Volume Fraction of Ether Is a Significant Factor in Controlling Conductivity in Proton Conducting Polyether Based Polymer Sol—Gel Electrolytes

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Supporting Information

ABSTRACT: We have synthesized several copolymers of methyl polyethylene glycol siloxane $(MePEG_7SiO_3)_m$ and methyl polypropylene glycol siloxane $(MePPG_nSiO_3)_m$ as hydrogen ion (H^+) conducting polymer electrolytes. These copolymers were prepared by a sol-gel polymerization of mixtures of the MePEG and MePPG monomers. We synthesized these H^+ conducting polymer electrolytes in order to study the relationship between observed ionic conductivity and structural properties such as viscosity, fractional free volume, and volume fraction of ether. We found that viscosity increased as the fraction of the smaller comonomer increased. For the MePPG_2/MePPG_3 copolymer, an increase in fractional free volume increased



the fluidity. The heterogeneous copolymers (PEG/PPG copolymers) obeyed the Doolittle equation, while the homogeneous (PEG/PEG and PPG/PPG) copolymers did not. The increase of FFV did not, however, correspond to an increase in conductivity, as would have been predicted by the Forsythe equation. The conductivity data did correspond to a modified Forsythe equation substituting Volume Fraction of Ether ($V_{f,ether}$) for FFV. We conclude that the proton conductivity of MePEG copolymers is more dependent on the volume fraction of ether than on the fractional free volume.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) use a polymer electrolyte to both physically separate the anode from the cathode and conduct hydrogen ions (H^+) between the electrodes. Polymer electrolytes have the advantage of being easy to chemically modify, and have properties that support ion mobility as well as mechanical durability.¹⁻³ Currently, Nafion, a sulfonated perfluorinated polymer, is the most widely used proton conducting polymer electrolyte. Nafion has the necessary chemical stability, mechanical properties, and ionic conductivity when hydrated for use in a PEM fuel cell. The major disadvantages of Nafion are its cost, poor hydrophobicity, and hydration dependent conductivity. Alternatively, membranes based on polybenzimidazole (PBI) and phosphoric acid have also been developed with an eye toward higher temperatures without the same water management requirements of Nafion.

The hydration dependent ionic conductivity in Nafion limits the operational temperature to below 80 $^{\circ}C.^{4}$ The platinum catalytic anode in a PEMFC has a low resistance to CO poisoning (which is commonly present in H₂ fuel streams produced from reforming of fossil fuels). These disadvantages necessitate the development of new anhydrous polymer electrolytes for PEM fuel cells, for which the U.S. Department of Energy has set an operational goal of 0.1 S/cm conductivity at 120 $^{\circ}C$ and 50% relative humidity.

Polyethylene glycol (PEG) and poly(ethylene oxide) (PEO), and the related polymer polypropylene glycol (PPG), conduct

small cations in the absence of water. Neither PEG nor PPG have the mechanical stability required to serve as a fuel cell membrane. However, attachment of PEG or PPG groups to an inorganic matrix can form a hybrid organic/inorganic material combining the mechanical properties of the inorganic portion with the anhydrous conductivity of PEG and PPG.^{5–12}

Siloxanes are easy to functionalize, and are chemically and mechanically stable, due to their chemical similarities to silica.^{13–15} Both PEG and PPG can be coupled to siloxanes by hydrosilylation reactions to form the inorganic/organic hybrid.^{5,16–22} Siloxane polymers are easily made from the acid catalyzed, sol–gel condensation of chlorosilanes or alkoxysilanes. Polymers formed by this condensation can exhibit the advantages of both the organic and inorganic portions, making them useful as polymer electrolytes.

We are interested in how the structure of the polymer electrolyte affects the ionic conductivity. In terms of studying the structure, we look to intrinsic properties of the polymer including viscosity, ionic conductivity, fractional free volume, and volume fraction of the ionically conductive ether component (i.e., either the PEG or PPG units).

Free volume theory is used to statistically evaluate glassy or amorphous polymer systems.²³ The free volume ($v_{\rm f}$) is defined as the virtual volume of the molecule (the total volume

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indirectly occupied through random molecular motions, $v_{\rm m}$) minus the hard sphere volume (van der Waals volume, $v_{\rm w}$) of the molecule.^{23–25} Free volume is a scalar quantity that is dependent on the sample size of the material but can be expressed as the sample size independent: molar free volume ($V_{\rm fr}$ eq 1).

When calculating the free volume of a polymer, the molar volume ($V_{\rm m}$, eq 2) is first calculated using the density and molecular weight of the molecule, and then, the molar van der Waals volume ($V_{\rm w}$) is calculated using the group contribution method developed by Bondi.^{24,26,27} Further, the fractional free volume (FFV, eq 3) is very useful in describing transport behavior in these systems, and is expressed as the ratio of molar free volume ($V_{\rm f}$) to total molar volume ($V_{\rm m}$). Fractional free volume is independent of sample geometry and volume and is useful for comparing the free volume of different materials.^{24,26,27}

$$V_{\rm f} = V_{\rm m} - V_{\rm w} \tag{1}$$

$$V_{\rm m} = \frac{\rm MW}{\rm d}$$
(2)

$$FFV = \frac{V_f}{V_m} = \frac{(V_m - V_w)}{V_m}$$
(3)

In free volume theory, the transport properties of a material (e.g., viscosity - η , conductivity - σ , and diffusion coefficient - D) are dependent on the free volume.^{28,29} For example, diffusion through a material is described as translation through openings in the free volume in a particle's vicinity.²⁵ Free volume, in this description, is a measure of the concentration of void space in a material.

