Streaming Potential of Microporous Membranes Made from Homogeneously Functionalized Polysulfone

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SYNOPSIS

Microporous membranes were prepared from chemically modified polysulfone. The substitution of the polysulfone was performed in solution using reactions known from polymer modification such as halomethylation, aminomethylation, and lithiation. Membranes can be prepared directly from halomethylated polysulfones which are consecutively converted heterogeneously in a second step to the final functionalized form. Sometimes, two-step reactions are necessary to yield the polymers from which the membranes were cast. In those cases where the reactions change the charge of the polymer, the success of the reaction can be demonstrated by streaming potential measurements. The advantage of this analytical method lies in the fact that the intact membrane is investigated.

INTRODUCTION

Often, polymers do not fit the demand for special applications when they are used in their originally chemical form. This problem can be solved either by blending the polymer or by chemical modification. These methods also are successfully applied to membranes when distinct properties are requested. Thus, charged membranes can be obtained by mixing a film-forming polymer which is neutral with an ion exchange polymer. Another possibility is to introduce ionic groups on a polymer. This implies that the chain length of the polymer remains unaltered; otherwise membrane preparation would be limited using this substituted polymer. The introduction of ionic groups on a polymer extends its application range as a membrane polymer, e.g., neutral polysulfone used for membranes for ultrafiltration or microfiltration is fit for reverse osmosis[1] or electrodialysis[2] after sulfonation. Furthermore, special microfiltration membranes can be prepared which sorb opposite charged particles from solutions. And, finally, the water uptake is increased.[3]

Other substituents allow the covalent bonding of special molecules such as chelates, crown ethers, and enzymes. Besides the sulfonation of polysulfone[1,4] there are many organic reactions for modifying polymers. One of the most common reaction for functionalizing small organic molecules is halomethylation. This reaction was used for modifying polysulfone. In general, a chloromethyl alkyl ether is used as reactive agent[5,6] with Friedel–Crafts catalysts like $SnCl_4$ or $ZnCl_2$ for halomethylation. The electrophilic substitution of the aromatic nucleus occurs in the bisphenol A part of the polysulfone. However, this agent is capable of forming methylene bridges which yield crosslinking of the polymers. This side reaction is less pronounced at lower reaction temperatures and when $ZnCl_2$ is used instead of $SnCl_4$ as catalyst. For example, the chloromethylation of polysulfone (PSU) can be performed with $ZnCl_2$ at 323 K.[5] Because of the toxicity of chloromethyl methyl ether, the corresponding n-octylether is the preferred agent. Organic molecules, which have been chloromethylated, can be further modified by nucleophilic substitution.[7] However, a higher activity for this nucleophilic substitution can be expected from the bromomethyl group which can be introduced on PSU using bromomethyl octylether.[8] The reaction of halomethylated polystyrene using nucleophiles can be found in the references.[7,9] In the case of the modified PSU, reactions with trialkyl amines have been published[6,10]. In the presence of $NaHCO_3$, the chloromethyl group can be trans-

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formed into an aldehyde using DMSO. An aromatic aldehyde group separated by an aromatic spacer from the polymeric backbone can be obtained with p-hydroxybenzaldehyde. Introduction of ester groups can be carried out using potassium acetate as was demonstrated with substituted polystyrene.[11] The chloromethylated polysulfone is suited to react with all kinds of amines. The resulting derivative is the next higher substituted amine, e.g., a primary amine yields a secondary aminated polysulfone. Besides the formation of functional groups side reactions like intramolecular or intermolecular crosslinking can also occur. Only trimethylamine yields the quaternary ammonia group; therefore, the reaction with this amine is used for the preparation of anion exchange polymer. Using bifunctional amines, crosslinking occurs via both active groups.

