

## Sulfonated Polysulfone

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### Synopsis

Polysulfone has been sulfonated to varying degrees using a sulfur trioxide-triethyl phosphate complex as the sulfonating agent. These conditions are suitable for surface sulfonation as well as solution sulfonation. The neutralized, sodium salt form is much more stable than the free acid form. The glass transition temperature of polysulfone is increased by as much as 130°C (i.e., to 310°C) by the introduction of  $-\text{SO}_3\text{Na}$  groups. Sulfonation also causes a major shift in the low-temperature ( $-100^\circ\text{C}$ ) transition of polysulfone. Compositions of intermediate degree of sulfonation, containing 0.5  $-\text{SO}_3\text{Na}$  groups per polysulfone repeat unit, are melt processable. This composition also displays the best balance of properties. Water absorption, which exerts a large influence on mechanical properties, ranges from 1% to 61%, depending upon degree of sulfonation and sorption conditions. Water absorption and desorption curves show non-Fickian behavior. Compositions of intermediate degree of sulfonation display optimum reverse osmosis desalination behavior. Gas permeability is significantly reduced by sulfonation. Overall behavior is consistent with an ionomer-type structure.

### INTRODUCTION

Sulfonation is a powerful and versatile polymer modification tool. Sulfur trioxide is a very reactive, inexpensive sulfonating agent. Its reactivity can be controlled over a wide range by the use of various complexing ligands. Sulfonated polymers can be prepared in the form of the free acid ( $-\text{SO}_3\text{H}$ ), a salt (e.g.,  $-\text{SO}_3^-\text{Na}^+$ ) or an ester ( $-\text{SO}_3\text{R}$ ).<sup>1</sup> The degree of sulfonation can be high or low, as desired. The polymers can be sulfonated before fabrication, or the fabricated article (e.g., film, fiber, molding, etc.) can be sulfonated in its final form, either uniformly or on the surface only.

Many homopolymers, random copolymers, and block and graft copolymers containing aromatic rings or double bonds can be sulfonated. For example, extensive sulfonation of polystyrene yields water-soluble polymers useful as thickeners and flocculants, and sulfonation of styrene-divinylbenzene random copolymers yields ion exchange resins.<sup>2</sup> Sulfonation improves the dyeability of propylene-styrene copolymer fibers.<sup>3</sup> Sulfonated poly(phenylene oxide) is claimed to be useful as an ion exchange resin and as a reverse osmosis membrane.<sup>4-7</sup> The sodium salt of sulfonated butyl rubber is reportedly stronger than the unsulfonated polymer.<sup>8,9</sup> Sulfonation of the center block of styrene-isoprene-styrene block copolymers yields piezodialysis membranes and biomedical polymers, and sulfonation of the styrene segments of these block copolymers, after hydrogenation of the center block, is claimed to

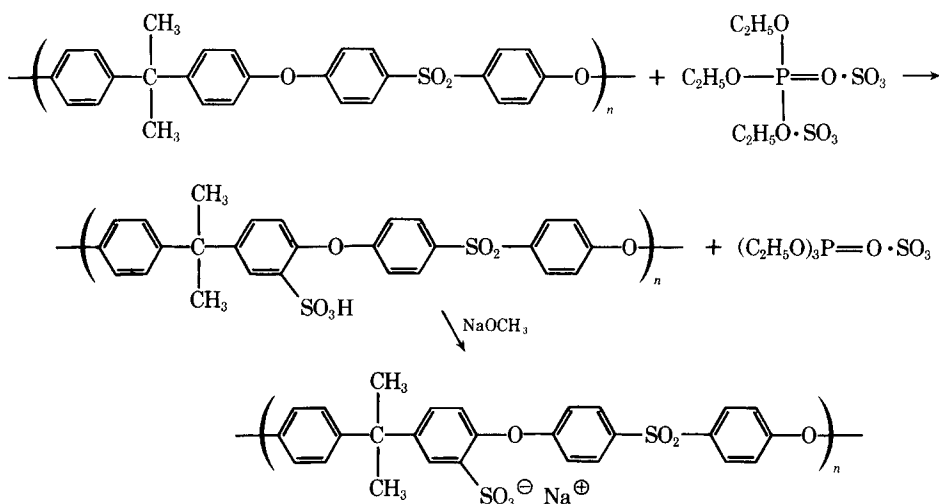
produce nonbrittle ion exchange resins.<sup>10-12</sup> Sulfonated polycarbonates, polyesters, and polyimides are also mentioned in the literature.<sup>13-15</sup>

Polysulfone is a high-performance, tough, high-temperature-resistant thermoplastic resin. As such, it is an excellent candidate for chemical modification by sulfonation. Sulfonated polysulfone membranes have been reported to be useful in desalination applications.<sup>16,17</sup> This paper describes the controlled sulfonation of polysulfone with a sulfur trioxide-triethylphosphate complex, and the effect which this modification exerts on thermal transitional behavior, melt processability, hydrophilicity, mechanical properties, and permeability properties.

## DISCUSSION

### Synthesis

Polysulfone was sulfonated at room temperature in 1,2-dichloroethane solution using a 2/1 sulfur trioxide/triethyl phosphate complex ( $\text{SO}_3/\text{TEP}$ ) as the sulfonating agent. The resulting polysulfone sulfonic acid was neutralized with sodium methoxide to produce the sodium salt:



Compositions ranging from low to high degrees of sulfonation, i.e., 0.1–1.0  $\text{SO}_3\text{Na}$  groups per polysulfone repeat unit, were synthesized by varying the  $\text{SO}_3/\text{polysulfone}$  ratio.

$\text{SO}_3/\text{TEP}$  was used as the sulfonating complex since the high reactivity of the  $\text{SO}_3$  can be conveniently controlled by varying the  $\text{SO}_3/\text{TEP}$  ratio and since this complex minimizes crosslinking due to sulfone-forming side reactions.<sup>18</sup> In a 1/1  $\text{SO}_3/\text{TEP}$  complex, the  $\text{SO}_3$  is relatively strongly bonded to the phosphoryl oxygen of the TEP. As a result, polysulfone was not extensively sulfonated by a 1/1 complex at room temperature, and refluxing did not increase the degree of sulfonation appreciably (see Table I). Sulfonation was very facile at room temperature with a 2/1  $\text{SO}_3/\text{TEP}$  complex due to the relatively weak bonding of the second mole of  $\text{SO}_3$  with one of the TEP ester oxygens. Higher reactivity can be attained by using 3/1 or 4/1 complexes,

TABLE I  
Effect of Reaction Conditions on Degree of Sulfonation

Reactant mole ratio (SO <sub>3</sub> /TEP/PSF)	Reaction temp.	Degree <sup>b</sup> of sulfonation (-SO <sub>3</sub> <sup>-</sup> /PSF) <sup>a</sup>				
		% Sulfur found <sup>a</sup>		Target	Found in	
		Free acid	Na salt		Free acid	Na salt
1/1/1	ambient	7.9	9.5	1.00	0.12	0.45
1/1/1	reflux	8.9	9.8	1.00	0.30	0.52
2/1/1	ambient	11.9	11.7	1.00	0.90	1.00
1/0.5/1	ambient	9.3	9.3	0.50	0.38	0.40
0.2/0.1/1	ambient	7.9	8.4	0.10	0.12	0.20
Unmodified PSF	—		7.2	—	—	—

<sup>a</sup> The free acid values are more indicative of degree of sulfonation than are the Na salt values. The consistently higher sulfur contents of the salt forms are probably due to the presence of sulfur-containing contaminants arising from reaction of excess SO<sub>3</sub>/TEP with isopropanol and/or NaOCH<sub>3</sub> during the neutralization step.

