

Synthesis and Characterization of Sulfonated Poly(phenylene oxides) as Membranes for Polymer Electrolyte Membrane Fuel Cells

B. VISHNUPRIYA, K. RAMYA, K. S. DHATHATHREYAN

Center for Energy Research, SPIC Science Foundation, 111 Mount Road, Guindy, Chennai 600 032, India

Received 19 March 2001; accepted 1 June 2001

ABSTRACT: The synthesis of a thermally stable proton conducting polymer based on poly(phenylene oxide) (PPO) was carried out using 2,6-dimethylphenol (DMP) and 2-allylphenol (AP) as monomers. The copolymers using the two monomers were prepared with DMP to AP molar ratios of 20:80, 40:60, 60:40, and 80:20. The polymers and the copolymers were blended with poly(vinylidene fluoride) and cast as membranes. All the membranes were sulfonated and characterized for their suitability as a polymer electrolyte membrane. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1792–1798, 2002

Key words: poly(phenylene oxide); copolymer; blend membrane; polymer electrolyte; fuel cells

INTRODUCTION

Oxidative polymerization of 2,6-disubstituted phenol gives the thermoplastic engineering plastic material poly(phenylene oxide) (PPO), which has excellent mechanical properties, good electrical characteristics, good heat resistance, low absorbability of water, and good dimensional stability. A manganese catalyst system and copper catalyst system are utilized for oxidative polymerization of a 2,6-disubstituted phenol.

Poly(2,6-dimethyl-1,4-phenylene oxide) is a versatile and well-known polymer with a high glass-transition temperature (T_g).^{1,2} PPO is modified by various electrophilic substitutions including bromination,^{3–6} carboxylation, and sulfonylation and ac-

ylation^{3,5} and by introduction of trialkyl-silyl, hydroxyethylene, and ethyleneoxytrialkyl-silyl groups in the polymer backbone.⁷

Yang and Hay⁸ polymerized 2,6-diphenylphenol (DPP) oxidatively to give a polymer with a T_g of 235°C and a melting point of 480°C. They also modified the properties of the polymer by synthesis of a series of DPPs containing substituents like F, Cl, Br, I, *t*-Bu, CN, and OPh at both the *o*- and *para* positions of the pendant phenyl groups. Cooper and Bennett⁹ synthesized dimers of 2,6-dimethylphenol (DMP) and DPP and polymerized the dimers to give perfect alternating copolymers using a copper chloride–pyridine catalyst. The DMP undergoes faster oxidative coupling than DPP.

The PPOs generally have low selectivity for gases and show the highest permeabilities to gases. This is attributed to the absence of polar groups in the polymer backbone. Sulfonation is carried out to improve the gas selectivity of this material.^{10–12} Sulfonated PPO (SPPO) is considered as a potential material for reverse osmosis

Correspondence to: K. Ramya (cerssf@md5.vsnl.net.in).

Contract grant sponsor: SPIC Science Foundation and Department of Science and Technology, Government of India; contract grant number: SP/S1/H-30/97.

Journal of Applied Polymer Science, Vol. 83, 1792–1798 (2002)
© 2002 John Wiley & Sons, Inc.
DOI 10.1002/app.2307

membranes and fuel cells. The gas separation properties of SPPOs were reported. The density and T_g of SPPO increased with an increasing degree of sulfonation of the polymer.¹³ Huang and Kim¹⁴ studied the synthesis and transport properties of SPPO thin film composites for reverse osmosis applications. Composite membranes were prepared with porous polysulfone supports and by dip coating of porous support materials like polypropylene, polyethylene, poly(vinyl chloride), poly(vinylidene fluoride) (PVDF), poly(tetrafluoroethylene), and so forth, with suitable ion conducting polymeric materials that were chemically synthesized.¹⁵

The PPOs were also synthesized by the electropolymerization route on suitable substrate materials like Cu, Fe, Pt, and so forth. These coatings found applications in metal protection. The process is carried out by anodizing (at the metal surface to be coated) hydroalcoholic solutions of phenol containing a suitable amine. The protective performance of PPOs synthesized using DMP¹⁶ or *o*-allyl phenol¹⁷ were reported. Bertinello et al.¹⁸ reported the growth of PPO coatings consisting of either a single copolymer layer or two homopolymer layers using phenol, 3-hydroxybenzyl alcohol, 2-fluorophenol, and 3-nitrophenol electrochemically on Zn sheets.

