Anion-Conductive Multiblock Aromatic Copolymer Membranes: Structure–Property Relationships

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ABSTRACT: Anion-conductive multiblock copoly(arylene ether sulfone)s (mPES) were synthesized with different block lengths and ion-exchange capacities (IEC) to maximize ion conductivity and explore the relationship between chemical structure and morphology in anion-exchange membranes (AEM). Nuclear magnetic resonance (NMR) relaxometry was used to probe water mobility and domain size. The multiblock copolymers were synthesized by polycondensation of separately prepared hydroxy-terminated oligomers with fluoro-terminated oligomers. The polymers were made ion-conductive through selective chloromethylation of one of the two block types, followed by quaternization and hydroxide ion exchange. The resulting block structure, in which one type is hydrophilic and one type is hydrophobic, was designed to ensure a nanophase-separated morphology. The multiblock copolymers exhibited higher anion conductivity than their random copolymer counterparts at the same IEC. The multiblock copolymer that exhibited the highest anion conductivity was not the one with the highest IEC, but it was the one with the shortest NMR relaxation times for water, indicating a greater fraction of water interacts with the ionic polymer segments. Higher IEC values led to increased water absorption, an effective dilution of the ionic groups, and increased NMR relaxation times for water.

1. INTRODUCTION

Fuel cells directly convert chemical energy to electricity and could potentially reduce pollution in transportation and other areas.1 The proton-exchange membrane fuel cell (PEMFC) has been extensively investigated as a power source in electric vehicles and stationary applications.2,3 In PEMFCs, Nafion, developed by DuPont in 1962, is the preferred polymer electrolyte.4 Nafion is a perfluorosulfonated copolymer that exhibits high ionic conductivity and dimensional stability. Nevertheless, commercialization of the PEMFC has been hampered by intrinsic drawbacks such as the use of expensive metal catalysts, limited lifetime due to degradation, complex water management schemes, the use of poison-vulnerable catalysts, and the slow rate of oxygen reduction under acidic conditions. These problems all originate from the use of protons as conductive species.

Anion-exchange membrane fuel cells (AEMFCs) have been investigated as an alternative to PEMFCs because many deficiencies can be addressed:5–9 (i) high pH provides kinetically favored oxidation of fuels, (ii) AEMFCs can operate with platinum-free catalysts, (iii) new routes are available for addressing water management, and (iv) the electro-osmotic drag of water from the air cathode to the fuel anode lowers fuel crossover. Despite these benefits, the AEMFC suffers from the low diffusion coefficient of hydroxide ions.8 A membrane with high ionic conductivity may be obtained by the formation of nanochannels to facilitate ion transport. Numerous studies have attributed Nafion’s high conductivity to nanochannels created through nanophase separation between a hydrophobic matrix and hydrophilic side groups.4,10

Attempts have been made to create proton conductivity in materials with Nafion-like morphology by incorporating monomers with perfluorocarboxy groups.11,12 Example alternative materials also include sulfonated poly(ether sulfone),13 hydrophilic–hydrophobic multiblock copolymers based on poly(arylene sulfone),14–16 and aromatic comb-shaped copolymers with highly sulfonated side chains.17 Attempts have also been made to create materials with hydroxide conductivity by use of sequential hydrophobic and hydrophilic blocks. Watanabe and co-workers18 prepared anion-conductive multiblock copoly(arylene ether)s that had higher hydroxide ion conductivity than their corresponding random copolymers. They attributed the enhanced conductivity of the multiblock copolymers to their well-developed phase-separated morphology. Although the conductivity of AEM multiblock copolymers has been reported, the systematic study of water mobility and domain size in these types of polymer membranes has not been studied. Understanding the relationships between polymer structure, morphology, and ion conductivity is important to find predictive pathways for improving conductivity.