A further possibility for introducing reactive substituents on substances with aromatique groups is the aminomethylation using N-chloromethylphthalimide. This method can also be applied to derivatize PSU.[10] The phthalimide group is split by hydrazine in a second reaction step. Functionalization of polymers with aromatic structure units can be carried out using lithium organic compounds. Thus, n-butyllithium is used for the modification PS,[12] polyoxyphenylene,[13] and PSU.[14] Often, the reaction is carried out in tetrahydrofurane. ^{1}H-NMR spectroscopy showed that the sulfone group in the PSU backbone is responsible for substitution of the aromatic nucleus in o-position adjacent to the SO_2 bridge. The lithiated PSU can further be converted with various agents like $(CH_3)_2S_2$, $(CH_3)_3SiCl$, or acetone.[15] CO_2 is a simple reagent for carboxylation at room temperature.[16]

EXPERIMENTAL

Preparation of Functionalized PSU

Halomethylation

For the investigations described herein the temperature for the halomethylation should not exceed 318 K. The reason for this restriction is the fact that the employed reaction conditions should also be suited for substituting ready PSU membranes. It pointed out that at higher temperatures the membranes lost their mechanical properties.[17] The chloromethylation was carried out with chloromethyl methyl ether in the presence of $SnCl_4$ or $ZnCl_2$, which was prepared by reaction of acetyl chloride with dimethoxymethane[18] without isolating the ether. The reaction mixture can be used directly for PSU conversion.[6,19] The bromomethylation was performed at 318 K according to Ref. 8. The reaction equation for the chloromethylation is

$$PSU - H + ClCH_2 - O - alkyl \rightarrow$$
$$PSU - CH_2Cl + HO - alkyl \quad (1)$$
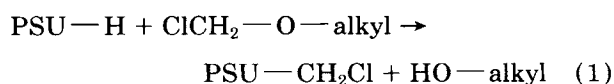
The solvent for the reaction mixtures was 1,2-dichloroethane. The reaction conditions and the results are listed in Table I.

Reaction of Chloromethylated PSU (CPSU) with Nucleophiles

In the following some reactions are described which yield polysulfone derivatives suitable for membrane preparations.

Table I   Reaction Conditions and Degree of Substitution for Halomethylation of PSU

| Expt No.[a]	Catalyst	Mol Ratio PSU/Ether/Catalyst	Reaction Time (h)	c_{PSU} (mmol L^{-1})	DS[b] EA	DS[b] ^{1}H-NMR
Br 1	$SnCl_4$	1 : 11.8 : 0.16	3	68	0.22	0.20
Cl 2	$SnCl_4$	1 : 19.4 : 0.16	1	60	0.88	0.83
Cl 2	$SnCl_4$	1 : 19.4 : 0.16	2	60	1.17	1.05
Cl 3	$SnCl_4$	1 : 19.4 : 0.16	3	60	1.24	1.22
Cl 4	$ZnCl_4$	1 : 9.7 : 0.11	7	120	0.19	0.16
ClO5	$SnCl_4$	1 : 19.4 : 0.16	2	60	1.15	1.02
ClO6	$SnCl_4$	1 : 19.4 : 0.16	4	60	1.25	1.16
ClO7	$SnCl_4$	1 : 9.7 : 0.16	5	48	1.22	1.23

[a] Br = bromomethyl octylether; Cl = chlormethyl methylether; ClO = chloromethyl octylether.
[b] DS = degree of substitution; EA = elementary analysis.

Dimethylsulfoxide (DMSO). The reaction was carried out at 428 K for 3 h using a mixture of 3.0 g CPSU (DS 0.8), 100 mL DMSO, and 7 g NaHCO$_3$. The polymer is soluble in the solvents normally used for polysulfone like DMF, DMAc, DMSO, and NMP. The degree of substitution was determined by ^{1}H-NMR to be about 0.80. The equation for this reaction reads as follows:

$$PSU—CH_2Cl + (CH_3)_2SO \rightarrow$$

$$PSU—CHO + (CH_3)_2S \quad (2)$$
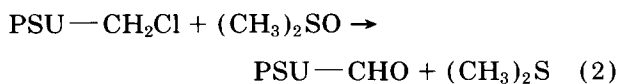
***p*-Hydroxybenzaldehyde.** The CPSU (15 g) was dissolved in 500 mL dioxane and the agent (6.11 g), KOH (2.8 g), and ethanol (20 mL) were added. The mixture was kept boiling for 24 h. The conversion did not come to completion. The DS of the PSU—CH$_2$Cl was 0.55, the DS for the resulting PSU—CH$_2$O—ArCHO was 0.42 and the remaining Cl corresponded to a DS of 0.11 in the feed product. The reaction can be described according to