The Stokes–Einstein equation (eq 4) predicts that an increase in fluidity (fluidity = η^{-1}) will result in an increase in the diffusion coefficient (*D*). The Nernst–Einstein equation (eq 5) predicts that an increase in the diffusion coefficient of either ion results in a proportional increase in the ionic conductivity.³⁰ Equations 4 and 5 together indicate that an increase in the fluidity will cause an increase in the ionic conductivity.

Stokes-Einstein Equation:

$$D_{\rm phys} = \frac{kT}{6\pi\eta R_{\rm H}} \tag{4}$$

Nernst-Einstein Equation:

$$\sigma_{\rm ION} = \frac{F^2}{RT} [z_+^{\ 2}D_+C_+ + z_-^{\ 2}D_-C_-]$$
(5)

Walden's rule (eq 6a) defines the relationship between fluidity and conductivity. In this equation, Λ is the molar equivalent conductivity and η is the viscosity. This rule generally holds true for ideal solutions in which there are no ion—ion interactions. However, in real electrolyte solutions, the fractional Walden rule (eq 6b) is a better descriptor of real physical observations.^{31,32} In eq 6b, α is a constant between 0 and 1, with $\alpha = 1$ representing ideal behavior (eq 6a); that is, viscosity is the only force impeding ionic mobility. Where 0 < α < 1, other forces are present that impede ionic mobility.

Walden's Rule:

$$\Lambda \eta = \text{constant}$$
 (6a)

Fractional Walden's Rule:

$$\Lambda \eta^{a} = \text{constant} \tag{6b}$$

Doolittle developed an empirical equation (eq 7) to describe the relationship between free volume and viscosity.^{29,33} Doolittle's relationship demonstrates that a smaller fractional free volume results in a smaller fluidity. In eq 7, A and q are material specific constants where A represents the fluidity extrapolated to zero free volume and q is a measure of the liquid's intermolecular forces. In addition, $V_{\rm m}$ and $V_{\rm f}$ are the total molar volume and molar free volume, respectively. The ratio $V_{\rm m}/V_{\rm f}$ is equivalent to the inverse fractional free volume (FFV⁻¹), and substitution results in eq 7a.

Doolittle's Equation:

$$\frac{1}{\eta} = A \, \exp\left[-q \frac{V_{\rm m}}{V_{\rm f}}\right] \tag{7}$$

$$\frac{1}{\eta} = A \exp\left[\frac{-q}{\text{FFV}}\right] \tag{7a}$$

Cohen and Turnbull combined the Stokes–Einstein equation (eq 4) with the Doolittle equation (eq 7), resulting in the Cohen–Turnbull equation (eq 8). In this equation, A incorporates all of the constants in eq 4 and γ is the same as q in the Doolittle equation.²⁵ The Cohen–Turnbull equation illustrates that, as the fractional free volume increases, the diffusion coefficient will also increase. Forsythe combined the Nernst–Einstein equation (eq 5) with the Cohen–Turnbull equation (eq 8), resulting in the Forsythe equation (eq 9).³⁴ The Forsythe equation shows that, when the fractional free volume is increased, the ionic conductivity (σ) should increase as well.

Cohen-Turnbull Equation:

$$D = A \, \exp\!\!\left[-\frac{\gamma}{\text{FFV}}\right] \tag{8}$$

Forsythe Equation:

$$\sigma = \left(\frac{ACF^2 Z^2}{RT}\right) \exp\left[\frac{-\gamma}{FFV}\right]$$
(9)

EXPERIMENTAL SECTION

Materials. Polyethylene glycol monomethyl ether $(CH_3(OCH_2CH_2)_nOH = MePEG_nOH, M_n = 350, n = 7.24;$ Aldrich) and polypropylene glycol monomethyl ether $(CH_3(OCH(CH_3)-CH_2)_nOH = MePPG_nOH, M_n = 148.2, 206.3, n = 2, 3;$ Aldrich) were dried at 60 °C under a vacuum for approximately 24 h prior to use. This paper will refer to poly(ethylene glycol) monomethyl ether $M_n = 350$ as $MePEG_7OH$, tri(propylene glycol) monomethyl ether $M_n = 206.3$ as $MePPG_3OH$, and di(propylene glycol) monomethyl ether $M_n = 148.2$ as $MePPG_2OH$. Copolymers of $MePEG_7$ and $MePPG_3$ will be referred to as $MePEG_7/MePPG_3$, $MePEG_7$ and $MePPG_2$ copolymers as $MePEG_3/MePPG_2$.

Triethoxysilane (Aldrich), allyl bromide (Acros), Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2%; Aldrich), and sodium sulfite (Fisher) were all used as received. Amberlite IRA-400(Cl) anion exchange resin (Aldrich) and Amberlite IR-

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120H cation exchange resin (Aldrich) were used as received. Phosphorus tribromide (99%; Aldrich) was prepared as a 1.98 M solution in dry diethyl ether using 55.91 g of phosphorus tribromide dissolved into 85.0 mL of dry diethyl ether. Sodium hydride (Aldrich) was rinsed thoroughly with hexanes and filtered prior to use to remove any mineral oil. Dry tetrahydrofuran (THF) and diethyl ether (Et_2O) were obtained from Fisher as Optima grade and dried using a PPT Glass Contour Solvent Purification System, under argon, immediately prior to use, and kept under an inert atmosphere.

