

Hydroxide-Ion Transport and Stability of Diblock Copolymers with a Polydiallyldimethyl Ammonium Hydroxide Block

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ABSTRACT: Base-stable amphiphilic diblock copolymers with a polydiallyl dimethyl ammonium hydroxide block were synthesized and characterized to quantify hydroxide-ion transport in the hydrated state; polystyrene was the hydrophobic block. The challenge of synthesizing a copolymer comprising blocks with very different solubility behaviors was addressed by a combination of reversible addition fragmentation chain transfer polymerization and ion metathesis. Both monomers used in the polymerization are commercially available on industrial scales. Hydroxide-ion conductivities of 0.8 mS/cm were achieved in hot-pressed membranes immersed in water at

room temperature despite relatively low water uptake (4.2 water molecules per hydroxide ion). The stability of the polydiallyl dimethyl ammonium hydroxide chains was investigated in 2 M NaOD at 60 °C. ¹H NMR spectroscopy studies showed no detectable degradation after 2000 hours. © 2017 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 2243–2248

KEYWORDS: base-stable; base; block copolymer; conducting materials; conductivity; diallyl dimethyl ammonium chloride (DADMAC); diblock copolymer; hydroxide conductivity; ion exchange

INTRODUCTION There is continuing interest in hydroxide-conducting polymer membranes that are stable at elevated pH and high temperatures for applications such as fuel cells and artificial photosynthesis.^{1–3} Ideally, the membrane should comprise continuous hydrophilic channels in a hydrophobic matrix.^{4–6} In such materials, ion transport is governed by the geometry and composition of the hydrophilic channels while the mechanical properties are governed by the rigidity and chemical stability of the hydrophobic matrix.⁷ Block copolymer self-assembly is a facile approach for creating well-defined microphase separated morphologies that can be tuned to independently control ion transport and membrane stability. In principle, materials containing conducting channels can also be obtained in homopolymer and random copolymer analogs, but systematic studies have shown that well-defined block copolymer morphologies have superior ionic conductivity.^{8,9}

In basic systems, chains of interest contain tethered cationic groups and free OH[−] counterions. The degradation reactions that occur under basic conditions (e.g. Hofmann elimination) limit the polymer backbone chemistries and the cations that

can be incorporated to the polymer.¹⁰ Most reports on diblock copolymer membranes for OH[−] transport are based on trimethyl ammonium and imidazolium cations,^{8,9} that are only marginally stable at high pH.^{11–13} To overcome this limitation, polymers using new monomers have emerged with increased stability by modifications in their chemical structures.^{14–18}

Diallyl dimethyl ammonium chloride (DADMAC) is a quaternary ammonium monomer with high charge density. Polymerized DADMAC (PDADMAC) is extensively used in industrial applications requiring a highly water soluble polymer for separation processes such as flocculation or flotation because of facile synthesis, monomer price, and low toxicity.¹⁹ Polymers used in these applications are synthesized by free radical polymerization, an approach that cannot be extended to obtain well-defined block copolymers. The copolymerization of DADMAC with a hydrophilic monomer has been previously reported.^{20,21} However, this approach results in polymers that dissolve in water, that is, not appropriate for applications that require membranes. Ameduri and coworkers conducted a radical copolymerization of the DADMAC

Additional Supporting Information may be found in the online version of this article.

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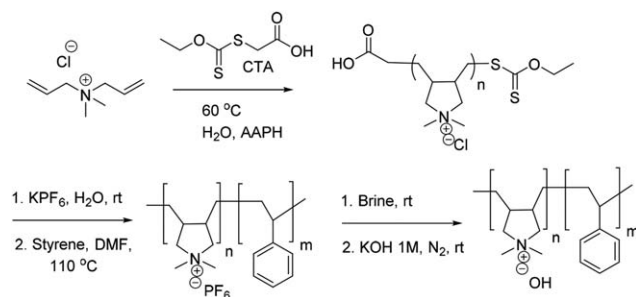


FIGURE 1 Synthesis of D(PF₆)S polymers (for simplicity, the RAFT endgroups have been left out in the block copolymers structural representation).

monomer with fluorinated comonomers to make insoluble random copolymers, and reported on conductivities of chloride and trifluoromethanesulfonylimide ions.²² In this work, we demonstrate the synthesis of a block copolymer comprising a PDADMAC block and a hydrophobic block (polystyrene, PS). We show that membranes of this copolymer are a suitable for applications where stable hydroxide-ion transport under strong basic conditions is required.