$$PSU—CH_2Cl + HOC_6H_4—CHO + KOH \rightarrow$$

$$PSU—CH_2OC_6H_4—CHO + KCl + H_2O \quad (3)$$
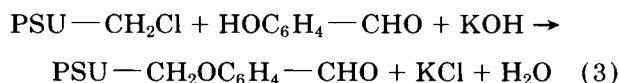
Potassium Acetate. The polymer was reacted with potassium acetate according to the experiments using the corresponding polystyrene.[11] Two grams of CPSU were dissolved in 60 mL DMSO, and, after adding 12 g acetate, the reaction was carried out at 303 K for 64 h. The resulting substituted PSU is soluble in *N*-methylpyrrolidone (NMP), DMSO, dimethylformamide (DMF), and dimethylacetamide (DMAc). For membrane preparation a 17% solution in NMP was used. The reaction scheme is as follows:

$$PSU—CH_2Cl + CH_3COOK \rightarrow$$

$$PSU—CH_2—OOCCH_3 + KCl \quad (4)$$
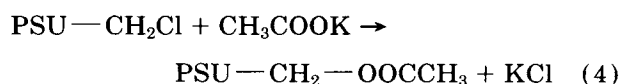
### Reactions of CPSU with Nitrogen-Containing Compounds

In the following some reactions are listed.

Diethanolamine. A solution of 25 g CPSU prepared with the chloromethyl octylether (DS of CPSU 0.67) in 500 mL DMF was added to 105 g diethanolamine. The reaction temperature was 308 K, and the reaction time was 3 h. In order to precipitate the substituted polymer, methanol was added to the reaction mixture. According to the IR spectra and the elementary analysis, the conversion

had occurred. The estimation of the DS by ^{1}H-NMR failed because of signal superposition. The reaction equation is

$$PSU—CH_2Cl + NH(C_2H_4OH)_2 \rightarrow$$

$$PSU—CH_2N(C_2H_4OH)_2 + HCl \quad (5)$$
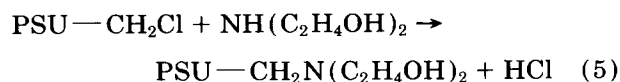
Trimethylamine. CPSU (8 g), prepared using chloromethyloctylether with a DS of about 0.55, was dissolved in 100 mL DMSO and 50 mL of a 45% solution of the agent in water were added. The mixture was agitated for 6 h at room temperature. The isolated product had a DS of 0.49. The reaction scheme is as follows:
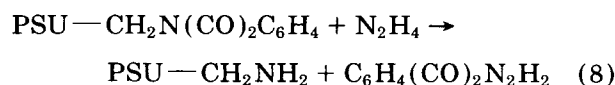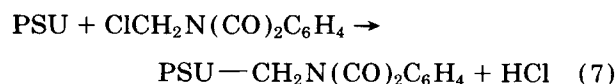
$$PSU—CHCl_2 + N(CH_3)_3 \rightarrow$$

$$PSU—CH_2N^+(CH_3)_3Cl^- \quad (6)$$
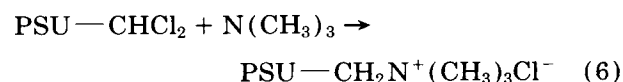
Dimethylamine. For this reaction, 0.2 m dimethylamine (33% in ethanol) dissolved in DMAc was mixed with 0.004 m CPSU (DS 1.22) in DMAc solution and agitated for 4 h at room temperature. The DS of the isolated product was estimated to 1.24 from the ^{1}H-NMR values. Membranes were prepared from DMSO and NMP dopes.

Ethylenediamine. A solution of 0.1 m CPSU in DMAc was dropped to a well-agitated solution of 15 m ethylenediamine in DMAc at room temperature. After 3 h the polymer was precipitated by adding 2-propanol and further purified. The product finally received is soluble in DMF, DMAc, and NMP. According to the ^{1}H-NMR signals, the —CH$_2$—NH$_2$ is present. This indicates that the reaction did not come to complete crosslinking. Furthermore, copper ions were chelated by the bidentate ligand. Mechanically stable membranes were prepared using a dope made from DMAc and LiCl as an additive.

