Development of New Ionomer Blend Membranes, Their Characterization, and Their Application in the Perstractive Separation of Alkenes from Alkene–Alkane Mixtures. I. Polymer Modification, Ionomer Blend Membrane Preparation, and Characterization

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ABSTRACT: In this contribution, the synthesis and characterization of novel ion-exchange blend membranes which contain the SO₃Ag group for the application in the perstractive separation of alkene–alkane mixtures, where the Ag^+ ion serves as facilitated transport site for the alkene via formation of a pi complex with the alkene double bond, is presented. In this part of the article, the synthesis and characterization of following blend membrane types are described: (1) acid-base blend membranes of ortho-sulfone-sulfonated polysulfone (PSU) with ortho-sulfone-diaminated PSU; (2) blend membranes of ortho-sulfone-sulfonated PSU with unmodified PSU; (3) blend membranes of ortho-sulfone-sulfonated PSU with ortho-sulfone disilylated PSU. The differently modified PSU types were characterized via ¹H nuclear magnetic resonance (¹H-NMR). The acid-base blend membranes were characterized via Fourier transfer infrared (FTIR) spectroscopy. It could be indirectly proved that formation of PSU- SO_3 —⁺H₃N–PSU ionic crosslinks takes place. Transmission electron microscopy (TEM) investigations of (1) and (2) yielded the results that these blends are inhomogeneous at the microscopic scale. Mechanical stabilization of these blends is accomplished by physical entanglement of the different macromolecules. The blends (3) were macroscopically inhomogeneous due to the strong difference in hydrophilicity of the blend components. Only the blend 90% PSU-SO3H-10% PSU[Si(CH3)3]2 formed a blended membrane. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 428-438, 1999

Key words: facilitated transport; alkene; SO_3Ag -containing polysulfone (PSU) blend membranes; blend of sulfonated and aminated PSU; blend of sulfonated and unmodified PSU

INTRODUCTION

Membrane technology can be considered as an alternative separation process to conventional technologies, such as distillation and extraction, especially in cases where physical parameters, such as boiling points and solubilities, overlap, or in the separation of azeotropic mixtures and heatsensitive compounds. For membrane processes to be cost-effective, membranes should have high selectivity and high throughput and the membrane material should be inexpensive. In facilitated transport, weak, reversible, complex-forming reactions between carrier ions confined to the

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Figure 1 Modified polysulfone Udel[®], in which X, Y are the positions for lithiation, silylation, sulfonation, and amination.

membrane and unsaturated hydrocarbons are used to increase olefin fluxes. As a result, selectivity for the recovery of olefins is increased.

Previous studies on facilitated transport through sulfonated polysulfone PSU Udel[®] membranes showed good separation factors for pentene-pentane mixtures, but pentene fluxes through the membranes were low.¹ In this study, olefin fluxes were increased using three concepts. The free volume of polymers is increased by introducing bulky groups unto the polymer backbone to decrease the packing density and the torsional mobility of the chains,^{2,3} and high gas permeabilities result.^{4,5} Methyl, nitrate, and halogen groups have been used successfully to increase polymer free volume.^{2,3,6} Masuda et al. reported high gas permeabilities through poly[(1-trimethylsilyl)–1-propyne] (PTMSP) membranes due to the excess free volume resulting from the bulky trimethylsilyl groups.⁵ The facilitated transport of olefin gases were investigated by introducing silver ions into the PTMSP membranes by complexation to the double bond of polyacetylene to form a poly[(1-trimethylsilyl)–1-propyne]–AgClO₄ complex membrane or by ion-exchange into poly-[(1-trimethylsilyl)–1-propyne]–graft poly(acrylic acid)–Ag⁺ complex membranes.^{7,8}

A second way of increasing olefin fluxes is by increasing the ion-exchange capacity of the ionomer membrane. Polysulfone ionomers with high ion-exchange capacities can be produced because there are two positions on the PSU repeat unit that can be substituted with the sulfonic acid group. However, 1.5- to 2-fold substituted ionomers are water-soluble. Dissolution can be prevented by stabilizing the ionomer membrane with a polymer containing basic groups where the saltforming reaction PSU–SO₃H + PSU–NH₂ \rightarrow PSU–SO₃–⁺H₃N–PSU takes place. Several studies



