Polysulfones and Their Derivatives: Materials for Membranes for Different Separation Operations

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SYNOPSIS

Polysulfones, as well as their derivatives obtained by chemical reactions, are versatile materials for membrane preparation. The selection of an optimum material clearly depends on the separation process for which the membranes will be used. Membranes made from these materials may serve diverse functions, ranging from an actual permselective separation barrier to a support for a thin membrane layer in a composite structure. Illustrative examples of polysulfone membranes useful in these various applications are given and compared with respect to their cross-sectional and/or their surface morphology as well as in their surface charge and chemical composition.

INTRODUCTION

Polysulfones rank second only to cellulose acetate as a commercial membrane material with applications in both large-scale production and laboratory scale. The diversity of these applications demand the use of a vocabulary that provides an efficient description of the particular membranes being considered. Various factors can be discussed. For example, the existence and distribution of pores within the cross section, the type and amount of charge on the polymer, and the detailed composition across the membrane between the upstream and downstream surfaces are important quantities.

Membranes that lack a more or less pronounced skin on one side are generally termed "homogeneous," as opposed to "asymmetric" membranes that possess such a well-defined layer. In electrodialysis, the term homogeneous is kept for those membranes that are prepared from one compound, whereas heterogeneous ones contain an inert film-forming material.

In common usage, the same term, e.g., "composite," may refer to membranes of vastly different structure, properties, and end-use application. For example, the well-known reverse osmosis (RO)

membrane made by FilmTec, the FT 30, is referred to as a "composite membrane." The FT-30 membrane consists of a polysulfone support layer and a polyamide separation layer sitting atop the microporous support layer.[1] Similarly, the Monsanto gas separation membrane is commonly referred to as a "composite membrane." Indeed, the Monsanto membrane also has two layers, but contrary to the FT-30, the principal separation function lies within the lower polysulfone part.[2] The upper silicone rubber part acts to seal the few commonly occurring pores in the active membrane surface. Yet another type of "composite" can be formed for gas separation and RO uses by chemically modifying the external surface of a standard polysulfone membrane. If surface pores exist prior to chemical treatment, they can persist in the chemically treated layer and may require subsequent treatment via the Monsanto-type procedure to produce an even more complex composite structure if the membrane is to be used for gas separation. For less demanding RO uses, post-treatment is not needed.

Alternatively, if the chemically modified polysulfone layer and the original polysulfone material can be made to form a miscible system in the presence of a solvent and compatibilizing additives, it is potentially feasible to form a phase-inverted asymmetric blend or interpenetrating network membrane. In this case, the chemically modified material will tend to be distributed throughout the skin and

the support structure, thereby diluting its effect as a separating agent.

In pervaporation, dense films made from polysulfone are used for separating water from ethanol/water mixtures.[3] There are still better polymers for preparing membranes for pervaporation;[4] however, for the purpose of this paper, an example should be selected where polysulfone membranes are applied. Experiments with membranes based upon polysulfone are performed and will be published soon.

For electrodialysis, membranes are made from polymers that possess fixed positive or negative charges. So, e.g., polysulfones can be treated with chlorosulfonic acid,[5] which results in cationic exchange polymers because of their negative fixed ionic groups. From this polymer cationic exchange membranes can be prepared by solvent casting.[6,7] The resulting dense film is called a homogeneous membrane, since it consists of only one compound. Bipolar membranes are used for special applications.[8] These membranes consist of one cation-exchange layer and one anion-exchange layer, and they can also be prepared from the corresponding polysulfone derivatives.[9]