Aminomethylation

The reaction was carried out under reflux using a solution of PSU in 1,2-diethylene chloride (0.18 m) with SnCl$_4$ as catalyst. A mixture of *N*-chlorophthalimide in the same solvent (0.72 m) was added to this solution. After 3 h the reaction was stopped by adding HCl. The DS can reach 0.80. The more effective catalyst is FeCl$_3$ (DS up to 1.45), but AlCl$_3$ can also be used. For converting this derivative into the aminomethylated PSU, a hydrazine/ethanol mixture was used. Since the substituted PSU is insoluble in this mixture, the reaction occurs heterogeneously using the polymer powder at 333 K for 6

h. The aminomethylated PSU is soluble in DMF, DMAc and NMP; membranes can be obtained using the casting solutions made from the mentioned solvents. The better possibility, however, was to cast membranes from the phthalimide–PSU derivative, which was heterogeneously reacted with hydrazine. The dope for the membrane preparation consisted of 14.5% b.w. of the polymer and 3.5% b.w. of LiCl in DMAc. The reaction equations are as follows

$$PSU + ClCH_2N(CO)_2C_6H_4 \rightarrow$$

$$PSU-CH_2N(CO)_2C_6H_4 + HCl \quad (7)$$

$$PSU-CH_2N(CO)_2C_6H_4 + N_2H_4 \rightarrow$$

$$PSU-CH_2NH_2 + C_6H_4(CO)_2N_2H_2 \quad (8)$$

Lithiation

The reaction was carried out according to Ref. 14. PSU (0.0754 m) was dissolved in THF (700 mL) and cooled down to 203 K. To this well-stirred solution 35 mL of a mixture were added which consisted of n-BuLi in hexene (0.056 m) and 25 mL THF. The reaction scheme is as follows:

$$PSU + n\text{-}C_4H_9Li \rightarrow PSULi + n\text{-}C_4H_{10} \quad (9)$$

The lithiated PSU was not isolated, but it was consecutively converted to a tertiary alcohol using acetone. Therefore, a solution of acetone (0.34 m) in THF (25 mL) was added after 30 min to the reaction solution mentioned above. The precipitate was stirred 30 min and then isolated and purified. The DS was about 0.6.

$$PSU-Li + H_3C-CO-CH_3 \rightarrow$$

$$PSU-C(CH_3)_2OH \quad (10)$$
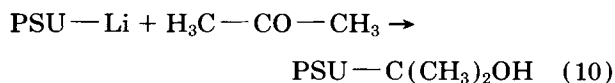
PSU—Li is also suited to yield primary aromatic amino groups.[20] For this purpose o-methylhydroxylamine was used as reagent. The lithiation reaction was carried out in the same way as mentioned above. Fifty milliliters of a solution of 7.1 g in 200 mL THF were added to the reaction mixture. The DS was about 0.12. The polymer is soluble in CH_2Cl_2, DMF, and DMAc. Membranes were prepared from DMAc solutions. They can be dyed by the β-naphthol coupling reaction:

$$PSU-Li + CH_3ONH_2 \rightarrow$$

$$PSU-NH_2 + LiOCH_3 \quad (11)$$
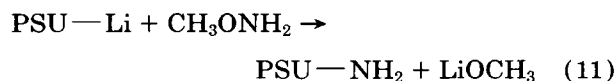
The carboxylation of polysulfone is performed by the reaction of lithiated PSU with CO_2 according to

$$PSU-Li + CO_2 \rightarrow PSU-CO_2Li \quad (12)$$

The preparation of the PSU–Li solution is carried out as described above. Pulverized CO_2 was added to this solution at temperatures of 203 or 273 K. The yield of substitution was about 1 mmol —COOH/g polymer. The product is soluble in DMF or DMAc.