Kuver and Potje-Kamloth¹⁹ prepared copolymers of sodium-4-hydroxybenzenesulfonate and 2-allylphenol (AP, varying molar ratios) electrochemically on Au and platinized carbon substrates and studied the methanol crossover properties of various membrane electrolytes for application in acid direct methanol fuel cells. The effectiveness of the methanol barrier depends on the concentration of the crosslinker in the polymer or in the monomer solution. We recently carried out studies on the electropolymerization of AP²⁰ on a porous conductive material and on the suitability of these membranes for direct methanol fuel cells. Sulfonated poly(2-allylphenylene oxide) is found to have lower permeability to methanol with a high ionic conductivity on the order of 10^{-3} S/cm.

This article reports the synthesis and characterization of various PPOs using DMP and AP as monomers. These polymers and copolymers were blended with PVDF and cast as membranes. The properties of the sulfonated membranes and their suitability for application in fuel cells were investigated.

EXPERIMENTAL

Synthesis of Polymer and Copolymer

The compounds used for polymerization were DMP (Acros), AP (E. Merck), CuCl, pyridine, chloroform, nitrobenzene, and anhydrous MgSO₄. The DMP was polymerized at 25–50°C by passing oxygen through a rigorously stirred phenol solution containing CuCl–pyridine catalyst. A desiccant, such as anhydrous MgSO₄, was added to remove the water formed during polymerization. This helps in avoiding catalyst hydrolysis. The amounts of the various components are 0.005M CuCl, 0.375M pyridine (N/Cu ligand ratio of 75), 0.2M DMP, and 0.2M MgSO₄.¹⁸

Copolymers of DMP with AP were prepared by adding the requisite monomers in molar ratios of 80 DMP/20 AP, 60 DMP/40 AP, 40 DMP/60 AP, and 20 DMP/80 AP and maintaining the same composition for the rest of the components. Pure polymer of AP was also prepared by using only AP as the monomer. The polymer and copolymers were then characterized using instrumental techniques like IR, NMR, and thermogravimetric analysis (TGA).

Curing and Crosslinking of Polymers

Curing was carried out by heating a known weight of the copolymer or polymer in an air oven at 150°C for 1 h. The extent of crosslinking was evaluated from the quantity of insoluble fraction remaining after the extraction of cured polymer with CHCl₃, which is a good solvent for the polymer or copolymer.

The percentage of solubility of these polymers in CHCl₃ was calculated as

$$\% \text{ solubility} = W_0 - W_1/W_0 \times 100$$

where W_0 is the initial dry weight of the polymer and W_1 is the weight of the insoluble material.

Preparation of Proton Conducting Membranes

The membranes were prepared by solvent casting techniques. The polymer or copolymer is dissolved in a known quantity of solvent. PVDF powder (Fluka) was dissolved in an equimixture of cyclopentanone and propylene carbonate. The two solutions were mixed thoroughly for 1 h to get a uniform blend solution. This solution was cast on a glass plate and oven dried at 100°C for 24 h in

an air oven. The membranes were peeled off the plate by immersing them in water. The membranes were then washed several times with water to remove residual solvents and crosslinked by heating them in a press at 150°C and a pressure of 5000 psi for 0.5 h. Subsequently, the membranes were sulfonated by immersing them in concentrated H₂SO₄ for a suitable time from room temperature to 80°C to attain proton conducting membranes.

Ion Exchange Capacity

The acidified membranes were soaked in 3M KCl solution, and the protons released by the membrane were neutralized using a NaOH solution of known concentration. The ion exchange capacity is calculated from the volume of soda necessary to obtain a pH of 7.

Water and Methanol Uptake Studies of Membranes

All membrane samples were oven dried at about 80°C and the dry weight was taken; samples were then immersed in the respective solvents at room temperature. After 48 h of equilibration the membranes were blotted dry to remove the excess liquid on the surface and quickly weighed.

Conductivity Measurements

The conductivity of the proton conducting membranes was tested by a complex impedance spectrum obtained using an EG&G PARC potentiostat/galvanostat (model 273) and a Schlumberger 1255 HF frequency response analyzer unit.