The operative mechanism of separation in all of the preceding applications involves essentially a "solution-diffusion" process of distinguishing between copermeating species. The very different process of "hydrodynamic sieving" also forms the basis for an important class of separations typically re-
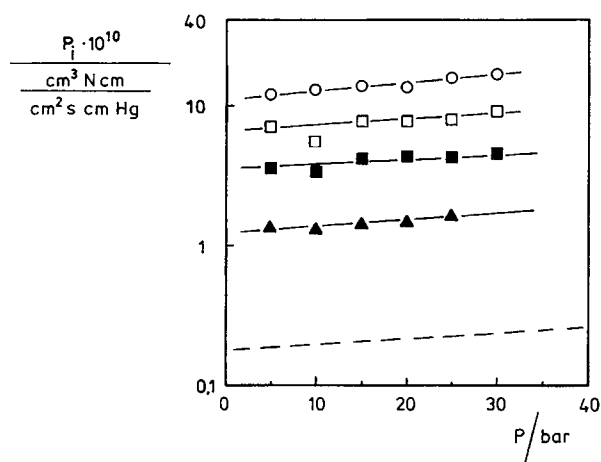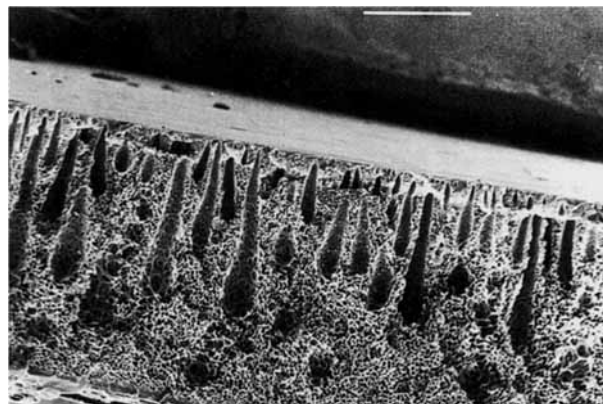

Figure 2 SEM photograph of a gas separation membrane made from a dense SPSF layer atop a PSF UF membrane.

ferred to as "ultrafiltration" and "microfiltration".

In ultrafiltration applications, many membrane producers offer asymmetric polysulfone-based membranes. Besides asymmetric membranes, so-called homogeneous membranes are available from some suppliers. The latter membrane type may also be referred to as symmetric because of its cross section. In the case of microfiltration, polysulfone is again a very popular material; however, different process conditions are used to produce larger pore dimensions needed for this type of application. Such microfiltration and ultrafiltration membranes are extended to the new field of biotechnology. In these cases, the asymmetric support and separating skin can be used for separation alone or in conjunction with enzymes to form a combined separator/reactor unit. Not surprisingly, the relatively inert and easily processed polysulfone membranes have been considered for these applications. In cases when it is desired to covalently fix enzymes to the membrane, a chemical modification is required to provide reactive groups for enzyme bonding. Because some reactions result in polymer chain degradation, occasionally the preparation of a mixture of the film-forming polysulfone and a polymer suitable for enzyme coupling is preferred, providing that the polymers are compatible and the casting solution does not possess a miscibility gap.[10] Such combinations, referred to briefly above, are known as polymer alloys[11] or interpolymers.[12] The solubility parameters are helpful in determining the compatibility as was demonstrated by using polysulfone and its sulfonated derivatives in the protonated and sodium salt form.[13]

As can be seen from these examples, polysulfones and their chemically modified derivatives are ver-

Figure 1 Permeabilities P_i of oxygen and nitrogen for an interpolymer membrane and heteropolymeric laminate membranes as function of pressure.[17] Dashed line, interpolymer membrane: SPSF/PSF (DS 0.25) at T 30°C; (O) laminate membranes: SPSF (DS 0.41)/PSF at T 30°C; (□) APSF (DS 0.48)/PSF at 25°C; (△) APSF (DS 0.72)/PSF at T 25°C; open symbols: oxygen; filled symbols: nitrogen.
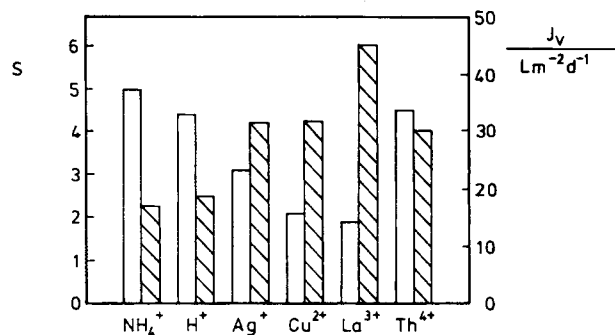
Figure 3 The influence of counter ions of laminate SPSF/PSF membranes on selectivity S and volume flow J_v. Open columns: selectivity; filled columns: volume flow.

satile materials used to form membranes that are useful for most kinds of separation operations where membranes are applied. In the following, a detailed explanation of the above-mentioned alternative for membrane designation is presented using laboratory-scale membranes prepared from these polymers.