In this study, a series of anion-conductive multiblock copoly(arylene ether sulfone)s (mPES) containing quaternary ammonium groups19 were synthesized with different lengths of...
hydrophobic and hydrophilic blocks to enable nanophase-separated morphologies. The corresponding random copolymers were also synthesized for comparison of the properties. The precise chemical structures of the copolymers were characterized by one- and two-dimensional (1D and 2D) NMR. The phase-separated morphologies of the copolymers were probed by measuring NMR spin−lattice (T₁) and spin−spin (T₂) relaxation times of water absorbed into the anion-conductive polymeric matrices. Compared to atomic force (AFM) and transmission electron microscopy (TEM), NMR relaxation time measurements can be used to obtain quantitative information on water mobilities and domain sizes without laborious sample preparation. The water mobility and domain size information extracted from the NMR relaxation times of water in the membranes was then correlated with ionic conductivity.

2. EXPERIMENTAL DETAILS

2.1. Materials. 4,4′-Difluorodiphenyl sulfone (FPS), bisphenol A (BPA), 1,1,2,2-tetrachloro ethane (TCE), trimethyl amine aqueous solution (50 wt %), and calcium hydride were obtained from TCI Co., Ltd. N,N-dimethylacetamide (DMAC), 4,4′-(hexafluoroisopropylidene) diphenol (HFHPA), and tin-(IV) chloride were obtained from Alfa Aesar. Chlormethyl methyl ether (CMME), potassium carbonate, and dimethyl sulfoxide-d₆ (DMSO-d₆) were obtained from Aldrich Chemical Co. Chloroform-d was obtained from Cambridge Isotopes Inc. for the NMR studies. All chemicals were used as received, unless otherwise specified.

2.2. Polymerization. A typical synthetic procedure for the hydroxy-terminated oligomer (for number of repeat units x = 6.7) is as follows. DMAC was dried by distillation in vacuo at 130 °C over CaH₂ and stored with activated 3A molecular sieves. FPS (1.63 g, 6.40 mmol), HFHPA (2.37 g, 7.04 mmol), K₂CO₃ (2.21 g, 16.00 mmol), and DMAC (20 mL) were mixed under dry conditions equipped with a condenser at room temperature for 10 min. The resulting mixture was heated to 120 °C by use of an oil bath for 3.5 h. HFHPA (0.79 g) was added to the mixture and allowed to react for 1 h at 120 °C to ensure that the ends were hydroxyl-terminated. The slightly viscous mixture was poured into hot water to precipitate the product. The reddish powder was washed with water and methanol several times. The product was collected, isolated by filtration, and dried at 80 °C for 24 h. The number of repeat units (x = 6.7) and molecular weight (MW = 4040 g/mol) were determined by ¹H NMR.

A similar synthesis, purification, drying, and ¹H NMR characterization procedure was followed to prepare a fluoro-terminated oligomer (number of repeat units y = 7.7). FPS (1.79 g, 7.04 mmol), BPA (1.46 g, 6.40 mmol), and K₂CO₃ (1.86 g, 12.80 mmol) were dissolved in 20 mL of dry DMAC and stirred at 110 °C for 7 h. After addition of 0.27 g of FPS, the reaction was allowed to continue for 4 h at 55 °C. The crude chloromethylated polymer was recovered by pouring the reaction mixture into methanol and washing with the precipitate with methanol several times.

The chloromethylated copolymers (CmPES or CrPES) (0.50 g) were quaternized by reacting with 50 wt % trimethylamine aqueous solution (10 mL) at room temperature for 24 h. The dry quaternized copolymer (QPES) was recovered by evaporating the residual trimethylamine in a Petri dish. The QPES (0.50 g) was dissolved in N,N-dimethylformamide (DMF; 3 mL) and the resulting solution was filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) membrane filter. A film was cast by pouring this solution into an aluminum dish, followed by drying in a vacuum oven at 80 °C for 24 h. The free-standing polymer films were about 100 μm thick and 3.5 × 3.5 cm. The chloride ions in the film were exchanged for hydroxide ions by soaking in 0.1 N KOH under nitrogen for about 12 h. After being washed several times with water, the QPES membranes in hydroxide form were stored in distilled water in a closed vial.

