Poly(phenylene oxide)-Based Polymer Electrolyte Membranes for Fuel-Cell Applications

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ABSTRACT: Poly(phenylene oxide)s were synthesized by the oxidative polymerization of 2-phenyl phenol (PP) and 2-allyl phenol (AP). The copolymers were also synthesized with 80 mol % PP and 20 mol % AP and with equimolar monomers. The polymers were characterized. Blends of these polymers with poly(vinylidene fluoride) were pre-pared. These blend membranes were sulfonated, and their suitability for applications in fuel cells was evaluated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 307–311, 2003

Key words: poly(phenylene oxide); blends; crosslinking; ionomers; membranes

INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been identified as promising power sources for vehicular transportation and for other applications requiring clean, quiet, and portable power.[1] The major obstacles preventing the commercial use of these fuel cells are the expensive materials used and the low performances at high temperatures (>100°C) and low humidity. The limiting factor in PEFCs is the membrane, which serves as a structural framework supporting the electrodes and transporting protons from the anode to the cathode.

One of the most promising routes to high-performance proton-conducting polymer electrolyte membranes is the use of hydrocarbon polymers for polymer backbones. The advantages of hydrocarbon polymers are that they are cheaper than the perfluorinated ionomers currently used and that these polymers can be suitably modified to absorb large quantities of water by the introduction of polar groups. The choice of a hydrocarbon-based polymer electrolyte depends on its ionic conductivity at a low humidity and/or an elevated temperature and its chemical degradation in oxidizing and reducing environments at elevated temperatures. The thermal characteristics and chemical stability of new materials will, therefore, determine their potential applications.

New membrane concepts include partially fluorinated membranes,[2] composite membranes,[3,4] and sulfonated aromatic polymer membranes. Chemically and thermally stable aromatic polymers such as polystyrene,[5] poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene),[6,7] poly(1,4-phenylene),[8] poly(oxy-1,4-phenylene),[9] poly(phenylene sulfide),[10] and poly-(benzimidazole)[11] have been employed as polymer backbones for proton-conducting polymer electrolytes. These aromatic polymers can easily be made to conduct protons by the introduction of ion-conducting groups.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a hydrophobic membrane material with a high glass-transition temperature that can be modified by electrophilic substitutions in the polymer backbone.[12,13] Sulfonated PPOs (SPPOs) are potential materials for reverse-osmosis membranes, and sulfonation is also known to improve the gas selectivity of these membranes. Kruczek and Matsuura[14] sulfonated high molecular weight PPOs to various ion-exchange capacities with chlorosulfonic acid and evaluated the physicochemical properties and gas transport properties. An increase in the ion-exchange capacity of SPPO resulted in an increase in O_2/N_2 and CO_2/CH_4 ideal selectivity and a decrease in O_2 and CO_2 permeability. Steck and Stone[15] polymerized 2,6-diphenylol into poly(2,6-diphenyl-1,4-phenylene oxide).This polymer was later brominated and sulfonated. The sulfonated polymer was analyzed as a polymer electrolyte for fuel cells and had a life of 500 h of continuous operation.

In our earlier article,[16] we reported the synthesis of poly(2-allyl-1,4-phenylene oxide), PPO, and the copolymer poly(2-allyl-1,4-phenylene oxide-*co*-2,6-dimethyl-1,4-phenylene oxide) with various monomer molar ratios, using a copper–pyridine catalyst system, and we evaluated the suitability of these polymers for applications in fuel cells. Copolymerization with a suitable monomer modifies the properties of PPO and

Polymer	Yield (%)
Poly(2-phenyl-1,4-phenylene oxide)	78
Poly(2-allyl-1,4-phenylene oxide)	60
Copolymer (80PP/20AP)	70
Copolymer (50PP/50AP)	57

enhances the possibility of obtaining materials suitable for various electrochemical applications. With the idea of improving the ionic conductivity and selectivity of PPO, we considered 2-phenyl phenol (PP) to be an ideal monomer because the extra phenyl ring is also susceptible to sulfonation. Suitable substitutions at this phenyl ring can produce new and improved properties, such as enhanced thermal stability, flexibility, rigidity, and solubility. 2-Allyl phenol (AP), because of its crosslinking behavior, imparts a fuel partitioning property and insolubility.