Methods. The density and concentrations of the polymer samples were measured gravimetrically, as has been previously described.³⁵ The concentrations of the MePEG₇SO₃H acid/MePEG_n copolymer mixtures were calculated by converting the mass of both the acid and the polymer to volume using their respective densities. Then, the mass of acid was converted to moles by using the acid's molecular weight and was divided by the total volume of the acid plus polymer (this method specifically assumes that the volumes are additive).

The viscosities of the polymer samples were measured using a Brookfield DV-III Ultra Programmable Rheometer. The CPE-40 spindle was used and the viscosities measured under a flow of dry nitrogen at three different rotational speeds which were averaged. The rotational speeds were selected to keep the torque in a range of 10–100%. The samples were dried at 50 °C under a vacuum prior to measurement.

Gel permeation chromatography (GPC) measurements were performed using two 30 cm PL Mixed-D analytical columns with a Polymer Laboratories ELS-2100 evaporative light scattering detector. Polystyrene molecular weight standards (PL-EasiCal PS-2, MW range 580–480 000) were used to calibrate the MW range prior to running unknown samples. THF was then allowed to elute through the column for 30 min to remove any remaining samples and to equilibrate the system. Unknown samples were made by dissolving 2–3 mg of sample in 1 g of THF.

AC-impedance measurements were performed using a PAR 283 potentiostat equipped with a PerkinElmer 5210 lock-in amplifier.¹⁶ Conductivity is determined from a Nyquist plot by the diameter of the high frequency semicircle.³⁶

NMR measurements were made with either a Bruker AC-300 or Bruker DRX-500 instrument.

Strong acid ion exchange columns were prepared by placing 50 mL (95 mequiv) of Amberlite IR-120H ion-exchange resin (1.9 mequiv/mL) in a chromatography column with a porous frit. Hydrochloric acid (1 M, 300 mL, 300 mequiv) was allowed to flow through the column to exchange all of the cation sites to H^+ . Deionized water was then allowed to flow through the column until the pH of the column was near neutral pH (~6.0–8.0). A strong base exchange column was similarly prepared with 50 mL (70 mequiv) of Amberlite IRA-400(Cl) strongly basic ion-exchange resin (1.4 mequiv/mL), followed by charging with sodium hydroxide (1 M, 225 mL, 225 mequiv), and rinsing with deionized water to a near neutral pH.

Synthesis. Scheme 1 describes the synthesis of MePEG and MePPG polymers (4a-c) from MePEG₇OH and MePPG_nOH (1a-c). Samples with the "a" designation were prepared from the MePEG₇OH as a starting material, while samples with the "b" and "c" designations were prepared from MePPG₃OH and MePPG₂OH, respectively. Table S1 (Supporting Information) summarizes preparation of the sol-gel copolymers.

*MePEG*₇ *Allyl:* (*MePEG*₇*OCH*₂*CHCH*₂) (2*a*) was prepared as previously described.^{5,16,17}



Synthesis of Tri(propylene glycol) Allyl Methyl Ether (MePPG₃OCH₂CHCH₂) (**2b**). MePPG₃ allyl (**2b**; Scheme 1) was synthesized analogously to the method used to prepare **2a**. Briefly, NaH (4.87 g, 202.9 mmol) was slurried with THF in an air-free round-bottom flask. MePPG₃OH (20.91 g, 101.5 mmol) was dissolved in THF and added dropwise to the NaH/THF slurry. Allyl bromide (19.63 g, 162.2 mmol) was dissolved in THF and added dropwise to the reaction mixture. A clear viscous liquid (**2b**) was recovered (18.11 g, 73.6 mmol, 72.5% yield). NMR (¹H, in CDCl₃), δ (ppm): 1.1 (s, 9H), 3.27–3.41 (m, 9H), 3.99 (d, 2H), 5.12 (dd, 2H), 5.83 (m, 1H). NMR (¹³C, in CDCl₃), δ (ppm): 17.02, 56.60, 58.98, 70.02, 72.89–75.85, 116.10, 135.45.

Synthesis of Di(propylene glycol) Allyl Methyl Ether (MePPG₂OCH₂CHCH₂) (**2c**). MePPG₂ allyl (**2c**; Scheme 1) was synthesized according to the method used to prepare **2b** using the following amounts: NaH (6.10g, 254.1 mmol), MePPG₂OH (25.13 g, 169.6 mmol), and allyl bromide (40.00 g, 330.6 mmol). A clear viscous liquid (**2c**) was recovered (22.34 g, 118.7 mmol, 70.0% yield). NMR (¹H, in CDCl₃), δ (ppm): 1.16 (s, 6H), 3.34–3.62 (m, 6H), 4.07 (d, 2H), 5.21 (dd, 2H), 5.91 (m, 1H). NMR (¹³C, in CDCl₃), δ (ppm): 17.35, 56.88, 59.25, 70.26, 73.19–76.05, 116.50, 135.48.

 $MePEG_7$ Monomers: $MePEG_7OCH_2CH_2CH_2Si(OEt)_3$ (3a) was prepared as previously described. ^{5,16,17}

Synthesis of $MePPG_3$ Monomer ($MePPG_3OCH_2CH_2CH_2Si$ -(OEt)₃) (**3b**). The MePPG₃ monomer was prepared analogously to **3a** using the following amounts: triethoxysilane (14.50 g, 88.4 mmol), **2b** (18.11 g, 73.6 mmol), and Karstedt's catalyst (~80 μ L). A clear viscous liquid (**3b**) was recovered (28.30 g, 69.0 mmol, 93.8% yield). NMR (¹H, in CDCl₃), δ (ppm): 0.57 (m, 2H), 1.07 (m, 9H), 1.17 (m, 9H), 1.58 (m, 2H), 3.29–3.54 (m, 9H), 3.80 (m, 6H).

