The Preparation of Microporous Membranes from Blends of Poly(2,6-dimethyl-1,4-phenylene oxide) and Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a chemically resistant polymer and, therefore, an attractive material for the formation of membranes. However, membranes of unmodified PPO prepared by an immersion precipitation possess very low hydraulic permeabilities at the filtration processes. The membranes with higher hydraulic permeabilities can be prepared from sulfonated PPO and/or from blends of unsulfonated PPO and sulfonated PPO. In conclusion, the mechanism of the formation of membranes from blends of unsulfonated PPO and sulfonated PPO is suggested. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 161–167, 1999

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INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an attractive material for the preparation of membranes, because it exhibits excellent film-forming and gas separation properties, and is resistant against a number of chemical agents, including aqueous solutions of strong acids and bases. The main interest in the application of unmodified and modified PPO membranes is directed to gas separations[1–5] to reverse osmosis,[6–9] and in a lesser extent to vapor permeation[3] and pervaporation.[10,11] PPO ultrafiltration membranes were prepared by immersion precipitation

by Broens et al.[12] from PPO solutions containing unmodified polymer dissolved in the binary solvent/nonsolvent mixture of trichloroethylene/octanol. These membranes, when used for the purification of aqueous solutions in an ultrafiltration process, had, however, very low permeabilities to water. In a former work, Schauer et al.[13] prepared membranes from a moderately sulfonated PPO (sulfur content: 1.2 wt %) by immersion precipitation method. Chloroform/1-butanol were used as solvent/nonsolvent binary mixtures. Membranes with water permeabilities up to 900 L/m² h MPa could be prepared. However, heterogeneous sulfonation of PPO powder in sulfuric acid depends on the porosity of the PPO powder and allows only a low degree of sulfonation.

The aim of this study was the preparation of PPO microporous membranes having higher permeabilities to water and bearing negative charges, which may improve antifouling properties. The negative charges should be generated by

a homogeneous and a newly developed heterogeneous sulfonation procedures.

EXPERIMENTAL

Homogeneous Sulfonation of PPO

PPO (10 g) (manufactured by Spolana Neratovice, Czech Republic) of different molecular weigths was dissolved in 200 g of 1,2-dichloroethane (45°C) and a calculated amount of chlorsulfonic acid in 50 g of 1,2-dichloroethane was added with stirring to the solution over a period of 30 min. The mixture was stirred at room temperature for at least 6 h, and then it was precipitated into methanol. The precipitated sulfonated product was removed by filtration, washed with distilled water, and dried and characterized by elemental analysis.

Heterogeneous Sulfonation of PPO

PPO (10 g) was first dissolved in 20 g of trichloroethylene and the solution was added under vigorous stirring to 100 g of sulfuric acid (98.0 wt %). During the addition to the sulfuric acid, the dissolved polymer is precipitated as a swollen heterogeneous gel with a small particle size. Then the mixture of swollen PPO particles and sulfuric acid was stirred at room temperature for 10–600 min. Finally, the PPO particles were removed by filtration, washed with distilled water, dried, and characterized by elemental analysis.

Membrane Preparation

The membranes were prepared from solutions containing PPO and/or sulfonated PPO (total amount of polymers: 10 wt %), chloroform as the solvent and 1-butanol as the nonsolvent (chloroform/1-butanol 85 : 15 by weight). The solutions (20°C) were cast on a glass plate as a 0.35-mm thick film; after 20 s evaporation time the films were immersed into a methanol coagulation bath; then after 20 min the glass plate with the membrane was transfered into a water bath.

Sulfonation of Membranes of Nonsulfonated PPO

The initially wet membranes prepared from a nonsulfonated PPO were immersed for approximately 1 min in a 25 wt %, subsequently in a 50 wt %, and finally in a 75 wt % aq. H_2SO_4 solution,

and then for a given time (2 min to 2 h) in 98 wt % H_2SO_4. The membranes treated by sulfuric acid were washed in 75, 50, and 25 wt % H_2SO_4, respectively, and finally in water.

