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ARTICLE

Synthesis and Characterization of Poly(phenylene)-Based Anion Exchange Membranes for Alkaline Fuel Cells

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ABSTRACT: Cationic polymer membranes that conduct free anions comprise an enabling area of research for alkaline membrane fuel cells and other solid-state electrochemical devices that operate at high pH. The synthesis of anion exchange membranes based on a poly(phenylene) backbone prepared by a Diels–Alder reaction is demonstrated. The poly(phenylene)s have benzylic methyl groups that are converted to bromomethyl groups by a radical reaction. Cationic polymers result from conversion of the bromomethyl groups to ionic moieties by quaternization with trimethylamine in the solid state. The conversion to benzyltrimethylammonium groups is incomplete as evidenced by the differences between the IEC values measured by titration and the theoretical IECs based on ^{1}H NMR measurements. The anion exchange membranes formed from these polymers have hydroxide ion conductivities as high as 50 mS/cm in liquid water, and they are stable under highly basic conditions at elevated temperatures.

Introduction

In recent years, interest has grown in the development of anion exchange membranes (AEM) for applications such as alkaline fuel cells and electrolyzers due to the low overpotentials associated with many electrochemical reactions at high pH[1,2] and the potential to forego noble metal catalysts.[3] AEMs serve as an interesting counterpoint to the more widely developed and understood proton or cation exchange membranes (PEM or CEM). However, there are no readily available anion exchange membranes that serve as a commercial standard for electrochemical applications such as DuPont's Nafion does in the field of cation exchange membranes.

The need for AEMs with the necessary conductivity, water swelling, and chemical stability is a key challenge in the development of alkaline fuel cells. Most commercially available AEMs are typically based on cross-linked polystyrene and are not very stable in alkaline environments. In addition, they are blended with other inert polymers and fabric supports that limit their ionic conductivities. Compared to the research on membranes for PEM fuel cells, there are very few reports of AEMs for alkaline membrane fuel cells.

A series of AEMs synthesized by radiation grafting of vinylbenzyl chloride onto partially or completely fluorinated polymers such as poly(ethylene-*co*-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), or poly(vinylidene fluoride) (PVDF) and their performance in alkaline fuel cell testing have been reported.[4−7] Several groups have reported the synthesis of AEMs made from poly(sulfone)s by performing a chloromethylation reaction on the polymer and then converting the chloromethyl groups into tetraalkylammonium cations in a subsequent step.[8−13] Such poly(sulfone)-based ionomers have also been evaluated as potential binders in the catalyst layers of alkaline fuel cells.[14] Syntheses of AEMs based on poly(vinyl alcohol)[15] and poly(ether−imide)s[16] have also been reported.

In nearly all of the cases cited above, the cationic quaternary ammonium (QA) groups were formed by the reaction of tertiary amines with benzylic chloromethyl groups on the polymer chains. Because of the reactivity of chloromethyl groups, they generally cannot be present during the polymerization reactions and therefore must be grafted on in a postpolymerization step. The chloromethylation reaction can be sluggish, often requiring long reaction times and large excesses of toxic reagents such as chloromethyl methyl ether. To avoid these problems, a novel approach to the formation of halomethyl groups by preparing polymers with benzylic methyl groups has been described. In this approach, poly(2,6-dimethyl-1,4-phenylene oxide) was prepared and then treated with bromine to convert the methyl groups into bromomethyl groups.[17,18] The bromomethyl groups could then be converted into QA groups in the same manner as chloromethyl groups. These poly(phenylene oxide)-based AEMs are promising candidates for alkaline fuel cells, and they can be blended and cross-linked with a chloroacylated poly(phenylene oxide) to further improve their mechanical properties.[19,20]

A key property in developing AEMs for fuel cells is the chemical stability of the cationic groups attached to the membrane. Even in an electrochemical cell without any added electrolyte, the localized pH within the ion-conducting channels of the membrane will be quite high. Also, despite the fact that alkaline fuel cells do not require temperatures as high as PEM fuel cells to achieve adequate reaction kinetics, elevated operating temperatures are expected to enhance hydroxyl transport to optimize fuel cell performance. This combination of high pH and elevated temperature can lead to chemical attack on the quaternary ammonium groups, most commonly by either an E2 (Hofmann degradation) mechanism or by an S_N2 substitution reaction. The elimination reaction pathway can be avoided by using quaternary ammonium groups that do not have beta hydrogens such as the benzyltrimethylammonium group. The substitution pathway cannot be avoided so easily, and several