<sup>b</sup> Degree of sulfonation calculated from curves in Fig. 3.

and maximum reactivity is achieved with uncomplexed SO<sub>3</sub>. Complexing agents other than triethyl phosphate, e.g., dioxane, pyridine, etc., can undoubtedly also be used.<sup>22</sup>

The reaction of polysulfone with a 2/1 SO<sub>3</sub>/TEP complex at room temperature is essentially instantaneous. Simultaneous addition of 1,2-dichloroethane solutions of polysulfone and of SO<sub>3</sub>/TEP to a reaction flask with good agitation resulted in the precipitation of polysulfone sulfonic acid on contact. The product can be isolated as the free acid, but conversion to a neutral salt (e.g., with sodium methoxide) before isolation is preferred. The free acid can undergo crosslinking (via sulfone formation) and acid-catalyzed thermal degradation, but sulfonate salts display a high order of thermal stability. Neutralization was carried out by adding isopropanol to the reaction slurry to dissolve the polysulfone sulfonic acid, followed by the addition of excess methanolic sodium methoxide. The product, which precipitated upon neutralization, was filtered and water-washed to extract the SO<sub>3</sub>/TEP neutralization by-products. Lightly sulfonated products, which do not precipitate upon neutralization, were isolated by coagulation with isopropanol. An alternative isolation procedure used for some products (both high and low degrees of sulfonation) was to filter the polysulfone sulfonic acid slurry, wash with 1,2-dichloroethane, dissolve in dimethylformamide, neutralize, and coagulate the resulting solution with isopropanol. This procedure gives a cleaner, more uniform product and should allow recycling of the sulfonating complex.

The preceding discussion describes solution sulfonation to produce uniform sulfonation throughout the product. Sulfonation of the surface of polysulfone films or pellets can also be achieved. This was done by immersion of 5-mil polysulfone films in a room temperature bath of SO<sub>3</sub>/TEP in either cyclohexane or tetrachloroethylene. These diluents are nonsolvents for polysulfone but are compatible with the SO<sub>3</sub>/TEP sulfonation complex. Neutralization of the sulfonated surface was carried out by immersion of the film in methanolic sodium methoxide. Under these conditions, sulfonation occurred on the film surface only.

TABLE II  
Solubility<sup>a</sup> of Sulfonated Polysulfone at  $-\text{SO}_3^-/\text{PSF} = 1.0$

Solvent	Sulfonated PSF		Unmodified PSF
	Free acid	Na salt	
Dimethylformamide	S	S	S
Dimethylsulfoxide	S	S	swells
Methylpyrrolidone	S	S	S
Diethylene glycol monoethyl ether	S	S	—
Triethyl phosphate	S	swells	—
Dimethylacetamide	S	—	S
4/1 1,2-Dichloroethane/isopropanol	S	I	—
5/1 Dioxane/methyl ethyl ketone	S	I	—
Hexamethylphosphoramide	swells	I	S
Dioxane	swells	I	S
Methyl ethyl ketone	swells	I	I
Tetrahydrofuran	I	I	S
1,2-Dichloroethane	I	I	S
Dichloromethane	I	I	S
Chlorobenzene	I	I	S
Heptane	I	I	I
Nitromethane	I	—	—
Acetonitrile	I	—	I
Isopropanol	I	I	I
Methanol	I	I	I
H <sub>2</sub> O	I	I	I

<sup>a</sup> Solubility at ~10 wt-% at room temperature; S = soluble, I = insoluble.

### Characterization

The solubility characteristics of sulfonated polysulfone in the free acid and the sodium salt forms are shown in Table II for a composition containing 1.0  $-\text{SO}_3^-$  group per polysulfone repeat until (abbreviated by 1.0  $-\text{SO}_3^-/\text{PSF}$ ). The free acid is soluble in several organic solvent systems, but the sodium salt was found to be soluble only in polar solvents such as DMF, DMSO, methylpyrrolidone, and diethylene glycol monoethyl ether. DMF is a good solvent for the preparation of solution-cast films.

The effect of sulfonation and subsequent neutralization on the reduced viscosity of polysulfone, for a composition sulfonated to the extent of 0.3  $-\text{SO}_3^-/\text{PSF}$  is shown in Table III. The reduced viscosity was essentially the same for polysulfone, polysulfone sulfonic acid, and the sodium salt. This

TABLE III  
Effect of Form and of Molding Conditions on Reduced Viscosity<sup>a</sup>

	Unmodified polysulfone	Sulfonated polysulfone <sup>b</sup>	
		Free acid	Na salt
Initial	0.35	0.39	0.33
Molded at 250°C	—	0.13	0.23
Dried at 90°C, then molded at 275°C	—	—	0.32

<sup>a</sup> 0.2 g/dl in DMSO at 25°C.

<sup>b</sup>  $-\text{SO}_3^-/\text{PSF} = 0.3$ .

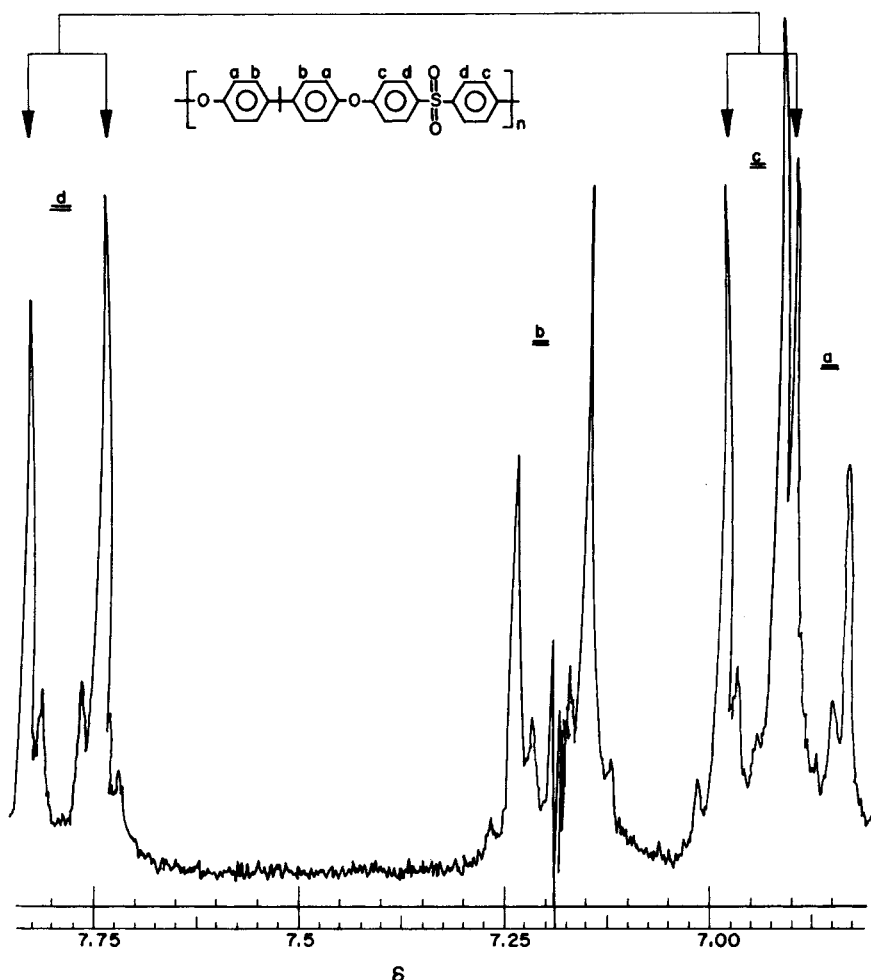
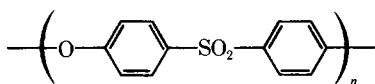