Molecular Weight Determination

Because of possible chain degradation, molecular weight measurements were performed with a Knauer unit fit with four Shodex columns of different cutoff ranging from 5×10^3 to 5×10^6 g mol^{-1}. Commercially available PSU 1700 from Union Carbide Corp. served for calibration.

Membrane Preparation

All membranes used in this investigation were prepared according to the phase inversion process. Optimum conditions were determined only with chloromethylated PSU. From this polymer membranes were prepared by casting solutions differing in their polymer concentration onto a glass plate which was then immersed in the precipitation bath consisting of distilled water of 288 K after a residence time at ambient air of 5 s. The solvents were varied also. The influence of different residence times were investigated as well. The slit width of the casting die was 0.2 mm, and the casting velocity was 1 m/min.

Membranes made from the other polysulfone substitutes were cast preferably from solutions in DMAc with 17% b.w. of the polymer; however, as mentioned in the different sections also other solvents can be used, and in addition LiCl is suited as a pore-forming agent. The same casting conditions as mentioned for CPSU membranes were employed.

Membrane Characterization

The membranes were characterized by means of their ultrafiltration behavior and their electrokinetic properties. In addition, the water content was estimated. Ultrafiltration measurements were performed in a thermostated closed loop unit. It consisted of four cells equipped with stirrers which were connected in series, a 5-L reservoir, and a membrane piston pressure pump. The volume flow in the testing

units was 0.4 L/min at 3 bar. Before each run the membranes were conditioned with distilled water at 3 bar for 24 h. Testing materials were pure water and dextran solutions prepared from samples differing in the molecular weight from 4000 to 200,000 g mol^{-1}. Thus, molecular weight cutoff could be determined.

In order to get information on the surface charge, measurements of the streaming potential U_s were performed using a cell described in Ref. 21, which allowed to estimate the pressure and the pH dependency as well. Silver/silver chloride electrodes were used; the concentration of the electrolyte solution (KCl) was about 10^{-3} m. Because of the problem using porous membranes the zeta-potential was not calculated from the experimental findings (see e.g. Ref. 22). Since the zeta-potential is a function of $U_s \kappa'/P$, where κ' is the electrolyte conductivity in the pore liquid, both $U_s \kappa'$ and U_s as functions of the transmembrane pressure difference can be used for investigating the electric behavior of the membranes.

RESULTS AND DISCUSSION

Molecular Weight Determination

The reactions mentioned above yield a more or less pronounced polymer chain degradation which in some cases can cause the loss of film-forming properties. On the other hand, crosslinking can occur as mentioned already. Therefore, gel permeation chromatography was used to get information on molecular weight changes. A more detailed investigation was carried out using chloromethylated polysulfone. The results are shown in Table II, which were obtained by computing $(\bar{M}_w/\bar{M}_n) - 1$. (This term is comparable to what is called dispersion in form of
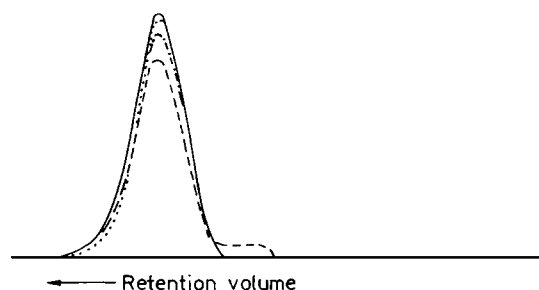

Retention volume

Figure 1   Gelchromatogram of modified PSU prepared via lithiation: (—) original PSU; (· · ·) PSU—NH$_2$; (-·-) PSU—C(CH$_3$)$_2$OH; (---) PSU—COOH.

$\bar{M}_w/\bar{M}_n$). In order to compare the substituted polymer with the untreated polymer in this case, the assumption was made that the substitution does not strongly change the physical and chemical properties as well. Therefore, the values obtained have only qualitative character and further measurements using the other substituted polysulfones were only carried out qualitatively. As can be seen from Figure 1, a crosslinking did not result when the PSU was lithiated and the reaction with acetone or methoxylamine was consecutively performed. The carboxylation, however, causes polymer bridging indicated by a shoulder at lower retention volumina.