Membrane and Casting Solutions Characterization

Permeabilities and rejections of prepared membranes were determined in an ultrafiltration stirred cell type GN 10-400 (Berghof GmbH, Eningen, Germany) at 0.05 MPa. The ultrafiltration experiments were carried out first with distilled water, then with a single solution of a test substance mixture (0.1 wt % aqueous solution of a dextran mixture with molecular weights from 650 to 215,000). Molecular size distributions of dextrans in permeates, in retentates and in original solutions, were determined using gel permeation chromatography (GPC). From the results of GPC the average pore diameter (D_{50}), the maximal pore diameter (D_{100}) and the corresponding molecular weigths were calculated by assuming a logarithmic normal distribution of the pore size.[14] The pore density was calculated from the average pore size and the water permeability by means of the Sampsson equation.[15]

The limiting viscosity numbers were measured with an Ubbelohde viscometer in a mixture chloroform/1-butanol (85 : 15 by weight) at 25°C.

The affinity between methanol and sulfonated PPO has been determined by turbidic titration. Methanol was added to the PPO solution (10 wt %) dissolved in chloroform/1-butanol (85 : 15 by weight) at 25°C until turbidity appeared. The turbidity point was detected visually.

RESULTS AND DISCUSSION

By the heterogeneous sulfonation of PPO powder only low to moderately sulfonated PPO polymers will be obtained, as the sulfonation reaction takes place only at the interface of sulfuric acid and PPO powder.[13,16] Generally, the sulfur content of the modified polymer does not exceed to 2.5 wt %. Contrary to this powder modifiing technique, the precipitation of the PPO solution with concentrated sulfuric acid generated a highly swollen PPO gel with very small particle sizes and, therefore, a high surface that can be more readily modified with sulfonic groups. Under such conditions there can be reached a degree of sulfonation simu-

Figure 1 Cross-section of an asymmetric membrane from the blend of heterogeneously sulfonated PPO with nonsulfonated PPO (ratio of polymers 50 : 50 by weight, see Table I, line 3).

Figure 2 Dependence of water flux at 0.05 MPa on the sulfur content in polymer: (1) membranes from heterogenously sulfonated PPO; (2) membranes from homogeneously sulfonated PPO; M_w is always 52,600.

lar to that which can be obtained by a homogeneous sulfonation technique.

The membranes prepared from unsulfonated and sulfonated PPO had an asymmetric structure, as can be expected for membranes prepared by immersion precipitation. A typical morphology is shown in Figure 1. However, more unexpected is the fact that the membranes prepared from the heterogeneously sulfonated PPO or from the blend of the heterogeneously sulfonated PPO with nonsulfonated PPO can be, in some cases, several orders more permeable to water than the ones prepared only from nonsulfonated PPO under the same conditions (Figs. 2 and 3) or from homogeneously sulfonated PPO. Under optimal condition membranes with water permeabilities as high as 5000 L/m^2 h MPa can be obtained.

All membranes reported in this article were prepared from casting solutions containing 10 wt % of total polymers, chloroform as the solvent, and 1-butanol as the nonsolvent (chloroform–1-butanol 85 : 15 by weight). Permeabilities of resulting membranes are (as it is always the case with the phase inversion membranes) strongly dependent on the polymer and the nonsolvent concentrations in the casting solution: Low concentrations of the membrane-forming polymer solution and/or a high content of a nonsolvent in the casting solution generate high water permeabilities. However, it was not possible to increase substantially 1-butanol concentration in the casting system: higher 1-butanol concentrations caused

polymer precipitation in the casting solution,[13] and second, it was not possible to use casting solution with substantially lower polymer concentrations: Mechanical strength of resulting membranes is then too low for membrane applications.[13] Finally, it is also necessary to stress that all results concerning heterogeneously sulfonated PPO given in Figures 2 and 3 refer to PPO sulfonated with 98.0% H_2SO_4—the change of conditions of sulfonation (temperature, amount of reagents in the sulfonation reaction, and especially of H_2SO_4 concentration) brought about the change of permeability values of resulting membranes.

Figure 3 Dependence of water flux at 0.05 MPa on the sulfonated polymer content in blends of nonsulfonated polymer with sulfonated polymers: (1) heterogenously sulfonated PPO, sulfur content 3.3%; (2) homogeneously sulfonated PPO, sulfur content 3.2%; M_w is always 52,600.