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approaches have been tried to reduce the susceptibility of the ammonium group to the substitution reaction. Tomoi et al. showed that by increasing the length of the alkylene spacer between the backbone of an aromatic polymer and the nitrogen atom of the ammonium group in their AEMs, chemical degradation in an alkaline environment was slowed substantially.[21] Bauer et al. prepared AEMs with more stable quaternary ammonium groups by using the diamine 4,4′-diazabicyclo-[2.2.2]octane (DABCO).[22] In that case, the quaternary ammonium groups were stabilized by the through space sharing of an electron pair from the nonquaternized nitrogen on the same DABCO molecule.

In addition to these attempts to prepare AEMs with more stable cationic groups, there is also evidence that QA groups are more stable under basic conditions than commonly thought. A study of the decomposition of ammonium cations by Macomber et al. indicates that controlled humidification of the AEM might present a viable strategy that could enable the use of AEMs with ammonium groups.[23] Varcoe et al. have reported a 233 h durability test of an alkaline fuel cell utilizing an AEM with benzyltrimethylammonium cationic groups.[24] Over the course of the test, the ion-exchange capacity of the AEM decreased by less than 5%, indicating reasonable stability under the operating conditions.

This article describes the preparation of AEMs based on a poly(phenylene) backbone prepared by a Diels−Alder polymerization. A series of cation exchange membranes based on the same poly(phenylene) have been previously reported.[25,26] From that work it was known that the poly(phenylene) backbone could be prepared with a high enough molecular weight to make mechanically robust membranes. In addition, the wholly aromatic polymer exhibited extremely good chemical stability. In order to make an AEM from the same polymer backbone, a similar polymer with benzylic methyl groups was prepared. The methyl groups were then converted to benzyltrimethylammonium groups after the polymerization.

Experimental Section

Materials. All reagents were purchased from commercial vendors and used without further purification unless specified. 1,4-Diethynylbenzene was recrystallized from ethanol and dried under vacuum prior to use. Bis(cyclopentadienone) (bCPD) and 4-phenylglyoxalylbenzil were prepared according to the procedure of Ogliaruso et al.[27] 4,4′-Dimethylbis(benzyl ketone) was prepared according to the procedure of Bhandari and Ray.[28] A sample of Tokuyama's Neosepta AHA membrane was purchased from Electrolytica, Inc.

Synthesis of Tetramethylbis(cyclopentadienone) (TMbCPD). The synthesis of TMbCPD was based on the published synthesis of a similar bis(cyclopentadienone).[29] A mixture of 4,4′-dimethylbis(benzyl ketone) (42.16 g, 176.9 mmol) and 4-phenylglyoxalylbenzil (29.98 g, 87.57 mmol) in ethanol (750 mL) was stirred and heated until a solution formed. A solution of KOH (4.91 g, 87.6 mmol) in water (10 mL) was carefully added, and the solution was heated at reflux for 1 h. The solution was then cooled to room temperature and stirred for 18 h. The resulting mixture was filtered; the filtrate was triturated with water and then with ethanol, and then it was dried under vacuum at 120 °C to yield TMbCPD as a dark purple solid (37.13 g, 57%).

Synthesis of TMPP Homopolymer and DAPP−TMPP Copolymers. The polymerization was based on the procedure of Fujimoto et al. with a few modifications.[25] A typical procedure for preparing DAPP−TMPP (1:1) is given here. To make the TMPP homopolymer, no bCPD was added. TMbCPD (3.96 g, 5.31 mmol), bCPD (3.67 g, 5.31 mmol), 1,4-diethynylbenzene (1.34 g, 10.62 mmol), and diphenyl ether (40 mL) were charged to a flask under argon. The mixture was frozen in a dry ice/acetone bath and was freeze−thaw degassed (two times) before heating at 180 °C for 24 h. The reaction was cooled to 100 °C, and toluene (40 mL) was added to thin the solution before cooling to room temperature. The solution was poured into excess acetone and the precipitate was dried, dissolved in toluene (40 mL), and reprecipitated into acetone. The resulting solid was dried under vacuum at 250 °C to yield a tan solid (7.37 g, 88%).

