined in Figure 1.

The final aim is to obtain a new material with improved gas permeability, employable in the field of membrane for gas separation and processable under conditions analogous to PSf. This

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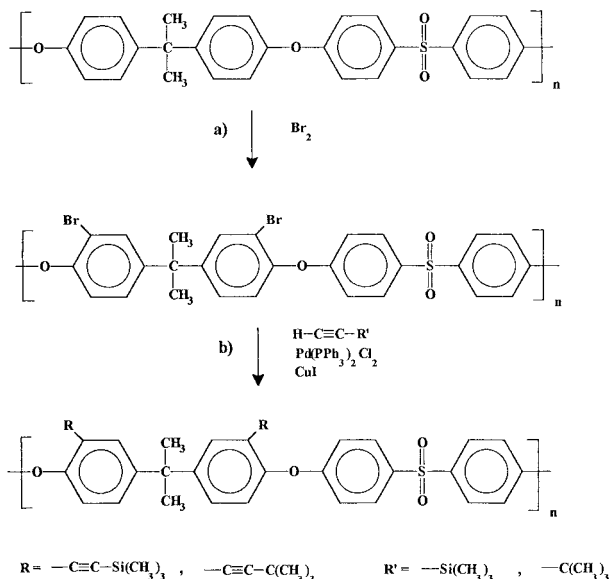


Figure 1 Reaction scheme for PSf modification.

article deals with the synthesis and characterization of PSf-based copolymers, the measurements of their permeation properties, and the preparation of the corresponding asymmetric membranes.

EXPERIMENTAL

Materials

Udel® 3500 with $M_n = 29,500$ and $M_w = 63,000$ (determined by gel permeation chromatography using polystyrene standard) was obtained from Union Carbide. Reagent grade bromine and chloroform were used as received for the bromination reactions. Trimethylsilylacetylene, *tert*-butylacetylene, *N*-methyl-2-pyrrolidone, triethylamine, triphenylphosphine, lithium chloride, palladium (II) chloride, and cuprous iodide were used as purchased from Aldrich Chemical Co.

Bromination of PSf

Bromination of the aromatic rings of the bisphenolic unit was achieved using a known procedure.² In a typical experiment, bromine (210 mmol) was added to a stirred solution of PSf (75 mmol) in chloroform (200 mL) at room temperature. The hydrogen bromide produced during the reaction was absorbed into a diluted solution of NaOH and the mixture was stirred at room temperature for 24 h. The brominated polymer was recovered by pouring the chloroform solution into a double volume of methanol and purified by redissolution in chloroform and reprecipitation from methanol. The recovered polymer was dried 24 h at 40°C under vacuum. The brominated polymers, listed in Table I, were obtained varying the molar ratio between bromine and PSf.

Alkynylation of PSf

Preparation of Palladium Catalyst

Bis(triphenylphosphine) palladium (II) chloride was prepared according to Hergenrother,⁶ by refluxing a stirred mixture of 1.77 g (10 mmol) of palladium (II) chloride, 0.85 g (20 mmol) of lithium chloride and 5.5 g of triphenylphosphine in 50 mL of disreathed methanol. The reaction mixture was heated for 1 h; the complex precipitated as yellow solid. The solid was filtered and dried under vacuum.

Reaction of Brominated PSf with Substituted Acetylenes

In a typical alkynylation experiment with trimethylsilylacetylene, a mixture of 3 g of brominated PSf and 250 mL of *N*-methyl-2-pyrrolidone were placed into a 500 mL round-bottom flask fitted with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas bubbler.

Table I Modification of PSf with Substituted Alkynes

Polymer	PSf Bromination Degree (mol %)	Mol Alkyne/mol Bromine	Final Polymer Composition (mol %)		
			R	Br	R
1	98	2.4	$-C\equiv C-Si(CH_3)_3$	6	92
2	50	2.4	$-C\equiv C-Si(CH_3)_3$	3	47
3	98	2.4	$-C\equiv C-C(CH_3)_3$	21	77
4	50	2.4	$-C\equiv C-C(CH_3)_3$	5	45

The alkynylations have been carried out at 80°C for 4.