Fig. 1. NMR spectrum of unmodified polysulfone.

does not guarantee, of course, that there were no molecular weight changes during sulfonation, since the degree of chain extension in solution (due to repulsive effects) of the more polar sulfonated species differs from that of unmodified polysulfone, i.e., solution viscosity values are not directly comparable. However, the similarity of the R.V. values does suggest that there was no drastic degradation or crosslinking upon sulfonation, at least for this composition.

Nuclear magnetic resonance spectra for unmodified polysulfone and sodium sulfonated polysulfone (1.0  $-\text{SO}_3\text{Na}/\text{PSF}$ ) are shown in Figures 1 and 2. Analysis<sup>19</sup> of these spectra indicates that sulfonation occurs predominantly (>80%) in one position and that this position is in the bisphenol A portion of the repeat unit rather than in the deactivated sulfone portion. This latter conclusion is supported by the observation that bisphenol S polyether,



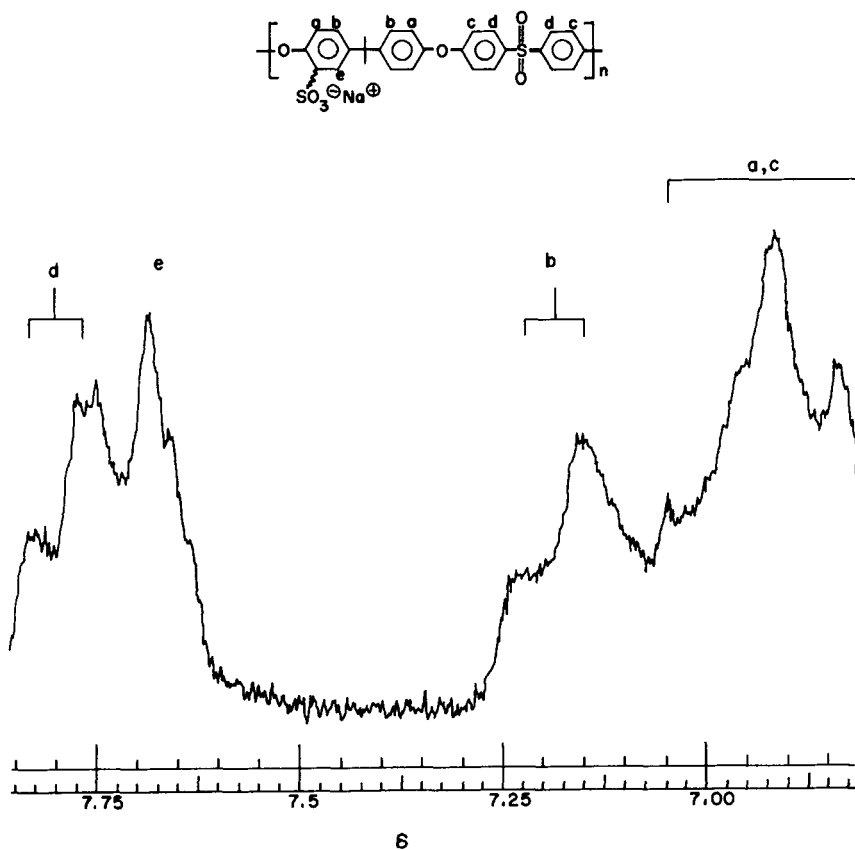


Fig. 2. NMR spectrum of sulfonated polysulfone ( $-\text{SO}_3\text{Na}/\text{PSF} = 1.0$ ).

did not undergo sulfonation under the conditions used to sulfonate polysulfone. It has been concluded, therefore, that sulfonation occurs in a bisphenol A aromatic ring at the position either ortho or meta to the ether bond. The ortho position is more probable based on electronic and steric considerations, and it is in this position that the sulfonate group has been placed in the synthesis equation shown above.

As was mentioned earlier, products were prepared with degrees of sulfonation ranging from 0.1 to 1.0  $-\text{SO}_3^-$  group per polysulfone repeat unit. Three methods were used to determine the degree of sulfonation: (a) elemental sul-

TABLE IV  
Characterization of Degree of Sulfonation  
( $-\text{SO}_3\text{Na}/\text{PSF}$  Repeat Unit)

Target	By sulfur analysis <sup>(a)</sup>	By ion exchange capacity <sup>(b)</sup>	By NMR <sup>(b)</sup>
1.00	0.90	1.15	1.01
0.50	0.38	0.56	0.57
0.10	0.12	0.14	—

(a) See Table I. (b) See Experimental section.

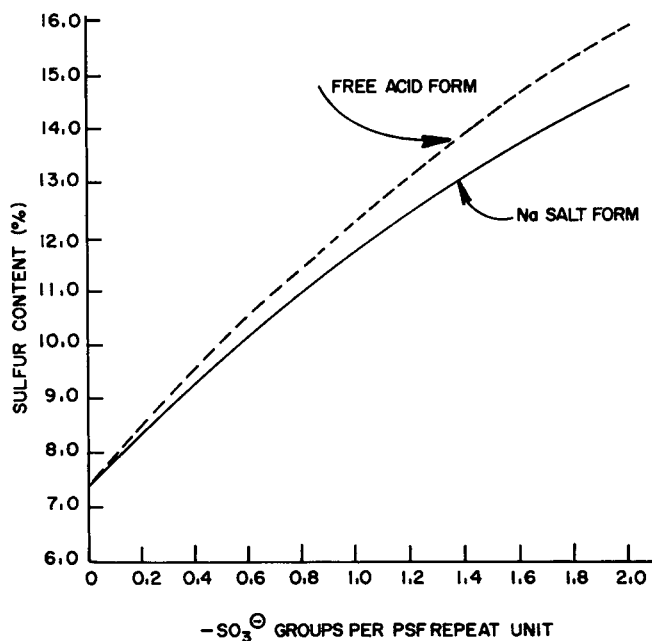


Fig. 3. Calculated relationship of sulfur content to degree of sulfonation.

fur analysis (using the calculated sulfur content vs degree of sulfonation relationships shown in Fig. 3); (b) ion exchange measurements (carried out by the method of Fisher and Kunin<sup>23</sup>); and (c) nuclear magnetic resonance measurements (via a technique<sup>19</sup> described in the experimental section). The compositions as determined by these techniques are in fairly good agreement, as can be seen from Table IV.