Bromination of TMPP Homopolymer and DAPP−TMPP Copolymers. Polymers were prepared with varying degrees of bromination. The procedure for preparing BTMPP with 2.20 $-CH_2Br$ groups per repeat unit is described. TMPP (13.27 g) was dissolved in 1,1,2,2-tetrachloroethane (215 mL) in a flask equipped with a magnetic stir bar and a condenser. The solution was heated to 85 °C, and *N*-bromosuccinimide (6.50 g, 36.5 mmol) and benzoyl peroxide (443 mg, 1.83 mmol) were added. After 3 h, the reaction was cooled and poured into excess ethanol. The precipitate was washed with water and ethanol twice and then dried under vacuum at room temperature to yield a tan solid (15.26 g).

Casting and Amination of Films. Solutions of brominated TMPP (BTMPP) or brominated DAPP−TMPP (DAPP−BTMPP) in chloroform (5−8% w/w) were filtered and poured into glass dishes, and the $CHCl_3$ was controllably removed by evaporating the solvent at room temperature from the dish over a 24 h period by partially covering the dish with an inverted beaker. The films were removed from the dishes by immersing them in water. To form the benzyltrimethylammonium functional groups, the films were immersed in a 45% w/w solution of trimethylamine in water in a closed container for 48 h at room temperature. They were then soaked in 1 M NaOH for 48 h to exchange the bromide ions for hydroxide ions. Finally, the membranes were immersed in deionized water for at least 24 h prior to analysis.

Characterization and Measurements. Gel permeation chromatography (GPC) was performed with a liquid chromatograph equipped with a Viscotek VE2001 isocratic pump and autosampler and a Viscotek VE3580 refractive index detector. The mobile phase was tetrahydrofuran, and the system was operated at 25 °C with a flow rate of 1.0 mL min^{-1}. The weight-average molecular weights were measured by calibration with polystyrene standards.

^1H NMR spectra of the polymers were obtained on a Bruker spectrometer using 5 mm o.d. tubes. Sample concentrations were about 5% (w/v) in MeOH-d_4 (for ATMPP) or in $CDCl_3$ (for all other samples) containing 1% TMS as an internal reference.

Ion exchange capacities were determined by a back-titration procedure described previously, and hydroxide ion conductivities were measured using an impedance spectroscopy method also described previously.[13]

Results and Discussion

The utilization of a Diels−Alder reaction to prepare poly(phenylenes) has been previously reported.[30−32] In those cases, however, very little was done to add functionality to the polymer once it was prepared. The scheme for the synthesis of the monomer and polymers used in this study is shown in Scheme 1. The key monomer, a tetramethylbis(cyclopentadienone) (TMbCPD), was prepared from 4-phenylglyoxalylbenzil and 2 equiv of 4,4′-dimethylbis(benzyl ketone). The Diels−Alder polymerization was conducted by heating equimolar amounts of the bis(cyclopentadienone)s and 1,4-diethynylbenzene in diphenyl ether with the loss of one carbon monoxide molecule for each Diels−Alder reaction. It is this loss of CO and the accompanying formation of a highly stable aromatic ring that makes the polymerization irreversible. To make the tetramethylpoly(phenylene) homopolymer (TMPP), no bCPD was used in the polymerization.

Because of the ambiguous regiochemistry of the Diels−Alder reaction, every other ring in the poly(phenylene) backbone has an uncertain substitution pattern (either 1,4- or 1,3-). In a study of