EXPERIMENTAL

If not otherwise stated, polysulfone 1700 manufactured by the Union Carbide Corp. was used as the basic material. In the following, the abbreviation PSF is used for polysulfone. For investigations where charged membranes were necessary, different derivatives have been prepared. Sulfonated polysulfone (in the following abbreviated as SPSF) can be syn-

thesized either by chlorosulfonation as described in Ref. 5 or by the reaction with the SO_3–triethyl phosphate complex in $C_2H_4Cl_2$.[14] Polysulfone with anion-exchange behavior can be obtained by the reaction with bromomethyl octyl ether[15] followed by amination. This PSF derivative (in the following abbreviated as APSF) can also be used for enzyme fixation. Another polymer used for preparing enzyme membranes is a polycondensate obtained by the reaction of bisphenol A with 2,4-dichloronitrobenzene.[10] The solvents for the polymers or polymeric mixtures (mostly N-methyl-2-pyrrolidone, NMP) were analytical grade. The membranes were conventionally obtained by either precipitating the as-cast film in water that sometimes contained additives like salts or surfactants or by evaporating the solvent at elevated temperature in an oven.

RESULTS AND DISCUSSION

Gas Separation (GS) Membranes

PSF films have an acceptable selectivity at 23°C of about 28 for the gas mixture CO_2/CH_4, but a rather low permeability of $1.6 \cdot 10^{-10}$ cm^3 (STP) cm/(cm^2 s cmHg).[16] These films are dense but, nevertheless, permeable for gases; thus, they are designated as membranes. If PSF and its sulfonated or animated derivatives in a weight ratio of 2.4 : 1 are dissolved in NMP, a clear solution is obtained.[17] After casting this solution onto glass plates and evaporating the solvent in an oven, a transparent film can be prepared. This blend membrane type possesses rather poor gas separation capabilities for O_2/N_2 mixtures.

Table I Reverse Osmosis Experiments Using SPSF and CA Membranes with CaCl₂ and CaSo₄ Solutions (Pressure 30 bar; Temperature 20°C)

	Membrane					
	CA		SPSF-1		SPSF-2	
Procedure	R_{NaCl} (%)	J_v (L/m²/d)	R_{NaCl} (%)	J_v (L/m²/d)	R_{NaCl} (%)	J_v (L/m²/d)
1. Characterization[a] 0.025 M NaCl	90.7	730	79.9	1790	93.3	940
2. Characterization[a] after 0.1 M CaCl₂ 10-day test	93.6	480	82.8	1260	95.1	700
3. Characterization[a] after 6 × 10⁻³ M CaSO₄ 10-day test	93.0	400	81.0	1170	95.2	620

[a] Characterization was performed using NaCl solution.

Table II   ED Membranes Made from PSF Derivatives

Membrane	DS	d (mm)	Water Content %	R_M (Ω cm^2)	Membrane Potential (mV)	Permselectivity (%)
Cation exchange	0.7	0.13	20	1.1	14.1	90
Anion exchange	0.9	0.04	12	0.6	15.6	95
Bipolar	0.7	0.9	16	2.5	—	—

DS: degree of substitution; d: membrane thickness; R_M: membrane resistance.