Figure 2 Assignment of aromatic protons for ¹H-NMR spectroscopy of PSU (unmodified, onefold modified, and twofold modified PSU repeating units¹²).

have been performed on the interaction of acid and base polymers.^{9,10} The ion-exchange capacities, degrees of swelling, and ionic resistances of the membranes can be controlled by changing the ratios of sulfonated to aminated polysulfone. A third method of increasing hydrocarbon fluxes is by producing ultrathin membranes. In laboratory studies, it has been shown that thin, nonsupported, sulfonated PSU membranes are not stable in pentene-pentane mixtures. More stable membranes can be produced by blending unmodified PSU with sulfonated PSU.¹¹ Membranes with different ion-exchange capacities, degrees of swelling, and ionic resistances can be produced by controlling the ratios of the two polymers.

PREPARATION OF POLYMERS

Polysulfone Udel® 1800 was used as the base polymer and was modified in the X and Y positions shown in Figure 1. In all modifications, the initial procedure was to deprotonize the polymer ortho to the sulfone bridge by reacting with butyllithium at -65 to -70° C.^{11,12} Polysulfone Udel® 1800 was dissolved in THF at ambient temperatures and under an argon atmosphere. First, 2–3 cm³ of 2.5 mol dm⁻³ butyllithium was added to the dissolved polymer to react with impurities in the reaction mixture. Butyllithium was added until a light orange color appeared as indication of the first lithiated polymer. Thereafter, a stoichiometric amount of 10 mol dm^{-3} butyllithium was added at -65° C to lithiate the polymer. The mixture was stirred for 1 h. Subsequently, the metalated polymer was reacted with different reagents to produce the silvlated, sulfochlorinated, and aminated PSU polymers.

Preparation of Sulfochlorinated PSU

A syringe was used to swiftly introduce sulfurylchloride in a 20% excess into the solution of the lithiated PSU.¹¹ The polymeric solution decolorized within seconds. Subsequently, 200 mL of H_2O were added to the solution, and the polymeric solution was allowed to warm to ambient temperature. During this time, the solution separated into two phases, with the upper solution containing the solution of sulfochlorinated PSU in THF, and the lower solution containing mainly H_2O , THF, Li salts, and hydrolysis products of excess sulfurylchloride. The upper phase was poured into a threefold excess of *i*-propanol,



Figure 3 Aromatic region of the ¹H-NMR spectrum of unmodified PSU, together with the assignment of aromatic protons.

where the sulfochlorinated PSU precipitated. The polymer was filtered off, washed thoroughly with i-prOH, and dried at 50-70°C under 50 mbar vacuum.

Preparation of Sulfonated PSU¹¹

The dried sulfochlorinated PSU (2 sulfochloride groups per repeating unit) was suspended in a 20-fold excess $H_2O(w/w)$, and heated under stirring to 90–95°C for 48 h. During this time, the polymer dissolved due to progressive hydrolysis of the sulfochloride group:

$$PSU-SO_2Cl + H_2O \rightarrow PSU-SO_3H + HCl$$

After complete dissolution of the polymer, the solution was dialyzed in a cellulosis-acetate dialysis tube to remove all HCl formed. Subsequently, the polymer was dried at 95°C in a drying oven. Then the polymer was milled and stirred under diethyl ether in order to remove H₂O residuals. Finally, the ether was evaporated at 95°C and under oil pump vacuum (10^{-1} mbar).

Preparation of Aminated PSU

PSU Udel[®] was aminated ortho to the sulfone bridge to obtain diaminated PSU by a procedure developed by Guiver et al.,¹³ which comprises the following stages:



Figure 4 Aromatic region of the 1 H-NMR spectrum of sulfochlorinated PSU, together with the assignment of aromatic protons.



Figure 5 Aromatic region of the 1 H-NMR spectrum of sulfonated PSU, together with the assignment of aromatic protons.



