

Development of Light-Induced Functionalized Asymmetric Polysulfone Membranes

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ABSTRACT: The introduction of functionality into asymmetric polysulfone membranes has widened their applicability. They are modified with acrylic acid with a light-induced technique. Fourier transform infrared, contact-angle, porometry, and atomic force microscopy studies have been carried out to characterize the membranes. The performance of the modified membranes has been investigated with permeation measurements. The salt rejection (NaCl and Na₂SO₄)

performance of the modified membranes shows evidence of functionalization on them. The modification of the membranes also develops the retention of small organic molecules (glucose and 2,4-dichlorophenol). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 609–614, 2007

Key words: FTIR; membranes; modification; morphology; separation techniques

INTRODUCTION

The attachment of functional monomers to polymer surfaces affords a convenient procedure for preparing membranes of different applicability. The modification of membranes has already been described by several authors with different objectives, such as fouling reduction,^{1,2} immobilization,³ and switchable permeability.⁴ Several techniques have been employed to impart specific properties to membranes.⁵ These include (1) a radiation technique,^{6–11} (2) glow-discharge, low-temperature plasma treatments,^{12–16} (3) redox reactions,^{17–20} and (4) a light-induced technique.^{21,22} Among the techniques, the light-induced technique has many advantages, including a low activation energy, rapid reaction rate, high monomer conversion and low monomer residue, and low- or room-temperature operation. In addition, it provides solvent-free formulations, which reduce the emissions of volatile organic pollutants.

The importance of polysulfones (PSs) as commercial membrane materials with applications in both large-scale and laboratory-scale production is due to its inherent chemical and thermal stability. Although the applications of PSs are diversified, modifications demand versatility. Modifications of the properties of PSs according to tailor-made specifications are important criteria for various applications.

Here, in this study, for the modification of asymmetric PS membranes, acrylic acid (AA) has been chosen. The monomer is water-soluble and photoresponsive. The attachment of AA has the ability to generate the functionality of the membrane surface so that it can be low-charge and show some potential to reject strong electrolytes as well as low-molecular-weight compounds. In other words, the objective of the work is to develop a functionalized asymmetric PS membrane that shows its capability for the nanofiltration range. The experimentation proves that modification can occur without a sensitizer for AA. Here, in this study, an experiment has been performed with our bench-scale PS (modified/unmodified) membranes, and a permeation experiment has been conducted with 2,4-dichlorophenol and glucose molecules to show the wide variation of the performances of the modified membranes.

EXPERIMENTAL

Materials and methods

PS (Udel P-3500; Solvay advanced polymers, Alpharetta, GA), dimethylformamide (Merck, Mumbai, India), and sodium lauryl sulfate were used to prepare the asymmetric membrane. AA (SRL, Mumbai, India) was used as a monomer to modify the PS membrane. 2,4-Dichlorophenol (SD Fine Chemicals, Mumbai, India), glucose (Glaxo, Mumbai, India), sodium chloride, and sodium sulfate were used in the membrane permeation experiments. Reverse-osmosis-treated water was used in the experiments.

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TABLE I
Experimental Conditions and AA Contents for the Modified PS Membranes

Membrane	AA (%)	Dipping time (min)	AA $\times 10^7$ (mol/cm ²)
Memb-I	1	10	2.9
Memb-II	5	10	3.4
Memb-III	10	10	5.1
Memb-IV	1	30	4.1
Memb-V	5	30	7.2
Memb-VI	10	30	10.2

Light-induced experiments were performed with a 125-W Philips HPR UV lamp (Turnhout, Belgium). The membrane samples were kept at a 5-cm distance from the light. The lamp generated 300–400-nm and 171 W/m² light. All experiments were carried out at the ambient temperature. The photoirradiation was carried out in a nitrogen atmosphere. The radiation density flux on the entire surface area was assumed to be constant in each run.

Methods

The PS membranes (15% w/w) in dimethylformamide were prepared over nonwoven polyester fabric (1 m wide) by a phase-inversion technique^{23–25} with a prototype casting machine. The choice of the dimethylformamide solution for dissolving the PS was preferred because the dissolution was slow and did not lead to fast and poorly controlled nonhomogeneous deformation.²⁶ The polymeric solution, cast onto the nonwoven fabric, then was dipped into the non-solvent bath (here water). Sodium lauryl sulfate was used in the gelation bath to control the pores in the membrane.