The same polymers in laminated form, i.e., composite membranes with improved separation properties, can be prepared in the following way: A very thin (10–20 μm) dry transparent ion-exchange membrane (sulfonated or aminated) made from the corresponding PSF derivatives is cast and kept on a glass plate rather than stripping it off for direct use. On top of this dense ion-exchange layer, a PSF solution is cast. After a very short residence time at ambient air, the glass plate is placed in a water bath where the precipitation of the supporting part for the entire membrane occurs. The result is a dense PSF-derived ion-exchange membrane sitting on a microporous PSF membrane containing different amounts of water. The permeabilities of oxygen and nitrogen through these two membrane types as a function of pressure are shown in Figure 1. The corresponding values for the symmetric interpolymer membrane are marked by a dashed line. The cross section of the membrane consisting of two layers can be seen in Figure 2. It should be added that the membranes used for these investigations are applied in wet conditions. The sodium ion was used as the counter ion. The influence of other counter ions upon selectivity and volume flow is shown in Figure 3. The ion exchange was performed by equilibrating the membrane in a solution containing the concerning chloride compound. To avoid membrane drying, the gas mixture was passed through a moistening device.

Reverse Osmosis (RO) Membranes

The membranes for RO application were prepared from a solution of SPSF in the form of the Li salt in NMP. The polymer was obtained by the chlorosulfonation process. The degree of sulfonation (DS) was about 50%. Using a casting solution of 30% by weight (b.w.), the membranes were formed by precipitation in a bath of various compositions. For the SPSF-1 membrane, the bath consisted of a 50 : 50 mixture of isopropanol and NaCl solution (20%

b.w.), whereas for the SPSF-2 membrane, the content of isopropanol was 82% and the NaCl solution contained only 8%.[9] To evaluate the suitable solvent and precipitation bath composition, the concept of the solubility parameters can be referred to as was shown for the RO SPSF membranes.[18] The above membranes have moderate rejection properties; they can be used for softening tap water at lower pressures. Table I shows the results of RO experiments for the two different SPSF membranes in comparison with a cellulose acetate (CA) membrane. The first line depicts the values of NaCl characterization; in the second one, the values are listed that result from the NaCl test after a 10-day reverse osmosis experiment using $CaCl_2$ solution. After a further experiment using a $CaSO_4$ feed solution for 10 days, an additional characterization completed the investigation (third line). It is reported that membranes made from this polymer suffer from remarkable fouling when the feed contains alkaline earth cations. As can be seen from the table, fouling due to calcium is not severe. It is a matter of membrane charge, but it occurs both in the CA and SPSF membranes if the low solubility product of calcium sulfate is exceeded.
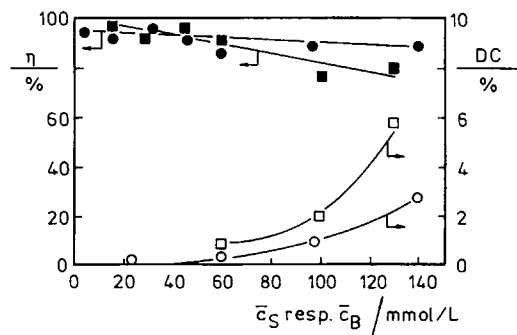

Figure 4   Acid–base production using bipolar ED membranes.[9] Effectiveness factor η and degree of contamination DC as function of acid $\bar{c}_S$ and base $\bar{c}_B$ concentration. (O) Acid; ($\square$) base.
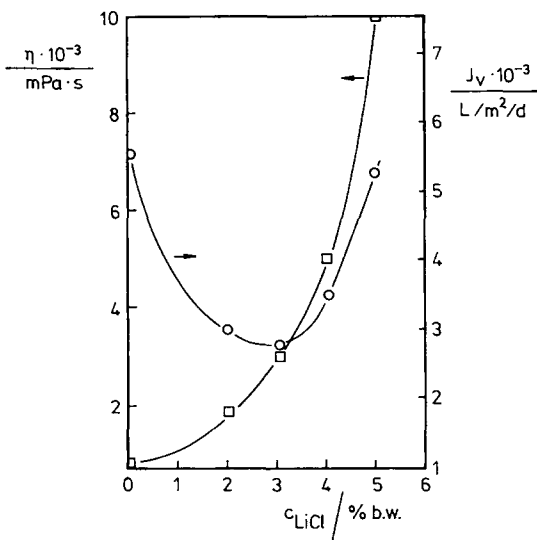
Figure 5 Influence of LiCl upon the viscosity of the PSF casting solution and upon the volume flow of ultrafiltration membranes made from the solution. Membrane testing conditions: pure water, 3 bar.