RESULTS AND DISCUSSION

The steps used to synthesize PDADMAC-containing block copolymers are shown in Figure 1. In the first step, PDADMAC homopolymers [D(Cl)] with number averaged molecular weights of 5 and 10 kg/mol were synthesized in water by ring-closing reversible addition fragmentation chain transfer (RAFT) polymerization using 2-((ethoxycarbonothioyl)thio)acetic acid as a water-soluble chain transfer agent (CTA) (see Supporting Information for more details).^{23,24} 2,2'-Azobis(2-methylpropanamide) dihydrochloride was used as a water-soluble radical initiator. At this point, molecular weights were estimated by monomer conversion (see Supporting Information). To confirm that, the polymerization was controlled and pseudo-living, kinetic studies were

performed. Monomer concentrations were calculated by taking aliquots at different times from the reaction vessel for analysis using ¹H NMR spectroscopy. Peak assignments and integrations can be found in the Supporting Information. There is some controversy surrounding the relationship between the observed splitting of the NMR peaks in PDADMAC and the different chemical environments surrounding the protons.^{25–28}

As shown in Supporting Information Figure S3, the plot of ln([M]₀/[M]) versus polymerization time is linear, a signature of controlled polymerization. ([M]₀ is the initial monomer concentration and [M] is the monomer concentration as a function of time). No evidence of an induction period was observed.²⁹ In previous work on DADMAC polymerization by RAFT, the “livingness” of PDADMAC polymerization is not clear.^{20,21} Using a water soluble Xanthate as a CTA, the molecular weight and polydispersity of PDADMAC can be predicted and controlled.

The chemical stability of PDADMAC in basic conditions at high temperatures was investigated by ¹H NMR spectroscopy. In a sealed NMR tube, 40 mg of the 10 kg/mol D(Cl) was dissolved in 0.7 mL of 2 M NaOD and heated in an oil bath at 60 °C. The NMR tube was removed from the oil bath for analysis at different times. Figure 2 shows ¹H NMR spectra of D(Cl) before and after exposure to 2 M NaOD at 60 °C for 2000 hours. The overlap of the two spectra indicates that there was no significant change in the chemical structure of the polymer after 2000 hours. (Signatures of glass degradation, white precipitates, were visible toward the end of the experiment.)

Steric hindrance and π-conjugation reduce the rates of S_N2 substitution and Hofmann elimination reactions.¹¹ Despite this, imidazolium-based polymers start degrading in 1 M KOH at 25 °C after just 24 hours.¹¹ Similarly, with quaternary amines, synthetic methods have been developed to increase stabilities of imidazolium containing monomers.

