Membrane Binders Based on Poly(phenylene oxide) Functionalized with Quaternary Ammonium Groups via a Hexyl Spacer

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Anion exchange membranes (AEMs) with hexyl pendant chains were synthesized by Friedel–Crafts acylation of 6-bromo-1-hexanoyl chloride on poly(phenylene oxide) (PPO), followed by the reduction of the ketone with triethylamine, and quaternization with a tertiary amine (trimethylamine, quinuclidine, or 1-methylimidazole).1–3 Operating in alkaline conditions presents distinct and attractive advantages to AMFCs and solid-state alkaline water electrolyzers.4–10 In the second experiment, TMA-C6-PPO AEM was immersed in nitrogen degassed 1 M KOH at 60 °C for 30 days. The ion exchange capacity of this AEM decreased 33% confirming previous results. The finding that PPO-based AEMs with hexyl spacers degrade in alkali suggests the hypothesis that alkyl spacers can be used to increase the alkaline stability is not valid for all backbones and conditions.

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There is an increasing interest in alkaline stable anion exchange membranes (AEMs), and solubilized AEM binders for applications in alkaline membrane fuel cells (AMFCs) and solid-state alkaline water electrolyzers.11–13 Operating in alkaline conditions presents distinct and attractive advantages to AMFCs and solid-state alkaline water electrolyzers, in comparison to acidic proton-exchange membrane fuel cells and water electrolyzers. Under alkaline conditions, it is possible to achieve faster oxygen reduction kinetics, more efficient water management, there is greater flexibility in the choice of fuels, and more importantly, presents the possibility of using non-precious-metal electrocatalysts.14 On the other hand, the hydrogen oxidation/evolution reaction is more sluggish in alkaline media.5–10

The majority of the AEMs evaluated and reported in the peer-reviewed literature comprise polymers functionalized with benzyl trimethylammonium groups or, similar cation groups attached to the benzyl carbon of polymer backbones like benzyl trimethyl ammonium resins lost approximately 30%. The authors believe that the close proximity of the ions to the polymer structure leads to limitations in ion dissociation, and thus conductivity, because of the absence of reactive benzylic carbons, which could be attacked by strong nucleophiles like hydroxide anions.

Hibbs11 synthesized poly(phenylene)-based anion exchange membranes with quaternary ammonium cations affixed to the benzene rings in the backbone by using six-carbon alkyl chains. The synthesis comprised three steps: 1) Friedel–Crafts acylation using 6-bromo-1-hexanoyl chloride, 2) reduction of the ketone proximal to the aromatic ring, and 3) quaternization with trimethylamine. He found that alkyl trimethylammonium was significantly more stable than benzyl trimethylammonium groups. Only a minimal (ca. 5%) decrease in the ion exchange capacity was observed for membranes immersed in nitrogen-degased 4M KOH at 60 °C for 14 days. The same test done on AEMs containing benzyl trimethylammonium cations resulted in a loss of 21% of their initial ion exchange capacity.

Ran and coworkers22 attached pendant chains (rod-coil grafted copolymers) with quaternary ammonium groups to a polyelectrolyte backbone. Their motivation was to improve the alkaline stability, and also enhance the ionic conductivity through nanophase separation between the hydrophobic polymer chains and hydrophilic graft chains to create a suitable pathway for high hydroxide ion mobility. In random copolymers, the placement of cations close to the polymer backbone, and the absence of degrees of freedom obstruct their movement, preventing an efficient phase separation. Common approaches to facilitate phase separation in AEMs are the concentration of ions into single units in statistical copolymers.22–25 stiff side groups26 or block copolymers.27 However, those approaches may lead to limitations in ion dissociation, and thus conductivity, because of the close proximity of the ions to the polymer structure.28
presence of long mobile pendant chains might favor phase separation without the drawbacks mentioned above.