Scheme 1. Synthesis of TMbCPD and DAPP−TMPP Copolymer

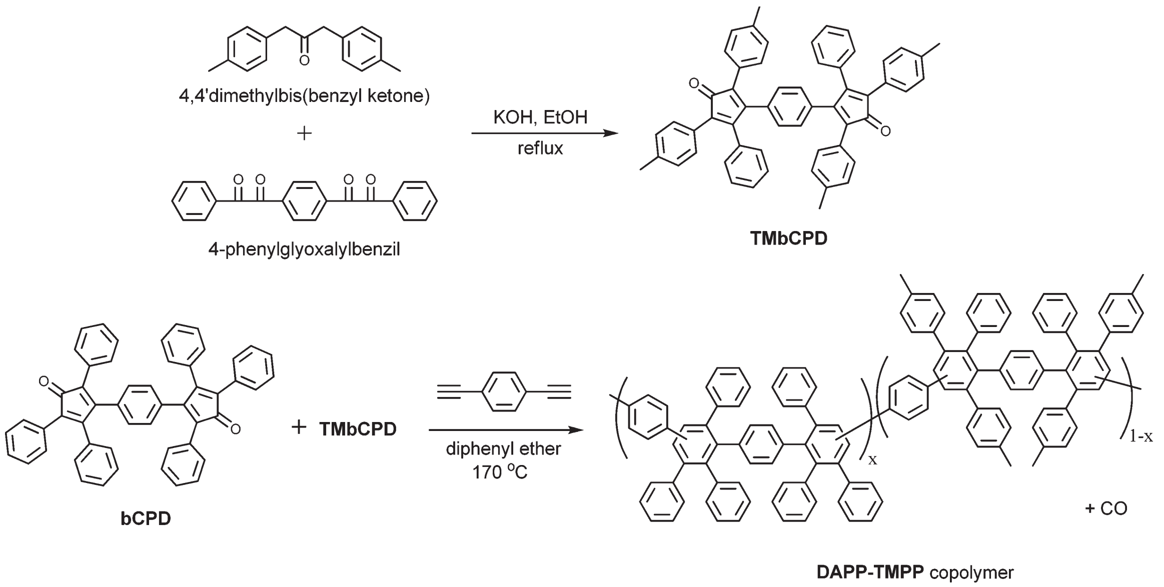


Table 1. GPC Molecular Weight Results for TMPP and DAPP−TMPP Copolymers

sample	$M_n \times 10^3$ (g mol^{-1})	$M_w \times 10^3$ (g mol^{-1})	PD
TMPP, batch 1	31	69	2.2
TMPP, batch 2	28	62	2.2
TMPP, batch 3	31	71	2.3
TMPP, batch 4	32	65	2.0
TMPP, batch 5	34	75	2.2
DAPP−TMPP (1:1), batch 1	32	79	2.5
DAPP−TMPP (1:1), batch 2	31	68	2.2

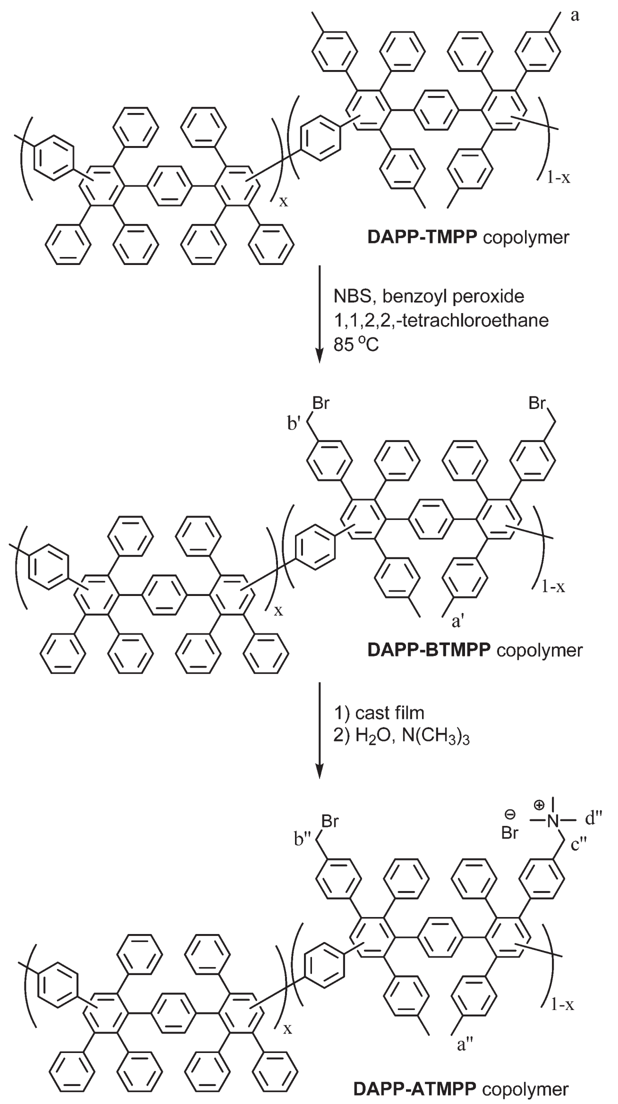
the catenation of Diels−Alder polymerizations by Stille and Noren, the authors found that the ratio of para- to meta-substituted rings formed at the reaction temperature used in the present study is about 57:43.[33] This irregularity in the backbone and the many aryl side groups prevent the polymer chains from packing closely together and becoming intractable like many other poly(phenylene)s. Consequently, both TMPP and DAPP−TMPP are soluble in common organic solvents such as toluene and chloroform. Molecular weight information for several batches of TMPP and DAPP−TMPP is given in Table 1. Molecular weights tended to be a lower than those previously reported for sulfonated DAPP,[25] but all of the samples listed in Table 1 could be cast into clear, creasable films. Obviously, the true molecular weights would increase upon the addition of pendant quaternary ammonium groups although this would not affect the average number of repeat units per chain.