RESULTS AND DISCUSSION

The poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2-allyl-1,4-phenylene oxide) polymers were prepared in good yield using the Cu-pyridine catalyst. Copolymers of DMP and AP were also prepared using the two monomers in molar ratios of 80 DMP/20 AP, 60 DMP/40 AP, 40 DMP/60 AP, and 20 DMP/80 AP.

Characterization of Polymers

IR Study

All the PPO polymers that were synthesized showed a distinctive band of aromatic ether groups at 1188 cm⁻¹.

Poly(2-allyl-1,4-phenylene oxide) showed three defined bands in the range of 3067–2800 cm⁻¹ that were due to allyl—CH stretching and a sharp band at 1640 cm⁻¹ that was attributed to —HC=CH₂— stretching. In the crosslinked sample the morphology of the bands at 3067–2800 cm⁻¹ changes and the band at 1640 cm⁻¹ disappears.

The copolymers of DMP and AP both show the aromatic ether bands and allyl group stretching peaks. On crosslinking of these polymers the peak at 1640 cm⁻¹ disappears completely, except in the polymer synthesized using 80% DMP and 20% AP. This may be due to partial crosslinking of the polymer because of the lower molar ratio of AP in the copolymer.

Sulfonation causes the appearance of two bands at around 1070 and 675 cm⁻¹, and the disappearance of the peaks at 825 and 750 cm⁻¹ indicates sulfonation in the phenyl ring and substitution of the aromatic ring, respectively.

NMR Study

Figure 1 shows the NMR curves of the homopolymers and the copolymer prepared using 60% DMP and 40% AP.

The homopolymer of AP showed signals at δ 3–4 for 2H due to ph—CH₂—CH=CH₂, at δ 4.5–5 for 2H due to ph—CH₂—CH=CH₂, at δ 5.5–6 for 1H due to ph—CH₂—CH=CH₂, and at δ 6–8 for 3H due to protons attached to phenyl ring.

The homopolymer of DMP shows signals at δ 1–2 for 6H due to ph—CH₃—CH₃ and at δ 6–8 for 2H due to aromatic protons.

The 60:40 DMP/AP copolymer showed signals at δ 1–2 for 6H due to ph—CH₃—CH₃, at δ 3–4 for 2H due to ph—CH₂—CH=CH₂, at δ 4.5–5 for 2H due to ph—CH₂—CH=CH₂, at δ 5.5–6 for 1H due to ph—CH₂—CH=CH₂, and at δ 6–8 for 5H due to aromatic protons. The copolymer thus shows peaks due to allyl group protons and methyl group protons. The ratio of the methyl groups of DMP to that of the allyl protons show that only half the value of the protons is obtained. The ratio of the monomers in the polymer is hence two units of DMP to one unit of AP only (2:1). This is not the same as the ratio of the amount of monomer taken. This difference in the ratios is attributed to the lesser reactivity of AP in the mixture of the monomers. This ratio of the monomers (DMP/AP) in the copolymer suggests a random or block copolymer formation and not an alternating polymer.