This article reports the synthesis and characterization of polymers and copolymers based on AP and PP. The copolymers were synthesized with an equal molar ratio of the two monomers or with a monomer ratio of 80% PP to 20% AP. The polymers were cast as membranes, and their properties were evaluated.

EXPERIMENTAL

AP (E. Merck, Germany), PP (E. Merck), CuCl, pyridine, chloroform, nitrobenzene, and anhydrous MgSO$_4$ (E. Merck) were used for polymerization. AP was polymerized by the passage of oxygen through a vigorously stirred phenol solution containing a CuCl/pyridine catalyst at 25–50°C. MgSO$_4$ (anhydrous) was used as a desiccant to remove water that formed during polymerization. In this way, catalyst hydrolysis was also avoided. The concentrations of the various components were as follows: 0.005M CuCl, 0.375M pyridine (N/Cu ligand ratio = 75), 0.2M 2,6-dimethyl phenol, and 0.2M MgSO$_4$.[17] Copolymers of AP with PP were prepared by the addition of the requisite monomers in the molar ratios of 80 PP/20 AP or 50 PP/50 AP, with the same composition maintained for the rest of the components. A pure polymer of PP was also prepared with only PP as the monomer.

The membranes were prepared by the blending of the polymer solutions with equimolar poly(vinylidene fluoride) in a suitable solvent[15] and by the casting of the solutions onto clean glass plates. They were dried at 100° C for 24 h in an air oven. The membranes were peeled off from the plate by immersion in water. The membranes were then washed several times with water for the removal of residual solvents. They were then sulfonated by immersion in concentrated H$_2$SO$_4$ for a suitable time from room temperature to 80°C, and proton-conducting membranes were obtained.

The polymer and copolymers were characterized with instrumental techniques such as IR, NMR, and thermogravimetry.

The equivalent weight was determined by a titration technique from the volume of sodium hydroxide necessary to obtain pH 7. The conductivity of the membranes was determined from the resistance of the membranes
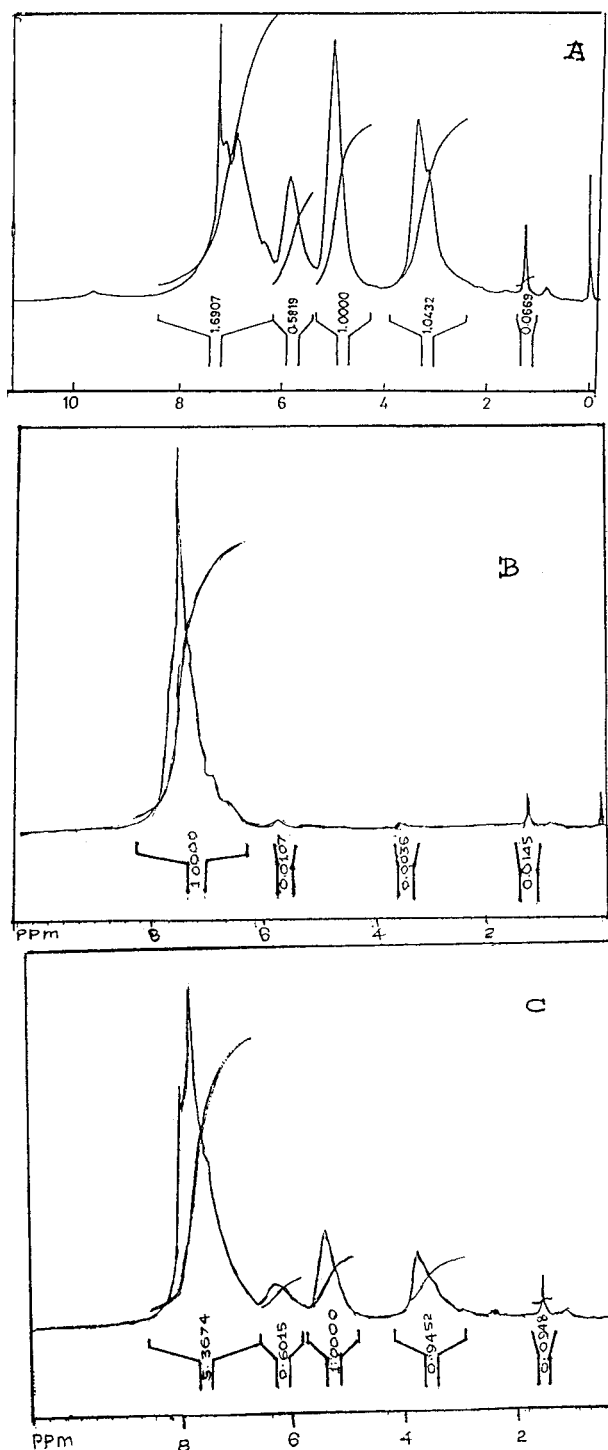