The bromomethylated poly(phenylene), BTMPP, was prepared by a radical bromination reaction on the TMPP repeat units of the parent polymer (Scheme 2). The fraction of methyl groups converted to bromomethyl groups was controlled by adjusting the amount of NBS used. Figure 1 shows the relationship between the amount of NBS used and the number of bromomethyl groups formed for several different batches of BTMPP and DAPP:BTMPP (1:1). In all cases, the reaction temperature was 85 °C, the reaction time was 3 h, and 0.05 equiv of benzoyl peroxide initiator (based on NBS) was used. The degree of functionality (DF) is defined as the number of bromomethyl groups per polymer repeat unit and thus has a maximum possible value of 4 for the TMPP homopolymer. In all cases, the DF achieved was approximately 75−85% of the DF that would have resulted if every NBS molecule had reacted to make a bromomethyl group. Figure 2 shows the ^{1}H NMR spectra of the TMPP homopolymer (top) and BTMPP (middle). The aromatic regions of these spectra contain many overlapping peaks, and individual peaks could not be assigned. Because of the irregularity of the regiochemistry of the polymer backbone, the protons of the methyl groups in TMPP were responsible for the group of peaks labeled a. Upon bromination, the b′ peaks appeared and the a′ peaks decreased in size. DF was measured by comparing the integrals of the a′ and b′ peaks.

The oversimplified illustration of the bromination reaction in Scheme 2 shows a polymer with a DF of two and which has exactly two bromomethyl groups per repeat unit (for the case where $x = 0$). Since the bromination reaction can occur independently at any of the methyl groups, there is actually a random distribution of bromomethyl groups among the repeat units, and the DF is merely an average value. For example, in a BTMPP homopolymer with a DF of two, the mole fractions of repeat units having 0, 1, 2, 3, and 4 bromomethyl groups are 1/16, 1/4, 3/8, 1/4, and 1/16, respectively. TMPP has a maximum potential DF of four, so AEMs prepared from TMPP (ATMPP) have a maximum theoretical IEC value of 3.4. DAPP−TMPP (1:1) has a potential DF of two, so AEMs prepared from DAPP−TMPP(1:1) (DAPP−ATMPP) have a maximum theoretical IEC value of only 2.0.

Table 2 lists the DF for several batches of BTMPP as well as the characterization data for the AEMs prepared from them by soaking in trimethylamine. The theoretical IEC values were calculated based on DF assuming 100% conversion of bromomethyl groups to benzyltrimethylammonium groups and 100% exchange of bromide ions for hydroxide ions. As the data show, the reaction to convert bromomethyl groups in BTMPP repeat units to benzyltrimethylammonium groups could only be carried out to 55−75% completion. So the ATMPP membranes each contain some unreacted bromomethyl groups, as illustrated in Scheme 2. This is similar to the incomplete quaternization of chloromethyl groups on a polysulfone under identical conditions reported previously[13] and is probably due to the fact that the quaternization reaction takes place within a solid membrane rather than in solution. Benzyltrimethylammonium groups are formed when BTMPP films are soaked in aqueous trimethylamine (Scheme 2). As the quaternary ammonium groups are formed, the membranes become hydrophilic and swell as they take up water. However, some of the bromomethyl groups are isolated in hydrophobic domains and therefore do not come into contact with the aqueous trimethylamine reagent.