2.4. Membranes. The chemical structures of the synthesized polymers were analyzed by a variety of NMR techniques: one-dimensional ¹H and ¹³C NMR, distortionless enhancement by polarization transfer (DEPT), and two-dimensional heteronuclear multiple bond correlation (HMBC). A Bruker Avance III 400 spectrometer with 5-mm sample tubes was used. Chloroform-d or DMSO-d₆ was used as the NMR solvent. ¹H spectra (16 scans) were collected at 400.13 MHz with a 7.5 s recycle delay. The ion-exchange capacities (IEC) and degrees of chloromethylation (DC) were determined from the respective ¹H NMR spectra. The ¹³C and DEPT NMR spectra were collected at 100.61 MHz. The HMBC analysis employed 32 scans, 128 increments along t₁, 1024 data points along t₂, 160 Hz as a one-bond coupling constant, and 10 Hz as a long-range coupling constant.

To ensure full hydration, the QPES membranes in hydroxide form were stored in distilled water for at least 1 week prior to NMR studies. A 3 × 10 mm membrane strip was loaded into a 7-mm solid-state NMR rotor, and ¹H NMR spin−lattice (T₁) and spin−spin (T₂) relaxation times were measured at 25 °C on a Bruker DRSX-300. The inversion recovery sequence 180°−τ−90° was used for the T₁ measurements, and the Carr−Purcell−Meiboom−Gill pulse sequence (CPMG) was used for the T₂ measurements with an interpulse delay of 0.2 ms.

The molecular weights of the polymers were determined by GPC on a Waters 2690 separations module with a 2410 differential refractive index detector, which was connected to Waters Styrage columns (HP 1, HP 3, HP 4). Tetrahydrofuran (THF) was used as the eluent and the solvent. The molecular weights were computed by a calibration curve based on polystyrene standards.

The water uptake of the membranes was evaluated according to eq 1: dx.doi.org/10.1021/jp311987v/J. Phys. Chem. C 2013, 117, 15468−15477
water uptake \( \frac{W_d - W_{wd}}{W_d} \times 100 \) (1)

where \( W_d \) is the dry mass of the membranes determined after drying in a desiccator and \( W_{wd} \) is the wet mass of the membranes without excess surface water after soaking for 24 h. The ionic conductivity measurements were performed in a four-probe electrochemical impedance spectrometer by use of a PAR 2273 potentiostat. The membrane strips (1 × 3 cm) were mounted in a conductivity cell and stabilized at a specific temperature (i.e., 25 or 60 °C) under nitrogen. The frequency region from 1 Hz to 2 MHz was scanned, where the impedance had a constant value. The ionic conductivity was calculated from eq 2:

\[ \sigma = \frac{L}{Z'(A)} \] (2)

where \( L \) is the length between sense electrodes (0.425 cm), \( Z' \) is the real component of the impedance response at high frequency, and \( A \) is membrane area available for hydroxide conduction.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Multiblock and Random Copolymers. A series of mPES multiblock copolymers were synthesized by polycondensation of separately prepared HO-terminated and F-terminated oligomers, as shown in Scheme 1. The length of each oligomer was carefully controlled by optimizing the polymerization time (i.e., 3.5–7
Figure 1. $^1$H NMR spectra of (a) HO-terminated oligomer ($x = 6.7$), (b) F-terminated oligomer ($y = 7.7$), and (c) resulting multiblock copolymer mPES-$X_{6.7}Y_{7.7}$. 
The integral ratio of 1H NMR peaks b' and b allows calculation of the degree of polymerization for the hydrophobic HO-terminated oligomer, which is $x = 6.7$ for the block shown in Figure 1a. In the same manner, the integral ratio of 1H NMR peaks c' and e allows calculation of the degree of polymerization for the F-terminated oligomer, which is $y = 7.7$ for the block shown in Figure 1b. The F-terminated oligomer will become the charge-carrying hydrophilic block after chloromethylation and quarternization, as described below. A summary of the oligomer lengths, which are assumed to correspond to block lengths after incorporation into the multiblock copolymers, is shown in Table 1, along with molecular weights and degrees of chloromethylation for the prepared copolymers.