Synthesis of MePPG₂ Monomer (MePPG₂OCH₂CH₂CH₂Si-(OEt)₃) (**3c**). MePPG₂ monomer (**3c**) was prepared in the same manner as **3a** using the following amounts: triethoxysilane (30.60 g, 186.6 mmol), **2c** (22.34 g, 169.6 mmol), and Karstedt's catalyst (~80 μ L). A clear viscous liquid (**3c**) was recovered (31.16 g, 88.5 mmol, 52.2% yield). NMR (¹H, in CDCl₃), δ (ppm): 0.56 (m, 2H), 1.07 (m, 6H), 1.16 (m, 9H), 1.60 (m, 2H), 3.25–3.54 (m. 6H), 3.76 (m, 6H).

Synthesis of MePEG₇ Polymer (MePEG₇OCH₂CH₂CH₂SiO_{1.5}) (**4a**). The MePEG₇ polymer (**4a**) was prepared as previously described. 5,16,17

Table 1. Fractio	nal Free Volumes	for PEG-PPG C	Copolymers and	MePEG ₇ SO ₃ H Acid
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polymers and copolymers		MW^a (g/mol)	D (g/mL)	molar volume $(V_{\rm m})^b$	van der Waals volume $(V_{\rm w})^c$	FFV^d	$V_{\rm f,ether}^{e}$
MePEG ₇ polymer		443	1.169	379	262	0.309	0.789
MePPG ₃ polymer		299	1.109	270	183	0.321	0.697
MePPG ₂ polymer		241	1.141	211	147	0.304	0.622
MePEG ₇ /MePPG ₃ copolymer	75:25 ^f	407	1.151	354	242	0.314	0.772
	50:50	371	1.137	326	222	0.317	0.751
	25:75	335	1.148	292	203	0.305	0.727
MePEG ₇ /MePPG ₂ copolymer	75:25	393	1.159	339	234	0.310	0.763
	50:50	342	1.156	296	205	0.308	0.729
	25:75	292	1.136	257	176	0.315	0.685
MePPG ₃ /MePPG ₂ copolymer	75:25	285	1.104	258	174	0.325	0.681
	50:50	270	1.116	242	165	0.318	0.663
	25:75	256	1.123	228	156	0.314	0.644
MePEG ₇ SO ₃ H		414	1.212	342	267	0.330	0.973

^aThe effective MW for copolymers represents the MW of one "repeat unit" of the polymer. One repeat unit of MePEG₇ polymer is defined as MePEG₇OCH₂CH₂CH₂CH₂SiO_{3/2}. ${}^{b}V_{m}$ for polymers and copolymers represents the weighted V_{m} calculated using the effective MW. ${}^{c}V_{w}$ for polymers and copolymers represents the weighted V_{m} calculated using the effective MW. ${}^{c}V_{w}$ for polymers and copolymers represents the weighted V_{m} calculated by the Bondi group contribution method. d Fractional free volume (FFV) is calculated according to eq 3. c The calculation of the volume fraction of ether ($V_{f,ether}$) has been reported. 17,20,37 f. The 75:25 ratio indicates that this copolymer is 75% mole fraction MePEG₃ polymer (Table S1, Supporting Information).

Synthesis of Sol–Gel Polymer ($MePPG_3OCH_2CH_2SiO_{3/2}$) (4b). The MePPG₃ polymer (4b) was prepared analogously to 4a using the following amounts: 3b (4.11 g, 10.0 mmol). The resulting gel 4b was a clear viscous liquid.

Synthesis of Sol–Gel Polymer ($MePPG_2OCH_2CH_2CH_2SiO_{3/2}$) (4c). The MePPG₂ polymer (4c) was prepared in the same manner as the MePEG₇ polymer (4a) using the following: 3c (4.38 g, 12.43 mmol). The resulting gel 4c was a clear viscous liquid.

Synthesis of Sol–Gel Copolymers. The sol–gel copolymers were polymerized in the same way as the MePEG₇ polymer (4a). Here, the two comonomers were mixed together and an excess (6 equiv) of slightly acidic water (pH ~ 3, one drop of conc. HCl in 100 mL of distilled water) was added. The millimoles and mole fractions of the comonomers are summarized in Table S1 (Supporting Information). The solution was mixed well and allowed to hydrolyze at room temperature for 12–24 h. The excess water and ethanol were removed by rotary evaporation, and the resulting gel was placed in a vacuum oven at 60 °C for 24 h. Table S1 (Supporting Information) shows the GPC results for these copolymers.

Synthesis of $MePEG_7SO_3H$ Acid $(MePEG_7(CH_2)_3SO_3H)$ was prepared as previously described.^{16,17,20–22,35,37}

End Group Analysis. End group analysis was performed on all of the prepared copolymers to test for uncondensed Si–OH from the sol–gel condensation to form the polymers. Test samples were mixed with chlorotrimethylsilane, $(CH_3)_3Si-Cl$, with which the uncondensed –OH groups reacted with to label each residual OH group with a trimethylsilyl group. We then measured the labeled samples by NMR and ratioed the integrated peak areas of the trimethylsilyl groups and the terminal MePEG methyl groups to quantitate the amount of unreacted –OH groups per polymer unit.