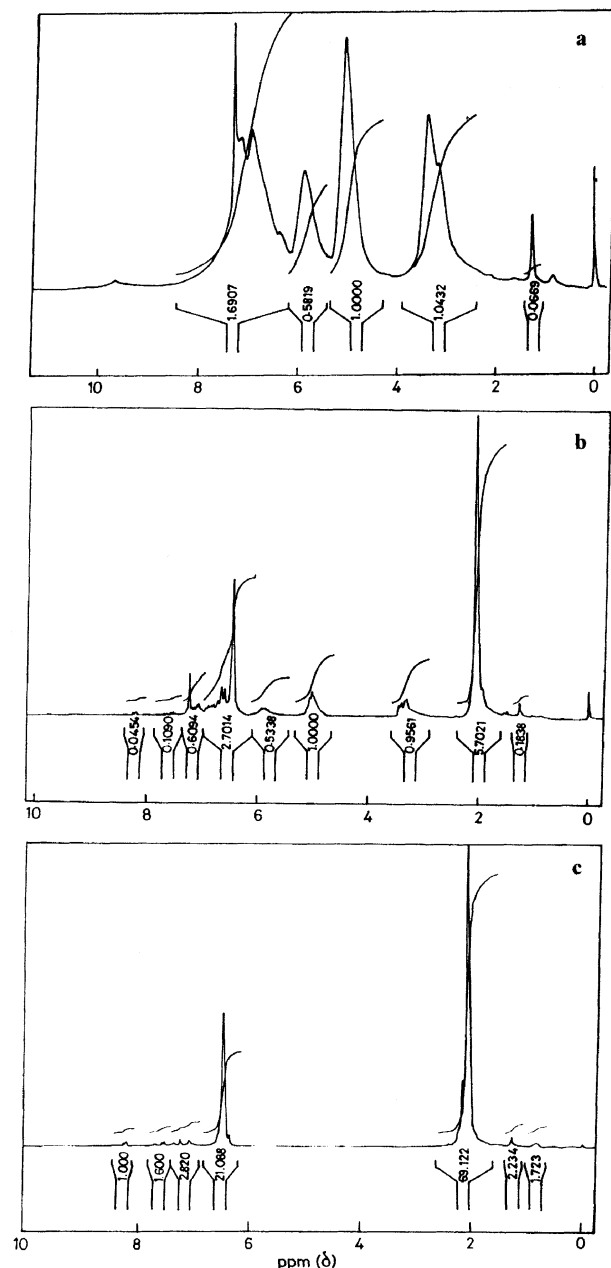


Figure 1 NMR spectra of (a) poly(2-allyl-4-phenylene oxide), (b) poly(2,6-dimethyl-co-2-allyl phenylene oxide) (60/40 copolymer), and (c) poly(2,6-dimethyl-4-phenylene oxide).

TGA Study

Poly(2,6-dimethyl-1,4-phenylene oxide), poly(2-allyl-1,4-phenylene oxide), and the copolymer prepared using 60:40 DM/AP were characterized using TGA.

The TGA curve of poly(2,6-dimethyl-1,4-phenylene oxide) shows three regions of weight loss.

The first one below 100°C may be attributed to moisture and low boiling residual solvents used for synthesis and precipitation of the polymer. The second small peak (5% weight loss) with a peak temperature of 339°C may be attributed to some residual high boiling solvent and impurities in the form of oligomers. The major chain scission of the polymer occurs at the peak temperature of 421°C. The char yield of the polymer at 594°C is 23.9% in an air atmosphere.

Poly(2-allyl-1,4-phenylene oxide) shows a weight loss below 150°C that is attributed to low and high boiling solvents and residual moisture. The weight loss of 3% at the peak temperature of 170.7°C may be attributed to chain scission of low molecular weight oligomer. The peaks at 312 and 437°C can be attributed to side chain scission (allyl group) and some main chain scission. Major degradation of the polymer occurs at the peak temperature of 480°C. The residual yield of the polymer is 16% at 594°C.

The monomer ratio of the copolymer of DMP and AP (60:40) shows a weight loss at the peak temperature of 112°C that may be attributed to solvents, moisture, residual monomer, small oligomers, and so forth. The weight loss at the peak temperature of 477°C (285–589°C temperature range) may be attributed to side chain scission of the allyl group and chain scission of the polymer. There is 35% copolymer residue at 594°C in an air atmosphere.

Poly(2-allyl-1,4-phenylene oxide) is less stable than poly(2,6-dimethyl-1,4-phenylene oxide) because the side chain (allyl group) degrades at lower temperature. The copolymer has higher stability than the polymer of AP and lower stability than the polymer of DMP.

The polymer film prepared by blending poly(2-allyl-1,4-phenylene oxide) and PVDF shows peaks due to residual solvents, monomers, and moisture at peak temperature of less than 100°C. The weight loss due to degradation of side chain, main chain PPO, and PVDF occurs at a peak temperature of 466°C (280–533°C temperature range, 92% weight loss) and the residual yield is 4.5%.

The side chain scission in the copolymers of PPO seems to be slightly delayed when blending with PVDF. There is only marginal improvement in the thermal stability with blending.

The DSC curves of poly(2-allyl phenylene oxide) shows a number of exotherms starting from 90°C. The 60:40 DMP/AP copolymer shows an

Table I Percentage of Solubility of Cured/Crosslinked Polymers

DMP/AP (%)	Solubility (%)
100/0	100
80/20	99.0
60/40	97.0
40/60	85
20/80	50
0/100	0

exotherm at 90°C. These could be due to curing of allyl groups.