Nie and coworkers\textsuperscript{35} combined cross-linked polymers and aromatic side groups to synthesize polysulfone-based AEMs. Through their experiments and analysis they concluded that the crosslinking favored AEM mechanical stability, and participated in the formation of large and stable ionic channels improving ionic conductivity. Hydroxide ion conductivities at 80 °C in the range 40 to 80 mS/cm were measured. They found that the AEM ionic conductivities dropped 6% after immersion in 1 M NaOH for 28 days.

Recently, several authors have independently proposed that alkyl pendant chains can be used to get stable AEMs by reducing the electronic interaction between the quaternary ammonium and the aromatic rings in the backbone. Some of these works contain computational analysis others contain studies with model compounds. Only a few works had actual experiments with AEMs containing the pendant chains. Analyzing the changes in NMR spectra and/or conductivity were the predominant methods to study the alkaline stability. NMR spectra can be difficult to analyze for large polymers where the NMR peaks are broad and can overlap, and ionic conductivity can be affected by many factors unrelated to the presence of the cation under study. For example, oxidation reactions leading to the formation of carboxylates can maintain similar levels of ionic conductivity, even if the quaternary ammonium group degrades (it is difficult to distinguish between anion and cation conductivity). We believe that any studies of alkaline stability should include NMR spectra and experimental measurements of the ion exchange capacity to determine the actual changes of the concentration of the fixed cations. Specifically, one should use the Volhard titration method to estimate the true anion exchange capacity. We have adopted this method in our previous works\textsuperscript{2,3,14,17,36,37}

It has been suggested that using aliphatic pendant spacer chains results in several advantages, including the formation of a well-hydrated and percolating phase resulting in high ionic conductivity, and lowering of degradation rates due to the presence of benzyl carbons.\textsuperscript{24,25} However, some of the reports attesting to these advantages are not entirely conclusive, as they do not contain all the experiments necessary to characterize the degradation of the AEMs. Because of these concerns, we believed that it would be worthwhile to consider (using the rigorous approach suggested above) whether the use of spacer chains indeed improved the alkaline stability of AEM based in aromatic backbones. In this work, we will evaluate the alkaline stability of an AEM with a six-carbon spacer chain. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is functionalized using a long flexible hexyl chain by a three stage procedure: 1) Friedel–Crafts acylation using 6-bromo-1-hexanoyl chloride, 2) reduction of the ketone in the benzyl carbon attached to the aromatic ring, and 3) quaternization by reaction with a tertiary amine. The stability of the AEM will be assessed by exposing them to alkali (1 M KOH) at 60 °C for up to 1 month. The AEMs (before and after exposure to alkaline solutions) were characterized using 1D (\textsuperscript{1}H NMR and \textsuperscript{13}C NMR) and 2D NMR (correlation spectroscopy, COSY, and \textsuperscript{1}H-\textsuperscript{13}C heteronuclear multiple-quantum correlation spectroscopy, HMOC), and by measuring the anion exchange capacity by Volhard titration.

We have selected PPO as base polymer for the studies because it is well documented that the material is stable in alkaline solutions. Arges and coworkers\textsuperscript{14} analyzed PPO before and after exposure to 1 M KOH and 6 M KOH via 2D-NMR spectroscopy and tensile tests and they did not observe any changes in the \textsuperscript{1}H-\textsuperscript{13}C HMOC spectrum and mechanical properties. These results prove that PPO by itself, before and after exposure to 1 M NaOH for 28 days, the AEM ionic conductivities dropped 6% after immersion in 1 M NaOH for 28 days.

Results and Discussion

The synthesis of AEMs based on poly(phenylene oxide) oxide with alkyl side chains was accomplished via Friedel–Crafts acylation of 6-bromo-1-hexanoyl chloride on the base polymer, poly(2,6-dimethyl-1,4-phenylene oxide (Polysciences, Inc.). The average molecular weight (M\textsubscript{w}) of PPO measured using GPC was 31,400 and the polydispersity was 2.4. The scheme for the synthesis is shown in Figure 1.