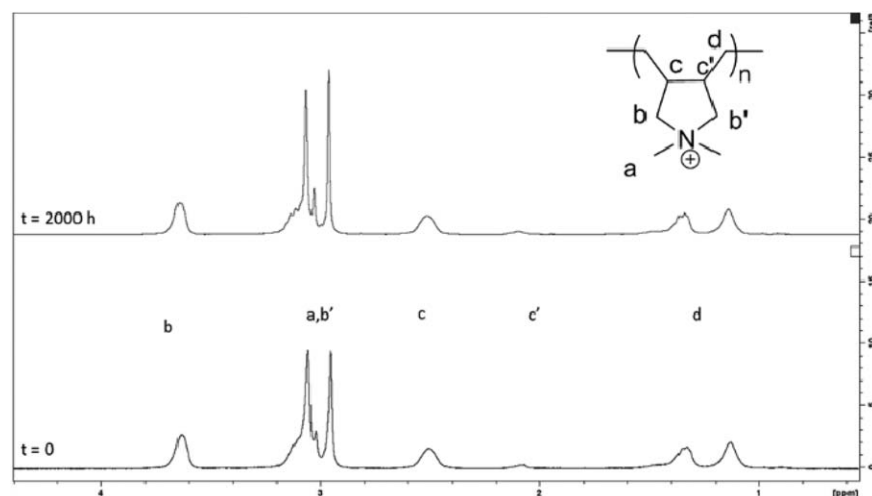


FIGURE 2 ¹H NMR spectra of DADMAC in 2 M NaOD solution in D₂O at time zero and after 2000 hours at 60 °C. The overlap of the two spectra is almost perfect indicating stability of the polymer.

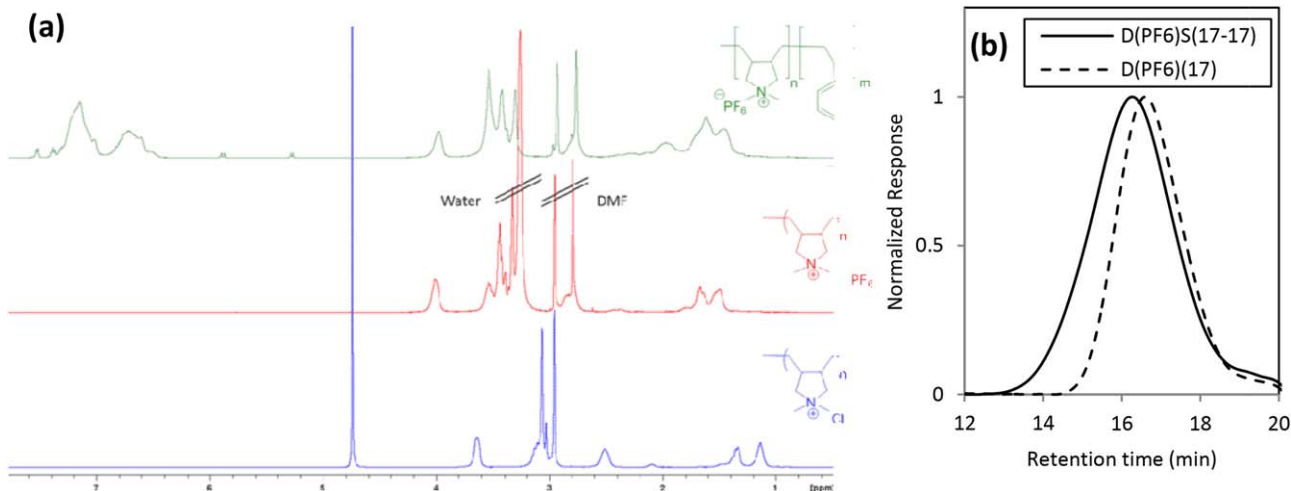


FIGURE 3 (a) ¹H NMR of polymer D(Cl), D(PF₆) precursors, and D(PF₆)S(17-17) diblock copolymers in D₂O, DMF-d₇ and DMF-d₇, respectively. (b) Refractive index signals from the GPC analysis of D(PF₆)(17) homopolymer and D(PF₆)S(17-17) block copolymer. [Color figure can be viewed at wileyonlinelibrary.com]

Holdcroft and coworkers as well as Coates and coworkers have been able to increase the stability of imidazolium by the addition of bulky substituents via multi-step synthesis.^{16,18,30} On the other hand, DADMAC is readily available in commercial scale. The fact that PDADMAC is stable in 2 M NaOD at 60 °C for 2000 hours without any structural modification is thus significant. Further work is necessary to determine the molecular basis for the observed stability. It is known that anti-coplanar conformations of the β-hydrogens relative to the charged nitrogen promote Hoffmann elimination. The observed stability under basic conditions may arise from the fact that these conformations are forbidden in PDADMAC.