AA solutions (in water) of different concentrations were spread on the PS membranes (asymmetric side) fitted on a glass tray for different times. The solutions were decanted from the membrane surface and photoirradiated for 10 min at the ambient temperature in a nitrogen atmosphere. The experimental details are shown in Table I.

Techniques

To confirm the presence of AA on the PS membrane, attenuated total reflection infrared spectroscopy

(with a PerkinElmer Spectrum GX, Norwalk, CT with a resolution of ± 4 cm⁻¹ and an incident angle of 45°) of the surface layer of the modified and unmodified membranes was performed.

The membranes were structurally characterized by atomic force microscopy (AFM). The images were obtained from a Multimode scanning probe microscope with a NanoScope IV controller (M/S Veeco, Santa Barbara, CA) in the tapping mode.^{25,27} The scan size was 2×2 μm^2 , and the scanning rate was 1.507 Hz. The direct information on the height was characteristic of the membranes. The roughness data are tabulated in Table II.

The porometric studies were performed with a capillary flow porometer (model 1500 AEX, Porous Materials, Inc., Ithaca, NY), the pores being considered capillaries. In this technique, the membrane samples were soaked in a liquid called Porewick (surface tension \Rightarrow 16 dyn/cm). The pressure of the nitrogen gas on one side of the wet membrane samples was then gradually increased. With increasing pressure, the gas removed the liquid from the smaller pores, and the gas flow rate increased. The gas permeation was measured up to 200 psi. The mean flow pore diameter and the corresponding flow pressure data are shown in Table III.

The contact angles in water were measured with a tensiometer (DCAT 21, Dataphysics, Filderstadt, Germany). This is based on an energy balance approach to the three-phase equilibrium, which results in Young's equation:^{28,29}

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

where γ represents the surface tension for the particular interface, sv is the solid vapor, sl is the solid liquid, and lv is the liquid vapor.

The permeability was measured at room temperature with a laboratory-made pressure cell. The effective membrane area was 0.00152 m². The water flux and salt rejection experiments with sodium chloride and sodium sulfate (2000 ppm) were performed. The permeability experiments for glucose (500 ppm) and 2,4-dichlorophenol (20 ppm) were of the short run type, each lasting for about 3 h. They were carried out at the laboratory temperature and an operating pressure of 0.34 MPa.

The salt rejection measurement was performed with the conductivity relationship, as the concentra-

TABLE II
Roughness Data (nm) of the Membranes

Unmodified PS membrane	Memb-I	Memb-II	Memb-III	Memb-IV	Memb-V	Memb-VI
9.239	7.747	9.268	9.843	8.499	10.603	13.893

TABLE III
Porometric Data of the Membranes

	Unmodified PS membrane	Memb-I	Memb-II	Memb-III	Memb-IV	Memb-V	Memb-VI
Mean flow pore diameter (μm)	0.101	0.080	0.077	0.05	0.047	0.04	0.035
Mean flow pressure (psi)	65.4	83.1	85.7	131.9	140.2	165.2	187.4

tions follow a direct relationship.^{30,31} The efficiency of the membranes in removing the studied solutes was determined as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where R is the rejection (%) and C_p and C_f are the concentrations for the permeate and the feed solution, respectively. The concentrations of the organic compounds in water were monitored with ultraviolet-visible (UV-vis) spectrophotometry.

The flux was calculated with the following relation:

$$\text{Flux} = \frac{v}{t \times A}$$

where v indicates the volume of the permeate (L), t is the time (days), and A is the effective membrane area (m^2).

The 2,4-dichlorophenol concentrations were analyzed with UV-vis absorption spectrophotometry. The glucose concentrations were measured with the phenol/sulfuric acid colorimetric method.³² The analysis of glucose was based on a condensation reaction with phenol in an acid medium, yielding a yellow-orange color.³³ The wavelength of detection was 291 nm for 2,4-dichlorophenol and 485 nm for glucose.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of the PS membrane and PS-AA membranes (1 and 10%). The strong reflectance at $1586\text{--}1488\text{ cm}^{-1}$ is related to the benzene ring stretching mode. The sulfone bands can be observed at 1151 cm^{-1} . Asymmetric C—O stretching frequencies occur at 1244 and 1014 cm^{-1} . These observations are similar to earlier reports^{34–37} in the literature.