Figure 2 shows the \textsuperscript{1}H NMR spectra for BrKC6-PPO and BrC6-PPO polymers. NMR peaks were assigned using 2D NMR (COSY and HMOC) spectra included in the ESI (Figs S1-S4 correspond to BrKC6-PPO and Figs S5-S8 belong to BrC6-PPO). For BrKC6-PPO,
the alkyl chain contained a ketone group in the benzyl position. Peak “i” (3.0 ppm) corresponds to the protons in the alkyl chain carbon adjacent to the ketone group. Additional assessment of the presence of the ketone group in the benzyl position was done using $^{13}$C NMR spectroscopy. The $^{13}$C NMR spectrum of BrKC6-PPO showed a peak at 206.7 ppm that was ascribed to the ketone carbon in the vicinity of the aromatic ring (Fig S3). The assignment was made using listings of chemical shifts of common groups, and by referring to related work. The peak at 3.39 ppm (“e”) corresponds to the protons in the bromomethyl group. The brominated polymer (BrKC6-PPO) had a DF of 0.31 mol of bromine per polymer repeat unit. This DF was selected to get final AEMs with ion exchange capacity (IEC) of approximately 1.8 mmol (chloride)/g. In this work, we decided to evaluate the alkaline stability of AEMs with IECs in the range 1.5–2.0 mmol/g, since these are typical values for AEMs employed in AEM fuel cells and solid-state alkaline water electrolyzers, and because we suspect that in some of the previous works, the AEMs evaluated had lower IECs, which led to an incorrect assessment of the alkaline stability. It is more difficult to accurately estimate changes in the IEC and ionic conductivity when the functionalization degree is low, because of the quantification limits of the analytical techniques. The second step in the synthesis involved the reduction of the ketone group in the pendant chain. This is a necessary step to minimize the degradation of the quaternary ammonium under alkaline conditions.94–98% of the ketone groups were reduced after optimization of the amount of triethylamine and trifluoroacetic acid used in the reduction step. The reduction of the ketone was confirmed by the changes in the $^1$H NMR spectra (Figure 2). Peak i initially observed at 3.0 ppm shifted to lower frequencies (peak i’ at 1.66 ppm) due to the loss of the adjacent electron withdrawing ketone group. The reduction of the ketone yielded a new methylene bridge whose protons resulted in a $^1$H NMR signal at 2.8 ppm (peak k’).

$^{13}$C NMR spectroscopy was also used to confirm the reduction of the ketone. The absence of any peak at approx. 207 ppm (initially present in the $^{13}$C NMR spectrum of BrKC6-PPO) presented definitive proof of the complete reduction of the ketone in the BrC6-PPO. The solutions obtained were cast onto glass plates and the solvent was dried in an attempt to get AEM films. Unfortunately, the films were too brittle and it was not possible to use them as membrane separators in alkaline membrane fuel cells or solid-state alkaline water electrolyzers. We initially believed that the reason for the brittleness of the AEMs was a reduction in the molecular weight of the polymer backbone during chemical modifications via Friedel-Crafts acylation or reduction of the ketone. However, the molecular weights (Mw) of BrKC6-PPO and BrC6-PPO as measured by using GPC were 51,100...
Table I. Properties of the solubilized AEM binders.

| AEMs       | Theoretical IEC (From $^1$HN M R) (mmol Cl$^{-}$/g) | Ionic conductivity* mS/cm |
|------------|--------------------------------------------------|---------------------------|
| TMA-C6-PPO | 1.8                                              | 1.2 ± 0.1                 |
| ABCO-C6-PPO| 1.7                                              | 0.7 ± 0.1                 |
| 1 M-C6-PPO | 1.7                                              | 0.6 ± 0.1                 |
| TMA-PPO    | 1.9                                              | 1.1 ± 0.1                 |

*The measurements were done at 25°C in a Swagelok Teflon conductivity cell loaded with 5 wt% solubilized AEM binder solution (in chloride form).