Curing and Crosslinking

Table I shows the percentage of the soluble compound after curing and dissolving the polymer in CHCl_3 . It can be seen that as the percentage of AP in the copolymer increases, the crosslinking density increases as indicated by the amount of insoluble compound in the CHCl_3 .

Ion Exchange Capacity

Figure 2 gives the ion exchange capacity of the homopolymers and the various copolymers when the polymers were sulfonated for a period of 3 h at room temperature in concentrated H_2SO_4 . It can be seen that the ion exchange capacity increases with an increase in the AP ratio in the copolymer. The sulfonation of the AP monomer is higher because of the +I effect of the allyl group and because one more position (the sixth position) is vacant when compared to DMP where the sixth position is occupied by a methyl group. From the equivalent weight it is evident that for every 2.4 monomer units in poly(2-allyl-1,4-phenylene oxide) there is 1 sulfonic acid group present whereas for every 25 units in poly(2,6-dimethyl-1,4-phenylene oxide) there is 1 sulfonic acid group present.

Water and Methanol Uptake Study

Figure 3 gives the water and methanol uptake of the SPPO-PVDF films (polymers and copolymers)

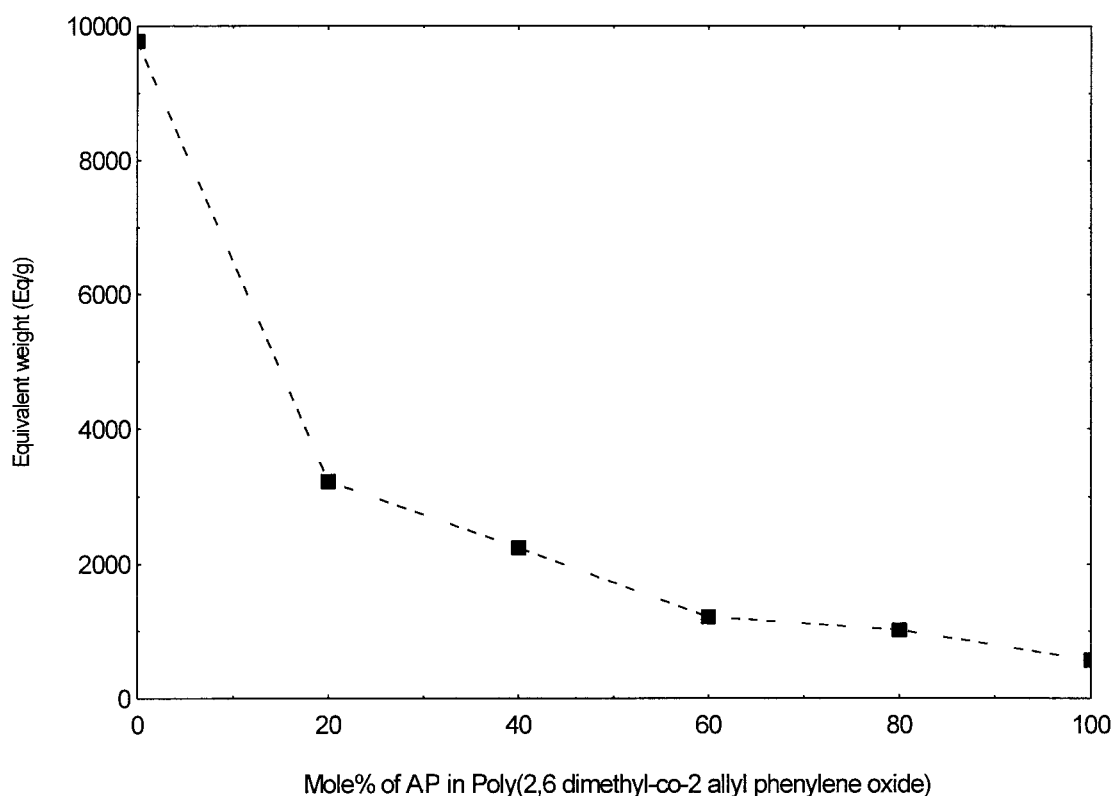


Figure 2 The equivalent weight versus molar percentage of allyl phenol in the copolymer.