Figure 6 Aromatic region of the ¹H-NMR spectrum of disilylated PSU, together with the assignment of aromatic protons.

 $\begin{array}{c} NaBH_4 \\ PSU-NNN \xrightarrow{} PSU-NH_2 \end{array}$

Preparation of Silylated PSU

A 10% excess of the required stoichiometric amount of chlorotrimethylsilane was added to the lithiated polymer solution, and the reaction temperature was allowed to increase to -20°C. The mixture discolored, which indicated completeness of the reaction, as follows:

 $PSU-Li + Cl-Si(CH_3)_3 \rightarrow PSU-Si(CH_3)_3$

The modified polymers were precipitated in isopropanol, filtered, washed with water and isopropanol, and dried under vacuum.

MEMBRANE PREPARATION

Blends of PSU-Sulfonic Acid and Diaminated PSU

The $PSU-NH_2/PSU-SO_3H$ blended membranes were prepared by dissolving the polymers in

NMP. The substitution degree of the aminated polymer was 1.67 amine groups per repeating unit, while the ion-exchange capacity of the sulfonated PSU was 2.6 meq/g dry polymer. Solutions of 14% sulfonated PSU and 20% aminated PSU were prepared and mixed in ratios of 70/30, 80/20, 88/12, and 93/7 w/w%. The polymer solutions were stirred well and cast onto a glass plate by means of a doctor's knife. Solvents were evaporated at 80–120°C under vacuum.

Blends of Sulfochlorinated PSU and Unmodified PSU and Its Hydrolysis

Sulfochlorinated PSU with a substitution degree of 1.87 groups per repeating unit and unmodified PSU polymers were dissolved in THF (15% solutions) and mixed in ratios of 70/30, 50/50, 30/70, 20/80, and 10/90 (w/w%) PSU to PSU–SO₂Cl. After stirring, polymer solutions were cast onto a glass plate using a doctor's knife. The solvent was evaporated at room temperature, and the final traces were removed at 60°C in a vacuum oven. The membranes were hydrolyzed by soaking in water at 90°C overnight.

Blends of Sulfochlorinated PSU and Silylated PSU and Its Hydrolysis

Sulfochlorinated (1.87 SO₂Cl per repeating unit) and Silylated PSU [2 Si(CH₃)₃ per repeating unit]



Figure 7 Aromatic region of the ¹H-NMR spectrum of aminated PSU, together with the assignment of aromatic protons.

were dissolved in THF, respectively, and mixed in ratios of 70/30, 50/50, 30/70, 20/80, and 10/90 (w/w%) PSU–Si(CH₃)₃ to PSU–SO₃H. Polymer solutions were cast onto a glass plate using a doctor's knife, and the solvent was evaporated at room temperature. Final traces of THF were removed at 60°C in a vacuum oven. Membranes were hydrolyzed by soaking in water at temperatures of 70–90°C.

POLYMER AND MEMBRANE CHARACTERIZATION

¹H Nuclear Magnetic Resonance

The degree of substitution for silvlated, sulfochlorinated, sulfonated, and aminated PSU polymers was determined from the integrals of proton signals in the aromatic regions of the respective ¹H nuclear magnetic resonance (¹H-NMR) spectra. The assignment of protons for substituted PSU (unmodified, onefold modified, and twofold modified PSU repeating units) is shown in Figure 2.

In Figure 3, the aromatic region of the ¹H-NMR spectrum of unmodified PSU is shown, together with the assignment of aromatic protons. The ¹H-NMR spectrum of sulfochlorinated PSU is given in Figure 4.

Integration of aromatic protons and comparison of the aromatic signals give a medium sulfochlorination degree of $1.87 \text{ SO}_2\text{Cl}$ groups per repeating unit. Hydrolysis of this polymer yields sulfonated PSU with an ion-exchange capacity of 2.6 meq SO₃H/g. From ¹H-NMR integral analysis (Fig. 5), the conclusion can be made that the hydrolyzed polymer also contains, in mean, 1.87 SO₃H groups per PSU repeating unit.