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and 43,100, and they were very close to the expected values of 49,000 and 44,000. The polydispersity of BrKC6-PPO and BrC6-PPO were 1.9 and 1.8 respectively; also very close to the starting polymer. Given the molecular weights and polydispersities were close enough to the expected values, we could conclude that the molecular weight of the polymer backbone did not decrease during the chemical modifications. The reasons for the brittleness of the films therefore were not related to the chemical procedure employed for the synthesis of the AEMs.

However, the AEMs were solubilized in isopropanol/water (1:1 weight) and could be used as binders for the fabrication of electrodes for the electrochemical devices mentioned above. The stability of these binders is equally important, and is worthy of study.2,4

The ionic conductivity of the solubilized AEM binders is shown in Table I. The chloride ion conductivity of TMA-C6-PPO binder was slightly higher than for TMA-PPO binder. The two materials also exhibited similar performance when used as electrode binders in a solid-state alkaline water electrolyzer.2 The substitution of trimethylamine by larger bases (ABCO and 1 M) slightly reduced the ion exchange capacity (larger molecular weight) and reduced the ionic conductivity by approximately 50%.

The alkaline stability of TMA-C6-PPO solubilized AEM binders was evaluated using two separate, complementary experiments. In the first experiment, the AEMs were dissolved in a mixture of 1 M NaOD + DMSO-d6. The experiments were done in polypropylene containers to avoid the reaction of the base with container walls (commonly reported for glass vessels). Polypropylene containers do not yield any products that can interfere in the NMR analysis under the experimental conditions. We did not detect any products through $^1$H-NMR analysis in 1 M NaOD solution kept in polypropylene containers for 1 month (60°C). Samples were taken at regular intervals and $^1$H NMR spectra were recorded at regular intervals and used to assess the alkaline stability. Figure 3 shows a comparison of the $^1$H NMR spectra of TMA-C6-PPO, before and after exposure to alkali for 1 month. The new peaks (A, B, C and D) that emerged in the NMR spectrum for TMA-C6-PPO after 1 month in 1 M NaOD + DMSO-d6 confirmed that this material was not stable in alkali. A similar comparison for TMA-PPO can be seen in Fig S12 in the ESI. The new peaks A1 and A2 that emerged in the NMR spectrum for TMA-C6-PPO after 1 month in 1 M NaOD + DMSO-d6 showed that the material was not stable in alkali. We did not attempt to calculate the degradation degree because the peak g overlaps with a large water peak.

Peak “D” (2.33 ppm) was attributed to the formation of tertiary amines (trimethylamine) during degradation of the quaternary ammonium group (Hofmann elimination or direct nucleophilic, $\mathrm{S_N2}$ reaction). Peak “B” was attributed to protons in alkene moieties formed during Hofmann elimination. Despite the assumption generally accepted that cation groups attached to long alkyl pedant groups (greater than n > 3 carbons) substantially improve cation stability in alkaline media,11,26,40,41 it is very likely they suffer from Hofmann elimination. Peaks “A” and “C” remain unidentified, but their presence suggests changes in the structure of the material.

Figure 4 shows the evolution of the ion exchange capacity for TMA-C6-PPO for the same alkaline stability experiment. The theoretical ion exchange capacity of TMA-C6-PPO was calculated by comparing the peak areas for peaks “a+b” and m’. The ion exchange capacity of TMA-C6-PPO decreased from 1.8 ± 0.1 mmol/g to 1.1 ±
0.1 mmol/g after 1 month in 1 M NaOD + DMSO-d6 (loss of 39% of the initial IEC).