In one experiment, MePEG₇ polymer (0.035 g, 0.079 mmol) was dissolved in 20 mL of toluene in an argon purged flask. Then, a large excess of chlorotrimethylsilane (0.5 mL, 4 mmol) was added. The reaction mixture was stirred for 6 h. Afterwards, 2.0 g of K_2CO_3 was added to quench any unreacted HCl and then stirred for 1 h. The solution was filtered, and the toluene and unreacted chlorotrimethylsilane (BP = 57 °C) was removed by rotary evaporation followed by evacuation to

~100 mTorr for 30 min. The resulting product was a clear and colorless viscous liquid. The integration of the ¹H NMR trimethylsilyl peak at δ = 0.10 ppm was ratioed to the -OCH₃ peak of the MePEG group, showing the presence of 5.7% uncondensed Si–OH groups in this polymer.

RESULTS AND DISCUSSION

Fractional Free Volume (FFV). We have previously described how to determine the V_w and FFV of a copolymer.^{20,24,26,27} The FFV data for our MePEG and MePPG polymers and their copolymers are shown in Table 1. The FFV values are based on the van der Waals volume as calculated by the Bondi group contribution method. These values are average values taken from many different sample types and generally have a small amount of error associated with them. However, due to the magnitude of the values, this error is much smaller than the differences in the values presented in Table 1. The density is also used in the calculation of FFV which was measured using a micro balance in triplicate. The error associated with these measurements is also insignificant to the tabulated values of FFV.

In general, the MePPG₃ polymer has greater FFV than the MePEG₇ polymer, and the copolymerization of MePPG₃ with the MePEG₇ polymer leads to copolymers with greater FFV as compared to the MePEG₇ polymer. While the differences in FFV seen in Table 1 appear to be small, we have found that these small differences in FFV can have a large effect on the ionic conductivity.^{20–22,37}

We have also described how to calculate the volume fraction of PEG ($V_{\rm f,PEG}$) of a copolymer.^{17,20,37} Note that we have previously called this term the volume fraction of PEG; however, we are also using polypropylene glycol in this paper; thus, we are switching our notation to the volume fraction of ether ($V_{\rm f,ether}$).^{5,16,17} The mass and density both were used to calculate the $V_{\rm f,ether}$ of these polymers. The error associated with the density measurements, as stated above, is not significant. The masses were measured on a standard analytical balance whose mass is accurate to ± 0.001 g; this is less than 0.01% of the masses of the samples measured and is also not significant.

The $V_{f,ether}$ data is also summarized in Table 1. Of note in these data is that several polymers have similar FFVs but very

Table 2. Ether Volume Fractions for PEG-PPG Copolymer Electrolyte Mixtures with 0.26 and 1.32 M MePEG₇SO₃H Acid

polymer		[MePEG ₇ SO ₃ H] (mol/L)	$V_{\rm f,ether,mix}{}^a$	FFV _{mix} ^b
MePEG ₇ polymer electrolyte	0.26	0.452	0.309	
		1.32	0.455	0.316
MePPG ₃ polymer electrolyte		0.26	0.446	0.322
		1.32	0.454	0.324
MePPG ₂ polymer electrolyte		0.26	0.441	0.306
		1.32	0.453	0.314
MePEG ₇ /MePPG ₃ copolymer electrolyte	75:25	0.26	0.450	0.315
		1.32	0.454	0.320
	50:50	0.26	0.449	0.318
		1.32	0.454	0.322
	25:75	0.26	0.448	0.307
		1.32	0.454	0.315
MePEG ₇ /MePPG ₂ copolymer electrolyte	75:25	0.26	0.450	0.312
		1.32	0.454	0.318
	50:50	0.26	0.448	0.310
		1.32	0.454	0.317
	25:75	0.26	0.445	0.316
		1.32	0.454	0.320
MePPG ₃ /MePPG ₂ copolymer electrolyte	75:25	0.26	0.445	0.325
		1.32	0.454	0.326
	50:50	0.26	0.444	0.319
		1.32	0.454	0.322
	25:75	0.26	0.443	0.316
		1.32	0.454	0.320

 ${}^{a}V_{f_{ether,mix}}$ for copolymer electrolytes is the weighted $V_{f_{ether,mix}}$ of the monomeric units and the MePEGSO₃H acid. ${}^{b}FFV_{mix}$ for copolymer electrolytes is the weighted FFV_{mix} of the monomeric units and the MePEGSO₃H acid.

Table 3. GPC Data for Copolymers with Weight Average	e Molecular Weight	: (M _w), Polydispersity	y Index (PDI)), and Number o	f
Monomers with the Percent Uncondensed Si–OH					

		"high" MW peak c		"low" MW peak d				
polymers and copolymers		$M_{\rm w}~({\rm Da})$	PDI ^a	no. of monomers ^b	$M_{\rm w}~({\rm Da})$	PDI ^a	no. of monomers ^b	% Si–OH ^e
MePEG ₇ polymer		3813	1.37	8.61	546	1.31	1.23	1.00
MePPG ₃ polymer		2652	2.43	8.86				2.30
MePPG ₂ polymer		3163	8.01	13.1				1.78
MePEG ₇ /MePPG ₃ copolymer	75:25	5017	1.53	12.3	550	1.55	1.35	1.44
	50:50	4140	1.51	11.2	577	1.50	1.55	4.74
	25:75	2794	4.70	8.33				4.96
MePEG ₇ /MePPG ₂ copolymer	75:25	4165	1.46	10.6	527	1.60	1.34	1.19
	50:50	4166	1.61	12.2	539	1.26	1.58	1.19
	25:75	3332	1.52	11.4	450	1.52	1.54	5.07
MePPG ₃ /MePPG ₂ copolymer	75:25	2191	4.57	7.69				1.07
	50:50	2485	2.98	9.20				1.96
	25:75	3813	3.06	14.4				1.19