## Properties

### *Thermal Transition Behavior*

The introduction of  $-\text{SO}_3\text{Na}$  groups into polysulfone increases the glass transition temperature ( $T_g$ ), by as much as  $130^\circ\text{C}$ . This is probably due to increased intermolecular association through the polar ionic sites, i.e., an ionomer effect, and also to increased molecular bulkiness. The increase in  $T_g$  is proportional to the degree of sulfonation. This effect is illustrated by the mechanical loss curves shown in Figures 5–8 and is summarized in Figure 4 and Table V. Compositions containing 0.5 and 1.0  $-\text{SO}_3\text{Na}/\text{PSF}$  displayed  $T_g$  values of  $240^\circ\text{C}$  and  $300^\circ\text{C}$ , respectively, compared to  $180^\circ\text{C}$  for unmodified polysulfone. Secant modulus measurements (see Fig. 9) indicated an even higher  $T_g$ , i.e.,  $310^\circ\text{C}$ , for the 1.0  $-\text{SO}_3\text{Na}/\text{PSF}$  composition.

Not surprisingly, the unneutralized, free acid form ( $\text{SO}_3\text{H}$ ) displays a significantly lower  $T_g$  than the sodium salt form, e.g.,  $230^\circ\text{C}$  for a 1.0  $-\text{SO}_3\text{H}/\text{PSF}$  composition (see Fig. 10). This demonstrates the importance of ionic intermolecular interaction in increasing  $T_g$  via an ionomer effect similar to that which occurs in carboxyl-containing polymers.

TABLE V  
Effect of Sulfonation on Mechanical Properties<sup>a</sup>

Degree of sulfonation (-SO <sub>3</sub> Na/PSF)	Tensile modulus, psi		Tensile strength, psi		Elongation, %		Pendulum impact strength, ft-lb/in <sup>3</sup>	<i>T<sub>g</sub></i> , °C <sup>b</sup>
	Ambient	H <sub>2</sub> O immersed	Ambient	H <sub>2</sub> O immersed	Ambient	H <sub>2</sub> O immersed		
1.0	175,000	35,000	5,600	1,200	17	30	89	280-300 (310) <sup>c</sup>
0.5	232,000	157,000	9,100	5,600	25	98	—	240
0.3	280,000	—	9,000	—	8	—	—	195
0.1	297,000	266,000	10,000	8,200	7	14	110	180
0	360,000	—	10,200	—	50	—	150	180

<sup>a</sup> Determined on 10-mil films; 1.0 -SO<sub>3</sub>Na/PSF composition cast from DMF solution; other compositions compression molded at 275°C.

<sup>b</sup> *T<sub>g</sub>* values determined from mechanical loss-temperature measurements.

<sup>c</sup> 310° *T<sub>g</sub>* value determined from secant modulus-temperature measurements.



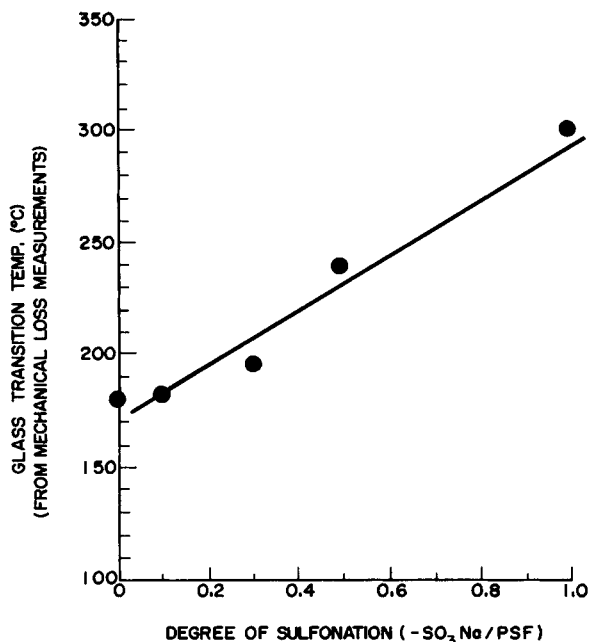


Fig. 4. Effect of degree of sulfonation on  $T_g$ .

$T_g$  is not affected by water sorption due to the  $T_g$  testing procedure used. Both wet and dry samples were examined at temperatures starting at  $-180^\circ\text{C}$  and increasing to  $>300^\circ\text{C}$ . Water diffuses from the samples during testing, especially between  $20^\circ\text{C}$  and  $100^\circ\text{C}$ , and virtually all the water is gone when the  $T_g$  temperature is reached. This results in a rise in modulus during the

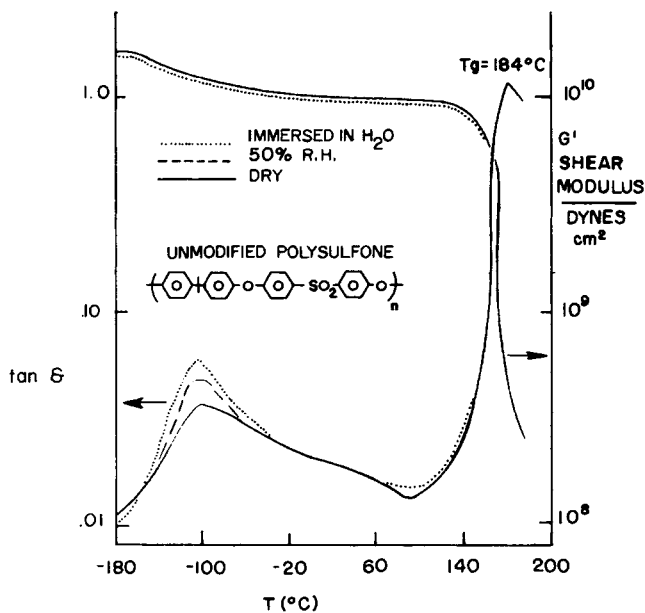


Fig. 5. Mechanical loss behavior of unmodified polysulfone.

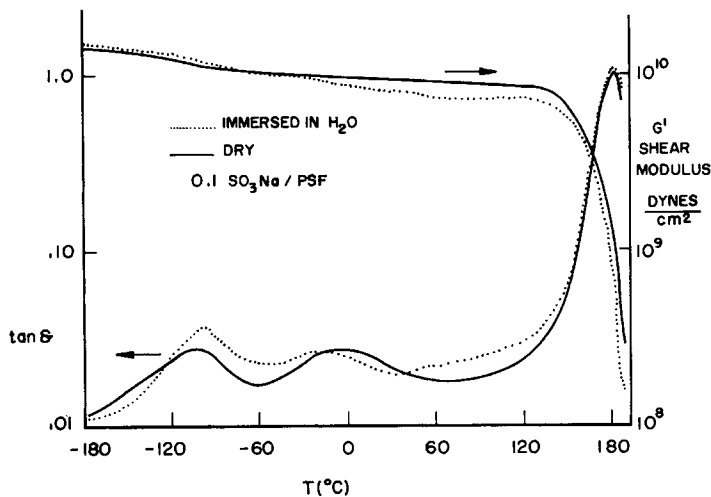


Fig. 6. Mechanical loss behavior of 0.1  $-\text{SO}_3\text{Na}/\text{PSF}$ .

test (see Figs. 9 and 11). The  $T_g$  values of wet samples were identical to those observed with predried specimens (see Figs. 5–8).