In the second alkaline stability test, performed to complement the results obtained in the first test, TMA-C6-PPO was immersed in nitrogen degassed 1 M KOH and kept in a sealed polypropylene vial in an oven at 60°C for 1 month. The motivation of this experiment was to evaluate the stability of the AEMs under alkaline conditions (1 M KOH) using an independent and complementary test, to validate the conclusions extracted by following the changes in 1H NMR peak areas (theoretical IEC). To assure the conclusions were strong, we decided to immerse the AEM material in 1 M KOH at 60°C and measure the ion exchange capacity using Vanilhed titration. The ion exchange capacity (in chloride form) of the AEM material decreased from 1.8 ± 0.1 mmol/g to 1.2 ± 0.1 mmol/g (33%) after immersion in 1 M KOH at 60°C for 30 days. These results (from a completely independent experiment) are in complete agreement with the NMR results that showed the AEM was not stable in alkali. 1H NMR spectroscopy performed in those AEMs after 1 month in 1 M KOH at 60°C (see Figs S13 & S14) showed similar degradation peaks to those observed in the alkaline stability experiments in NaOD + DMSO-d6.

Similarly, AEMs where trimethylamine was attached directly to the benzyl carbon in PPO (TMA-PPO), without any spacer, exhibited a decrease in the ion exchange capacity (measured using Vanilhed titration) of 18% under same conditions (from 1.8 ± 0.1 mmol/g to 1.4 ± 0.1 mmol/g). The fact that PPO-based AEMs with hexyl spacers degraded faster than variants without the spacer suggests that the generally accepted hypothesis that alkyl spacers can be used to increase the stability of the AEMs is not valid for all backbones and conditions, and most specifically, do not apply for PPO with a six-carbon alkyl spacer.

1H NMR spectra of ABCO-C6-PPO and 1M-C6-PPO showed clear signs of AEM degradation after 1 week in 1 M NaOD + DMSO-d6 (see Figs. S15 to S18). We did not attempt to quantify the degradation degree (as we have done for TMA-C6-PPO) because the protons in methyl groups attached to the quaternary ammonium (usually employed to estimate the loss of fixed groups during degradation experiments) overlapped with a large water peak. However, the presence of new peaks (see Fig. S16) and the substantial decrease in peak height for the protons in the methyl groups attached to the quaternary ammonium seems to confirm these AEMs also degrade as in the case of TMA-C6-PPO. We will continue our work with pendant chains and imidazolium cations to extract quantitative conclusions about the degradation rates.

We are aware of similar works reporting better stability of AEMs prepared with ammonium cations tethered to the backbone with long alkyl chains.11,39 Our results are contrary to those reported. At this point, we do not have conclusive answers as to why this contradiction exists. We can only reiterate that we have carefully performed the experiments in the present study and have validated the results using multiple independent approaches, and we are confident in our results. Among the possible reasons for the contrary results are the differences in the experimental conditions employed in the alkaline stability tests such as time, temperature, concentration, as well as differences in the polymer backbones employed. However, we believe that these alone cannot account for the drastic differences observed in the results. We intend to continue to explore the tethered systems to resolve the existing disparity in results.

**Experimental**

**Addition of a six-carbon chain to polyphenylene oxide (BrKC6-PPO).** — The addition of a pendant chain to poly(p-phenylene oxide) (PPO) was carried out following a slight modification of the method described by Hibbs.11 PPO (10 g, 83.3 mmol polymer repeat units) was dissolved in chlorobenzene (500 mL) in a round bottom flask and flushed with nitrogen. The flask was chilled in an ice bath and 6-bromohexanoyl chloride (19.1 mL, 121.1 mmol) was added. Finally, 5 g of aluminum (III) chloride (Lewis acid catalyst) was added to the flask, the ice bath was removed, and the mixture allowed to react overnight. The yield for the acylation reaction was approximately 25% and resulted in a polymer with a degree of functionalization (DF) of approximately 0.31 mol of bromomethyl groups per polymer repeat unit. The brominated polymer was recovered by precipitation in methanol (approx. 2.5 L), and purified by re-dissolving in chlorobenzene and precipitating in methanol again. The DF was determined from the 1H NMR peak areas (see Fig. S1 in supplementary information).