Table 1. Structural Characteristics of Multiblock and Random Copoly(arylene ether sulfone)s before and after Chloromethylation

<table>
<thead>
<tr>
<th>Oligomer Repeat Units (x/y)</th>
<th>mPES$^a$</th>
<th>CPES$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$n$</td>
<td>PDI</td>
<td>M$n$</td>
</tr>
<tr>
<td>mPES-X$_6$Y$_3$</td>
<td>6.7/3.4</td>
<td>34.5K</td>
</tr>
<tr>
<td>mPES-X$_6$Y$_3$</td>
<td>9.2/3.4</td>
<td>24.9K</td>
</tr>
<tr>
<td>mPES-X$_6$Y$_3$</td>
<td>11.3/3.4</td>
<td>25.3K</td>
</tr>
<tr>
<td>mPES-X$_6$Y$_3$</td>
<td>6.7/2.5</td>
<td>18.4K</td>
</tr>
<tr>
<td>mPES-X$_6$Y$_3$</td>
<td>6.7/7.7</td>
<td>22.8K</td>
</tr>
<tr>
<td>mPES-X$_6$Y$_3$</td>
<td>6.7/11.1</td>
<td>22.2K</td>
</tr>
<tr>
<td>rPES</td>
<td>55.3K</td>
<td>2.4</td>
</tr>
<tr>
<td>rPES</td>
<td>18.8K</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^a$PES = copoly(arylene ether sulfone)s. $^b$CPES = chloromethylated copoly(arylene ether sulfone)s. $^c$x = number of repeat units in hydrophobic block; y = number of repeat units in block that ultimately becomes hydrophilic. M$n$ = number-average molecular weight; K = kg/mol. PDI = polydispersity index. Degree of chloromethylation = number of chloromethyl groups per Y-type repeat unit.

The GPC elution curves for the mPES copolymers were unimodal and shifted to shorter elution times from those of the oligomers (cf. Figure 2), showing that the polymerization was successful. The target molecular weight ($M_n$) of the mPES was ca. 30 kg/mol. This allowed solvent casting of a free-standing film.

Random copoly(ether sulfone)s (rPES) were prepared in a one-pot polycondensation reaction of FPS, HFBPA, and BPA in the presence of K$_2$CO$_3$. The feed ratio of each monomer was controlled to give rPES copolymers with the same overall ratio of repeat units as a given mPES copolymer. DEPT-135 $^{13}$C NMR spectra for rPES and mPES are shown in Figure 3. A majority of the peaks for the multiblock copolymer, seen in Figure 3a, are sharp singlets. In contrast, most of the peaks for the random copolymer, seen in Figure 3b, are multiplets. The randomly distributed repeat units in the rPES cause the peak splitting. These results clearly show that the multiblock copolymers have highly ordered structures compared to the random copolymers.