Polysulfone displays a low temperature secondary relaxation transition at  $-100^\circ\text{C}$ , which is enhanced in magnitude by water sorption (see Fig. 5). It has been proposed<sup>20</sup> that this transition in dry polysulfone is due to a relaxation attributed to the aryl ether group, and that water absorption results in complexing of water with the sulfone group which produces a relaxation peak that overlaps the aryl ether relaxation. The  $-100^\circ\text{C}$  transition is influenced significantly by sulfonation. The free acid form displays a  $-100^\circ\text{C}$  transition

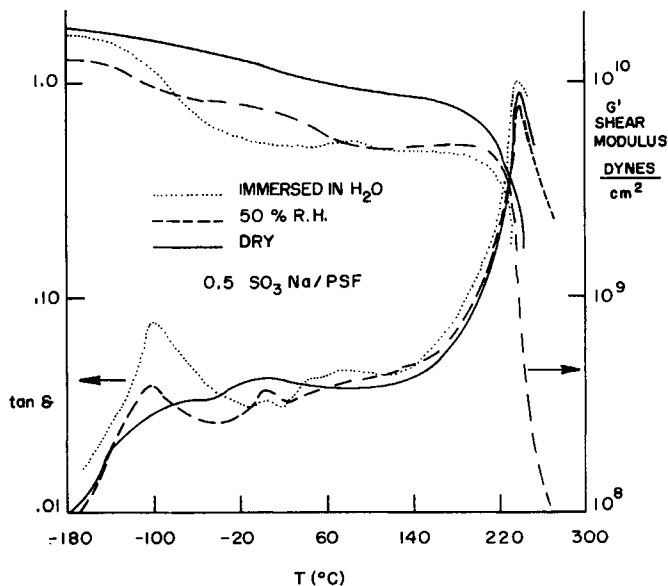


Fig. 7. Mechanical loss behavior of 0.5  $-\text{SO}_3\text{Na}/\text{PSF}$ .

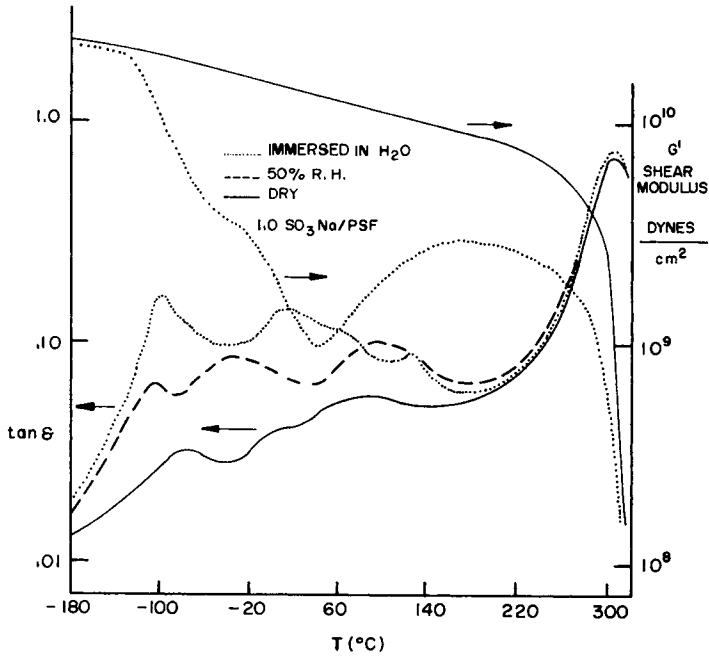


Fig. 8. Mechanical loss behavior of 1.0  $-\text{SO}_3\text{Na}/\text{PSF}$ .

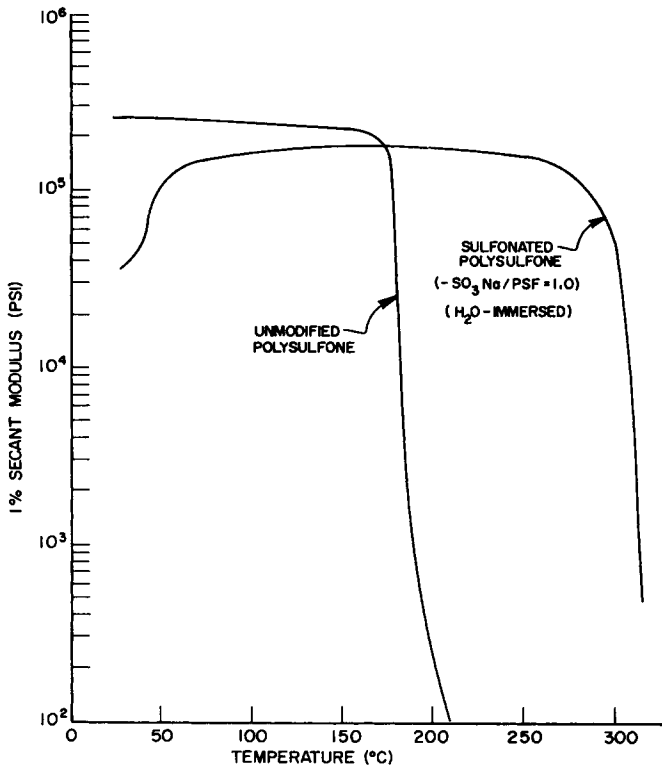


Fig. 9. Secant modulus-temperature relationships.

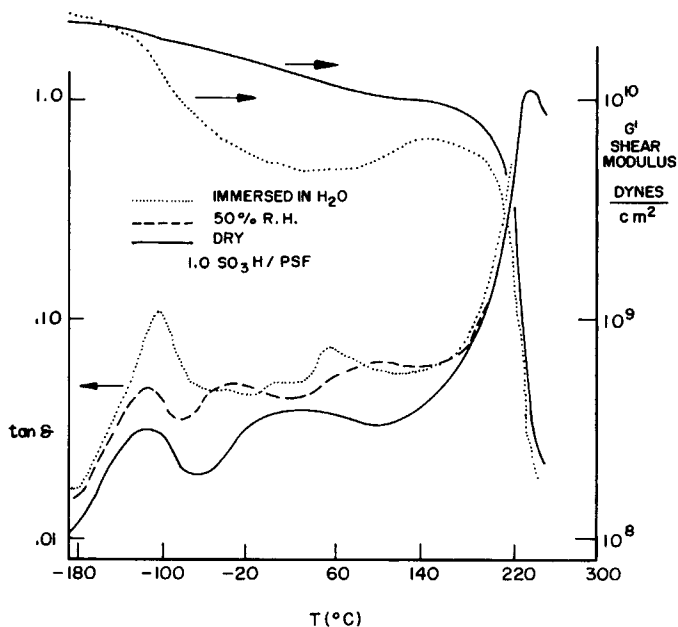


Fig. 10. Mechanical loss behavior of 1.0 —SO<sub>3</sub>H/PSF (acid form).