The 1726-cm^{-1} reflectance of C=O stretching can be well observed in the AA-modified membrane. There is a shifting (maximum $\sim 6\text{ cm}^{-1}$ for PS2) as the molecular environment is different than that of the individual monomer, which exhibits C=O stretching at 1720 cm^{-1} .²⁷ The absence of 3080- , 984- , and 927-cm^{-1} frequencies suggests that there is no unsaturation ($=\text{CH}_2$) on the surface of the PS membrane.

The probable mechanism for photoinduced modification is shown in Figure 2. It involves the following steps:²¹ (1) the absorption of light by the phenoxyphenyl sulfone chromophores in the PS chain; (2) photoexcitation resulting in the homolytic cleavage of a C—S bond at the sulfone linkage and in the random cleavage of the polymer backbone, yielding two radical sites at the ends of the polymer chains; and

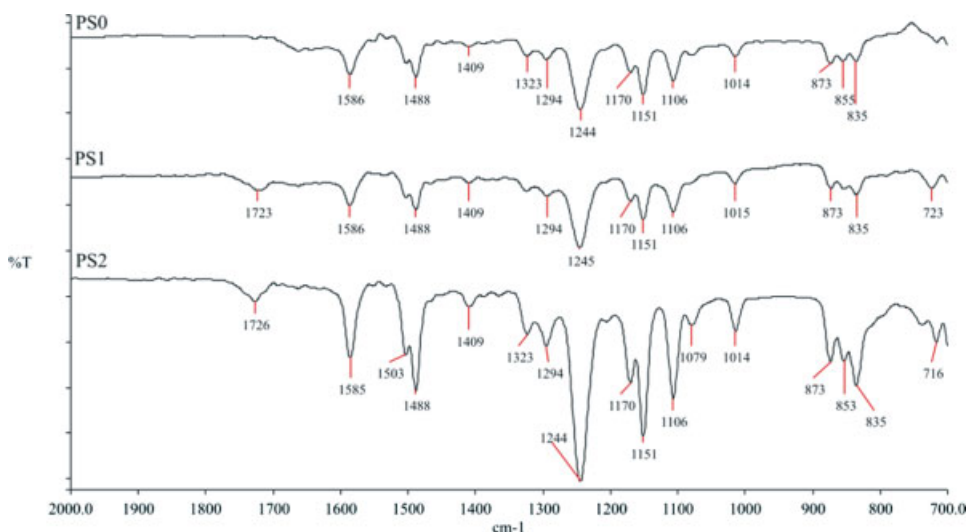


Figure 1 FTIR spectra of PS and AA-modified PS membranes. The conditions were as follows: a dipping time of 30 min, an AA concentration of 1%, and a photoirradiation time of 10 min for PS1 and a dipping time of 30 min, an AA concentration of 10%, and a photoirradiation time of 10 min for PS2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