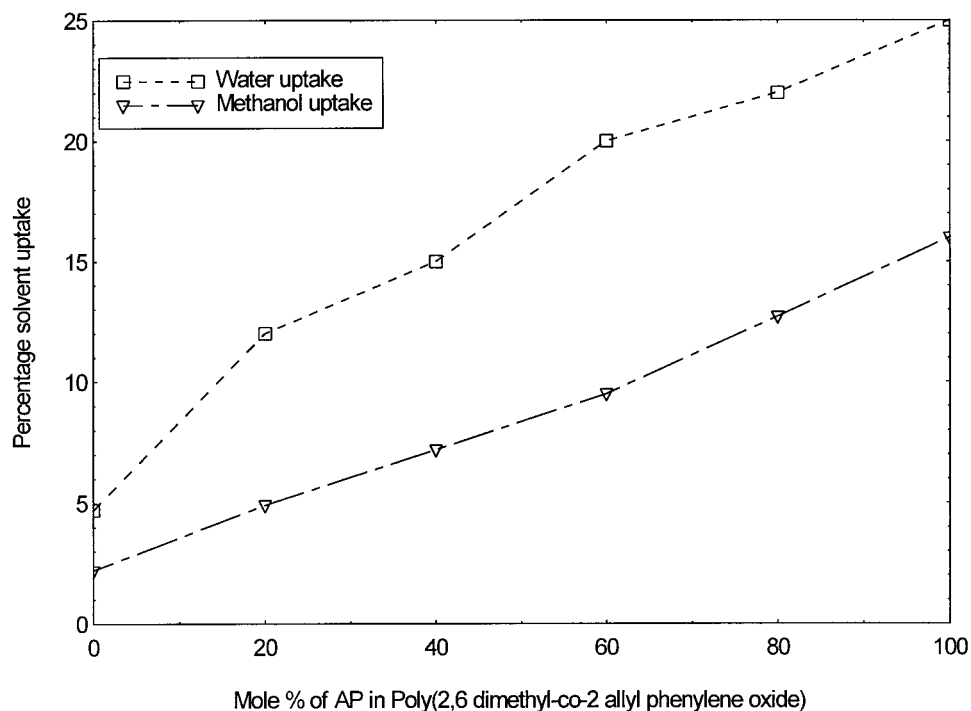


Figure 3 Solvent uptake curves in the homopolymers and copolymers.

after saturation (48-h equilibration). It can be seen that the water and methanol uptake increases with the increase in sulfonation, meaning that it follows the same trend as the ion exchange capacity. The maximum water uptake for the sulfonated AP polymer is 25% and the methanol uptake is 15%.

Conductivity Measurements

Table II shows the conductivity of the polymer blend films for a fixed sulfonation time and at room temperature. The pure AP polymer shows very high conductivity on the order of 10^{-3} S/cm. The conductivity of the polymer shows the same trend as that of the ion exchange capacity. Table

Table II Conductivity of Blend Membranes

DMP/AP (%)	Conductivity (S/Cm)
100/0	4.0×10^{-5}
80/20	3.0×10^{-5}
60/40	7.0×10^{-5}
40/60	4.1×10^{-4}
20/80	5.6×10^{-4}
0/100	4.4×10^{-3}

III shows the variation of the conductivity with the ion exchange capacity. It can be seen that the conductivity increases with the increase in the number of sulfonic acid groups in the polymer.

Table IV shows the conductivity of the poly(2-allyl-1,4-phenylene oxide) polymer with varying amounts of PVDF. Films could only be prepared with equal or higher amounts of PVDF. Higher percentages of the polymer did not yield stable films that could be sulfonated. Also, higher percentages of PVDF yielded films with higher resis-

Table III Dependence of Conductivity on Extent of Sulfonation for Blend Membrane Containing 60:40 DMP/AP

Sulfonation Conditions	Equivalent Weight (eq/g)	Conductivity (S/Cm)
3 h at room temp. immersion	2240	7.0×10^{-5}
3 h at room temp. immersion and 90 min of boiling in concn H_2SO_4 at 80°C	1346	2.1×10^{-4}

Table IV Conductivity of Blend Membranes of Poly(2-allyl-1,4-phenylene oxide) (PAPPO)-PVDF with Varying PVDF Percentages

PVDF/APPO (%)	Equivalent Weight (eq/g)	Conductivity (S/Cm)
50/50	567	4.5×10^{-3}
60/40	872	2.1×10^{-4}
70/30	1066	5.1×10^{-5}
80/20	1554	1.6×10^{-5}
100/0	—	8.4×10^{-6}

tance. Hence, all the blended films were prepared with equal quantities of the two polymers.