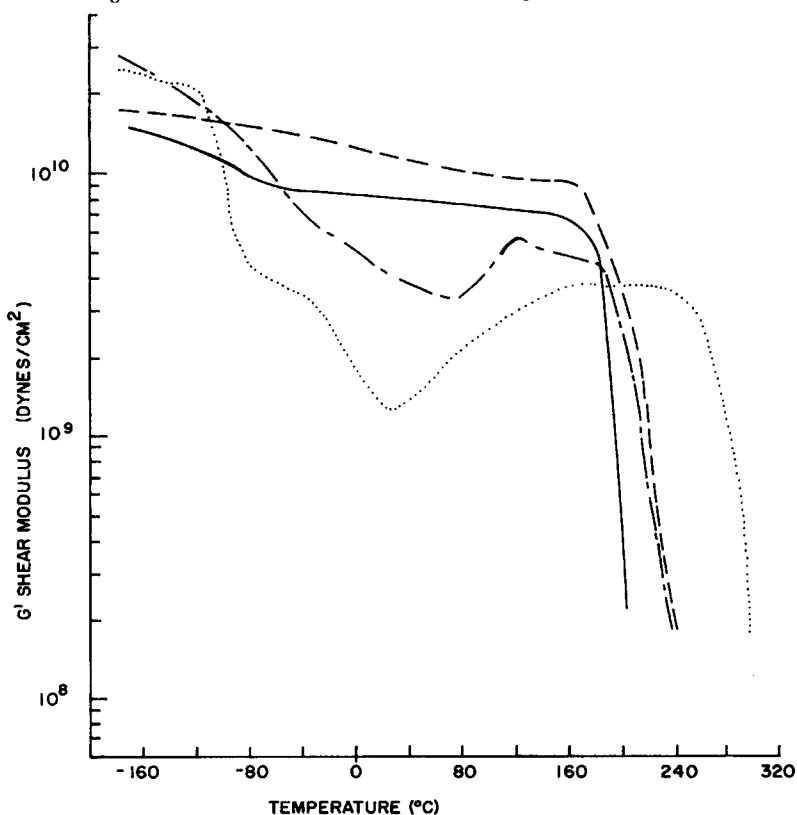


Fig. 11. Shear modulus-temperature relationships. (————) unmodified PSF; (---) 1.0 —SO<sub>3</sub>Na/PSF; molded; ambient; (-·-·-) 1.0 —SO<sub>3</sub>Na/PSF; molded; H<sub>2</sub>O-immersed; (·····) 1.0 —SO<sub>3</sub>Na/PSF; cast; H<sub>2</sub>O-immersed.

which is enhanced by water sorption to a much greater degree than is unmodified polysulfone (see Fig. 10). However, the sodium salt forms display different behavior (see Figs. 5–8). With dry samples, the  $-100^{\circ}\text{C}$  transition of these materials is significantly reduced in magnitude and shifted to higher temperatures, especially at the higher sulfonation levels. Upon exposure to water, however, the  $-100^{\circ}\text{C}$  transition is restored and enhanced in magnitude. This behavior can be explained based on the ionomer concept. The transitional shift to higher temperatures could be due to intermolecular “clustering” of the highly polar  $-\text{SO}_3\text{Na}$  groups which would increase the energy barrier which must be overcome to allow relaxation. Restoration of the  $-100^{\circ}\text{C}$  transition could be the result of dissociation of these clusters via water solvation of the  $-\text{SO}_3\text{Na}$  groups.

The sulfonated polysulfones also display some other small transitions, intermediate to the  $-100^{\circ}\text{C}$  relaxation and the  $T_g$ . However, the origin of these transitions is too complex to resolve within the scope of this investigation.

### Melt Processability

Compositions of low to medium degree of sulfonation in the sodium salt form were melt processable. Compression molding at  $275^{\circ}\text{C}$  gave good quality films for systems of 0.1–0.5  $-\text{SO}_3\text{Na}/\text{PSF}$ . The mechanical properties reported in Table V for these materials were measured on molded films. Reduced viscosity data (Table III) indicate that no extensive degradation occurred under these conditions if the polymer was dried before molding.

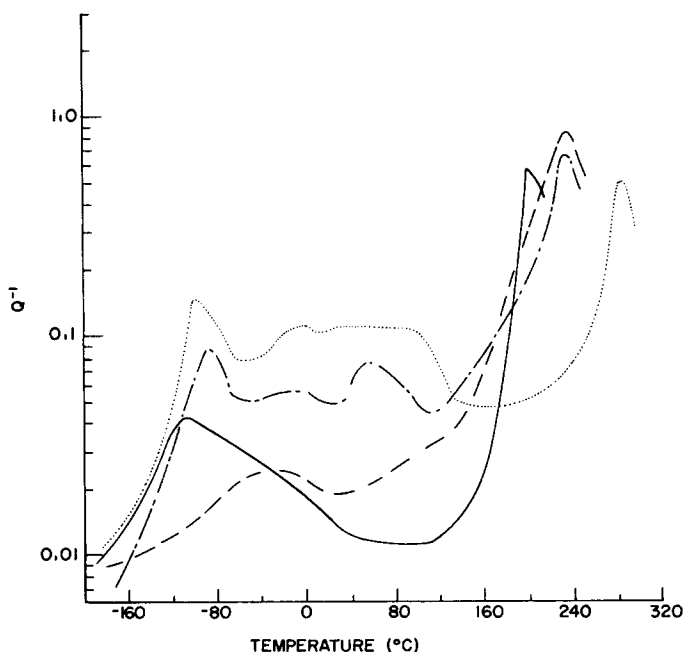


Fig. 12. Mechanical loss-temperature relationships: (.....) 1.0  $-\text{SO}_3\text{Na}/\text{PSF}$ ; cast;  $\text{H}_2\text{O}$ -immersed; (---) 1.0  $-\text{SO}_3\text{Na}/\text{PSF}$ ; molded;  $\text{H}_2\text{O}$ -immersed; (- - -) 1.0  $-\text{SO}_3\text{Na}/\text{PSF}$ ; molded; ambient; (————) unmodified PSF.

TABLE VI  
 Effect of Sulfonation on Hydrophilicity

Degree of sulfonation (—SO <sub>3</sub> Na/PSF)	Ion exchange capacity, <sup>a</sup> meq/g	Water sorption <sup>b</sup> (% weight increase)		Advancing <sup>b</sup> contact angle, °
		5 days ambient	1 day water immersion	
1.0	2.16	11.9	61.4	52
0.5	1.15	5.9	24.5	—
0.1	0.30	1.0	5.0	—
0 (PSF)	—	0.5	1.9	70
Surface sulfonation				
Na salt	—	—	—	62
Free acid	—	—	—	74

<sup>a</sup> See Experimental section.

<sup>b</sup> Measured on 10-mil film.

Some degradation was observed when the important drying step was omitted. Many condensation polymers, including unmodified polysulfone and the polycarbonates, require a drying step before melt processing.

Much poorer compression molding behavior was observed with free acid forms, regardless of degree of sulfonation, and with Na salt forms of highly sulfonated compositions. Attempts to mold free acid forms, even at lower temperatures (e.g.,  $\leq 250^\circ$ ), gave highly discolored, degraded films (Table III), probably due to acid-catalyzed degradation. The poor melt processability of highly sulfonated compositions in the salt form (1.0 —SO<sub>3</sub>Na/PSF) is primarily due to the high  $T_g$  of these materials which makes high molding temperatures necessary. Compression molding of such a material at 300°C yielded an incompletely fused, somewhat discolored film. The  $T_g$  of the molded film was lower than that of a cast film prepared from the same polymer (235°C vs. 280°C), indicating that some degradation had occurred during molding (see Figs. 11 and 12). Exhaustive NaOCH<sub>3</sub> treatment to ensure neutralization of the last traces of free acid should improve the melt processability of these systems by minimizing acid-catalyzed degradation.