To make PDADMAC-containing membranes that are stable in water, this hydrophilic polymer needs to be copolymerized with a hydrophobic monomer. Given that PDADMAC has been synthesized under pseudo-living conditions, the living ends should, in principle, allow for chain-extension. However, as PDADMAC is only soluble in water, chain extension with a hydrophobic monomer is challenging. To overcome this challenge, the solubility of PDADMAC was modified by anion exchange metathesis.³¹ The D(Cl) homopolymers were dissolved in water and a saturated solution of KPF₆ was added drop-wise with continuous stirring (Fig. 1). The polymers in the hexafluorophosphate form D(PF₆) precipitate naturally as the reaction proceeds toward completion. These polymers were isolated by filtration and the remaining salts were washed off with a mixture of acetone/water (50/50 by weight). Based on monomer conversion and CTA concentration, we expect the number average molecular weights of the two D(PF₆) polymers to be 8 and 17 kg/mol (see Supporting Information for details). For simplicity, we refer to the two homopolymers as D(PF₆)(8) and D(PF₆)(17) and the corresponding Cl precursors D(Cl)(8) and D(Cl)(17), respectively. The hydrophobic D(PF₆) homopolymers, now soluble in dimethylformamide (DMF), were chain-extended with

styrene using standard conditions as reported in the Supporting Information (Fig. 1).³² The formation of diblock copolymers was confirmed by ¹H NMR spectroscopy and gel permeation chromatography (GPC) and is shown in Figure 3.

¹H NMR spectra of the PDADMAC precursor homopolymers and the diblock copolymer are shown in Figure 3(a). A comparison of the NMR spectra of D(Cl) and D(PF₆) shows the effect of changing solvent and counterion on spectral features. The appearance of new peaks between 6.8 and 7.2 ppm in the block copolymer spectrum is attributed to the presence of PS [Fig. 3(a)]. Based on the ¹H NMR data, the number averaged molecular weight of the PS block is 17 kg/mol for D(PF₆)(17) and 32 kg/mol for D(PF₆)(8) (see Supporting Information for details). We refer to this copolymers as D(PF₆)S(17-17) and D(PF₆)S(8-32). To confirm that PS homopolymer was not present in the sample, the block copolymer was washed with acetone, a selective solvent for PS. The ¹H NMR spectra obtained before and after washing were identical.

GPC analysis was performed with a Malvern OMNISEC triple detector GPC system equipped with refractive index, four-capillary differential viscometer, and right angle and 7° low-angle light scattering detectors. Analysis was performed at 35 °C with a mobile phase of DMF with 0.02 M ammonium acetate and 5% acetic acid. Two C-MBHMW-3078 columns (300 × 7.8 mm) from Malvern were used to provide separation. A narrow PMMA standard (65 kDa) was used to calibrate the detectors for the determination of absolute molecular weight and molecular weight distribution. The refractive index GPC trace of D(PF₆)(17) is shown in Figure 3(b). Absolute weight-averaged molecular weight of the homopolymer, calculated using the light scattering signal, was 18 kg/mol. This value is in close agreement with the value estimated using monomer conversion of 17 kg/mol for D(PF₆). The dispersity, *D*, of the D(PF₆)(17) was estimated

TABLE 1 Block Copolymers Used in This Study

Polymer	M_n , D(PF6) (kg/mol)	M_n , S (kg/mol)	Φ_D	IEC (meq/g)	d (nm)
D(PF6)S(17-17)	17	17	0.68	1.78	7.6
D(PF6)S(8-32)	8.5	32.5	0.16	0.74	7.0

M_n by ^1H NMR spectroscopy. The d values are calculated by SAXS. ϕ_D were calculated using pure component densities.