Scheme 2. Bromination of DAPP−TMPP and Formation of DAPP−ATMPP Membranes



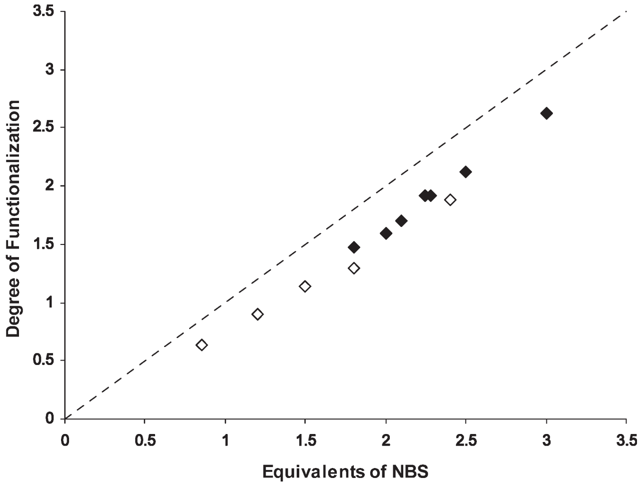


Figure 1. Efficiency of bromination in the synthesis of BTMPP (filled symbols) and DAPP−BTMPP (open symbols). Equivalents of NBS are per polymer repeat unit. Degree of functionalization = number of bromomethyl groups per repeat unit. The dashed line indicates the maximum theoretical DF (i.e., 100% efficient usage of NBS).

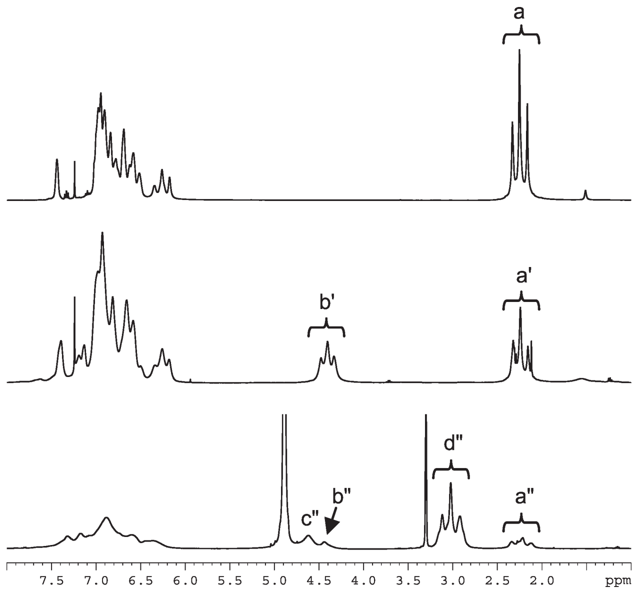


Figure 2. ^{1}H NMR spectra of TMPP (top), BTMPP (middle), and ATMPP (bottom).

The incomplete conversion of bromomethyl groups to benzyltrimethylammonium groups can be seen in the ^{1}H NMR spectrum of ATMPP (Figure 2, bottom). After amination, new peaks (c″ and d″) near 4.65 and 3.0 ppm were evident and were assigned to the methylene unit and the methyl groups of the newly formed QA group, respectively. The b″ peak indicates the presence of some unreacted bromomethyl groups, and its integral relative to that of the c″ peak is consistent with the difference between the theoretical and measured IECs. The peaks in the ^{1}H NMR spectrum of ADAPP are rather broad, presumably due to agglomeration of the ionomers in methanol solution, and precise integral values for c″ and b″ were difficult to obtain.

Not surprisingly, the water uptake values for the ATMPP membranes increase as the IEC increases although the rate of increase is greater at higher IEC values. This is most easily observed in the hydration numbers (λ) given in Table 2 which show fewer water molecules per QA group (25−26) at IECs below about 1.4 whereas ATMPP samples with IECs above 1.4 have hydration numbers that are significantly higher (39−47). Interestingly, these water uptake values for ATMPP are ~2 times greater than they are for cation exchange membranes prepared from the same poly(phenylene) backbone.[25] The increase in hydration numbers for ATMPP at higher IECs is indicative of an increase in the connectivity of the hydrophilic domains. As the number and size of the hydrophilic domains increase, a percolation threshold is reached, above which the hydrophilic domains are interconnected, and there are few, if any, isolated ionic groups which are not fully hydrated. BTMPP films with DF values above about 2.4 become so hydrophilic during the quaternization reaction that the membranes dissolve in the aqueous trimethylamine (in Table 2, this is indicated as infinite water uptake).