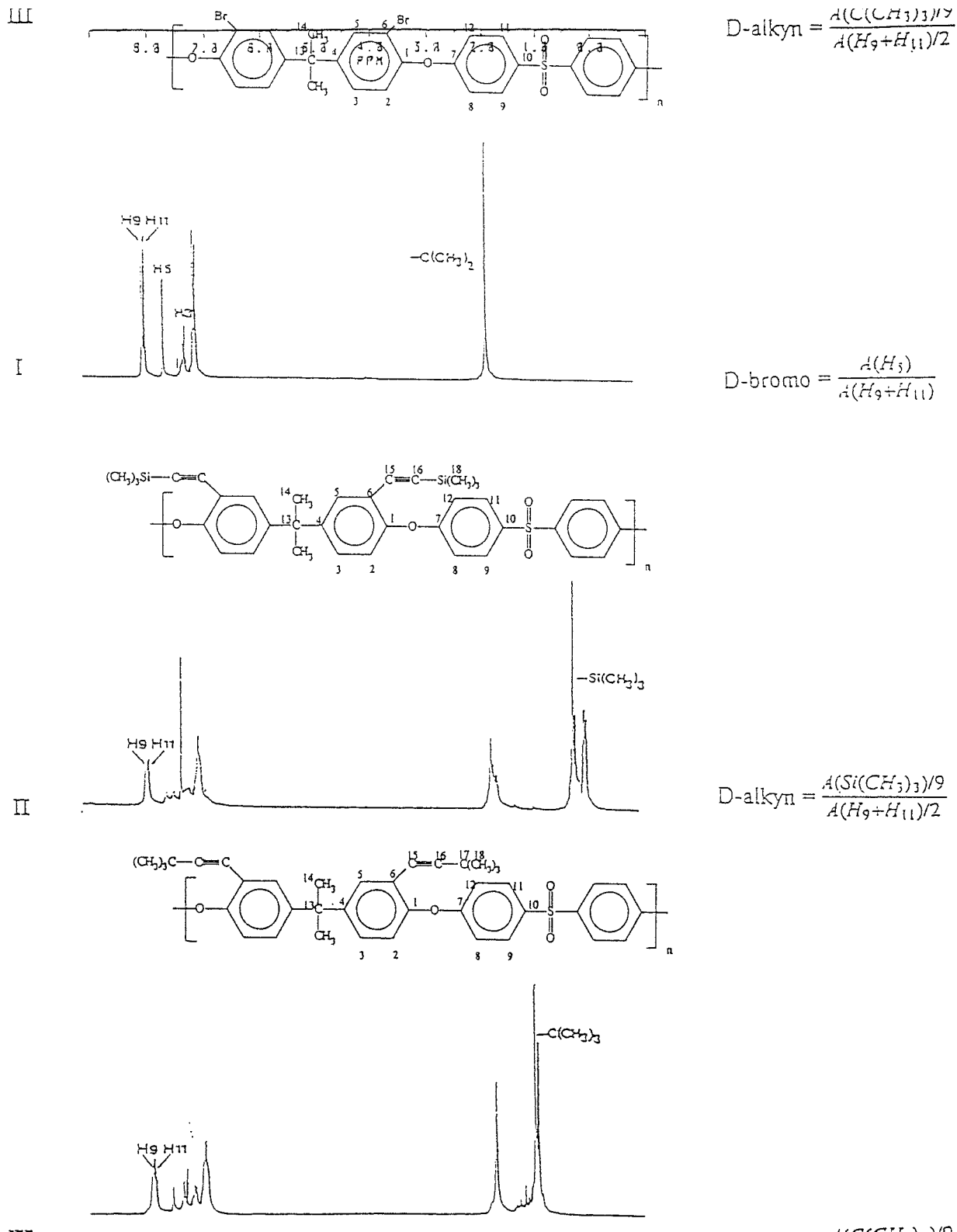


Figure 2 Comparative ¹H-NMR spectra of brominated (I) and alkyne-substituted PSf (II) (III).

Table II ^{13}C -NMR Chemical Shift of Unmodified and Modified PSf

Carbon	Unit			
	A	B	C	
			$-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$	$-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3$
1	152.9	149.6	153.4 ^a	149.4–152.6 ^a
2	119.8	122	120.4	121.4
3	128.4	127.6	128.6	128.1
4	147.1	148.6	146.8	146.7
5	128.4	132.1	132.2	131.5
6	119.8	115.7	116.4	115.6
7	161.9	161	161.1–161.8 ^a	161.0–161.9 ^a
8	117.7	117.1	117	116.7
9	129.7	129.8	129.6	129.6
10	135.4	135.7	135.4 ^a	135.6 ^a
11	129.7	129.8	129.6	129.6
12	117.7	117.1	117	116.7
13	42.4	42.5	42.5 ^a	42.3 ^a
14	30.9	30.7	30.9	30.5
15			101.3	105.1 ^a
16			99.7	74.3
17				27.8
18			-0.4 ^a	30.4

^a multiplet.