Figure 1 NMR curves for (A) poly(2-allyl-1,4-phenylene oxide), (B) poly(2-phenyl-1,4-phenylene oxide), and (C) poly(2-allyl-1,4-phenylene oxide-*co*-2-phenyl-1,4-phenylene oxide).
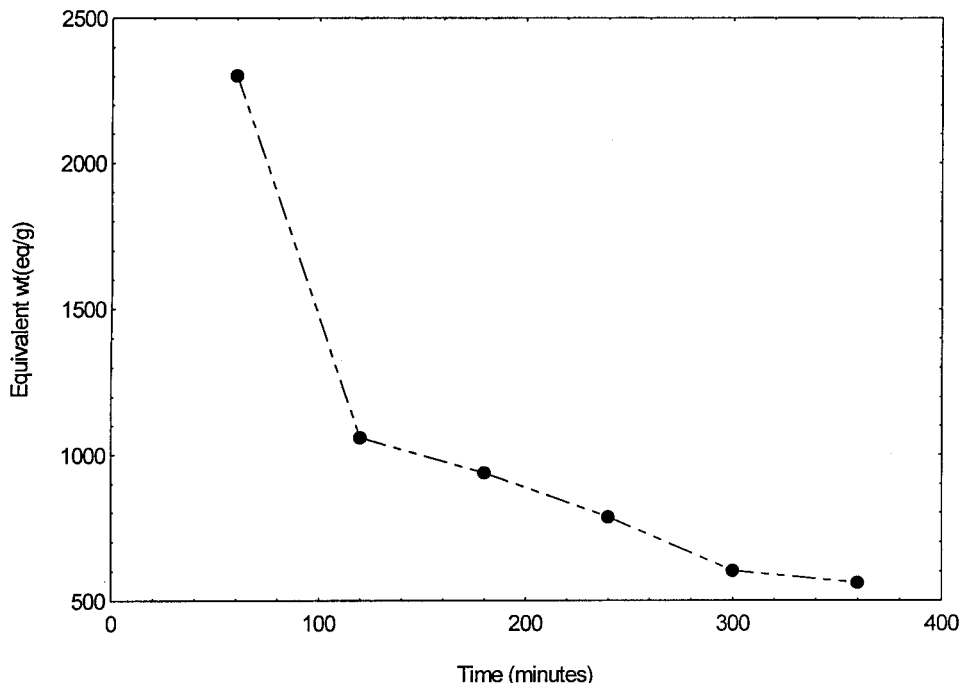
Figure 2 Equivalent weight of poly(2-phenyl-1,4-phenylene oxide) at various sulfonation times.

obtained through impedance techniques. Water and methanol uptakes were measured by the calculation of the weight increase in a membrane when a dry membrane was soaked in water or methanol.