Ultrafiltration Measurements

As can be seen from Figure 2, membranes with larger pores can be obtained using the DMAc solution.[23] In Table III the influence of solvents on membrane characteristics are listed. Increasing polymer concentration in the casting solution decreases the transmembrane water flow of the resulting membrane. The concentration was varied between 14.5

Table II   Number Average Molecular Weight and Weight Average Molecular Weight for Halomethylated PSU

Type	$\bar{M}_n$ (10^{-3} g/mol)	$\bar{M}_w$ (10^{-3} g/mol)	U ($\bar{M}_w/\bar{M}_n$) $- 1$	Reaction Conditions		
				(h)	T (K)	DS
PSU 1700	2.55	3.70	0.45	—	—	—
PSU—CH$_2$Br	2.48	3.88	0.57	3	318	0.22
PSU—CH$_2$Cl[a]	3.41	6.80	1.0	1	318	0.88
PSU—CH$_2$Cl[a]	2.83	5.36	0.9	3	298	0.72
PSU—CH$_2$Cl[b]	2.92	6.00	1.1	2	318	1.15
PSU—CH$_2$Cl[b]	2.74	4.90	0.8	2	208	0.55

[a] Reaction with chloromethylmethyleterer.
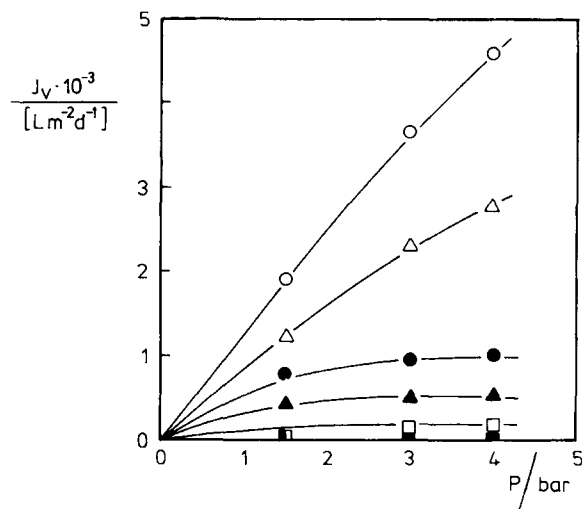[b] Reaction with chloromethyloctylether.

Figure 2 Volume flow for chloromethylated PSU membranes made from different casting solutions. Open symbols: pure water flow; filled symbols: 1 wt % dextran solution (MW 4000–200,000 g mol⁻¹). Solvents: (O) DMAc; (△) NMP; (□) DMF. $T = 20°C$.

and 20.5. As well known from PSU membrane preparation, additives in the casting solution also change the membrane porosity. Table IV shows some results for lithium chloride. In all cases the polymer content was 14.5 wt % in DMAc solution. The casting conditions are mentioned above. The tests were performed at 1 bar. Increasing LiCl concentration shifts the cutoff to higher molecular weights, indicating increasing transport area in the membrane surface.

Electrokinetic Measurements

Membranes prepared from chloromethylated polysulfone and those obtained by conversion using neutral reagents show the same behavior as other solids when they are in contact with water or dilute solutions of salts: They preferentially adsorb anions because of their greater polarizability and lower hydration. Electroneutrality requires the accumulation of counterions in the vicinity. These two arrays of

Table III Influence of Solvents on PSU—CH₂Cl Membrane Properties

	DMAc	NMP	DMF
Water content (%)	70.0	69.2	60.5
Porosity	74.1	73.3	65.2
Thickness (mm)	0.095	0.098	0.075
Cutoff (10³ g/mol)	56	42	13