A: PSf; B: brominated PSf; C: alkynylated PSf.

The mixture was heated until dissolution of brominated PSf and nitrogen was bubbled through the mixture for 1 h. Under nitrogen, 142 mg (0.2 mmol) of bis(triphenylphosphine) palladium (II) chloride, 19 g of cuprous (I) iodide, 3 mL of triethylamine and 1.66 mL (12 mmol) of trimethylsilylacetylene were added, then the reaction mixture was heated at 100°C for 4 h.

Alkynylated polymer was precipitated by pouring it into 2 L of water, washed with methanol, and purified by dissolution in chloroform and reprecipitation in methanol and finally dried 24 h at 80°C under vacuum. The same procedure was used in experiments with *tert*-butylacetylene but the reactions in this case were carried out in a sealed tube. The polymers with different degree of alkynylation, listed in Table I, were obtained varying the molar ratio between alkyne and brominated PSf.

Techniques

200 MHz ^1H and ^{13}C -NMR spectra were recorded from CDCl_3 solutions on a Bruker AC200 spectrometer. FT-IR spectra were recorded from

KBr pellets on a Perkin-Elmer 1760 spectrophotometer.

Differential scanning calorimetry (DSC) were performed with a Perkin-Elmer DSC7 at a heating and cooling rate of 10°C/min under nitrogen. A GPC instrument model 440 Waters was equipped with six Ultrastayragel columns with porosities of 10^6 , 10^5 , 10^4 , 10^3 , $5 \cdot 10^2$, 10^2 Å, and it was run at 25°C with CHCl_3 as a solvent. The set of columns was calibrated by polystyrene standards.

Gas permeability coefficients were obtained by measuring the steady flux of pure gas through 50 μm (ca.) thick dense films cast from CHCl_3 solution, using a LYSSY GPM 200 apparatus at 35°C, where the feed is kept at atmospheric pressure and the permeate accumulates in a He-filled circuit, whose composition is regularly detected by a Varian 3400 Gas Chromatograph.

The same equipment was employed in order to measure gas permeation of flat asymmetric membranes, prepared by means of a phase inversion technique, coagulating in water a 32% w/w polymer solution in formyl piperidine. Mass density of films was measured at 23°C using a density gradient column filled with an aqueous solution of sodium bromide, calibrated to ± 0.0004 g/cm³.