Table I   Permeation and Porosity Characteristics of Membranes Prepared from Blends of PPO (M_w = 52,600) and Sulfonated PPO Based on PPO (M_w = 52,600), Heterogeneous Sulfonation, Sulfur Content 3.3%

PPO/SPPO[a]	J_w[b] (L/hm^2)	M$_{50}$[c] (g/mol)	M$_{100}$[d] (g/mol)	D$_{50}$[e] (nm)	D$_{100}$[f] (nm)	Pore Density[g] $\times 10^{-7}$
100 : 0	1.5	380	6300	1.2	4.4	1100
75 : 25	0.2	850	31,600	1.8	9.0	2
50 : 50	270	8400	464,000	5.0	30.2	580
25 : 75	227	39,000	7,780,000	9.9	107.3	240
0 : 100	≤1	—	—	—	—	—

[a] Ratio (weight) nonsulfonated/sulfonated PPO (M_w always 52,600) in the casting solution.
[b] Water flux at 0.05 MPa.
[c] Equivalent molecular weights of dextran molecules at the rejection of 50%.
[d] Equivalent molecular weights of dextran molecules at the rejection of 100%.
[e] Hydrodynamic equivalent diameters corresponding to M$_{50}$.
[f] Hydrodynamic equivalent diameters corresponding to M$_{100}$.
[g] Number of pores per cm^2 membrane area.

Rejection and porosity characteristics of the blend membranes exhibiting high hydraulic permeabilities are given in Table I. However, it should be emphasized that all calculations of pore sizes[14] have been based on permeabilities and rejections of water solutions, and therefore, the values express the effective pore sizes with respect to aqueous medium.

The considerable increase of permeabilities of some membranes prepared from the heterogeneously sulfonated PPO (Fig. 2) or from the blend of the heterogeneously sulfonated with nonsulfonated PPO (Fig. 3) can plausibly due to an interplay of several phenomena: (a) increased hydrophilicity of sulfonated PPO; (b) changed affinity of the precipitant (methanol) to the polymer; (c) influence of the viscosity of the casting solution; and (d) inhomogenity of the polymer chains comprising sulfonated parts and nonsulfonated parts.

Increased Hydrophilicity of the Polymer

Nonsulfonated PPO is an extremely hydrophobic polymer. By sulfonation the polymer becomes more hydrophilic.[13] It is evident that increased hydrophilicity at the surface of pores makes the membrane more wettable to the aqueous solutions and, thereby, more permeable but, on the other hand, increased swelling in water resulting from increased hydrophilicity of the bulk of the polymer decreases pore sizes and, therefore, the permeabilities.

To differ between the influence of wettability and pore characteristics, membranes prepared from the nonsulfonated PPO were subsequently sulfonated at the surface by the immersion in concentrated H$_2$SO$_4$ (separation results not presented here). Although those membranes that were sulfonated for a period shorter than ca. 30 min showed a very small increase in permeability to water, those membranes that were immersed in H$_2$SO$_4$ for a longer time were highly swollen in water and were not at all permeable to water in ultrafitration experiments.

Changed Affinity of the Precipitant

The affinity between PPO and methanol is changed by the sulfonation (Fig. 4). Methanol is a very effective precipitant for nonsulfonated PPO. With an increased degree of sulfonation of PPO a

Figure 4   Maximal addition of methanol to 10 g of solution of homogeneously sulfonated PPO in chloroform/1-butanol (85 : 15 by weight) not causing turbidity in solution.

Figure 5 Dependence of water flux at 0.05 MPa on the sulfonated polymer content in blends of nonsulfonated polymers with heterogenously sulfonated polymers (sulfur content 2%): (1) sulfonated PPO M_w = 52,600, nonsulfonated PPO M_w = 52,600; (2) sulfonated PPO M_w = 52,600, nonsulfonated PPO M_w = 208,000; (3) sulfonated PPO M_w = 208,000, nonsulfonated PPO M_w = 52,600; (4) sulfonated PPO M_w = 208,000, nonsulfonated PPO M_w = 208,000.

higher concentration of methanol is needed to precipitate the polymer from solution, and, in the end, PPO with sulfur content of about 5.5% is soluble in methanol, and therefore, of course, no membranes can be prepared by this method. The affinity between PPO and methanol is not significantly influenced by the kind of sulfonation technique.

Viscosity Influence

It was shown[17,18] that two distinctly different types of phase separation are responsible for the formation of asymmetric membranes: gelation (or crystallization) and liquid–liquid phase separation. The boundary of the gel region in the ternary phase diagram is more or less a viscosity boundary. If the coagulation path intersects the binodal in the ternary phase diagram first, the liquid–liquid phase separation occurs, and the resulting structure is rather porous. If the coagulation path enters the gel region before intersecting the binodal, the phase separation occurs by gelation, and less porous membranes can be anticipitated.