The ADAPP−ATMPP copolymer membranes all have hydration numbers (31−37) that fall between the two ranges seen for ATMPP. Thus, it is probably the case that these membranes have IECs below the percolation threshold, but they are hydrated more effectively than ATMPP samples with IECs below 1.4. This can be explained as a result of the copolymer structure which forces the ionic groups to be located on half as many repeat units as they would be on an ADAPP homopolymer with the same IEC. This results in an ionic clustering effect which allows for the formation of hydrophilic microdomains even though the membrane itself does not exhibit phase separation.

Table 2. Results for ATMPP and DAPP−ATMPP

sample	DF[a]	theoretical IEC (mequiv/g)[b]	measured IEC (mequiv/g)	water uptake (%)	λ
ATMPP	1.38	1.46	0.93	42	25
ATMPP	1.49	1.56	0.99	44	25
ATMPP	1.65	1.72	1.04	48	26
ATMPP	1.92	1.93	1.42	101	40
ATMPP	1.98	1.98	1.39	97	39
ATMPP	2.13	2.09	1.57	122	43
ATMPP	2.19	2.14	1.25	101	45
ATMPP	2.63	2.48	N/A	∞	∞
ADAPP−ATMPP (1:1)	0.63	0.74	0.40	23	32
ADAPP−ATMPP (1:1)	0.90	1.03	0.70	39	31
ADAPP−ATMPP (1:1)	1.14	1.27	0.80	46	32
ADAPP−ATMPP (1:1)	1.30	1.43	0.89	54	34
ADAPP−ATMPP (1:1)	1.80	1.88	1.15	78	37

[a] Degree of functionalization = (number of bromomethyl groups/repeat unit). [b] Calculated from DF assuming complete amination, ion exchange, and water removal upon drying.

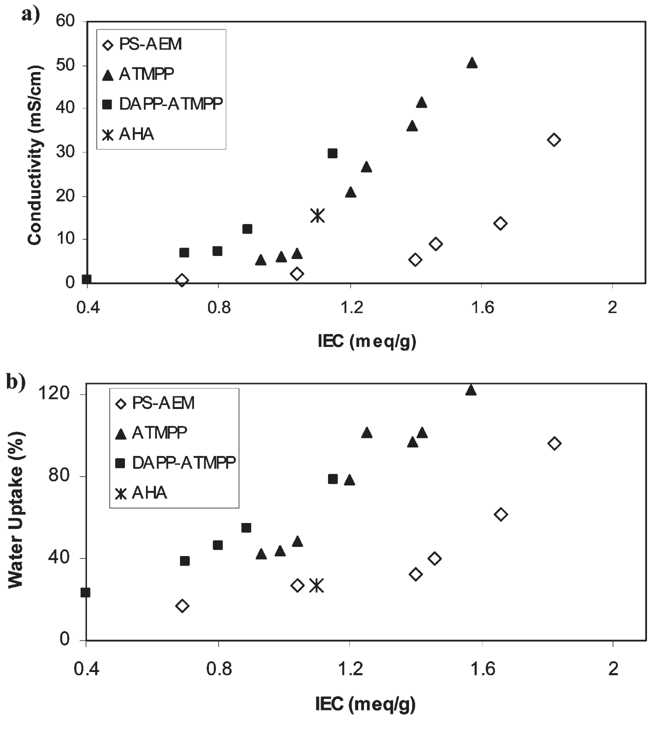


Figure 3. (a) Hydroxide anion conductivity and (b) water uptake versus ion exchange capacity for ATMPP, ATMPP/DAPP, polysulfone (PS−AEM), and Tokuyama AHA membranes.

The hydroxide ion conductivities of the ATMPPs and DAPP−ATMPPs are given in Figure 3a along with the data for a series of polysulfone-based AEMs (PS−AEM) previously reported for comparison.[13] The maximum conductivity measured for an ATMPP sample was 50 mS/cm, which is in line with the highest reported AEM conductivities reported to date. The conductivities of ATMPP samples are all higher than those for PS−AEMs with similar IEC values, and this is because of the inability of the polymer chains to pack closely together as described above. The extra space between the chains allows for greater water swelling (Figure 3b) and the increase in water content leads to greater ion conductivities. The equivalent conductivity and water uptake trends for the DAPP−ADAPP(1:1) copolymers are shifted to even lower IECs than they are for ADAPP. This is because of the ionic clustering effect discussed above. While this clustering is not as effective as it would be in a true block copolymer, it promotes overlap of the hydration shells and thus the formation of ion channels for greater conductivity. Data for a commercially available AEM, Tokuyama's Neosepta AHA membrane, are also included in Figure 3 for comparative purposes. The AHA membrane was not necessarily designed for use in a fuel cell, but it is one of very few available AEMs that are stable in a strongly basic environment.