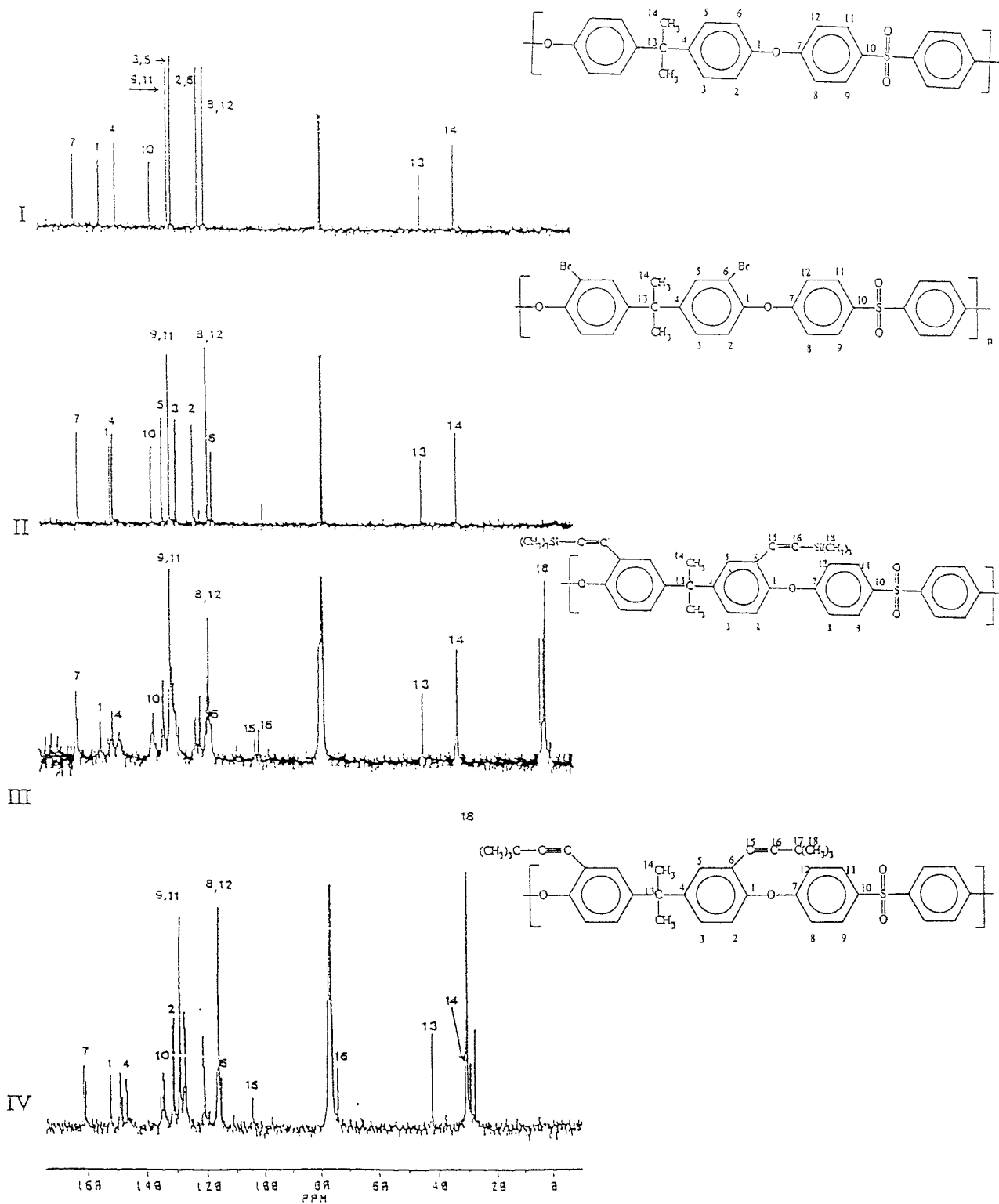


Figure 3 Comparative ^{13}C -NMR spectra of PSf (I), brominated PSf (II), and alkynylated PSf (III) (IV).

RESULTS AND DISCUSSION

The bromination-alkynylation process offers a new modification way to introduce pendant ethynyl groups, starting from commercial polysulfone (Fig. 1).

As reported in the literature, under proper reaction conditions, bromination of PSf is an electrophilic, regiospecific substitution, that does not require any catalyst, bromine attaches selectively the ortho positions to the aryl ether linkage in the bisphenol portion of the repeating unit, activated by the oxygen atoms.

On the other hand, the ortho-ether position in the phenylsulfone portion is unreactive to the bromination reaction, due to the influence of the sulfone group. Depending of the molar ratio between bromine and PSf, the degree of bromination can be varied as shown in Table I.

The bromination degree of our polymers ranged between 50 to 98%. The ratio between the well separated signals in $^1\text{H-NMR}$ spectra (Fig. 2) relative to aromatic hydrogens in brominated bisphenolic units (7.5 ppm) and aromatic hydrogens in unsubstituted sulfone unit of PSf (7.82 ppm) gives the degree of bromination (D_{Br}), according to the following relationship:

$$D_{\text{Br}} = \frac{A_{7.5}}{A_{7.82}},$$

where $A_{7.5}$ = integral of protons H_5 at 7.5 ppm and $A_{7.82}$ = integral of protons $\text{H}_9, \text{H}_{11}$ at 7.82 ppm.

Brominated PSf was subsequently alkynylated with trimethylsilylacetylene or *tert*-butylacetylene employing the C—C coupling reaction. An aryl-alkynyl coupling can be obtained in high yield by reaction of monosubstituted acetylenes with aromatic halide, in the presence of copper (I) iodide, a base, and a palladium salt as a catalyst.

Here, the catalytic-active specie tetrakis(triphenylphosphine) palladium (0) was formed *in situ*⁷ starting from a mixture of copper (I) iodide and bis(triphenylphosphine) palladium (II) chloride.