Table IV Influence of LiCl on PSU—CH₂Cl Membrane Properties

LiCl (% in casting soln)	3.5	4.5	5.5
Water content (%)	74.7	75.2	75.2
Porosity	78.3	78.7	78.7
Thickness (mm)	0.106	0.096	0.103
Cutoff (10³ g/mol)	398	1000	1412

different charges are called the electrical double layer, whose solution half is composed of two layers, namely, the fixed or STERN layer and the diffuse one. If the liquid is moved charges are moved too, and an electrokinetic potential between fixed charges and shearing boundary is created which is called streaming potential. This streaming potential of the membranes made from PSU with the —CH₂Cl, —CH₂OOCCH₃, and —CH₂OC₆H₄CHO groups is negative as can be seen from Figure 3, where the U_s values are plotted versus the applied pressure. According to the theory of Helmholtz and Smoluchowski[24] and Schmid,[22] respectively, the potential increases with increasing pressure. The other two lines in the figure stem from the experimental findings using membranes which were substituted with N-containing reagents. Consequently, the streaming potential is positive. The isoelectric point (IEP) of the membranes can be determined from
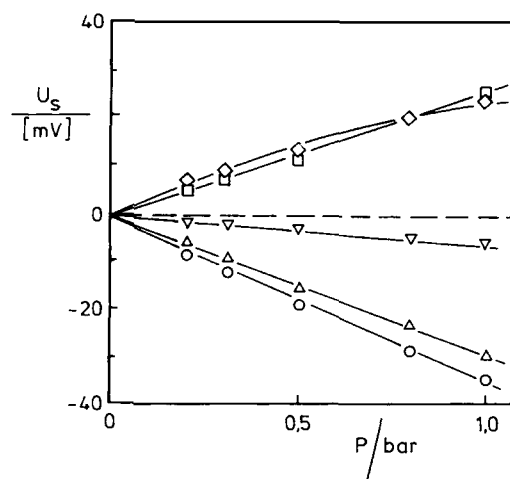

Figure 3 Streaming potential of functionalized PSU membranes made via chloromethylation: (O) CPSU; (△) PSU—CH₂—OOCCH₃; (▽) PSU—CH₂—OC₆H₄-CHO; (◇) PSU—CH₂—N(CH₃)₂; (□) PSU—CH₂—N(C₂H₄OH)₂. Electrolyte KCl ($c = 10^{3}$ mol L⁻¹).

the pH dependency. This is shown in Figure 4. In the pH range investigated the CPSU membrane increasingly sorbs anions from the solution, and the measured potential is shifted to higher negative values. The same can be seen for both the other neutral membranes, yet at low pH they are positively charged. The isoelectric point is about pH 4. For membranes with amino groups the IEP lie above pH 7. At low pH the basic amino groups are protonated; with rising pH values the amount of dissociating groups becomes smaller and reaches zero because of the low basity of alkylamines. Below zero potential these membranes behave like the "neutral" membranes, they sorb negatively charged anions. In Figure 5 the streaming potential is plotted for three membranes based on phthalimidomethylated PSU. Two of them have negative values; they are not reacted with hydrazine in a second reaction and can be designated as neutral. One is an interpolymer membrane made from a mixture of phthalimidomethylated and original PSU. After treating this membrane type with hydrazine, the streaming potential becomes positive. From this change of the surface charge it can be derived that the reaction has been carried out successfully. The pH dependency of membranes made via lithiation is shown in Figure 6. The membrane with carboxylic groups shows the same behavior as weakly organic acids. With increasing pH the dissoziation increases, and therefore the measured potential is shifted to higher
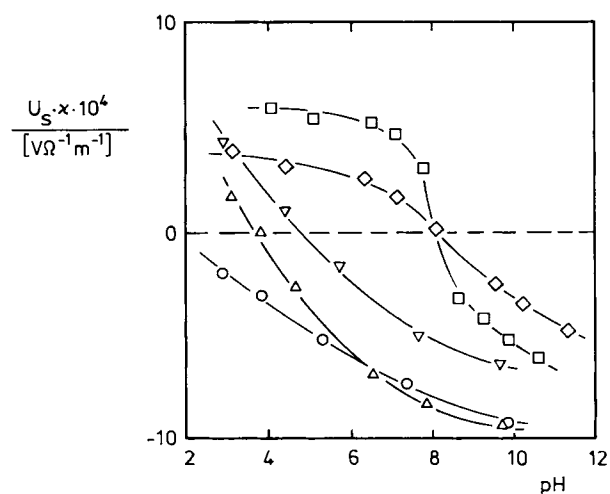