to be 1.2. The refractive index GPC trace of the corresponding diblock copolymer is also shown in Figure 3(b). The shift in peak position toward lower retention time confirms chain extension. Both the homopolymer and the diblock copolymer are unimodal. The measured dispersities, \mathcal{D} , of the D(PF6) homopolymer and the D(PF6)S(17-17) block copolymer was measured to be 1.20 and 1.75, respectively. We are not sure of the reason for the high measured dispersity of the copolymer: it may be due to the dispersity of our copolymers or due to interactions between the columns and one of the blocks. Given the charged and hydrophilic nature of the D(PF6) and the neutral and hydrophobic nature of PS, choosing the perfect columns and solvent system for GPC analysis is challenging. GPC conditions optimized for D(PF6) are very different from those optimized for PS. The characteristics of the two hexafluorophosphonated polymers used in this study are summarized in Table 1. The volume fractions of the ion-containing blocks in D(PF6) samples, ϕ_D , were calculated using pure component densities of PS, $\rho_S = 1.080 \text{ g/cm}^3$ and D(PF6), $\rho_D = 1.454 \text{ g/cm}^3$, ignoring volume changes in mixing. The value of ρ_D was measured in our laboratory using AccuPyc II 1340 Series Pycnometer. M_n values were estimated using monomer conversion measured by ^1H NMR spectroscopy, and confirmed by GPC with triple detection for D(PF6)(17) only.

Thermogravimetric analysis of D(Cl)(17) and D(PF6)(17) shows degradation temperatures of 280 and 380 °C, respectively (Supporting Information Fig. S4). Interestingly, differential scanning calorimetry (DSC) of D(Cl) and D(PF6) did not show either a glass or melting transition below their degradation temperatures. Wide angle X-ray scattering experiments show that the ionic block is crystalline, independent of the anion (Supporting Information Fig. S5).

In Figure 4, we show SAXS profiles of the two diblock copolymers D(PF6)S(17-17) and D(PF6)S(8-32), where scattering intensity is plotted as a function of magnitude of the scattering vector, q . The SAXS profile of D(OH)^{B-32} are devoid of signatures of microphase separation and the ionomer peak. In contrast, broad scattering peaks are seen in D(PF6)S(17-17) and D(PF6)S(8-32). The domain spacing, d , of the periodic structure is calculated by the equation $d = 2\pi/q^*$, where q^* is the magnitude of the scattering vector at the peak. The domain spacing values corresponding to the copolymers are given in Table 1. This length scale is commensurate with the "ionomer" peak seen in related systems.³³ This length scale is much smaller than that expected

from ordered block copolymer morphologies. We attempted several transmission electron microscopy (TEM) experiments (SAXS and TEM using ruthenium tetroxide as a staining agent) aimed at detecting microphase separation. None of the micrographs contained signatures of microphase separation. We note in passing that the unexpected lack of signatures of microphase separation in anion-containing block copolymers has been reported before.⁹ The reason for weak (or undetectable) microphase separation in these systems remains unclear.

Membranes of polymers D(PF6)S(8-32) and D(PF6)S(17-17) were prepared by hot pressing the polymers for 20 minutes at 120 °C. The in-plane conductivity, σ , of D(PF6)S(8-32) and D(PF6)S(17-17) immersed in water was measured as a function of increasing temperature from 21 to 71 °C (Fig. 5). After completion of the first run, the sample was heated to 71 °C and cooled in steps. At each temperature, we waited until stable conductivity values were obtained (in some cases up to 24 hours). The conductivities obtained during the first run are in reasonable agreement with those obtained during the second run. The values plotted in Figure 5 are the average of conductivity data obtained for two different