### Hydrophilicity

The enhancement of hydrophilicity produced by the sulfonation of polysulfone is illustrated by the water-film contact angle data<sup>24</sup> shown in Table VI. Solution sulfonation to the extent of 1.0 SO<sub>3</sub>Na/PSF reduced the contact angle of polysulfone by  $\sim 20^\circ$ . A surface-sulfonated and subsequently neutralized film displayed an intermediate contact angle. Interestingly, a film which was surface sulfonated to the same extent, but not neutralized, displayed no reduction in contact angle, suggesting that "wettability" may be due mainly to the ionic nature of the sodium salt in these systems.

The ion exchange capacities of compositions ranging from 0.1 to 1.0 SO<sub>3</sub><sup>-</sup>/PSF were found to be 0.3 to 2.2 meq/g (see Table VI). The effect of degree of sulfonation over this range on hydrophilicity is illustrated by the water sorption behavior of cast films (see Table VI). Moisture pickup from the atmo-

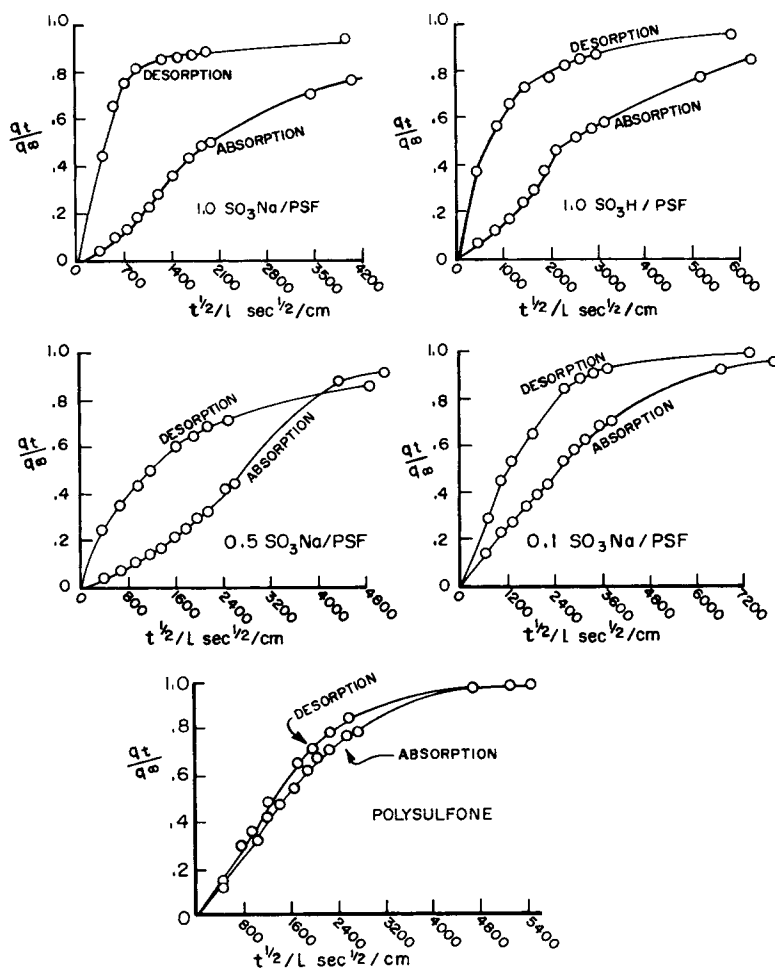


Fig. 13. Water sorption behavior.

sphere at ambient conditions ranged from 1% to 12%. Upon immersion in room temperature water for one day, the water pickup was 5% to 61% for these compositions.

Water absorption and desorption curves are shown in Figure 13. The data indicate non-Fickian behavior, similar to that reported for swelling agents in cellulose and polystyrene systems.<sup>25,26</sup> This behavior is typical and expected for materials which have glass transitions above the sorption testing temperature. The degree of non-Fickian behavior increases with increasing level of sulfonation.

### Mechanical Properties

The effects of degree of sulfonation and of water immersion on the room temperature mechanical properties of sodium sulfonated polysulfone are shown in Table V. The decreasing modulus with increasing degree of sulfonation is presumably due to the plasticizing effect of the water absorbed during ambient conditioning of the test films. Modulus was further reduced

TABLE VII  
Reverse Osmosis Water Desalination Membrane Tests<sup>a</sup>

Degree of sulfonation (—SO <sub>3</sub> Na/PSF)	% Water sorption	Permeate flux, gal-mil/ft <sup>2</sup> -day	% Salt rejection
1.0	61.4	1.00	0
0.5	24.5	0.14	95
0.1	5.0	0.009	—
0 (PSF)	1.9	<0.0001	—

<sup>a</sup> Tests carried out on dense 1-mil cast films; 0.1% NaCl at 1500 psig.

upon water immersion. Tensile strength decreased with increasing degree of sulfonation, and was reduced by water immersion. Elongation reached a maximum at 0.5 —SO<sub>3</sub>Na/PSF, and all compositions increased in elongation upon water immersion. Pendulum impact strength also was maximum at this intermediate degree of sulfonation and was unaffected by water immersion. The 0.5 —SO<sub>3</sub>Na/PSF composition displayed the most attractive overall combination of mechanical properties.

### Reverse Osmosis Desalination and Gas Permeability

The reverse osmosis technique for water desalination entails forcing a salt solution through a permselective membrane at pressures sufficiently high to overcome the osmotic forces which tend to drive water in the opposite direction. These membranes must allow water to permeate at a high rate but must reject permeation of the salt molecules to a high degree. The current state-of-the-art compositions are cellulose acetate asymmetric membranes. However, these membranes exhibit a reduction in permeation rate with time, due to creep-induced compaction, and are susceptible to chemical and biological degradation.

The excellent mechanical creep and stability properties of polysulfone recommend it highly for reverse osmosis membrane applications. However, the water permeability of unmodified polysulfone is very low. It was found that sulfonation dramatically increases the permeability of polysulfone and that salt rejection is high at intermediate degrees of sulfonation due to ionic repulsion effects.

Reverse osmosis desalination tests<sup>21</sup> were carried out on dense 1-mil films of sodium sulfonated polysulfone ranging in composition from 0.1 to 1.0 —SO<sub>3</sub>Na/PSF using a 0.1% NaCl feed at 1500 psig pressure (see Table VII). At 0.1 —SO<sub>3</sub>Na/PSF, the permeate flux was unacceptably low. At the other extreme, 1.0 —SO<sub>3</sub>Na/PSF, permeate flux was very high but zero salt rejection was observed due to the excessive hydrophilic nature of this composition. The intermediate composition, 0.5 —SO<sub>3</sub>Na/PSF, displayed a very attractive combination of high (95%) salt rejection and good permeate flux. It may be possible to increase salt rejection even further, to the desired 99.2% level, by minor variation in this intermediate range of sulfonation to "fine-tune" the system. The permeate flux was constant throughout the 120-hr test period, indicating that no compaction had taken place, and the film displayed a very low degree of swelling.