Again, the degree of substitution (D_{alkyn}) can be determined by the analysis of $^1\text{H-NMR}$ spectra (Fig. 2), and it was calculated using the relative areas of the $-\text{Si}(\text{CH}_3)_3$, or $-\text{C}(\text{CH}_3)_3$, and aromatic H_9 and H_{11} resonances as below:

$$D_{\text{alkyn}} = \frac{A_x/9}{A_{7.82}/2}$$

where A_x = integral of methyl protons $\text{R}-(\text{CH}_3)_3$ at 0.3 ppm for $\text{R}=\text{Si}$ or integral of methyl protons at 1.0 ppm for $\text{R}=\text{C}$; $A_{7.82}$ = integral of protons $\text{H}_9, \text{H}_{11}$ at 7.82 ppm.

Depending on the molar ratio between alkyne and brominated PSf, the substitution degree was in the range of 92–47% for $\text{R} = \text{Si}$ and 77–45% for $\text{R} = \text{C}$.

The $^{13}\text{C-NMR}$ spectra support the $^1\text{H-NMR}$ results. $^{13}\text{C-NMR}$ assignments, listed in Table II, confirm the structure of all products. Figure 3 represents some typical spectra of unmodified PSf and modified PSf samples.

Comparing the spectrum of brominated PSf with unmodified PSf it is clear that the substitution on C_6 gives rise to a minimal change in the chemical shift of the carbons in the sulfonic portion of molecular repeating unit; on the contrary, the chemical shift of the carbons in the bisphenolic portion are clearly influenced. In particular, the signals of C_2 and C_6 , which are magnetically equivalent in unmodified PSf, are split in a characteristic doublet in disubstituted copolymers; this is evidence for aromatic substitution ortho to the ether linkage on the bisphenolic portion. Other isomers are not evident.

As far as alkynylated PSf is concerned, the signals at 0 ppm in spectra III are related to methyl groups in $-\text{Si}(\text{CH}_3)_3$. The peaks at 99.7 and 101.3 are due to C_{15} and C_{16} quaternary carbons in the $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$. The signals at 115.7 and 116.4 ppm are related to the C_6 aromatic-substituted carbon. In spectrum IV, the quaternary carbons due to the triple bond of $-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3$ group, give signals at 74.3 and 105.1 ppm: the signals at 30.4 and 115.6 ppm are respectively due to the CH_3 in the *tert*-butyl group and to C_6 aromatic substituted carbon.

The FT-IR spectra, reported in Figure 4, support the NMR results. Spectrum III of Figure 3 shows a very strong and sharp absorption band, at 2150 cm^{-1} due to $-\text{C}\equiv\text{C}-\text{Si}$ stretching. The absence of absorptions at 3300 cm^{-1} due to the terminal $-\text{C}\equiv\text{CH}$ groups in acetylenic reagents, is a evidence of alkynylation on polymer backbone. The $-\text{C}\equiv\text{C}-\text{C}$ group gives rise to a less pronounced band at 2200 cm^{-1} visible in spectrum IV. Other typical absorption is present at 840 cm^{-1} ($\text{Si}-\text{CH}_3$ symmetry deformation).

Thermal Analysis

T_g values reported in Table III for brominated PSf show that the bromination lowers the T_g of un-

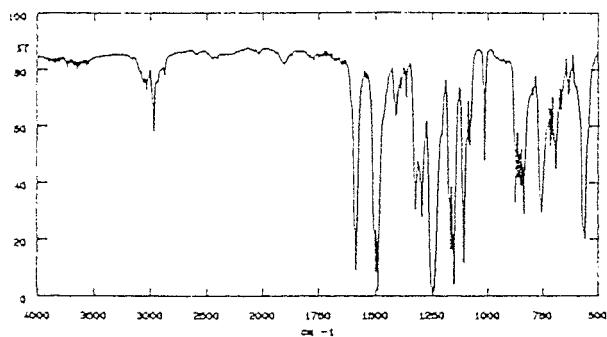
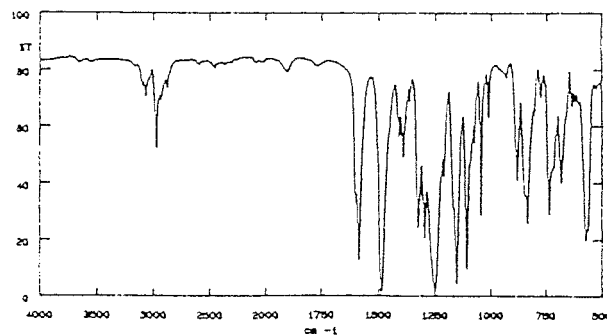
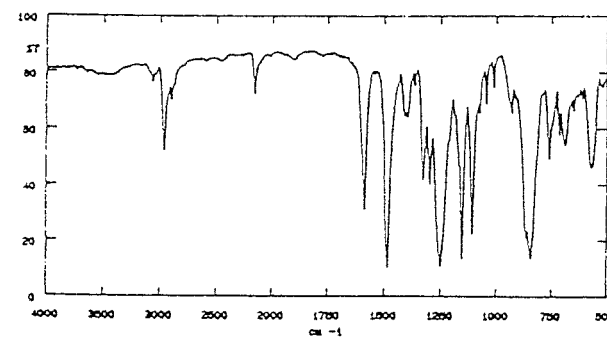
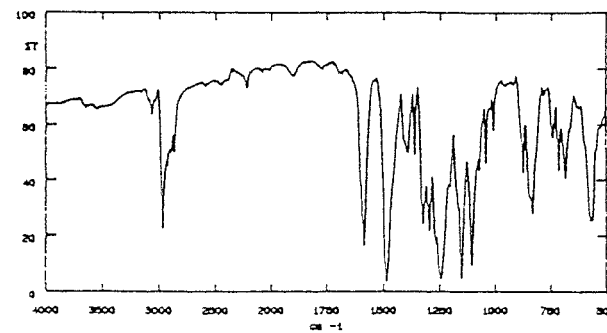
PSf
IPSf-Br
IIPSf-C≡C-Si(CH₃)₃
IIIPSf-C≡C-C(CH₃)₃
IV