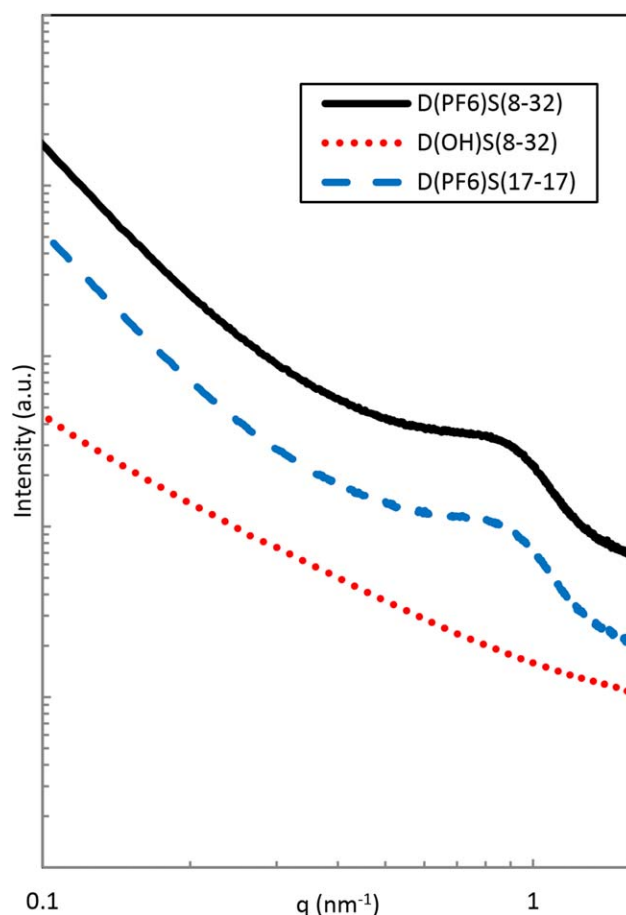


FIGURE 4 SAXS profiles of dry polymer membranes D(PF6)S(8-32), D(PF6)S(17-17), and D(OH)S(8-32). [Color figure can be viewed at wileyonlinelibrary.com]

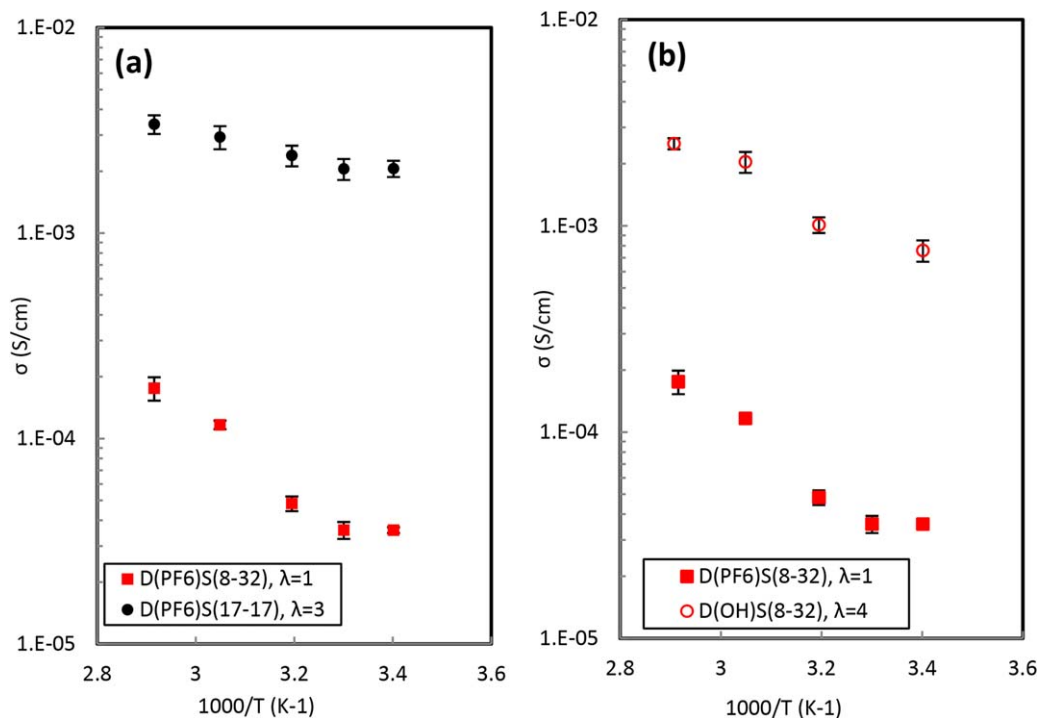


FIGURE 5 (a) Conductivity as a function of inverse temperature for D(PF6)S(8-32) and D(PF6)S(17-17). (b) Conductivity as a function of inverse temperature for D(PF6)S(8-32) and D(OH)S(8-32). [Color figure can be viewed at wileyonlinelibrary.com]