RESULTS AND DISCUSSION

Poly(2-allyl-1,4-phenylene oxide), poly(2-phenyl-1,4-phenylene oxide), and the copolymer poly(2-allyl-1,4-phenylene oxide-*co*-2-phenyl-1,4-phenylene oxide) were prepared by the oxidative polymerization of the respective phenols. Table I gives the yields of the various polymers produced. The yield of the polymer prepared with PP was higher than that of AP. This was due to the higher reactivity of PP with respect to that of the allyl group present in AP. The yield of the copolymers was lower than that of the polymer prepared from PP.
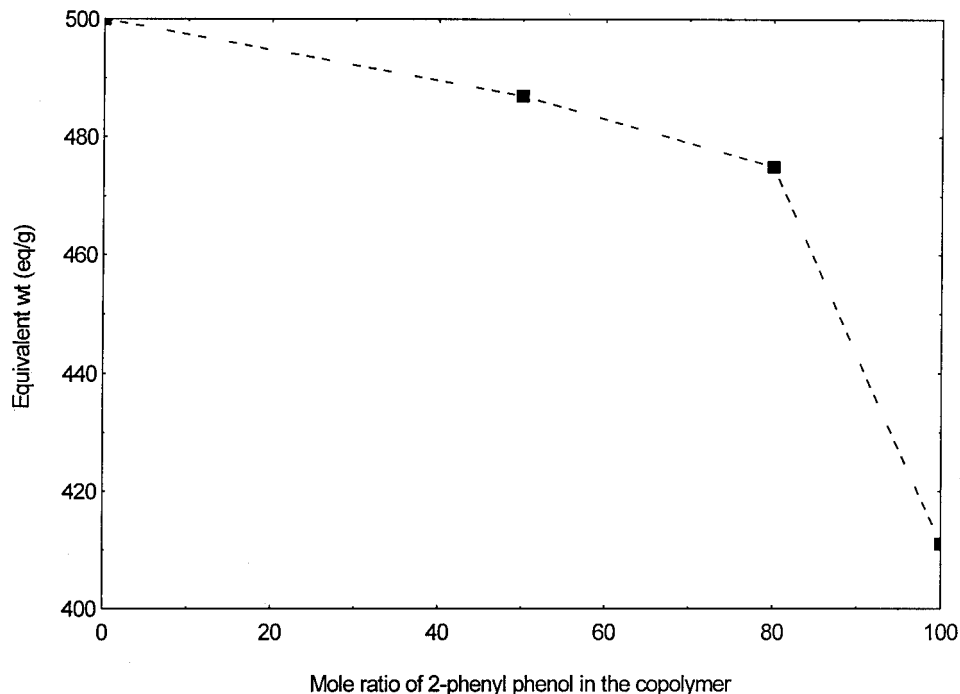

Figure 3 Equivalent weight variations with the molar ratio of PP in the polymer for a fixed period of sulfonation.

TABLE II
Conductivity of the Membranes

Membrane type	Conductivity (S/cm)
Homopolymer of PP	1.2×10^{-2}
Homopolymer of AP	4.4×10^{-3}
Copolymer (80 PP/20 AP)	1.5×10^{-2}
Copolymer (50 PP/50 AP)	2.5×10^{-3}

Polymer characterization

The IR spectra of all the PPO samples synthesized showed distinctive aromatic ether bands at 1188 cm^{-1}. The polymers containing AP showed allyl stretching peaks at 1640 cm^{-1}. These peaks disappeared with the thermal crosslinking of the samples at 140°C. With sulfonation, the appearance of a band at 1080 cm^{-1} and the disappearance of peaks at 825 cm^{-1} indicate substitution in the phenyl ring. The appearance of a broader peak around 3360 cm^{-1} is indicative of water absorbed by the sample because of sulfonic acid groups introduced into the polymer.