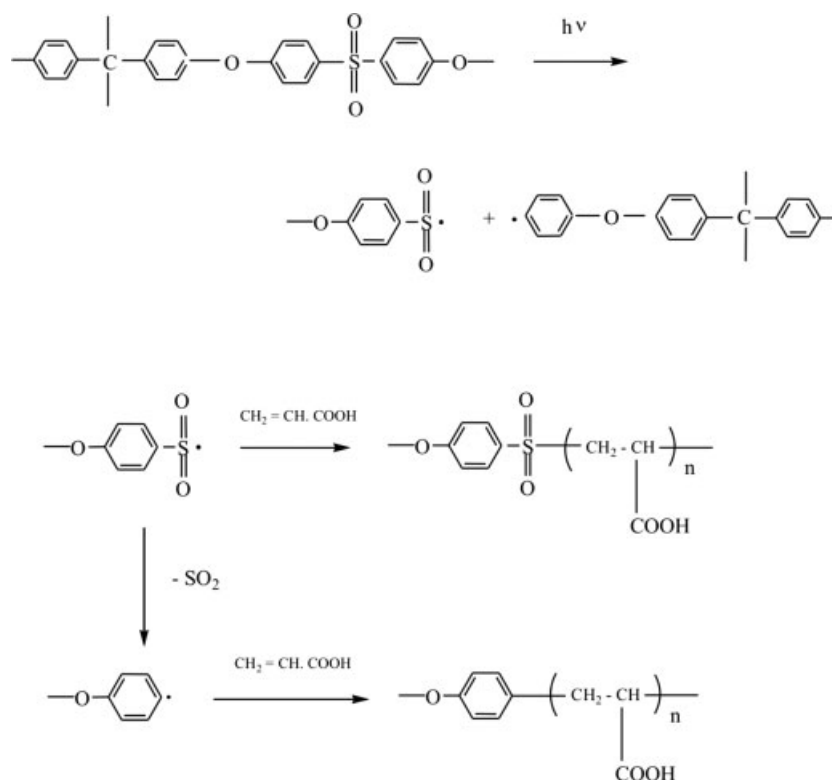


Figure 2 Proposed mechanism for the photoinduced modification of PS with AA.

(3) the reaction of AA with the aryl and sulfonyl radical. Alternatively, the sulfonyl radical may lose sulfur dioxide to generate an additional aryl radical, which also may initiate polymerization.

The weight differences of the modified membranes are due to the presence of AA on PS. Table I shows that with the increase in the dipping time as well as the concentration, an increase in the weight is

reflected systematically, and it is in the range of 10^{-6} – 10^{-7} mol/cm².

The micrographs of Memb-III and Memb-VI are shown in Figure 3. They show visual evidence of AA on the PS membranes. As shown in Tables I and II, the roughness increases with the AA content on PS. Initially, with a low content of AA, the roughness is rather low with respect to PS.

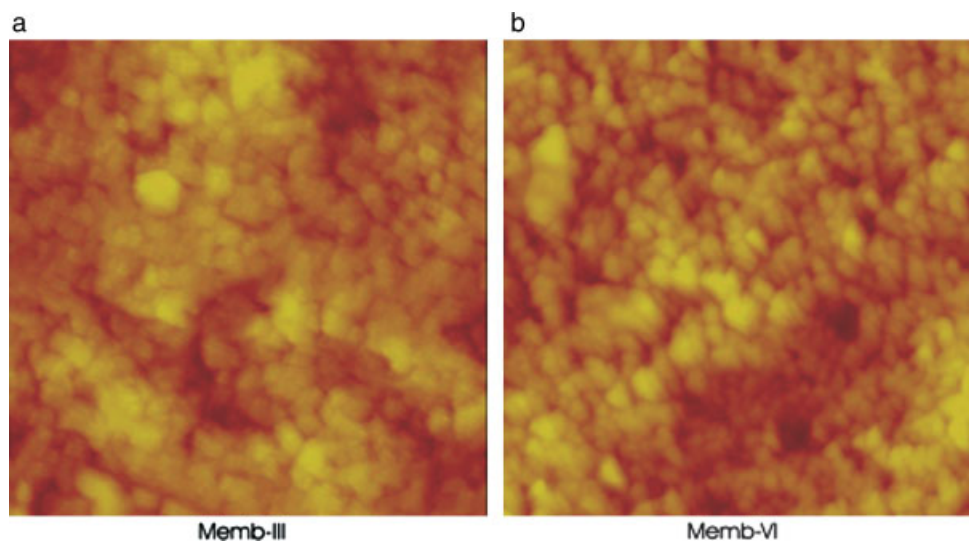


Figure 3 AFM for the modified membranes: (a) III and (b) VI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Performance of the Salt Rejection of the Membranes

Membrane	Water flux ($\text{lm}^{-2} \text{d}^{-1}$)	NaCl		Na ₂ SO ₄	
		Rejection (%)	Flux ($\text{lm}^{-2} \text{d}^{-1}$)	Rejection (%)	Flux ($\text{lm}^{-2} \text{d}^{-1}$)
Unmodified PS membrane	13,644	3.2	11,844	4.2	12,033
Memb-I	4169	4.5	3,790	15	3,695
Memb-II	3032	9	2,653	39.39	2,558
Memb-III	2464	14.4	2,132	43	2,085
Memb-IV	3790	5.6	3,506	24.2	3,222
Memb-V	2464	13.6	2,132	45.45	2,085
Memb-VI	1421	20.4	1,042	50.0	1,137

Feed concentration = 2000 ppm; pressure = 0.34 MPa.