Figure 4 Comparative FT-IR spectra of PSf (I), brominated PSf (II), and alkyne-substituted PSf (III) (IV).

Table III Glass Transition Temperatures and Molecular Weight of Modified PSf

Polymer	R	Composition (mol %)			Molecular Weight	
		R	H	T_g (°C)	M_w	M_n
PSf	H	0	0	200	63,000	29,500
1	—C≡C—Si(CH ₃) ₃	92	6	^a	56,000	21,500
2	—C≡C—Si(CH ₃) ₃	47	3	^a		
3	—C≡C—C(CH ₃) ₃	77	21	^a	70,500	30,000
4	—C≡C—C(CH ₃) ₃	45	4	^a		
5	H	0	98	185	57,000	31,000
6	H	0	50	187		

^a Not clearly measurable because of the presence of exothermal transition.

modified PSf, this effect could be due to an increase of intermolecular packing distance not counterbalanced by the increase in backbone rigidity.

The T_g of alkynylated copolymers are not clearly measurable because of the presence of an exothermal transition, probably due to crosslinking reactions of triple bonds; in fact, after these thermal treatments, the solubility of polymers clearly decrease.

Further investigations would be necessary to clarify the nature of these reactions and the possibility to obtain cured materials with improved solvent resistance for different applications.

Gas Permeation Properties

Gas transport properties of polysulfones obtained by condensation of a bisphenol and a dihalogenated diphenylsulfone have been extensively investigated. The effects of chemical modifications of bisphenol monomer on polymer structure, and hence, on gas transport, were so compared: methyl groups on bisphenol rings,^{11,12} bisphenol connecting groups,¹³ and nitro groups on bisphenol rings,¹⁴ the latter being obtained by nitration of PSf. As far as we know, no gas transport properties of brominated polysulfones are reported in the literature, differently from other polymers such as polyphenylene oxide (PPO)^{15,16} and polycarbonates.¹⁷

Gas permeabilities of alkynylated polysulfones and of their brominated intermediates are reported in Table IV. A comparison among gas transport properties of derivatives studied in the present article and those of derivatives reported

by literature^{11–14} has been performed in terms of fractional free volume (FFV).

The free volume of a polymer can be obtained from mass density measurements by subtracting a calculated occupied volume, V_0 , from the specific volume, V . The specific free volume (SFV) and FFV are given by

$$\text{SFV} = V - V_0 \quad \text{FFV} = (V - V_0)/V$$

The group contribution method¹⁸ has been used to calculate the Van der Waals volume (V_w) of the polymer, closely related to V_0 by the following expression.¹⁹

$$V_0 = 1.3V_w$$

V_w for a large number of molecular moieties have been tabulated,^{18,20} so that V_w can be easily calculated.

In this case, V_w of each repeat unit of modified PSf (brominated, alkynylated, and unmodified) has been first separately calculated and then combined according to their molar fractions in order to obtain molar V_w . Volumetric properties of modified PSf (V , SFV, and FFV) are reported in Table V.