Figure 6 Whole water content $\bar{W}_W$ and dextran rejection as function of the degree of substitution for SPSF membranes. ($\lozenge$) Pure PSF; ($\square$) SPSF (type A); ($\triangle$) SPSF (type B); (O) PSF/SPSF (type B). Filled symbols: R (dextran solution 1% b.w.; pressure 1.5 bar); open symbols: water content, RU = repeating unit.

Electrodialysis (ED) Membranes

ED membranes made from PSF have a good mechanical stability, which is demonstrated by a long-term heat exposure using 1N HCl.[7] However, they are rarely used in commercially run units. Contrary to this, for laboratory-scale investigations, they are well suited.[19] An ED stack that was operated with a charcoal suspension in the electrode compartments[20] was fitted out with APSF, SPSF, and a bipolar membrane made from both these polymers.[9] All the membranes used for the experiments described in this paper were prepared from the different polymer solutions by solvent evaporation. The bipolar membrane is obtained by casting one solution onto the dried film consisting of the opposite-charged polymer. The values of the membrane properties are shown in Table II. In Figure 4, results
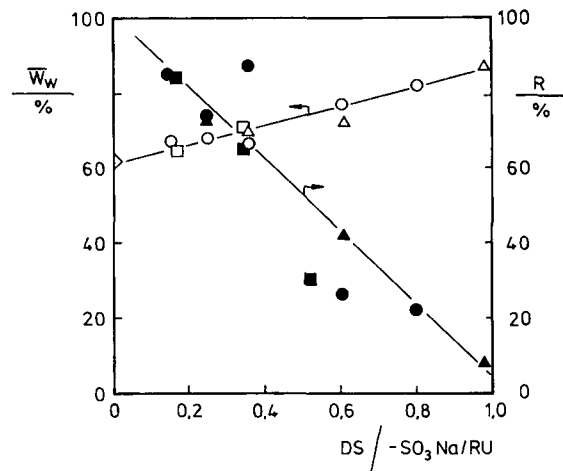
are demonstrated from an experiment for producing acid and base, respectively, using a 0.22M NaCl solution. In this figure, the effectiveness factor η for both the acid and the base and the degree of impurity in the product compartments are plotted versus concentration.

Ultrafiltration (UF) Membranes

The UF membranes for use in this study were made from PSF, SPSF, and a mixture from both these polymers. The common phase inversion procedure was used to produce good-quality asymmetric membranes. To increase the viscosity of the pure PSF casting solution, LiCl was added. The result is shown in Figure 5. From this figure, the influence of LiCl upon the water flow across the membrane is also depicted. For preparing UF membranes with fixed

Table III Ultrafiltration Membranes Made from PSF, SPSF. and a Mixture of PSF/SPSF

Polymer	Polymer Content in NMP Solution (% b.w.)	DS	J_w (L/m²/d)	J_v [a] (L/m²/d)	Water (%)
PSF	20	—	590	345	69
SPSF (type A)	30	0.165	580	360	66.5
SPSF (type B)	30	0.34	710	600	70.6
SPSF/PSF	30	0.6[b]	2400	1400	78.2

[a] Dextran solution 1% b.w. (see text); membrane preparation: casting die width 0.225 mm, residence time at ambient air 180 s.
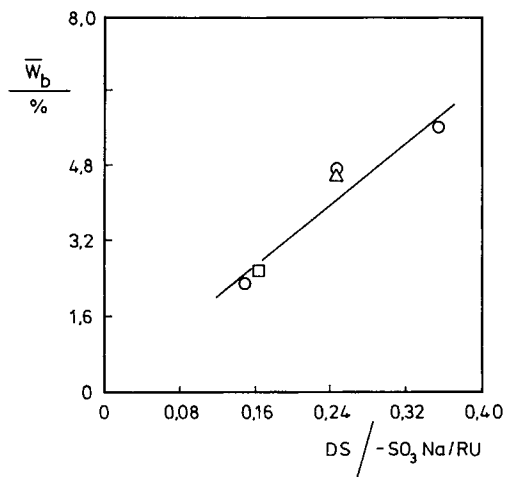[b] DS of the mixture, DS of the pure SPSF (type B) = 0.763.