**Reduction of the ketone in BrKC6-PPO.** — The protons in the α-position of the ketone group are acidic and can form enolate anions that are strong nucleophiles, which can degrade quaternary ammonium. Hibbs had previously pointed out this problem and reported accelerated degradation in AEMs containing ketone groups.11 Polyphenylene-based AEMs containing a six-carbon pendant chain and a ketone group in the benzyl position lost approx. 90–95% of the initial ion exchange capacity after 15 days in 4M KOH at 90°C (Argon degassed). To minimize the degradation of the AEMs, the ketone groups were reduced with the aid of triethylsilane.11 Brominated poly(p-phenylene oxide) with a six-carbon pendant chain containing the ketone group (BrKC6-PPO) (5 g, 28.6 mmol polymer repeat units, DF = 0.31) was dissolved in 1,2-dichloroethane (400 mL), followed by the addition of 290 mL of trifluoroacetic acid and 30 mL of triethylsilane (185 mmol). The reduction reaction was carried out under reflux conditions (temperature approx. 100°C) for 24 hours. The amounts of triethylsilane and trifluoroacetic acid were optimized to assure the reduction of the ketone was around 94–98% [area b/area b + area b′] (See Fig S5). The reduced polymer (BrC6-PPO) was recovered and purified as follows.

First, the reaction mixture was mixed with 500 mL of 30 wt% KOH (in DI water) and stirred for 30–60 min to neutralize the trifluoroacetic acid. The resultant organic phase (1,2-dichloroethane) was recovered in a separating funnel, and washed with DI water until the pH of the aqueous phase was in the interval 5–7. The resulting organic phase containing the brominated polymer (BrC6-PPO) was poured into DI water and the mixture was heated to evaporate the 1,2-dichloroethane and precipitate the polymer in the water.

Finally, the crude precipitate was dissolved in chloroform and re-purified in ethanol. This purification step was repeated three times. The purified product (white powder) was recovered by centrifugation and dried in a vacuum oven at 60°C overnight. The purity and degree of functionalization (DF) was measured using NMR (Fig. S5).

**Synthesis of anion exchange membranes.** — TMA-C6-PPO, ABCO-C6-PPO and 1M-C6-PPO. 0.5 g of the brominated polymer was dissolved in 50 mL of DMSO-d6 at 60°C with moderate stirring. The solution was heated to 60°C and the TMA chloride (2.5 mmol) was added in portions with rapid stirring. The reaction mixture was stirred for 5–7 hours and then cooled to room temperature. The precipitated material was recovered by centrifugation (10 000 g for 15 min) and washed with DMSO-d6. The material washed at least three times with 20 mL of DMSO-d6. The resulting precipitate was precipitated in 1 M NaOD by pouring the aqueous phase containing the polymer into 1 M NaOD and stirred for 30 min. The precipitate was recovered by centrifugation (10 000 g for 15 min). The precipitate was dried in a vacuum oven at 60°C.

![Figure 4. Evolution of theoretical ion exchange capacity (obtained from 1H NMR spectra) of TMA-C6-PPO solubilized anion exchange membrane binder. The experiments were done in 1 M NaOD + DMSO-d6 at 60°C.](image-url)
(BrC6-PPO) was dissolved in 9 mL of N-methyl-2-pyrrolidone (Fisher Scientific, extra dry 99.9% stored over molecular sieves). Then, the required amount of organic base (either trimethylamine, 1-azacyclo [2.2.2] octane, or 1-methylimidazole) was added and the reaction allowed to proceed for 24–72 hours. The ratio of the organic base to bromobenzyl groups was 1:1 for 1-azacyclo [2.2.2] octane and 1-methylimidazole, and 3:1 for trimethylamine. The reaction temperature was 60 °C for the reaction with 1-azacyclo [2.2.2] octane and 1-methylimidazole, and 30 °C for trimethylamine (to minimize the loss of base due to the high volatility of trimethylamine). Finally, the solution was cast on a 3.5" × 3.5" glass plate on a leveled surface in an oven at 70 °C to evaporate the solvent. The anion exchange materials (in bromide form) were washed in deionized water and ion exchanged to the chloride form by immersion in 1 M NaCl for 24 hours.