3.2. Synthesis and Characterization of Chloromethylated and Quarternized Multiblock Copolymers. Multiblock copolymers were chloromethylated by the Friedel–Crafts reaction with CMME and SnCl$_4$ in TCE solution (cf. Scheme 1). The resulting chemical structures (CmPES) were characterized and the degree of chloromethylation was evaluated by 1H NMR. A new peak at 4.53 ppm in the 1H NMR spectrum of CmPES shown in Figure 4, was assigned to the methylene protons of the chloromethyl groups. New peaks at 6.85, 7.15, and 7.35 ppm indicated that substitution of the -CH$_2$Cl groups changed the chemical shift of the BPA aromatic protons. The presence of these new peaks in the NMR spectra of the CmPES materials shows that the chloromethylation reaction was successful. The degree of chloromethylation (DC) in Table 1 was obtained by integrating the 1H NMR peak areas and comparing the ratio of the -CH$_2$Cl methylene protons to the dimethyl BPA protons. Previous studies reported the undesirable gelation of polymers caused by cross-linking during chloromethylation.$^{22}$ GPC evaluation of the CmPES materials was conducted to examine whether the molecular weight changed due to chloromethylation. As shown in Table 1 and Figure 2, the CmPES copolymers do not exhibit significantly different molecular weight characteristics from their mPES precursors and therefore did not undergo excessive branching or cross-linking during chloromethylation.

It was expected that Friedel–Crafts alkylation of the chloromethyl groups should selectively occur at the BPA moiety, which is more electron-rich than hexafluoroisopropylidenedi-phenyl and diphenylsulfone groups. The disappearance of the peak at 6.9 ppm in Figure 1, peak h, after chloromethylation proves that chloromethyl groups are attached at the ortho position to oxygen of the BPA. The two-dimensional HMBC spectrum was also obtained to verify the location of the chloromethylated product CmPES-X$_6$Y$_7$.7.7.23

Cross-peak 1 in Figure 5 is assigned to correlate the aromatic protons (H$_i$) with the aromatic quaternary carbon (C$_q$) of the BPA. Cross-peak 2 correlates the aromatic quaternary carbon C$_q$ with the aromatic proton H$_i$. Cross-peak 3 shows that the aromatic proton H$_i$ is coupled to another aromatic quaternary carbon (C$_q$) to which the chloromethyl group is attached. The position of the -CH$_2$Cl groups are shown by the position of cross-
peak 4. This peak shows the correlation between C and the methylene protons (H) of the chloromethyl groups.

The quaternary ammonium salt of CmPES was formed by immersing the dried powder in an aqueous trimethylamine solution. The quaternized copolymer (QmPES) had different solubility characteristics from CmPES. The QmPES was soluble in aprotic polar solvents such as DMSO, DMF, and DMAc. H NMR was used to investigate the chemical structure and completion of the chemical reaction for QmPES polymers, as shown in Figure 4b. The position of the amino methylene protons (4.63 ppm) shifted slightly downfield from that of the chloromethylene protons (4.53 ppm). The ratio of the integrated peaks between amino methylene protons and dimethyl protons of the BPA was consistent during the quaternization reaction. This comparison confirmed completion of the reaction. The integrated peak value for the trimethyl protons also supports quantitative quaternization.

The ion-exchange capacity (IEC) of the QPES copolymers was computed from eq 3:

\[
\text{IEC} = \frac{(DC)y}{xM_{\text{w,phob}} + yM_{\text{w,phil}}} \times 1000
\]

where DC is the degree of chloromethylation, \(M_{\text{w,phob}}\) is the repeat-unit molecular weight of the hydrophobic block, and \(M_{\text{w,phil}}\) is the repeat-unit molecular weight of the hydrophilic block. The IEC values for the copolymers are summarized in Table 2.

3.3. Membrane Formation, Water Uptake, and Hydroxide Ion Conductivity of QmPES and QrPES. Free-standing QPES membranes were obtained by solution casting from DMF. The chloride ion was exchanged for hydroxide in the membranes immediately before measuring the water uptake and ionic conductivity to minimize the effect of converting the hydroxide into carbonates through contact with CO₂ in air. Water uptake is particularly important for ion-exchange polymers used as ionomers in fuel cell electrodes. Typically, ionic conductivity is proportional to water uptake. However, excessive water uptake can swell the polymer and result in poor reactant transport within the electrodes. Thus, the optimum ionomer has moderate water uptake and high conductivity. Table 2 gives the water uptake at room temperature and hydroxide ion conductivity at 25 and 60 °C.