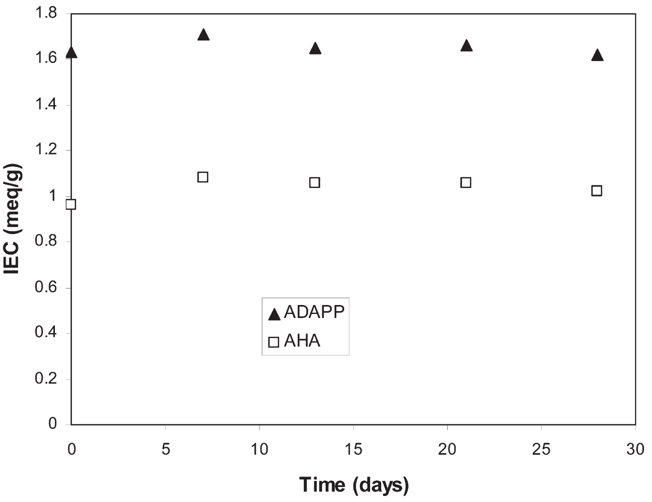


Figure 4. Stability of anion exchange membranes in 4 M NaOH at 60 °C.

These results point out the potential benefits of designing a similar membrane with a true block copolymer structure. The use of ionic and nonionic blocks would drive the formation of hydrophilic and hydrophilic domains within the membranes. The hydrophilic blocks would have high localized concentrations of ionic groups and large hydration numbers for the rapid movement of charge carriers. The hydrophobic blocks would serve to anchor the chains in place while keeping the overall water swelling of the membrane from becoming too large for the membrane to be useful.

The chemical stabilities of ADAPP, PS−AEM, and Tokuyama's AHA were tested by immersing samples in a stirred aqueous solution of NaOH (4 M) held at 60 °C for 28 days. The test results are shown in Figure 4. After only a few days, the PS−AEM samples became extremely brittle and broke apart due to the mechanical agitation of the stir bar. This embrittlement was almost certainly due to degradation of the poly(sulfone) backbone and indicates that membranes based on this type of polymer are probably not suitable for use in alkaline fuel cells. Because of the susceptibility of benzyltrimethylammonium groups to attack by the $\mathrm{S_N}2$ mechanism, it was anticipated that the IECs of all of the AEMs would decrease somewhat during the test. However, the ADAPP and AHA membranes did not exhibit any changes in appearance or flexibility during the testing, nor was there any measurable change in their IEC values. While this one set of testing conditions may not exactly duplicate the conditions in an operating alkaline fuel cell, the benzyltrimethylammonium groups on both of these membranes were surprisingly stable, and the test indicates that the ADAPP membranes are suitable for use in alkaline fuel cells.

Conclusions

Tetramethylpoly(phenylene) homopolymers and copolymers were synthesized via Diels−Alder condensation and were converted to cationic polymers in two steps: bromination and amination. The formation of benzyltrimethylammonium groups takes place with the membrane in the solid state so not all of the bromomethyl groups are converted to QA groups. The membranes thus formed are robust and creasable. They have water uptakes that range from 23 to 122% and hydroxide ion conductivities that range from 1 to 50 mS/cm. The ADAPP membranes have greater conductivities and water uptakes than poly(sulfone)-based AEMs with similar IECs due to irregularities in the linearity of the poly(phenylene) backbone and bulky side groups which prevent efficient packing of the polymer. The DAPP−ADAPP copolymers have higher conductivities and water uptakes than ADAPP homopolymers with similar IECs. It was hypothesized that this is due to the effect of having the cationic groups on only half of the repeat units in the copolymers resulting in a cooperative hydration effect. A test of the stability of ADAPP membranes under high pH conditions showed no degradation and indicated that these membranes are good candidates for use in electrochemical devices such as alkaline fuel cells.

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