Table III lists the porometric data for the unmodified and modified PS membranes. In the case of the unmodified PS membranes, the mean flow pore diameter is 0.101 μm . With an increase in the AA content on PS, the mean flow pore diameter decreases. The minimum mean flow pore diameter is 0.035 μm for Memb-VI. The mean flow pore pressures for the unmodified and modified membranes follow the reverse trend, as expected.

Comparing the contact angles of unmodified and modified membranes, we can see that with an increase in the AA content, the contact angle decreases. The maximum decrement of the contact angle is 2.48° for the modified membrane with respect to the unmodified PS membrane. A smaller contact angle indicates a more hydrophilic surface.²³ The decrement of the contact angle provides evidence of AA on the membrane and also suggests that a hydrophilic nature appears in the modified membrane.

To prove the efficiency of the modified membranes for the desalination of water, the permeation experiments were performed with synthetic water containing sodium chloride and sodium sulfate (2000 ppm). The membranes were dipped in water for 36 h before the experiment. The performance results of the experiments are shown in Table IV. The rejection ability of the membranes can be explained by the functionalized (—COOH) membrane. Different theories are described in the literature to explain the removal of electrolytes.³⁸ Because of the presence of the —COOH group, the salt rejection ability of the membrane could be explained by the well-accepted electrical and preferential sorption theoretical models. The rejection order of the ions

($\text{SO}_4^{2-} > \text{Cl}^-$) through the membranes can be explained by the greater hydrated size ($\text{SO}_4 = 3.79 \text{ \AA}$, $\text{Cl}^- = 3.32 \text{ \AA}$) and valence of the sulfate ions. The increase in the rejection with the AA-modified membrane can also be explained with the preferential sorption theory suggested by Sourirajan.³⁹ As the AA content (with increasing concentration and dipping time) increases on the membrane surface, the preferential layer of water that builds up at the membrane solution interface becomes greater; it is enriched with water and depleted of electrolytes. The higher rejection of the divalent anionic salt (Na_2SO_4) in comparison with the monovalent anionic salt (NaCl) clearly suggests the operation of Donnan's ion-exclusion phenomenon, in which electrostatic interactions play an important role. The maximum rejections of NaCl and Na_2SO_4 are 20.4 and 50% for Memb-VI. However, the membrane modified by 1 h of dipping in AA (10%) gives the same performance in terms of salt rejection as that dipped for 30 min in the same concentration.

The glucose (low-molecular-weight and neutral) molecule permeability is checked to show the wide variation of the performances of the modified and unmodified membranes. The glucose rejection of the membranes shows the following trends: Memb-III > Memb-II > Memb-I > unmodified PS and Memb-VI > Memb-V > Memb-IV > unmodified PS (Table V). This suggests that with the increase in the AA content on the PS, the glucose retention is greater. The glucose retention of the membranes shows pore-blocking evidence for the membranes, which is already reflected in the porometric data. The glucose rejection of the unmodified PS membrane is 9.2%,

TABLE V
Performance of the Membranes in the Retention of Glucose and 2,4-Dichlorophenol

Membrane	Unmodified PS membrane	Memb-I	Memb-II	Memb-III	Memb-IV	Memb-V	Memb-VI
Glucose	9.2	23	34	42	38	62	78
2,4-Dichlorophenol	10.5	23.6	25.5	35	36.2	39.3	58

but its maximum is 78% for the modified membranes.

The remediation of the water pollutant (2,4-dichlorophenol) has been also tested. The performance data are tabulated in Table V. The rejection of 2,4-dichlorophenol by the membranes shows a trend similar to the glucose rejection data. In comparison with the glucose rejection, the modified membranes show low phenolic rejection because of the relatively low molecular weight with respect to glucose and the polarity of the molecule.^{39,40}

CONCLUSIONS

AA-modified PS membranes have been prepared with a light-induced technique without a sensitizer. Fourier transform infrared (FTIR), AFM, contact-angle, and porometric studies provide evidence for the modified membranes:

1. The salt rejection behavior of the membrane correlates with the content of functionality on the membrane. The rejection of the ions follows the order of $\text{SO}_4^{2-} > \text{Cl}^-$.
2. The retention of organic molecules (glucose and 2,4-dichlorophenol) also depends on the AA content on the membrane.
3. The retention of glucose by the modified membrane, higher with respect to 2,4-dichlorophenol, is due to the higher molecular weight and low polarity of glucose.

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