The ¹H-NMR spectrum for silvlated PSU is shown in Figure 6. From the spectrum, the conclusion can be made that the silvlation degree is 2 per repeating unit, as intended.

The aromatic region of the ¹H-NMR spectrum of aminated PSU is given in Figure 7. Integration of the aromatic and NH_2 group protons leads to the result that the amination degree of the PSU is 1.67 NH_2 groups per repeating unit.

Fourier Transform Infrared Spectroscopy

Infrared (IR) spectroscopy was used to investigate the interaction of amine and sulfonic groups in the blended membranes.⁹ The IR spectra of sulfonated and aminated PSU are shown in Figure 8. The most characteristic band of PSU with $-SO_2$ —OH groups is at 922 cm⁻¹ due to the S—O stretching vibrations, as described in the literature,^{14,15} while characteristic bands for PSU with



Figure 8 IR spectra of sulfonated and aminated PSU.

NH₂ groups are at 1670 cm⁻¹ due to the in-plane bending vibration, at 1300 cm⁻¹ due to C—N stretching of primary aromatic amines, and at 980 cm⁻¹ due to out-of-plane bending vibrations.^{15,16} Common to both polymers are the R—SO₂—R groups, and characteristic bands are in the 1120 cm⁻¹ region due to symmetric S=O stretching vibrations and in the 1230 cm⁻¹ region due to asymmetric S=O stretching vibrations.^{14,15} Identification of the exact bands is difficult due to the overlapping with the symmetric S=O stretching vibrations of aromatic sulfonates in the 1260–1150 cm⁻¹ region and the asymmet-

ric S=O stretching vibrations in the 1080–1000 cm^{-1} region.

To study the interactions between the sulfonated and aminated blends, the focus was on the band at 922 cm⁻¹ assigned to the S—O stretching vibration. As shown in Figure 9, the intensity of this band increases as the sulfonate content of the membranes increases. The intensity of the N—H out-of-plane vibration at 980 cm⁻¹ decreases, as the amine content of the membranes decreases. Transfer of the proton from the —SO₃H groups to the —NH₂ group to form the —SO₃— and —NH₃⁺ ionic groups results in a decrease in the intensity



Figure 9 IR spectra of sulfonated and aminated PSU blends (50/50 Blend: 50 wt % PSU–SO₃H; 50 wt % PSU–NH₂. 70/30 Blend: 70 wt % PSU–SO₃H; 30 wt % PSU–NH₂. 80/20 Blend: 80 wt % PSU–SO₃H; 20 wt % PSU–NH₂. 88/12 Blend: 88 wt % PSU–SO₃H; 12 wt % PSU–NH₂).



Figure 10 Dependence of peak intensities of the sulfonate content of blended membranes before and after treatment with HCl at 80°C.

of the S—O stretching vibration due to the increase in molecular symmetry of the sulfonate group.¹⁷ The electron pair of the SO₃— would be delocalized among the three oxygen atoms so that all sulfur-oxygen bonds would be equal. Treating the blends with HCl to protonize the SO₃— groups and comparing the intensities of S—O stretching vibrations before and after treatment enabled indirect observation of the PSU–SO₃H/

 $\mathrm{PSU-NH}_2$ interactions. To analyze the interactions, the S—O stretching bands at 922 cm⁻¹ were normalized based on the band at 1010 cm⁻¹. This band is characteristic of PSU Udel[®] polymers (ring vibration of a 1,4-substituted aryl ether).¹⁸ Shown in Figure 10 is the dependence of S—O—H stretching vibration intensities on the sulfonate content of the blended membranes. The intensity for membranes not treated with HCl



Figure 11 TEM micrographs of sulfonated and aminated PSU blend before treated with HCl: (a) $3900 \times$ enlarged; (b) $105,000 \times$ enlarged.