Figure 1 gives the NMR curves of poly(2-allyl-1,4-phenylene oxide), poly(2-phenyl-1,4-phenylene oxide), and the copolymer poly(2-allyl-1,4-phenylene oxide-*co*-2-phenyl-1,4-phenylene oxide) prepared with an equimolar mixture of the two monomers. The homopolymer of AP showed signals at $\delta = 3–4$ for 2H due to ph—$\textbf{CH}_2$—CH=CH$_2$, at $\delta = 4.5–5$ for 2H due to ph—CH$_2$—CH=$\textbf{CH}_2$, at $\delta = 5.5–6$ for 1H due to ph—CH$_2$—$\textbf{CH}$=CH$_2$, and at $\delta = 6–8$ due to 3H attached to the phenyl ring.

The homopolymer of PP showed a broad signal between $\delta = 6$ and $\delta = 8$ (8 aromatic H). The copolymer (50/50) of AP and PP showed signals between $\delta = 3$ and $\delta = 4$ for 2H due to ph—$\textbf{CH}_2$—CH=CH$_2$, between $\delta = 4.5$ and $\delta = 5$ for 2H due to ph—CH$_2$—CH=$\textbf{CH}_2$, between $\delta = 5.5$ $\delta = 6$ for 1H due to ph—CH$_2$—$\textbf{CH}$=CH$_2$, and between $\delta = 6–8$ for 11H due to aromatic protons.

The copolymer, therefore, showed peaks due to both allyl group protons and phenyl group protons. The ratio of the allyl groups of AP to the phenyl protons (total) showed that 1 mol of AP reacted with 1 mol of PP. This means that the type of copolymer formed could be a random, block, or alternate copolymer. However, the yields of the homopolymers suggest that the reactivity of the monomer PP was higher than that of AP. Therefore, the possibility of the formation of alternate copolymers was negligible compared to the formation of a block copolymer that may be random.

Thermal characterization

Poly(2-phenyl-1,4-phenylene oxide) showed a weight loss below 100°C due to moisture and a low-boiling solvent and a weight loss below 400°C due to oligomers and other impurities. The major chain scission

occurred at 604°C. Poly(2-allyl-1,4-phenylene oxide), however, showed a weight loss below 150°C due to moisture and the solvents and below 400°C chain scission of allyl groups and oligomers; the major degradation of the polymer was around 480°C. The copolymer prepared from equimolar amounts of PP and AP had a major weight loss around 571°C. Therefore, the thermal stability of the polymer prepared with PP was greater than that of the polymer prepared from AP. The copolymer had thermal properties of both polymers. Therefore, it was more stable than the polymer prepared with AP but less stable than the polymer prepared with PP.

Polymer membranes prepared by the blending of the polymers with poly(vinylidene fluoride) followed by sulfonation had lower stability than the nonsulfonated polymers. This was due to the lower degradation temperatures for sulfonic acid groups introduced with sulfonation.

The copolymer and polymer prepared from AP and PP were soluble in solvents such as dimethylformamide, CHCl$_3$, and dichloroethane. The solubility of the thermally cured polymers in the aforementioned solvents decreased with an increase in the crosslink density. This method of crosslinking one of the polymers in the matrix is useful in restricting the leaching of the polymer from the matrix. For direct methanol fuel cells, the crosslinked structure could provide a restriction of methanol permeation from the anode compartment to the cathode compartment, thereby preventing losses during the operation of the cells.

Figure 2 gives the equivalent weight of poly(2-phenyl-1,4-phenylene oxide) for various time intervals of sulfonation. As the time of sulfonation increased, the sulfonation level in the polymer increased. Figure 3 gives the equivalent weight of the polymers and copolymer as a function of the molar fraction of PP used. There was only a marginal change in the equivalent weight with the increase of PP in the polymer.