Figure 5   Streaming potential of membranes made from amidomethylated PSU: ($\square$) PSU—$CH_2N(CO)_2C_6H_4$; ($\triangle$) PSU—$CH_2N(CO)_2C_6H_4$/PSU—interpolymer (14: 3.3%); ($\blacktriangle$) after reaction with hydrazine (PSU—NH_2/PSU).

values. Opposite to this acidic membrane, the strong sulfonic acid group is not depending on the pH investigated as was demonstrated using membranes heterogeneously modified.[17]

CONCLUSION

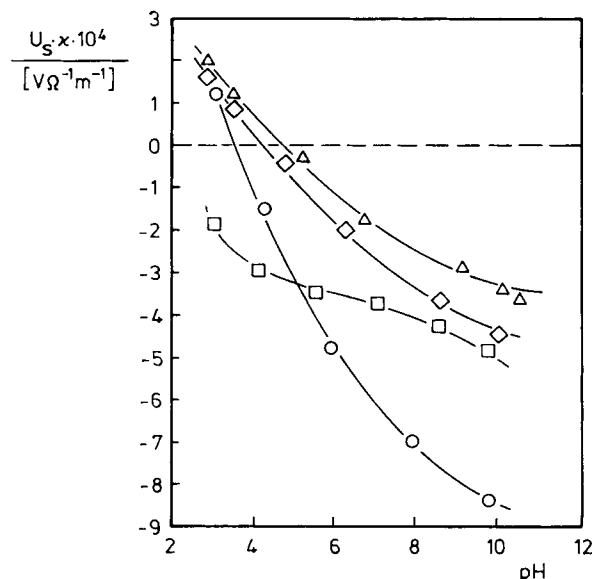Polysulfone is a versatile polymer for membrane preparation. Its broad application range can still be

Figure 4   Potential $U_s\kappa$ as function of the pH for different membranes prepared from CPSU: ($\bigcirc$) CPSU; ($\triangle$) PSU—CH_2-OOCCH$_3$; ($\triangledown$) PSU-CH_2—OC$_6$H$_4$CHO; ($\lozenge$) PSU—CH_2—N(CH$_3$)$_2$; ($\square$) PSU—CH_2N(C$_2$-H$_4$OH)$_2$.

Figure 6   Potential $U_s\kappa$ as function of pH for different PSU membranes prepared via lithiation: ($\bigcirc$) PSU; ($\triangle$) PSU—C(OH)(CH$_3$)$_2$; ($\lozenge$) PSU—NH$_2$; ($\square$) PSU—COOH.

extended by chemical modification. In this paper various homogeneous phase reactions are described such as halomethylation, aminomethylation, and lithiation. The first and the last methods allow further derivatization; thus various functionalized polysulfones can finally be obtained. In all cases, reaction conditions were selected which are regarded as to avoid substantial polymer degradation. Thus, the film-forming properties of the resulting polymers were hardly altered, which was important, since the applied reactions should also be applicable to heterogeneous reactions using commercially available membranes.[17] The membranes obtained from all polymers could be cast using solutions mostly made from dimethylacetamide. Only in those cases where the polymer was not soluble in appropriate solvents like the quaternary ammonium salts was a membrane cast from the precursor polymer, which was finally converted heterogeneously into the aminated form.

By determining the molecular weight of the polymers modified it could be shown that they either degraded or crosslinked by the reactions used. However, this change in the molecular weight of the substituted polysulfones was not serious, since the membrane-forming properties were preserved. Membranes cast from them were suited for ultrafiltration purposes.

For analyzing membrane polymers, elementary analysis or IR spectroscopy are useful. However, to apply these methods the membranes are disintegrated. In order to get information on the intact membrane, a nondestructive test was applied. Streaming potential measurements were used in order to estimate the surface charge of the membranes prepared from the differently modified polysulfones. By this method only the accessible groups within the pores are determined. From the results quantitative information on zeta-potential of the membranes cannot be obtained because the pore geometry is not known. Nevertheless, these measurements can be used for indicating that the reaction has successfully been carried out. Furthermore, from the pH dependency of the streaming potential the isoelectric point of the membrane can be determined. These measurements are simple methods for the characterization of porous membranes made from substituted polymers.

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