Since the DC of the membranes is approximately the same (cf. Table 1), the IEC is mostly determined by the ratio of the lengths of the charge-carrying hydrophilic to hydrophobic blocks (y/x). As shown in Table 2 and Figure 8c, water uptake generally increases with increasing IEC values for the multiblock copolymer membranes. However, the ionic conductivity does not exhibit a clear dependence on IEC (Figure 8a). Moreover, it should be noted that QmPES-X₆.₇Y₃.₄ showed the highest anionic conductivity in comparison to the other AEMs in spite of its moderate IEC and water uptake. A comparison between multiblock and random copolymers with similar IEC and y/x values, for example, mPES-X₆.₇Y₃.₄ versus rPES-X₆.₆₇N₃.₃N and mPES-X₆.₇Y₇.₇ versus rPES-X₅.₅N₀.₅N, clearly reveals that the multiblock copolymers exhibit higher ionic conductivity. The high conductivities of multiblock copolymer AEMs are not simply a result of the IEC and water uptake. Rather, the nanophase morphology is important; the specific nanophase structure of the multiblock material facilitates ionic transport.

3.4. Morphology and Water Transport in QPES Membranes. Hydroxide conductivity in these AEMs is directly proportional to ion concentration and ion mobility. Ion
concentration is relatively easy to evaluate from the ion-exchange capacity (IEC). On the other hand, effective ion mobility is less straightforward to assess because it is affected by polymer morphology such as the degree of phase separation and the shape and size of the domains (i.e., channels).

Several attempts to relate ion mobility to underlying polymer morphology have been reported for proton conductivity in PEMs. Systematic studies of the relationship between morphology and conductivity have employed block copolymers with controlled segment lengths and water contents. However, such systematic studies of hydroxide ion mobility and conductivity in AEMs have not appeared. Watanabe and co-workers used scanning transmission electron microscopy (STEM) to examine the morphology of multiblock AEMs, but they did not correlate ion mobility with block lengths or ion concentrations.

While imaging experiments provide a visualization of the morphology, the information does not directly show ion/water transport or provide a quantitative metric for evaluating different materials. In addition, imaging techniques suffer from complicated and sometimes inconsistent sample preparation procedures. In contrast, NMR measurements enable direct characterization of local molecular dynamics and ion/water movement through domains inside membranes. Specifically, NMR spin–lattice (T1) and spin–spin (T2) relaxation times provide direct indications of the restricted motions of water in confined environments or near surfaces. The spin–lattice NMR relaxation time (T1) has been used to examine water confinement and physical interactions of water molecules with the polymer in Nafion. Sierra-Martin et al. measured T2 to detect motional confinement of water molecules in a poly(NIPAM) microgel. They found that T2 could be correlated with changes in water mobility and degree of confinement. Morphological differences between random and multiblock copolymers in PEMs were revealed by analyzing bound versus free water through T2 values (water associated with sulfonic acid groups relaxed faster).

The nature of the ion/water channels in the copolymers synthesized here were investigated by examining NMR relaxation times by use of the inversion recovery pulse sequence for T1 measurements and the CPMG pulse sequence for T2 measurements. The relaxation times, summarized in Table 2, correspond to water in the membranes rather than the polymer protons. This is confirmed by the absence of peaks at 7–8 ppm belonging to the polymer, as shown in Figure 6. In addition, the water content in the membranes was high enough (8.4–54.7%) so that the NMR peaks due to water dominate the NMR spectrum.