Figure 12 Transmission electron micrograph (3900× enlargements) of blends of PSU–NH₂ and PSU–SO₃H post-treated with HCl: (a) blend of 30/70 PSU–NH₂/PSU–SO₃H; (b) blend of 20/80 PSU–NH₂/PSU–SO₃H; (c) blend of 12/88 PSU–NH₂/PSU–SO₃H; (d) blend of 7/93 PSU–NH₂/PSU–SO₃H.

levels off due to interactions between the sulfonate and amine groups. After treatment with HCl, the —SO₃— groups are protonized, and the acid/base reactions are reversed; thus, an excess acidity is introduced into the blends, which is indicated by the ion-exchange capacity of the blends, which is much higher after the HCl treatment:

$$\begin{split} \text{PSU-SO}_3 &\longrightarrow ||||| \text{H}^+ ||| \text{H}_2\text{N}-\text{PSU} + \text{HCl} \rightarrow \\ \\ \text{PSU-SO}_3\text{H} + [\text{Cl}^- + \text{H}_3\text{N}-\text{PSU}] \end{split}$$

As a result, the intensities of the S—O—H stretching vibrations increase linearly with the sulfonate content of the membranes.

Electron Microscopy

The miscibility of PSU–NH₂ and PSU–SO₃H polymers was investigated by transmission electron microscopy (TEM), and the contrast of blended polymers was enhanced by silver impregnation.¹⁹ Figure 11 represents a TEM micrograph of sulfonated PSU and aminated PSU blended membranes before treatment with HCl and indicates that silver is distributed evenly through the cross section of the membrane. The dark spots in Figure 11(a) and (b) represent microphases in the blended membrane matrix. No phase separation between the sulfonated and aminated PSU was observed, indicating that the interaction of sulfonated and aminated



Figure 13 TEM micrographs of PSU/PSU–SO $_3H$ blends (3900 \times enlargements): (a) 50/50 ratio; (b) 30/70 ratio.





Figure 15 TEM micrograph of PSU–Si(CH₃)₃—PSU–SO₂H blended membrane ($3900 \times$ enlargement).

regions of the PSU polymers resulted in the two ionomers being compatible.

After treating the membranes with HCl, the polymers became immiscible in microscopic regions, as shown in the electron micrographs of the blended membranes in Figure 12. The polymers separated into charged phases, which contained large amounts of silver (dark areas) and smaller, neutral, or positively charged areas with less silver (light oval-shaped areas). Post-treatment of the membranes with 8% HCl at 80°C protonized (partially) both the sulfonate and amine groups, forcing the reverse reaction to take place and phases to separate. The extremely high ion-exchange capacities compared to the theoretical ionexchange capacities confirmed this and indicated that the system did not exist as a frozen-in nonequilibrium structure.9 Membranes were stabilized by physical entanglement of the polymers. which was enhanced by the initial acid/base interaction. As shown in the TEM micrographs of Figure 13, phase separation was observed in the membrane matrix of sulfonated PSU and unmodified PSU blends. Membranes were stable due to the entanglement of polymers.

Silylation of polysulfone increased the hydrophobic nature of the polymer, while sulfonation of polysulfone increased the hydrophilic nature of the polymer. As a result the polymers are not compatible and in a series of membranes containing 70/30, 50/50, 30/70, 20/80, and 10/90 (w/w %) PSU–Si(CH₃)₃ to PSU–SO₃H, only the 10/90 ratio formed a blended membrane. As shown in the scanning electron microscopy (SEM) micrograph of Figure 14(a), all other membranes formed two layers of polymer on top of each other. The layers

differ in hydrophilic/hydrophobic nature and separate into two layers during drying of the membranes. Elemental analyses of the two layers are shown in Figure 14(b) and indicate that the one layer consists of PSU-SO₃H and the other layer consists of PSU-Si(CH₃)₃. The 10/90 w/w % mixture of PSU-Si(CH₃)₃ and PSU-SO₃H formed a blended membrane and, although silver was distributed evenly throughout the cross section of the membrane, an extent of incompatibility was observed due to circular structures in the membrane matrix shown in Figure 15. Physical entanglement of polymer chains in the blended membrane stabilizes the PSU–SO₃H polymers, which are normally soluble in water at this ion-exchange capacity.

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