Characterization of the AEMs.— The following NMR spectroscopy experiments were performed on a Bruker Avance 360 MHz NMR spectrometer: 1) 1H NMR spectra (collected at 360 MHz); 2) 13C NMR spectra (collected at 90 MHz – proton decoupled), 3) correlation spectroscopy (COSY) and 4) 1H–13C heteronuclear multiple-quantum correlation spectroscopy (HMQC). Additional details regarding the NMR experiments are presented in the ESI and in our previous papers.14,16,17

The ionic conductivity was measured by placing the solubilized AEMs in 5 wt% binder in chloride counter-ion form in a Swagelok Teflon conductivity cell between two platinum electrodes. Teflon Swagelok fittings help to keep the electrodes in place and prevent the leakage of the solution. The conductivity was determined using electrochemical impedance spectroscopy (EIS) (15 mV amplitude within a 300 kHz–100 Hz frequency range). The high frequency resistance (intercept with real axis at high frequencies), permits the evaluation of the leakage of the solution. The conductivity was determined using Volhard titration.29 The ionic conductivity was measured by placing the solubilized AEMs in a mixture of 1 M NaOD and 3:1 for trimethylamine. The reaction temperature was 60 °C to evaporate the solvent. The anion exchange capacity (mol/g), Anion exchange capacity of TMA-C6-PPO calculated using 1H NMR peaks, decreased 39% after 1 month in 1 M NaOD (from 1.8 ± 0.1 mmol/g to 1.1 ± 0.1 mmol/g).

In a second experiment, performed to unequivocally evaluate the alkaline stability of TMA-C6-PPO, the material was immersed in nitrogen degassed 1 M KOH at 60 °C. The ion exchange capacity decreased from 1.8 mmol/g to 1.2 mmol/g (33%) after immersion in the alkaline solution for 30 days, confirming the results obtained independently using NMR spectroscopy. 1H NMR spectroscopy performed in those AEMs after 1 month in 1 M KOH at 60 °C (see Figs S13 & S14) showed similar degradation peaks observed in the alkaline stability experiments in NaOD + DMSO-d6.

These results do not represent any improvement over the AEMs where the trimethylamine cation is attached directly to the benzyl carbon (TMA-PPO). The ion exchange capacity of TMA-PPO (measured using Volhard titration) decreased by only 18% after immersion in 1 M KOH for 1 month (from 1.8 ± 0.1 mmol/g to 1.4 ± 0.1 mmol/g). The results obtained in this work suggest that PPO-based AEMs with hexyl spacers (TMA-C6-PPO) do degrade in alkaline conditions and that the generally accepted hypothesis that alkyl spacers can be used to increase the stability of the AEMs is not valid for all backbones and conditions.

Conclusions

In this work, we synthesized AEMs binders via Friedel–Crafts acylation of 6-bromo-1-hexanoyl chloride on poly(phenylene oxide). The resulting brominated polymer was treated with triethylsilane under reflux to reduce the ketone to form methylene bridge, to avoid the degradation of quaternary ammonium by enolates formed in alkaline solutions. The resulting brominated polymer was quantized by reaction with trimethylamine. 1-D (1H NMR and 13C NMR) and 2-D (COSY and 1H–13C HMQC) NMR proved the formation of the desired products for each synthetic step. The alkaline stability of the AEMs was evaluated using two separate, complementary experiments. In the first experiment, the AEMs were dissolved in a mixture of 1 M NaOD + DMSO-d6 and kept at 60 °C. 1H NMR spectra showed signs of AEM degradation after 1 week in alkaline solution. The ion exchange capacity of TMA-C6-PPO calculated using 1H NMR peaks, decreased 39% after 1 month in 1 M NaOD (from 1.8 ± 0.1 mmol/g to 1.1 ± 0.1 mmol/g).

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