^{*a*}PDI = M_w/M_n . ^{*b*}No. of monomers is calculated by dividing M_w by the weighted monomer molecular weight. ^{*c*}"High" MW peak is the peak observed with the highest M_w when more than one peak is present. ^{*d*}"Low" MW peak is the peak observed with the lowest M_w when more than one peak is present. ^{*e*}" uncondensed Si–OH is equal to ¹H NMR –OTMS divided by 3 Si–OH per monomer times 9 protons per TMS.

different $V_{f,ether}$. For instance, the MePEG₇ polymer, the MePPG₂ polymer, and the MePEG₇/MePPG₂ copolymer all have a smaller variation in FFV (Table 1: 0.304–0.315, a 4% variation) but have a much larger variation in the range of the $V_{f,ether}$ value (Table 1: 0.622–0.789, a 27% variation).

It appears that in this system we have small variations in FFV but much larger variations in $V_{f,ether}$. We have probed the effect of FFV on the transport properties by incorporating bulky groups such as diphenyl siloxane and isobutyl siloxane.²⁰ In this report, we are adding free volume using PPG groups that lower the volume fraction of conducting ethers. Thus, we are able to make a better comparison about the relative contributions of fractional free volume and volume fraction of ether to the observed transport properties.

The calculation of the volume fraction of ether in a mixture of MePEG_nSO₃H acid and MePEG_n and MePPG_n copolymers $(V_{f,ether,mix})$ has also been described previously.^{17,20,37} Table 2 shows the calculated values of the FFV and the volume fractions of ether in the copolymer/acid electrolyte mixtures. In the 1.32 M acid containing polymer electrolytes, $V_{f,ether,mix}$ is dominated by the contributions of the added MePEG₇SO₃H acid. For the low concentration 0.26 M acid containing polymer electrolytes, $V_{f,ether,mix}$ for the MePEG₇ based polymers had larger values than the shorter MePPG_n based polymers. In this

case, the lower concentration of the MePEG₇SO₃H acid contributes a much smaller amount to the overall $V_{\text{f,ether}}$.

Gel Permeation Chromatography (GPC). GPC analysis was performed to determine the effects of cross-linking in the polymerization of the MePEG_n and MePPG_n polymers and copolymers. Evidence of cross-linking and the degree of polymerization can be determined from GPC analysis from the mass and polydispersity index (PDI). The GPC analysis results for the MePEG_n and MePPG_n polymers and copolymers are summarized in Table 3. The GPC data allows us to predict the structure of our polymers based on the previous work of Ghosh et al.³⁵ Two peaks were observed in the GPC for many of the copolymers that correspond to the polymer and dimer peaks. There is only one peak observed for several of the copolymers because the monomer and "dimer" of these copolymers have a small M_w . The ELS detector has difficulty detecting these low M_w components (ELS sensitivity $\propto MW^2$).^{17,20,37}

For the polymers that have two peaks, there is a low molecular weight peak that corresponds to a mixture of monomers and dimers. For high MW peaks, the M_w , M_n , and PDI support the formation of T₈ silsesquioxane clusters (Scheme S1, Supporting Information).³⁵ In these high MW peaks, the number of monomer units ranges from approximately 8 to 15 for the high MW peaks. We have previously noted that the polystyrene MW standards used to obtain the $M_{\rm w}$ and $M_{\rm n}$ values appear to systematically underestimate the actual molecular weight of glycol based polymers by up to 40%.¹⁶ We did not use PEG based calibration standards so that our data would be comparable to other data for polymer electrolytes that use polystyrene calibration standards. In the low MW peaks, the M_{w} , M_{n} , and PDI support the formation of T₂ dimer clusters where one silicon atom is connected to one other silicon atom with one or more Si-O-Si bonds.

For both of the copolymers with the longer MePEG₇ (i.e., the MePEG₇/MePPG₃ and MePEG₇/MePPG₂ copolymers), the number of monomer units in the high MW peak decreased as the mole fraction of PPG increased. This likely indicates the presence of incomplete T_8 clusters (i.e., open T_7 or T_6 clusters; Scheme S1, Supporting Information). We have characterized the formation of these incomplete clusters in a previous publication.³⁵ For the MePPG₃/MePPG₂ copolymers, the number of monomer units increased, perhaps indicating the presence of a ladder type structure.

We also infer from these results that the rate of polymerization is greater for the MePPG polymers, and relatively slower for the MePEG polymer. The reaction was carried out for 12– 24 h so that the sol–gel reaction would complete hydrolysis of the ethoxy groups and reach equilibrium. The smaller MePPG₂ and MePPG₃ comonomers have less steric hindrance, which likely allows the condensation reaction to proceed faster than it does for the larger MePEG₇ comonomer. It is also noteworthy that the MePPG₂ had the highest number of monomer units in the high molecular weight peak, indicating that its polymerization rate is the fastest.³⁸ Here a faster rate of polymerization may make a polymer more likely to adopt the ladder geometry than the T₈ silsesquioxane geometry.