The conductivities of the various prepared polymers are given in Table II. The conductivity of the polymer prepared with PP was higher than that of the polymer prepared with AP by one order of magnitude for almost similar ion-exchange capacities. This could be attributed to the better network formation of the ion-conducting groups for PP, as both the backbone phenyl ring and the side phenyl present at the ortho position were capable of being sulfonated. In the poly-

TABLE III
Solvent Absorption in Various Polymers

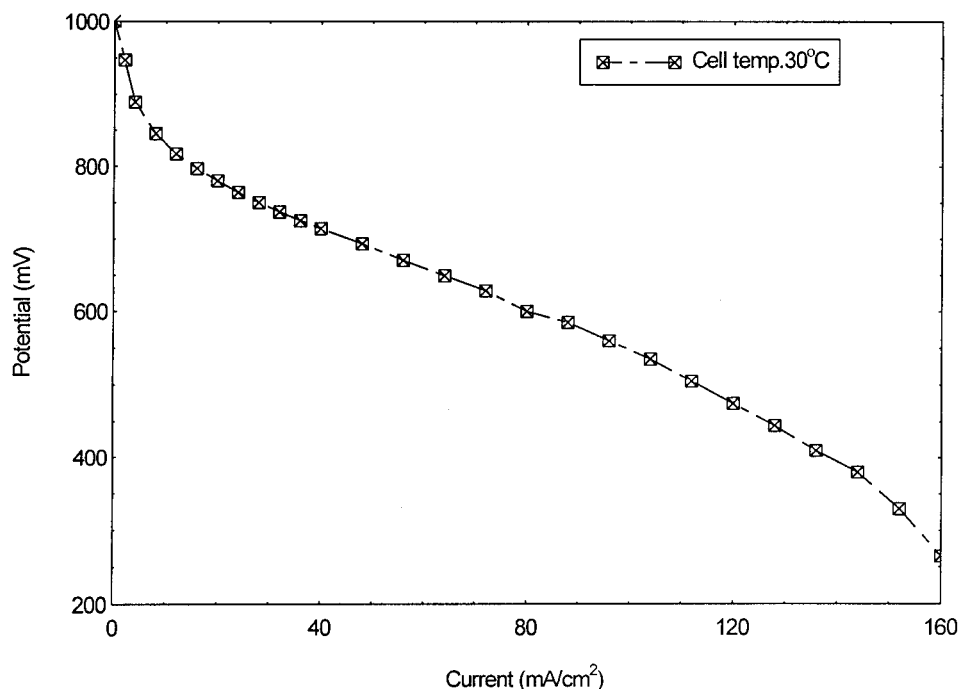| Membrane type	Water uptake (%)	Methanol uptake (%)
Homopolymer of PP	50	19
Homopolymer of AP	15	5
Copolymer (80 PP/20 AP)	47	17
Copolymer (50 PP/50 AP)	24	15

Figure 4 Fuel-cell polarization curve with H_2 and O_2 as reactants for a cell area of 25 cm^2.

mer prepared with AP only, one phenyl ring present in the backbone could be sulfonated. The copolymers prepared with various amounts of PP showed lower conductivity than poly(2-phenyl-1,4-phenylene oxide).

The methanol and water absorption of the polymers is shown in Table III. The polymer prepared from PP had the highest water and methanol absorption. The observed trend was similar to the conductivity order of the polymers. The methanol absorption in these polymers was lower than that of water. The presence of aromatic phenyl rings and the crosslinked structure of the polymer for copolymers containing AP were responsible for the lower methanol absorption.

Figure 4 gives the polarization curve for the polymer blend membrane made of 50% poly(2-phenyl-1,4-phenylene oxide) and 50% poly(vinylidene fluoride). A maximum current density of 160 mA/cm^2 was obtained in a 25-cm^2 test cell with standard Center for Energy Research electrodes used in the membrane. This shows that further optimization of the blend composition and bonding of the electrodes are required for improved performance.

CONCLUSIONS

New polymer electrolyte membranes based on poly-(phenylene oxides) were synthesized by the oxidative polymerization of PP and AP. A technique for the preparation of polymer electrolyte blend membrane was discussed. The polymers had good thermal properties and could easily be converted into polymer electrolytes. Fuel-cell experiments carried out with poly(2-phenyl-1,4-phenylene oxide) showed promising results.

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