The plot in Figure 5 summarizes CO₂ permeabilities (P_{CO_2}) of polysulfones with different bisphenol moieties obtained from both polymerization of modified bisphenols^{11–13} and chemical modification of bisphenol A based polysulfone (ref. 14; present work), as a function of FFV. The straight line represents the correlation between P_{CO_2} and FFV as calculated by Mac Hattie et al.¹² in the former group of derivatives, while the data

Table IV Permeability to Gases of Modified PSf

Polymer	R	Composition (mol %)		Permeability (Barrer) ^a				Selectivity	
		R	Br	CO ₂	CH ₄	O ₂	N ₂	CO ₂ /CH ₄	O ₂ /N ₂
PSf	H	0	0	5.7	0.26	1	0.21	21.9	5
1	—C≡C—Si(CH ₃) ₃	92	6	36.5	3.1	8.4	2.1	11.8	4
2	—C≡C—Si(CH ₃) ₃	47	3	18.5	1.22	3.76	1.24	15.1	3
3	—C≡C—C(CH ₃) ₃	77	21	28.2	2.6	6.5	1.7	10.8	3.8
4	—C≡C—C(CH ₃) ₃	45	5	16.4	1	3.3	0.9	16.4	3.7
5	H	0	98	14.2	1.3	2.9	1.3	11.3	2.2
6	H	0	50	5.5	0.8	1.7	0.95	6.8	1.8

$$^a 1 \text{ barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

related to modified PSf's are clearly more scattered.

As a rule, symmetric tetrasubstitution of ortho hydrogens with methyl groups in bisphenol A results in a high degree of chain stiffness, meaning higher FFV and gas permeability with respect to unmodified PSf. On the contrary, asymmetric disubstitution (one methyl group for each bisphenol ring) leads to highly packed chains, with lower FFV and gas permeability than PSf.

Chemical modification of PSf leads to asymmetric bisphenol substitution: nitration does not affect more than one ring¹⁴ while bromination, and alkynylation as a consequence, results in the functionalization of one position for each ring.² Such an asymmetry can contribute to explain the poor FFV and permeabilities of nitrated PSf, in addition to the polarity of —NO₂ group. Moreover, randomness of partial chemical modification is

probably a cause of the scattering shown by modified PSf in Figure 5.

Gas permeability of brominated PSf is to be considered overestimated, because dense films obtained from such derivatives were very brittle as pointed out by the low selectivities measured on them (Table IV). In any case, their relatively low FFV (and permeability) is well explained in terms of asymmetric substitution: Br and CH₃ have almost the same V_w , 14.6 and 13.67 cm³/mol, respectively.¹⁸

Apart of scattering, alkynylated polysulfones, bearing either —Si(CH₃)₃ or —C(CH₃)₃ groups, show both higher FFV and permeability (up to six times) than unmodified PSf: molecular structure (Table III) states that a bisphenol moiety bears about 1 to 2 R—C≡C groups (an average of 0.5 to 1 for each aromatic ring): a very asymmetric and random substitution. Nevertheless, the rigid,

Table V Volumetric Properties of Modified PSf

Polymer	R	Composition (mol %)		V cm ³ /g	SFV cm ³ /g	FFV
		R	H			
PSf	H	0	0	0.802	0.124	0.155
1	—C≡C—Si(CH ₃) ₃	92	6	0.896	0.15	0.167
2	—C≡C—Si(CH ₃) ₃	47	3	0.864	0.145	0.168
3	—C≡C—C(CH ₃) ₃	77	21	0.837	0.135	0.162
4	—C≡C—C(CH ₃) ₃	45	5	0.861	0.157	0.182
5	H	0	98	0.66	0.108	0.164
6	H	0	50	0.718	0.114	0.158

V = specific volume.

SFV = specific free volume.

FFV = fractional free volume.