For the polymers with the highest fraction of $MePEG_7$, the PDI was between 1.3 and 1.6, indicating a small dispersity in the polymer's molecular weight. The polymers with higher fractions of PPG, especially $MePPG_2$, had considerably higher PDI values ranging from 2.4 to 8.0, indicating a much more random polymerization compared to those polymers with the

higher MePEG $_7$ fractions. This more random polymerization is also consistent with a faster polymerization and an open-ended ladder geometry.

End Group Analysis. End group analysis was performed to determine if the copolymers were completely condensed, and if the presence of the copolymer altered the degree of polymerization. The end group analysis results are also included in Table 3. The copolymers ranged from 1 to 5% uncondensed Si–OH. These relatively low numbers indicate that the condensation was nearly complete, as would be expected from a completely condensed T_8 silsesquioxane cluster. The highest percentage of uncondensed silanols was in the copolymers with the highest fraction of PPG. These could be caused by size incompatibilities or differences in polymerization rates. Both occurrences would be expected to increase the amount of uncondensed silanols.

Viscosity. The viscosities of the copolymers were measured to determine the relationship between fractional free volume and viscosity for these copolymers. The viscosity data taken at 25 °C is summarized in Table S1 (Supporting Information). The viscosity of the pure polymers decreases in the order MePPG₂ < MePPG₃ < MePEG₇. We also see a similar decrease for the MePPG₃/MePPG₂ copolymers in the order 25% MePPG₃ < 50% MePPG₃ < 75% MePPG₃.

The viscosities of the MePPG₃/MePPG₂ copolymers follow the same trend as their calculated FFV values. However, in the heterocopolymers (MePEG₇/MePPG₃ and MePEG₇/ MePPG₂), the order of viscosity is 75% > 25% > 50%. This odd arrangement seems counterintuitive, but this trend is in fact following the calculated FFV trend.

Figure 1 shows the Doolittle plot of all the copolymers at 25 °C. The best fit line for all of the data points together (i.e., the



Figure 1. Doolittle plot for all MePEG/MePPG copolymers. The best fit linear line is shown for the MePPG₃/MePPG₂ copolymers (y = -2.2601x + 6.138, $R^2 = 0.983$, *p*-value = 0.0009) and MePEG₇/MePPG_x copolymers (y = -0.3294x + 0.3625, $R^2 = 0.0505$, *p*-value = 0.628817).

pure polymers, heterocopolymers, and homocopolymers grouped together) had a poor R^2 value (0.0063) and a high *p*-value (0.8059), indicating that there is no correlation between FFV and viscosity for these samples (note: the best fit for all the data is not shown in Figure 1).

On further inspection, the linear fit of just the MePPG₃/ MePPG₂ homocopolymers (solid circles and solid line in Figure 1) yielded a very good R^2 value (0.983) and a significant *p*-value (0.0009), indicating that there is a strong relationship for these copolymers. Furthermore, when all of the MePEG/MePPG heterocopolymers were grouped together (i.e., both the MePEG₇/MePPG₂ copolymers and MePEG₇/MePPG₃ copolymers; open circles in Figure 1), the correlation again showed a much smaller slope, a poor R^2 value (0.0505), and a high *p*-value (0.6282). This indicates that the heterocopolymers with heteromonomers do not follow the Doolittle equation.

There are two considerations to take into account. First, there is a clear mismatch of monomer sizes that may affect the viscosity, and second, there is also a great difference in the slopes (-2.26 and -0.329 for the MePPG homopolymers and $MePEG_7/MePPG_x$ heterocopolymers) which, as mentioned above, is the material specific constant q in eq 7a. This result agrees with our previous results,²⁰ where the Doolittle fit for heterogeneous copolymers showed only a moderate R^2 value (0.5340), a low *p*-value (0.0020), and a shallow slope (-0.611). Those results indicated that the FFV and viscosity were correlated, but the moderate R^2 and shallow slope suggest the correlation is not strong, and the low p-value indicates a significant correlation. The *p*-value is likely to be larger if the slope is small, and much more likely to be small with a larger slope; that is, it is harder for the correlation to occur randomly if the slope is larger. If this were the case, then the *p*-value may not be indicative of a correlation and the FFV and viscosity may only be moderately correlated for that set of heterogeneous copolymers.

These taken together indicate that the structures of the different copolymers are significantly different (as mentioned above in the GPC and end group analysis discussion). That is, differences in reactivity and associational forces make the MePPG/MePPG homocopolymers have a different structure from the MePEG/MePPG heteropolymers. Also, this difference in structure results in a significant difference in the transport properties of the MePEG/MePPG heterocopolymers.

lonic Conductivity. The ionic conductivities of the copolymers were measured to determine the relationship between ionic conductivity and FFV for these copolymers. Figure 2 shows a Forsythe plot correlating the molar equivalent ionic conductivity (Λ) with the inverse of FFV for all copolymers at 25 °C according to the Forsythe equation (eq



Figure 2. Forsythe plot with fractional free volume for all MePEG₇/MePPG_x copolymers with the best fit linear line shown. y = -1.1883x - 2.6406, $R^2 = 0.0030$, *p*-value = 0.7966.

9). The linear best fit shown has a small slope, a very low R^2 value (0.0030), and a large *p*-value (0.7966). These results clearly indicate that the Forsythe equation is not obeyed for this set of copolymers. This is an interesting lack of correlation, because we have previously observed a correlation between ionic conductivity and the volume fraction of PEG in a polymer, which we used as a proxy for free volume. This correlation, however, existed for MePEG based polymers and mixtures of MePEG based polymers.^{16,17} From our previous studies using the volume fraction of PEG, we understand that ionic conductivity results from the rearrangement of ether units. For this work, the $V_{f,PEG}$ concept has been extended to include the ethers of PPG, making $V_{f,ether}$.