The influence of the casting solution viscosities (of molecular weights of used samples of PPO) can be seen in Figure 5. Curve 1 relates to the permeabilities of membranes prepared from the blends of PPO and sulfonated PPO prepared by the way

of heterogeneous sulfonation from the same polymer having a molecular weight M_w = 52,600; curve 2 shows the permeabilities of membranes prepared from the blends of PPO with M_w = 208,000, and of sulfonated PPO prepared from the polymer having molecular weight M_w = 52,600; curve 3 relates to the blends of PPO with M_w = 52,600 and of sulfonated PPO prepared from the polymer having molecular weight M_w = 208,000; and curve 4 to the blends of PPO with M_w = 208,000 and of sulfonated PPO prepared from the same polymer (M_w = 208,000). Limiting viscosity numbers in chloroform/1-butanol (85 : 15 by weight) of samples based on the polymer with M_w = 52,600 (sulfonated or unsulfonated) were in the range of 0.29–0.35 dL/g; those of samples based on the polymer with M_w = 208,000 were in the range of 0.56–0.65 dL/g, limiting viscosity numbers of mixtures of both molecular weights corresponded to their weighted average. It can clearly be seen that lower viscosities of casting solutions resulted in higher permeabilities of prepared membranes.

Inhomogenity of the Sulfonated Polymer Chains

Figure 6 shows relative sulfur contents in the surface layer (8.3 nm) (skin side) of membranes prepared from blends of sulfonated polymers with a nonsulfonated polymer. The sulfur contents were obtained by the ESCA analysis. It can be seen that: (1) the relative sulfur content in the surface layer of membranes containing PPO ho-

Figure 6 Relative intensity of the signal corresponding to sulfur in the surface layer (8.3 nm) of membranes in dependence on the sulfonated polymer content in blends of nonsulfonated polymer with sulfonated polymers: (1) heterogenously sulfonated PPO, sulfur content 3.3%; (2) homogeneously sulfonated PPO, sulfur content 3.2%.

mogeneously sulfonated in solution is much lower than that of membranes containing PPO sulfonated in suspension; and (2) the relative sulfur content in the surface layer of membranes containing PPO sulfonated in solution increases lineary with the sulfur content in the bulk of the membranes, while the relative sulfur content in the surface layer of membranes containing PPO sulfonated in suspension reaches the maximum at the membrane compositions corresponding to the highest values of permeabilities (compare Fig. 3) and then remains (virtually) constant, although the sulfur content in the bulk of membrane polymer further increases. This can be explained by heterogeneous sulfonation of the polymer in suspension. Polymer chains near the surface of the swollen polymer particles are sulfonated with sulfuric acid to a higher degree than the chains inside of the particles. Therefore, the heterogeneous sulfonation generates modified polymers with heterogenously distributed sulfo groups on the polymer chain.

It is plausible that during and after the immersion of the cast film into a methanol bath the highly sulfonated polymer chain units of the heterogeneously sulfonated polymer become oriented toward the polar precipitant and will form the surface during the formation of the membrane. Slightly sulfonated or unsulfonated PPO chains remain more inside of the membrane. High permeabilities (to water and aqueous solutions) of the membranes prepared from the heterogeneously sulfonated PPO and from blends of heterogeneously sulfonated PPO with nonsulfonated PPO can be explained by this chain orientation: by the connection of advantageous way of precipitation of slightly sulfonated or unsulfonated PPO parts in methanol and of low swelling of these parts in water with hydrophilic domain structured surface. A similar mechanism of the formation of membranes is described for the mixtures of polysulfone and polysulfone–poly(ethylene oxide) block copolymers.[19] Such structured membranes are used in the medical field nowadays.[20,21]

CONCLUSIONS

Microporous membranes with high permeabilities to aqueous solutions can be prepared from heterogeneously (nonuniformly) sulfonated PPO and from the blends of heterogeneously sulfonated PPO with nonsulfonated PPO. Based on the results of this study, a hypothesis of the sulfonation process can been made: block copolymers comprising hydrophobic blocks of unsulfonated PPO and hydrophilic blocks of sulfonated PPO are generated by the heterogeneous sulfonation of PPO. So structured polymer chains can form organized structures during the precipitation in polar coagulants. Domains of the hydrophilic parts will be located at the membrane surface and will form hydrophilic surface of otherwise hydrophobic membranes. It follows from the hypothesis that the block copolymers containing hydrophilic and hydrophobic chain parts are the best suited polymers for the preparation of microporous membranes, which will be applied in the filtration of aqueous solutions.

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