Figure 7 Bound water $\overline{W}_b$ as function of the degree of substitution of SPSF membranes. For symbols, see legend of Figure 6.

negative charges, SPSF in its sodium salt form was used. In addition, the substitution mode for preparing the SPSF material was different. For type A, chlorosulfonic acid, and for type B, the SO_3–triethyl phosphate complex, was used; type C was a mixture of PSF and type A. The concentration of the fixed ions was different, as can be seen from Table III, where the characterization values are also listed. The experiments were carried out at a transmembrane pressure of 1.5 bar. Besides the pure water volume flow (J_w), that of a 1% b.w. solution of a dextran mixture (J_v) was also measured. Different dextrans were used for solution preparation, so that the molecular weight was in the range 4000 to 40,000 g/mol. In general, inserting ionic groups into a membrane polymer yields a higher water content in the membrane made from it compared to the unsubstituted polymer. As can be seen from the results in Table III, the water content of the pure PSF membrane (see first row) is higher than that of the membranes prepared from cation-exchange material. This can be explained by the lower solid concentration in the casting solution, which yields a membrane with a higher pore volume and, consequently, with a higher water content. Under comparable membrane-casting conditions, the PSF membrane contains less water than do the substituted PSF membranes, which can be seen from Figure 6, where the entire water content is plotted as function of the degree of substitution. In this figure, the rejection R is also shown as function of the DS. R is the overall dextran rejection using the mixed solution. This line suggests a linear rejection/DS dependency. Yet this

is due to the more open membranes resulting from higher DS of the polymer rather than to the increasing charge of the membrane.

Drying these membranes carefully under distinct conditions provides more information about the state of the water.[21] The prerequisite is nonshrinkable membranes, which is approved for SPSF membranes at a DS below 0.4. Plotting the drying rate (g water/m^2 membrane/min) of a membrane vs. the drying time (min), a drying curve is obtained with more or less pronounced sections. These sections can be attributed to the water states within the membrane, e.g., bulk water, capillary water, and bound water. The amount of the latter can be calculated from the final section. Increasing the degree of substitution yields an increasing bound water amount (Fig. 7). It can be assumed that a part of this water is hydration water of the ionic groups within the membranes.

Enzyme Membranes (EM)

To chemically bond enzymes to a membrane, chemically reactive groups are needed. Further, an appropriate enzyme-fixing reaction should be chosen that runs without destroying the enzyme activity and without reducing remarkably the membrane characteristics. As to the PSF molecule, the best-suited positions for substitution are the aromatic groups of the bisphenol A unit. By Friedel–Crafts acylation with a p-nitro substrate followed by reduction, a p-aminoacyl derivative of PSF can be obtained. By this procedure, however, the film-forming
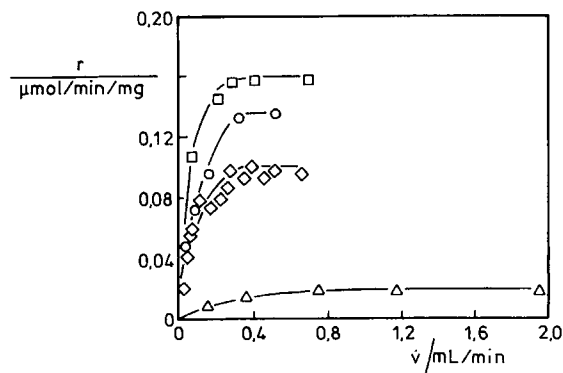