In our heterocopolymers, both the MePEG and MePPG have repeating ether units, and can thus both participate in the overall ionic conductivity. Figure 3 shows a modified Forsythe



Figure 3. Forsythe plot with volume fraction of ether ($V_{f,ether}$) for all MePEG₇/MePPG_x copolymers with the best fit linear line shown. y = -13.1827x - 9.2248, $R^2 = 0.6146$, *p*-value < 0.00001.

plot with molar equivalent conductivity (Λ) correlated with $V_{f,ether}$ (instead of FFV) for all copolymers at 25 °C. The linear best fit shown has a much greater slope than the Forsythe correlation with FFV shown in Figure 2. In addition, the correlation in Figure 3 has a much greater R^2 value (0.6146) and a small *p*-value (<0.0001), indicating a significant result. These values indicate that there is a correlation between the $V_{f,ether}$ and the equivalent conductivity, indicating that the MePPG_x copolymers behave similarly to our previously studied MePEG based polymers with respect to the mechanism of ionic conductivity.^{16,17,20,37} Further support for this mechanism is derived from the Arrhenius activation plots (Figure S1, Supporting Information) which are curved and obey the VTF equation. It is well-known that this behavior is indicative of ion transport that is associated with a rearrangement of the polymer segmental units.

Walden Plot. Figure 4 is the Walden plot for the 1.32 M polymer electrolytes. It should be noted that these samples are far below the ideal Walden line. The ideal Walden line has a slope of $\alpha = 1$ and passes through the origin. The data was fit to a linear best fit based on the fractional Walden rule (eq 6b) where α is the slope of the line for this relationship. For the 1.32 M copolymer electrolytes, the α values ranged from 0.2155



Figure 4. Walden plot for all 1.32 M polymer electrolytes with linear best fit lines shown: (●) 100% MePEG₇; (○) 100% MePPG₃; (▼) 100% MePPG₂; (△) 75% MePEG₇/25% MePPG₃; (■) 50% MePEG₇/50% MePPG₃; (□) 25% MePEG₇/75% MePPG₃; (◆) 75% MePEG₇/25% MePPG₂; (◇) 50% MePEG₇/50% MePPG₂; (▲) 25% MePEG₇/75% MePPG₂; (△) 75% MePPG₃/25% MePPG₂; (●) 50% MePPG₃/50% MePPG₂; (○) 25% MePPG₃/75% MePPG₂.

to 0.5611. No trend was observed for the α values for any of the copolymer series.

The Walden plots shown give further evidence that the FFV of these copolymer systems is not correlated with the ionic conductivity. The fact that there is no correlation suggests that, while viscosity is dependent on the FFV, the ionic conductivity is not related to FFV. This is most likely due to the mechanism of ionic conductivity being dependent on hydrogen bond acceptors such as the ether oxygens in the PEG and PPG. In addition, the low α values in the Walden plot indicate that forces other than viscosity are impeding ion mobility (i.e., polymer rigidity, small dissociation constant, and/or ion pairing).

The lower right region of the Walden plot that these polymer electrolytes fall within also defines electrolytes that are not completely ionized. Electrolytes in this region demonstrate ionic conductivity that is considerably smaller than an ideal electrolyte of the same viscosity. One possibility is that the low ionic conductivity results from ion pairing, possibly indicating incomplete dissociation of our MePEG₇SO₃H acid in these anhydrous copolymers. Studies are currently underway to measure the acidity constant of the MePEG₇SO₃H acid in a model PEG system. This would allow us to have direct evidence of the extent of dissociation in systems of this type.

CONCLUSIONS

The anhydrous electrolytes explored in this work are inorganic/ organic hybrid polymer electrolytes containing ether oxygens that can conduct H⁺ ions in the absence of water. The sol–gel condensation reactions result in a small fraction of uncondensed Si–OH groups for all of the copolymers. GPC analysis provided evidence that there is a dispersity in the polymer sizes synthesized, from a group of monomers and dimers, to silsesquioxane T₈ clusters, to ladder type structures with up to 15 monomer units. The copolymerization of the MePPG₃ with MePPG₂ allows for alteration of FFV to include values between the two pure polymers. This work and the work by Ghosh et al. suggest that, for the single component polymers (i.e., those with only MePPG or MePEG), the FFV can be systematically changed, while, for heterocopolymers, there seems to be no overall correlation between FFV and polymer composition. Only the MePPG₂/MePPG₃ homocopolymers followed the Doolittle equation, with the heterocopolymers found to have no correlation to viscosity.

While there was no relationship found between FFV and ionic conductivity, there was, however, a strong correlation between ionic conductivity and $V_{\rm f,ether}$ observed. These two observations together provide further evidence that proton conduction, in this polymer system, proceeds through rearrangement of the ether units in the PEG or PPG segmental units. The results of this experiment show that, for heteropolymers, free volume is less of a contributor to ionic conductivity than the volume fraction of ether present.

ASSOCIATED CONTENT

S Supporting Information

Table S1 describing the preparation of the MePEG/MePPG copolymers, Scheme S1 showing condensed and incompletely condensed polymer cluster structures, and Figure S1 showing an Arrhenius activation plot for all 1.32 M polymer electrolytes with VTF best fit lines. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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