membranes from both runs. The PF₆⁻ conductivity for sample D(PF6)S(17-17) varies from 2 mS/cm at room temperature to 3 mS/cm at 71 °C. On the other hand, for polymer D(PF6)S(8-32), the PF₆⁻ conductivity increases from 0.03 mS/cm at room temperature to 1 mS/cm at 71 °C. The difference in conductivity is attributed to the different ion exchange capacity (IEC), 1.78 meq/g for D(PF6)S(17-17) compared with 0.74 meq/g for D(PF6)S(8-32). Ionic conductivity in polymer electrolyte membranes depends crucially on water content. For these samples, water uptake was very low, $\lambda = 1.5$ for D(PF6)S(8-32) and $\lambda = 3.4$ for D(PF6)S(17-17), which was expected given the hydrophobicity of the polymers.

Conductivities of block copolymers with mobile ions (such as PF₆⁻) are complex functions of morphology, water uptake, and nature of the fixed ion. The conductivities of our polymers are an order of magnitude smaller than those of aqueous mixtures of ionic liquids with PF₆⁻ anions³⁴ but higher than that of neat polymers with PF₆⁻ anions.³⁵

Ionic exchange from PF₆⁻ to OH⁻ was attempted by standard procedures.³¹ Membranes were immersed in a 1-M KOH solution under nitrogen to avoid CO₂ contamination. The solution was changed three times a day for 1 week. Elemental analysis by ion-selective electrode method shows that after this procedure the sample still contained 16% of fluorine, indicating that only 28% of the PF₆⁻ ion was exchanged for OH⁻. Hence, a new ion exchange approach was developed. Polymer D(PF6)S(8-32) was dissolved in DMF. A solution water/DMF (50/50 by weight) saturated with NaCl was added dropwise to the DMF solution, and this resulted in the formation of a white

suspension. This observation suggests efficient exchange of PF₆⁻ to Cl⁻ ions. This polymer, D(Cl)S(8-32), was isolated by filtration, dried under vacuum at 50 °C, and hot-pressed to obtain a 450 μ m thick membrane. The membrane was immersed in a 1 M KOH solution under nitrogen for 12 hours. The solution was changed every three hours. The formation of D(OH)S(8-32) was confirmed by the absence of fluorine (0.0%) or chlorine (0.04%) in elemental analysis.

The in-plane hydroxide conductivity of D(OH)S(8-32) immersed in water under nitrogen was measured as a function of increasing temperature from 21 to 71 °C (Fig. 5). The values plotted in Figure 5 are the average of conductivity data obtained for two different membranes from both runs. The hydroxide conductivity of these membranes is a factor of 14 higher than that of the hexafluorophosphate conductivity, from 0.03 mS/cm for D(PF6)S(8-32) compared with 0.8 mS/cm for D(OH)S(8-32), at room temperature. There are three possible reasons for this increase: ¹ water uptake increases from $\lambda = 1.5$ to 4.2, ² the larger diffusion coefficient of OH⁻ relative to PF₆⁻ due effects such as the Grotthuss mechanism,^{36,37} and ³ differences in extent of counterion condensation.^{3,38} The OH⁻ conductivity measured after executing the thermal cycles described above was 2.5 mS/cm and within experimental error of that measured in the beginning of the experiment (both measurements were conducted at 71 °C).

CONCLUSIONS

In conclusion, two different DADMAC-based block copolymers were synthesized by combining RAFT polymerization

and ion metathesis. ^1H NMR spectroscopy indicates that these membranes are stable in 2 M NaOD at 60 °C for over 2000 hours. The hydroxide-ion conductivity of one of the copolymers was 0.8 mS/cm at room temperature, despite low water uptake (4.2 water molecules per hydroxide ion). The lack of detectable signatures of microphase separation was surprising given chemical structure of the monomers. The simplicity of the synthetic route provides facile access to new hydroxide-conducting polymer membranes for further investigation of the relationship between molecular structure and ion transport.

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