Figure 8 Rate r of the urea–urease reaction as function of volume flow $\dot{v}$ for different urea concentrations.[22] c_{urea}: ($\square$) 0.05 mol/L; ($\bigcirc$) 0.03 mol/L; ($\Diamond$) 0.015 mol/L; ($\triangle$) 0.002 mol/L. Temp: 25°C; pH of the solution: 6.65. Membrane: PSF (14% b.w.) and animated product of bisphenol A/2,4-dichloronitrobenzene (8% b.w.).
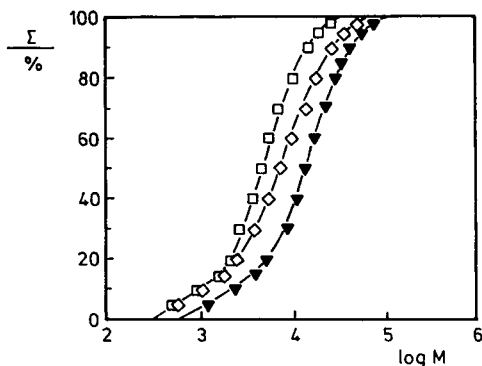
Figure 9   Sum curves for feed and permeates for different membranes suited for enzyme fixation.[22] Testing conditions: 3 bar, 25°C; solution: 1% b.w. dextrane; mixture of molecular weights from 4000 to 40,000 g/mol. (▼) Feed; (□) interpolymer membrane (PSF 14% b.w. + bisphenol A/2,4-dichloronitrobenzene condensate 8% b.w.). (◇) interpolymer membrane (PA 14% b.w. + bisphenol A/2,4-dichloronitrobenzene condensate 8% b.w.).

properties of the polymer are lost due to polymer chain degradation. However, this polymer can be dissolved together with the pure PSF in NMP, yielding a clear solution from which membranes can be obtained by the phase-separation process. To these membranes, enzymes can be fixed using the diazonium reaction.[10] Instead of the PSF derivative, the animated product of bisphenol A-2,4-dichloronitrobenzene is also suited in conjunction with PSF for membrane preparing. The casting solution consisted of a 8 : 14% bw mixture in NMP (78% bw). Urease was fixed to this ultrafiltration membrane by the diazonium reaction. The activity and the membrane behavior was determined with urea. Fig-

ure 8 shows the reaction rate of the urea–urease reaction as function of the volume flow through the membrane. Prior to enzyme fixation, the membrane was characterized with a dextran solution of the same composition as mentioned above in the ultrafiltration section. Figure 9 demonstrates the molecular weight distribution of the permeate and of the feed for differently prepared membranes. In addition, this figure contains the values of an experiment with a membrane made from an aliphatic/aromatic polyamide instead of PSF. The homogeneous reaction of bromomethyl octyl ether with PSF (abbreviated as BrPSF) results in a polymer with preserved film-forming properties. Enzymes can be fixed directly to membranes cast from this polymer as could be shown for urease.[22]

CONCLUSION

As was demonstrated in the investigations presented in this paper, polysulfones offer a wide range for membrane preparation. For special applications, there exist better-suited materials, e.g., for high-rejecting reverse osmosis membranes. Yet, in general, the polysulfones can not be beaten, above all if one takes into consideration that these polymers can be chemically modified in solution and in the state of the ready membrane.[23] Tailormade membranes are available for the various fields of application. Furthermore, from these polymers, all types of membranes can be prepared; additionally, they are miscible with some other polymers, forming blends from which membranes can be cast as well. Table IV lists those membranes used in these investigations, ar-

Table IV   Cross-Section Structure and Composition of PSF-Based Membranes

Membrane Operation	Cross-Section Structure			
	Asymmetric		Symmetric	
	Polymer	Composition	Polymer	Composition
Gas separation	APSF/PSF	Laminated	PSF, SPSF, APSF	Homopolymer
	SPSF/PSF	Laminated	PSF/SPSF	Interpolymer
Reverse osmosis	SPSF	Homopolymer		
Electrodialysis	SPSF/APSF	Laminated	SPSF, APSF	Homopolymer
Ultrafiltration	PSF, SPSF	Homopolymer		
Enzyme-loaded	PSF/SPSF	Interpolymer		
membrane	BrPSF	Homopolymer		
	PSF/P[a]	Interpolymer		

[a] Non-PSF polymer.

ranged according to their cross-section structure and composition for the various membrane-separation processes. All membranes described herein were in flat form, because this is the appropriate form for laboratory-scale preparation.

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