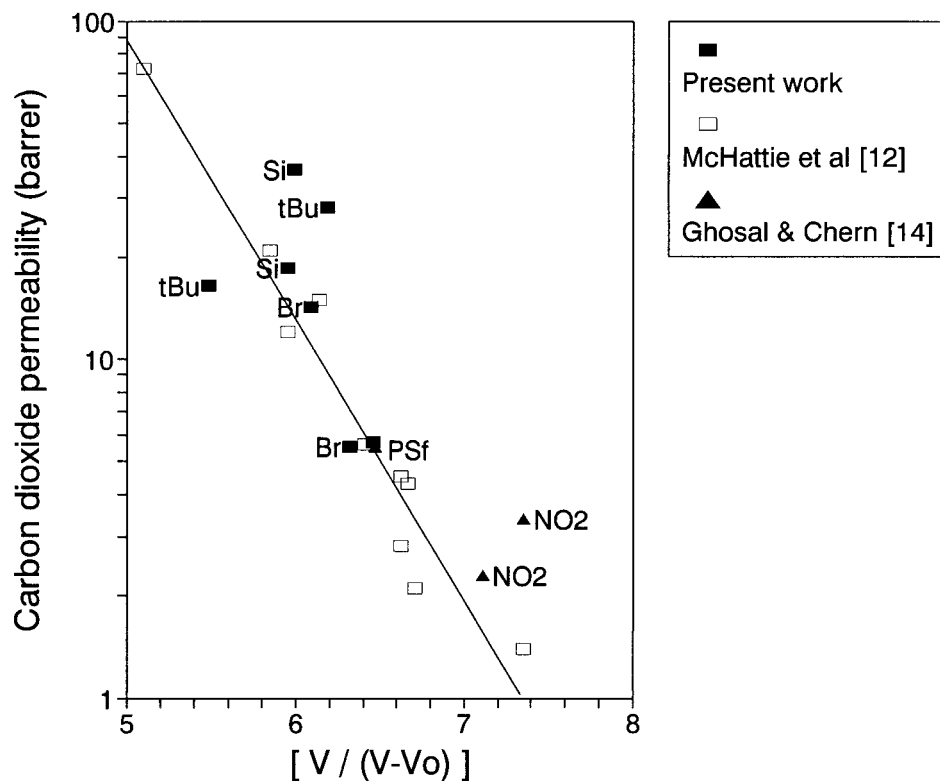


Figure 5 Comparison of CO₂ permeability coefficient dependence on fractional free volume for different polysulfones. Polysulfones of this work: PSf = unmodified polysulfone; Br = brominated intermediates; Si = $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$ containing derivatives; tBu = $-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3$ containing derivatives.

linear and cylindrical shaped $\text{R}-\text{C}\equiv\text{C}$ group is effective in preventing a close packing of polymer chains at a comparable extent as a symmetric tetramethyl substituted PSf.¹¹ Poor permselectivity of alkynylated polysulfones has to be related to randomness of substituted repeat units along the polymer chain, causing a very broad distribution of free volume in the structure. This behavior confirms again that the chemical modification of existing polymers is not effective in improving selectivity and permeability at the same time.²¹

Formability of asymmetric membrane by coagulation in water has been proved on derivative 1, the most permeable. The polymer is freely soluble in formyl piperidine, at least up to 32% w/w, typical concentration for obtaining gas separating membrane. After phase inversion of the above solution in a water bath, a 108 μm thick asymmetric membrane has been recovered. Its permeation properties (P/l) are reported on Table VI, compared to permeability coefficients (P) of parent polymer. From the $P/(P/l)$ ratio a skin thickness (l) about 1 μm can be calculated.

CONCLUSIONS

According to the literature, commercial polysulfone was brominated at room temperature and no catalyst. NMR spectroscopy showed that two

Table VI Gas Permeation of Asymmetric Membrane Made of Modified PSf (Derivative 1)

Gas	Permeance, P/l (GPU) ^a	Permeability, P (Barrer) ^b
CO ₂	37.5	36.5
CH ₄	3.5	3.1
O ₂	11.8	8.4
N ₂	2.9	2.1
Selectivity		
CO ₂ /CH ₄	10.7	11.2
O ₂ /N ₂	4.1	4

$$^a 1 \text{ GPU (Gas permeation unit)} = 10^{-6} \frac{\text{cm}^3 (\text{STP})}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

$$^b 1 \text{ barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

bromine atoms per repeat unit substituted exclusively on the ortho position to the ether linkage of the bisphenol portion. The brominated polymers were subsequently alkynylated by displacement of bromine with substituted acetylenes, using a palladium catalyst. This pathway leads to a series of new copolymers containing up to 90% of pendant unsubstituted ethynyl groups.

Although the separation factors decrease, the new materials show improved gas permeation properties, up to six times greater than unmodified PSF.

These results demonstrate that the reaction reported here represents a powerful preparative method for the controlled introduction of different kinds of substituents in aromatic polymers starting from easily available polymeric precursor, as an alternative to the synthesis and polymerization of specialty monomers. The capability to control the type and the degree of substitution could provide a method for designing materials for a wide range of applications.

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