As shown in Table 2, the sample that exhibits the highest ion conductivity (15.7 mS/cm at 25 °C and 37.7 mS/cm at 60 °C) is the multiblock copolymer mPES-X6.7Y7.7. The random copolymer with the same IEC (1.38 meq/g), rPES-X0.67Y0.33, exhibited much lower conductivity (5.7 mS/cm at 25 °C and 13.6 mS/cm at 60 °C), but it also absorbed less water (16% versus 24.5%). However, despite the higher water content, the multiblock exhibits a T2 relaxation time that is significantly shorter (20.2 ms) than T2 for the random copolymer (50.2 ms) (cf. Figure 7). The same relationships are also observed for
consistent with previously reported studies in which the authors claimed that multiblock copolymer AEMs with well-developed phase-separated morphologies utilize water molecules in hydrophilic blocks more efficiently than random copolymers for hydroxide ion transport.

The sample that exhibits the highest ion conductivity, mPES-X$_{6.7}$Y$_{3.4}$, is not the sample with the greatest IEC or water uptake, in contrast to many, but not all, published reports on PEM polymers. Conductivity versus IEC is shown in Figure 8a for the multiblock copolymers. The samples with IEC values greater than 1.38 meq/g exhibit lower conductivities than the mPES-X$_{6.7}$Y$_{3.4}$ multiblock copolymer. This trend is similar to the one shown for a plot of conductivity versus water uptake in Figure 8b. The sample with the highest conductivity does not absorb the most water. Such trends have been reported in the literature by Peckham et al. for an a,a,b-trifluorostyrene-based PEM: maximum conductivity was reached at IEC = 2 meq/g after which the conductivity decreased and finally leveled off with increasing IEC. Tsang et al. also observed the same trend for proton-conductive fluoronic ionic graft copolymers. Both publications attributed this nonlinear relationship to a dilution of the available sulfonic acid groups caused by a significant increase in water. As shown in Figure 8c, water uptake increases monotonically with IEC, as is often observed and expected. Figure 8d shows that $T_2$ also generally increases with IEC, especially for the two multiblock copolymers with IEC > 1.38 meq/g, indicating that the fraction of water that interacts with the ionic polymer segments decreases for the higher water contents. The observed relationships are indeed interesting and warrant further study.

For the following group of multiblock copolymers that do not contain the most conductive sample (i.e., mPES-X$_{6.7}$Y$_{3.4}$, mPES-X$_{6.7}$Y$_{3.4}$, and mPES-X$_{6.7}$Y$_{11.1}$, T$_1$ and T$_2$ increase as the length of the hydrophilic segment (y) increases for the same hydrophobic segment length ($x=6.7$). This trend is consistent with the concept that longer hydrophilic blocks generate morphologies with larger aqueous domains, and is consistent with the water uptake values (8.4%, 47.5%, and 57.5%). No significant effect on the NMR relaxation times is observed for the multiblock copolymers that have the same hydrophilic segment length (y = 3.4) but different hydrophobic segment lengths of $x=11.3$ and 9.2.

A series of multiblock copolymers was also synthesized in which the hydrophobicity of the hydrophobic segments was increased beyond those described here. The idea was to create more strongly phase-separated multiblock copolymers to examine whether the channel structure could be made more efficient, and therefore more conductive, for a given IEC and water content. The same trend was observed for conductivity

Table 2. Water Uptake, Ion Conductivity, and Water NMR Relaxation Times in QPES Membranes