The copolymer prepared using 60% DMP with 40% AP was subjected to a long conductivity test. The membrane was tested for 15 days. The conductivity did not deteriorate even after 15 days but showed marginal improvement of 6.1×10^{-5} to 1.004×10^{-4} S/cm in 3 days and remained almost constant thereafter.

Solid polymer membranes comprising SPPO alone or blended with PVDF were found to be vulnerable to degradation from peroxide radicals.²¹ The copolymer made with 20% DMP and 80% AP membrane was boiled in 30% H₂O₂ solution for 30 min and left in the same solution for 3 days. The membrane was then treated with dilute H₂SO₄ and later washed with distilled water, and the conductivity was measured. The conductivity remained the same, showing that there was no degradation of the polymer.

CONCLUSION

Polymers and copolymers of DMP and AP were prepared with varying molar ratios of the monomers and characterized. Membranes were cast from a suitable solvent with PVDF in varying weight ratios. The sulfonated poly(2-allyl phenylene oxide)PVDF blend membrane was found to have the highest conductivity of 4.4×10^{-3} S/cm. The conductivity of the membrane depended on the ion exchange capacity and it increased with the increase in the level of sulfonation. These

membranes could be used as polymer electrolytes in polymer electrolyte fuel cells, direct methanol fuel cells, reverse osmosis, and other applications.

The authors wish to thank the SPIC Science Foundation and Department of Science and Technology of the Government of India for the support extended to carry out this research.

REFERENCES

- Toi, K.; Morel, G.; Paul, D. R. *J Appl Polym Sci* 1982, 27, 2997.
- Aguilar-Vega, M.; Paul, D. R. *J Appl Polym Sci Part B* 1993, 31, 1577.
- Mahajan, S. S. *Polym Plast Tech Eng* 1991, 30, 27.
- Chern, R. T.; Sheu, F. R.; Jia, L.; Stannet, V. T.; Hopfenberg, H. B. *J Membr Sci* 1987, 35, 103.
- Percec, S. *J Appl Polym Sci* 1992, 33, 191.
- Story, B. J.; Koros, W. J. *J Membr Sci* 1992, 67, 191.
- Pedretti, U.; Gandini, A.; Roggero, A.; Sisto, C.; Valentini, C.; Assogna, A.; Stopponi, A. U.S. Pat. 5,169,416, 1992.
- Yang, R.; Hay, A. S. *Synthesis* 1992, 467.
- Cooper, G. D.; Bennett, J. G., Jr. *J Org Chem* 1972, 37, 3.
- Fu, H.; Jia, L.; Xu, J. *J Appl Polym Sci* 1991, 51, 1405.
- Kruczek, B.; Vujosevic, R.; Chowdhury, G.; Khulbe, K. C.; Matsuura, T. Presented at the Eighth Annual North American Membrane Society Meeting, Ottawa, Canada, 1996.
- Hamza, A.; Chowdhury, G.; Matsuura, T.; Sourirajan, S. *J Appl Polym Sci* 1995, 29, 4029.
- Percec, S.; Li, G. In *ACS Symposium Series 264*; Benham, J. L.; Kinstle, J. F., Eds.; American Chemical Society: Washington, DC, 1998; p 16.
- Huang, R. Y. M.; Kim, J. J. *J Appl Polym Sci* 1984, 29, 4017.
- Nakano, N.; Azuma, R.; Nakashima, M.; Horiguchi, M. U.S. Pat. 5,409,785, 1995.
- Bruno, F.; Pham, M. C.; Dubois, J. E. *Electrochim Acta* 1977, 22, 451.
- Mengoli, G.; Bianco, P.; Daolio, S.; Munari, M. T. *J Electrochem Soc* 1981, 128, 2276.
- Bertoncello, R.; Furlanetto, F.; Glisenti, A.; Musiani, M. M. *J Electrochem Soc* 1995, 142, 410.
- Kuver, A.; Potje-Kamloth, K. *Electrochim Acta* 1998, 43, 2527.
- Ramya, K.; Vishnupriya, B.; Dhathathreyan, K. S. *J New Mater Electrochem Syst* 2001, 4, 115.
- Cabasso, Y. Y. Pat. WO 9724777A1, 1997.