TABLE VIII  
Effect of Sulfonation on Gas Permeability

Degree of sulfonation ( $-\text{SO}_3\text{Na}/\text{PSF}$ )	Permeability, <sup>a</sup> cc-mil/100in <sup>2</sup> -24 hr-atm.					
	He	H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>
1.0	405	270	82	20	6	1
1.0 (acid form)	862	762	187	37	8	—
0.5	915	900	214	55	9	5
0.1	1200	1085	330	88	14	—
0	1800	1650	920	200	34	20

<sup>a</sup> Dry films cast from DMF solution.

The above test results were obtained with dense 1-mil films. In practice, desalination materials are used in the form of asymmetric membranes or hollow fibers in order to achieve thin membrane walls and high surface area, and thus maximum permeation rates. Sulfonated polysulfone is amenable to the solution techniques currently employed to prepare these structures. In addition, the melt processability of the salt form of intermediate degree of sulfonation compositions provides another optional fabrication technique. For example, hollow fibers could be produced by melt spinning as well as by solution spinning.

The surface sulfonation of polysulfone, as described earlier in the synthesis section, provides still another optional fabrication technique. Surface sulfonation of thin films or hollow fibers (inside, outside, or both) could produce useful desalination structures directly. Furthermore, surface sulfonation and neutralization, followed by extraction of the unsulfonated portion, could yield extremely thin structures which would be difficult or impossible to produce by normal casting techniques. For example, when the surface-sulfonated, neutralized 5-mil polysulfone film described earlier was immersed in methylene chloride (good solvent for PSF, nonsolvent for PSF  $-\text{SO}_3\text{Na}$ ) for 5 min, the center of the film dissolved, leaving intact the two "skins" of sodium sulfonated polysulfone. The "skins," which appeared to be tough, amounted to 0.5 wt.-% of the total film, and were estimated to be of the order of 0.01 mil in thickness. It should be possible to vary the skin thickness by changing the sulfonation diluent to achieve varying degrees of film swelling during sulfonation and therefore varying depth of sulfonation. This technique could be applied to films, solid fibers, or hollow fibers (inside, outside, or both).

Gas permeability data on dry films, cast from DMF solution, are presented in Table VIII. Sulfonation reduced permeability to all gases tested (He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>). The drop-off in permeability was proportional to the degree of sulfonation. Furthermore, permeability was significantly lower with the sodium salt form than with the free acid form. These observations are consistent with the expectation that permeability should be lower with systems which are tightly packed due to ionic intermolecular association.

## CONCLUSIONS

Sulfonated polysulfone has been synthesized using a 2/1 SO<sub>3</sub>/triethyl phosphate complex. Conditions have been defined (a) for thorough sulfonation in solution and for surface sulfonation only, (b) for extensive or slight sulfona-

tion, and (c) for isolation in the free acid form or in the neutral sodium salt form. The degree of sulfonation was characterized by sulfur content, ion exchange capacity, and NMR, with good agreement. The sulfonation site was found to be almost exclusively in the bisphenol A portion of the polysulfone repeat unit, most likely in the position ortho to the ether group.

The sodium salt form is much more stable and easily handled than the free acid form. Sodium salt forms of compositions of low to intermediate degree of sulfonation (0.1 to 0.5  $\text{—SO}_3\text{Na/PSF}$ ) are compression moldable. All compositions are soluble in polar solvents such as DMF and good quality films can be cast from these solutions. The  $T_g$  of polysulfone is dramatically increased, by as much as  $130^\circ\text{C}$ , by the introduction of  $\text{—SO}_3\text{Na}$  groups. Hydrophilicity, as determined by water sorption and contact angle measurements, can be varied over a wide range by controlling degree of sulfonation. Mechanical properties, before and after water immersion, are also dependent upon degree of sulfonation. The best combination of mechanical properties was displayed by the 0.5  $\text{—SO}_3\text{Na/PSF}$  system.

Compositions of intermediate degree of sulfonation display very promising reverse osmosis desalination properties, i.e., 95% salt rejection together with a good permeate flux level. Low and high degree of sulfonation compositions exhibited unsatisfactory desalination performance due to low permeate flux and low salt rejection, respectively. It may be possible to make very thin film and hollow fiber desalination structures via surface sulfonation followed by extraction of unsulfonated portions. Gas permeability is significantly reduced by sulfonation. The overall properties of sodium salt forms of sulfonated polysulfone are consistent with an ionomer-type structure.

## EXPERIMENTAL

The following is a typical sulfonation procedure for synthesizing a 1.0  $\text{—SO}_3\text{Na/PSF}$  composition in 1,2-dichloroethane solution using a  $\text{SO}_3/(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ /polysulfone repeat unit ratio of 2/1/1. Other degrees of sulfonation can be achieved by varying the ratio.

A 2/1  $\text{SO}_3/(\text{C}_2\text{H}_5\text{O})_3\text{PO}$  complex in 1,2-dichloroethane solution was prepared by adding 28.3 ml (54.2 g; 0.68 mole) of sulfur trioxide to a solution of 57.6 ml (61.8 g; 0.34 mole) of triethyl phosphate in 415 ml 1,2-dichloroethane. The temperature of the solution was kept below  $25^\circ\text{C}$  by adding the  $\text{SO}_3$  slowly and by cooling the solution with an ice bath. This solution and a solution of 150.0 g (0.34 repeat unit) of PSF (abbreviation for Union Carbide Polysulfone P-1700) in 1000 ml of 1,2-dichloroethane were added simultaneously via addition funnels to a 5-liter reaction flask containing 1100 ml 1,2-dichloroethane under vigorous agitation. The solutions were added at equivalent rates over a 10-min period at room temperature. A heavy precipitate formed upon contact of the two solutions, and the temperature rose from  $25^\circ\text{C}$  to  $34^\circ\text{C}$ . Stirring of the resulting slurry was continued for 30 min. If the free acid form of the product was desired, the slurry was filtered, washed twice with 1,2-dichloroethane, and dried at  $60^\circ\text{C}$  in vacuo to give a tan, hard, horny material. However, if the sodium salt form was desired, 550 ml isopropanol was added to the reaction slurry to dissolve the free acid precipitate. An excess of sodium methoxide (73.4 g; 1.36 moles) in 300 ml methanol was

then added to the reaction solution. The neutralized product, which precipitated, was filtered, washed twice with isopropanol and twice with distilled water, and dried to constant weight at 90°C in vacuo. The yield was 169.7 g (92.0%) of a white powder. An alternative procedure used in some cases for obtaining the sodium salt form was to filter the free acid precipitate, wash with 1,2-dichloroethane, dissolve in dimethylformamide, neutralize, and coagulate with excess isopropanol.

Solution-cast films were prepared from 10% solutions in dimethylformamide in a 100°C circulating air oven followed by water soaking and drying at 100–200°C. Film water sorption data were obtained by comparison of the weight of the water-immersed film with that of the subsequently vacuum-dried film. Ion exchange data were obtained by the method of Fisher and Kunin.<sup>23</sup> Nuclear magnetic resonance measurements were obtained by the method of Kopf<sup>19</sup> in DMSO solution. The degree of sulfonation by NMR was calculated from the ratio  $f = 12 - 4R/2 + R$ , where  $f$  = mole fraction of sulfonated repeat units and  $R = A_{abc}/A_{de}$ , where  $A_{abc}$  and  $A_{de}$  = the areas of the peaks due to  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  protons (see Figs. 1 and 2).<sup>19</sup> Dynamic mechanical testing was carried out with a torsion pendulum instrument based on the design of Nielson.<sup>27</sup>

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