<table>
<thead>
<tr>
<th></th>
<th>y/x°</th>
<th>IEC (meq/g)</th>
<th>water uptake (%)</th>
<th>conductivity (mS/cm)</th>
<th>$T_1$ (ms)</th>
<th>$T_2$ (ms)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>at 25 °C</td>
<td>at 60 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mPES-X$<em>{11.3}$Y$</em>{1.4}$</td>
<td>0.30</td>
<td>1.06</td>
<td>13.5</td>
<td>2.4</td>
<td>309</td>
<td>28.0</td>
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<tr>
<td>mPES-X$<em>{6.7}$Y$</em>{1.4}$</td>
<td>0.37</td>
<td>1.45</td>
<td>18.0</td>
<td>4.9</td>
<td>304</td>
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<tr>
<td>mPES-X$<em>{6.7}$Y$</em>{1.5}$</td>
<td>0.51</td>
<td>1.38</td>
<td>24.5</td>
<td>15.7</td>
<td>224</td>
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</tr>
<tr>
<td>mPES-X$<em>{6.7}$Y$</em>{1.7}$</td>
<td>0.37</td>
<td>1.02</td>
<td>8.4</td>
<td>3.2</td>
<td>229</td>
<td>22.2</td>
</tr>
<tr>
<td>mPES-X$<em>{6.7}$Y$</em>{11.1}$</td>
<td>1.15</td>
<td>2.28</td>
<td>47.5</td>
<td>13.9</td>
<td>483</td>
<td>95.6</td>
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<tr>
<td>rPES-X$<em>{6.7}$Y$</em>{3.4}$</td>
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<td>2.17</td>
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<tr>
<td>rPES-X$<em>{6.7}$Y$</em>{11.1}$</td>
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<td>1.38</td>
<td>16.0</td>
<td>5.7</td>
<td>212</td>
<td>50.2</td>
</tr>
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</table>

“Ratio of hydrophilic/hydrophobic repeat units.

Figure 6. $^1$H NMR stacked plot of CPMG spectra for QmPES-X$_{6.7}$Y$_{3.4}$ as a function of the number of cycles (n).

Figure 7. Signal intensity for CPMG spectra of QmPES-X$_{6.7}$Y$_{3.4}$ and QrPES-X$_{6.7}$Y$_{3.3N}$ as a function of the number of cycles. These copolymers are characterized by the same IEC (1.38 meq/g). The water in the multiblock exhibits a shorter $T_2$ relaxation time, despite a greater water content in the random copolymer. Another pair of multiblock and random copolymers with approximately the same IEC, mPES-X$_{6.7}$Y$_{7.7}$ (IEC = 2.28 meq/g) and rPES-X$_{6.7}$Y$_{6.5N}$ (IEC = 2.17 meq/g): the multiblock copolymer exhibits higher water uptake and conductivity and a lower $T_2$ value. For this to occur, the water molecules that are present in the multiblock must be more closely interacting with the solid polymer than the water in the random copolymer. This implies that the water in the random copolymer pools in a fashion that is inefficient for ion conductivity. This observation is...
versus IEC; that is, the most conductive sample was not the one with the greatest IEC. These results and the usage of these newly synthesized multiblock copolymers as membranes and/or ionomers in hybrid polymer electrolyte fuel cells and alkaline direct methanol fuel cells will be described in a future publication.

4. CONCLUSIONS

A systematic study of the effect of block lengths and the degree of randomness on the ionic conductivity in a series of multiblock and random aromatic copolymers containing quaternary ammonium groups was undertaken. The polymers were synthesized by a polycondensation reaction. The reaction conditions were optimized and the length of the blocks, overall molecular weight of the polymers, and degree of chloromethylation were controlled. NMR techniques, including DEPT-135 and two-dimensional HMBC, were used to investigate the degree of randomness and the position of chloromethyl groups within the aromatic copolymer backbone. Quaternary ammonium and anionic conductive membranes were prepared with reasonably high conductivity despite the low water uptake: 37.7 mS/cm at 60 °C in mPES-X6.7Y3.4 with 24.5% water. NMR relaxation times as a function of IEC, (c) water uptake as a function of IEC, and (d) T1 as a function of IEC for the series of multiblock copolymers with properties summarized in Tables 1 and 2.

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■ AUTHOR INFORMATION

Notes
The authors declare no competing financial interest.

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Figure 8. (a) Conductivity at 60 °C as a function of IEC, (b) conductivity at 60 °C as a function of water uptake, (c) water uptake as a function of IEC, and (d) T1 as a function of IEC for the series of multiblock copolymers with properties summarized in Tables 1 and 2.


